

3D Printing of Flexible and Efficient Polymeric Piezoelectric Energy Conversion Materials

Submitted by

Nikita Alexeyevich Shepelin

B.Sc. Nanotechnology (Hons)

ORCID: 0000-0002-5446-9213

August 2020

Thesis submitted in total fulfilment of the requirements for the degree of
Doctor of Philosophy

DEPARTMENT OF CHEMICAL ENGINEERING

THE UNIVERSITY OF MELBOURNE

The work described in this thesis was carried out within the Department of Chemical Engineering at the University of Melbourne and the Note Issue Department at the Reserve Bank of Australia as part of a Ph.D. program funded by the Australian Research Council's Linkage program (LP160100071) entitled "Printable Technologies for High Security Documents and Consumer Products".

Thesis submission date: 18 August 2020

Completion seminar date: 4 August 2020

Doctoral Committee:

Prof. Amanda V. Ellis	Primary Supervisor
Prof. Greg W. Dicinoski	Co-supervisor
Dr Peter C. Sherrell	Co-supervisor
Prof. Frank Caruso	Chair

ABSTRACT

The unique capability of piezoelectric materials to convert between mechanical and electrical energy holds tremendous potential in enabling a range of emerging applications. Polymers, as soft and biocompatible materials, are excellent candidates for the use in powering wearable and implantable electronics, as well as for the primary sensing mechanism in soft robotic interfaces. However, piezoelectric polymers are sparsely utilised due to their chemical and structural complexity, and the tremendous energetic cost to maximise their energy conversion efficiency. Fluoropolymers have piezoelectric figures of merit rivalling those of the widely used ceramics and are therefore promising to investigate. The common processing techniques for fluoropolymers revolve around solution casting from toxic, hazardous, and/or high boiling point solvents, which require lengthy solvent evaporation times and arduous post-processing by electrical poling, applying high electric fields to align the dipoles. Recent advances in three-dimensional (3D) printing show promise in order to process fluoropolymers into piezoelectric devices, inducing shear forces on the polymer chains during extrusion toward greater alignment and tailored architectures.

In this work, pathways to improving the piezoelectric output of a fluoropolymer, poly(vinylidene fluoride-*co*-trifluoroethylene) (PVDF-TrFE) were thoroughly investigated. The solvent evaporation-assisted (SEA) 3D printing technique was adapted to printing fluoropolymers, investigating the effects of layer-by-layer deposition on the optical, polymorphic and electromechanical properties. In combination with 3D printing, two classes of nanoscale additives were further investigated, single-walled carbon nanotubes (SWCNTs) and transition metal carbides (MXenes), to elucidate their role in the evolution and alignment of the piezoelectric polarisation.

The first part of the thesis focused on the development and optimisation of 3D printing capabilities for fluoropolymers. A binary solvent mixture was optimised by Hansen solubility parameters and the rheological properties were thoroughly probed to optimise the polymer concentration. The effects of printing parameters were further investigated in order to minimise spreading of the resultant ink post-printing. The polymers, 3D printed

up to 19 layers were transparent and exhibited piezoelectricity, with minimal changes in the electroactive phase fraction and without electrical poling. These results confirmed that shear stresses impart partial polarisation on the extruded materials, and provided a strong foundation for the further studies investigated in this thesis.

The second study of this thesis critically investigated the effects of the incorporation of SWCNTs, as a nanoscale additive, into the PVDF-TrFE coupled with the developed 3D printing process. The composites were printed as single-layer films, found to be transparent at carbon nanotube loadings up to 0.05 wt%, with low haze. The piezoelectric properties were investigated through two techniques, piezoresponse force microscopy (PFM) and bulk electromechanical characterisation, finding the greatest enhancement in piezoelectric properties at a 0.02 wt% loading of the SWCNTs from both techniques. Molecular dynamics (MD) simulations of the carbon nanotube interface with the polymer confirmed a polarisation enhancement effect, providing the first report of polarisation in the absence of electrical poling. Furthermore, the composites were found to be recyclable in pure acetone, a green and low boiling point solvent, allowing the printed piezoelectric polymers to be reprinted, with minimal changes in the chemical, physical and electroactive properties.

The final part of this thesis utilised two-dimensional (2D) MXene nanosheet additives as a model non-piezoelectric system to deduce and provide the first report on the mechanism of physical polarisation locking in the PVDF-TrFE, building on the knowledge of the first two studies. The composites were printed directly from acetone as a physical gel, allowing for a faster solvent evaporation rate and therefore improved crystallisation kinetics. MD simulations found a suppressed electroactive phase fraction of the polymer directly adjacent the surface of the additive, confirmed experimentally by Raman microscopy and differential scanning calorimetry. Furthermore, the MD simulations found the polarisation vector direction was locked perpendicular to the basal plane of the MXene, which was governed by electrostatic interactions. PFM results confirmed the dipole locking phenomenon, whereby the polarisation magnitude increased logarithmically with an increase in the MXene loading, while demonstrating the transition metal carbide had no discernible out of plane polarisation. Direct piezoelectric effect measurements *via* macroscale electromechanical testing showed that the composite material exhibited a larger

piezoelectric coefficient relative electrically poled polymer, implying that physical poling and polarisation locking from a nanomaterial template can impart greater polarisation than standard electrical poling techniques.

In summary, this thesis has developed and applied a fundamental understanding of the origins of piezoelectricity in fluoropolymers and how this phenomenon can be controlled at the nanoscale. The implications of this research are far-reaching, enabling commercial viability of piezoelectric materials in a multitude of emerging applications.

DECLARATION

This thesis comprises only my original work towards the degree of Doctor of Philosophy except where indicated in the preface; due acknowledgement has been made in the text to all other materials used; and the thesis is fewer than 100,000 words in length, exclusive of tables, maps, bibliographies and appendices.

Nikita Alexeyevich Shepelin, BSc Nanotechnology (Hons)

The University of Melbourne

PREFACE

During the course of this Ph.D. project, several manuscripts have been prepared and published in peer-reviewed journals. They are listed below with their publication status at the time of submission of this thesis. Parts of the presented work were carried out as collaborations and the contributions of others are presented below each citation. The work towards this thesis has not been submitted for other qualifications and has not been undertaken prior to enrolment. No third-party editorial assistance was provided in preparation of this thesis. This Ph.D. project has been financially supported by the Australian Government Research Training Program Scholarship (Fee Offset) and the Australian Research Council Linkage Program (LP160100071).

Chapter 2: N.A. Shepelin, A.M. Glushenkov, V.C. Lussini, P.J. Fox, G.W. Dicinoski, J.G. Shapter and A.V. Ellis. New developments in composites, copolymer technologies and processing techniques for flexible fluoropolymer piezoelectric generators for efficient energy harvesting. *Energy & Environmental Science*, **12**(4), 1143-1176 (2019). DOI: 10.1039/C8EE03006E

This review was written with the close oversight of Dr Alexey Glushenkov and Prof. Amanda Ellis, who provided suggestions on the content to be presented in this publication, as well as the structure and layout. All authors read the final draft and provided input.

Chapter 3: N.A. Shepelin, V.C. Lussini, P.J. Fox, G.W. Dicinoski, A.M. Glushenkov, J.G. Shapter and A.V. Ellis. 3D printing of poly(vinylidene fluoride-trifluoroethylene): a poling-free technique to manufacture flexible and transparent piezoelectric generators. *MRS Communications*, **9**(1), 159-164 (2019). DOI: 10.1557/mrc.2019.19

This communication was written with the oversight of Prof. Joseph Shapter and Prof. Amanda Ellis, discussing the relevance of the data in detail and providing recommendations on the layout. Prof. Amanda Ellis contributed to the conception of the research. Dr Vanessa Lussini provided assistance with the electromechanical characterisation and aspects of device fabrication. All authors assisted with the analysis of collected data. All authors read the final draft and provided input.

Chapter 4: N.A. Shepelin, P.C. Sherrell, E. Goudeli, E.N. Skountzos, V.C. Lussini, G.W. Dicinoski, J.G. Shapter and A.V. Ellis. Printed recyclable and self-poled polymer piezoelectric generators through single-walled carbon nanotube templating. *Energy & Environmental Science*, **13**(3), 868-883 (2020). DOI: 10.1039/C9EE03059J

This research article was written with the oversight of Dr Peter Sherrell and Prof. Amanda Ellis, providing suggestions on the content and layout. Prof. Amanda Ellis contributed to the conception of the research. Dr Eirini Goudeli and Emmanuel Skountzos undertook the Molecular Dynamics simulations and contributed to the analysis of the resultant data. Dr Vanessa Lussini provided assistance with the electromechanical measurements and provided the commercial materials used as controls. All authors contributed to the analysis of the data. All authors read the final draft and provided input.

Chapter 5: N.A. Shepelin, P.C. Sherrell, E.N. Skountzos, E. Goudeli, J. Zhang, V.C. Lussini, B. Imtiaz, K.A.S. Usman, G.W. Dicinoski, J.G. Shapter, J.M. Razal and A.V. Ellis. Interfacial piezoelectric polarization locking in printable $\text{Ti}_3\text{C}_2\text{T}_x$ MXene-fluoropolymer composites. *Submitted for publication to Nature Communications on 25 August 2020*.

This communication was written with the oversight of Dr Peter Sherrell and Prof. Amanda Ellis, providing critical recommendations on the content to be included, the structure and the layout. Dr Peter Sherrell and Prof. Amanda Ellis contributed to the conception of the research. The Molecular Dynamics simulations were carried out by Emmanuel Skountzos and Dr Eirini Goudeli, who contributed to the analysis and contextualisation of the resultant data. Jizhen Zhang, Ken Usman and Prof. Joselito Razal synthesised the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets used in this research. Dr Vanessa Lussini prepared the solvent cast PVDF-TrFE films. Beenish Imtiaz undertook the Fourier transform infrared spectroscopy characterisation and contributed to the analysis of the resultant data. All authors assisted with the final analysis of the data. All authors read the final draft and provided input.

ACKNOWLEDGEMENTS

This thesis has come together with the invaluable input of many of those around me. First and foremost, I would like to thank my supervisor, Prof. Amanda Ellis, who has dedicated significant time and effort into this project. Amanda, you gave me the opportunity to join your research group six years ago, as part of a Summer Research Scholarship in order to gain research experience. Throughout all this time, you have shown the utmost dedication to science and the development of researchers around you, and I believe this thesis is a testament to that fact. You have provided incredibly valuable guidance throughout my candidature, which has ultimately enabled me to be a better scientist and researcher. Your passion in scientific research is evident from the many discussions we had during this time—always keeping me on track and finding a way out when I was stuck with the project.

When I first arrived in Melbourne, I had the pleasure of meeting Dr Alexey Glushenkov, who joined the project as a postdoctoral fellow. Alexey, throughout the time working together on the project, you have taught me a tremendous amount on everything ranging from how to write a paper, to electrochemistry, to even the latest developments in world news. I found our discussions to be highly stimulating, and your guidance and knowledge has helped in more ways than you can imagine.

I would like to also thank Dr Peter Sherrell who joined the project part-way through and instantly made an impact on the research. When you joined, I was at a low point with my research and every experiment seemed to be not working for almost a year. Quickly, you were able to put all the data into perspective and helped me finalise the entire dataset. As my co-supervisor, you have kept helping me grow, pushing my academic writing to a more multidisciplinary level. Your networks allowed the final chapter to be realised and you have enabled many collaborations. It has been a pleasure to work alongside you.

Additionally, this project has involved significant input from the Reserve Bank of Australia by Dr Greg Dicinoski, Dr Vanessa Lussini, Dr Phillip Fox, Dr Nicole Cain and Dr Sani Muke, as well as from the University of Queensland by Prof. Joseph Shapter. I would like to thank you all collectively for your contribution to the project, questioning me whenever possible to ensure the work made sense and supporting me at every turn. Our monthly meetings kept me focused, and the regular presentations have admittedly made the task of writing this thesis much easier. Greg, I wish to thank you for all the times you have so quickly reviewed and edited my work, even when it was sent to you with a very short deadline. As my co-supervisor, you have supported the research I have undertaken, both in my yearly reviews and during my time at the RBA laboratories. Vanessa, you have always been there to help me make my arguments in the meetings, especially when it came to explanations of the weird effects we saw on the oscilloscope. Thank you for your expertise and your assistance in the lab. Joe, I am extremely grateful for the time you have put into supporting me, your guidance and willingness to contribute despite the time requirements of your position clearly demonstrate your passion for science.

During the collaborative work, Dr Eirini Goudeli, Emmanuel Skountzos, Jizhen Zhang and Prof. Joselito Razal have provided invaluable contributions to the project. Thank you for the time you have spent in meetings with us, trying to make sense of all the data on the project. Your diverse expertise allowed this research to develop into solid and exciting findings.

To the members of the Ellis Research Group, both past and present, you have made the Ph.D. experience truly enjoyable. The many discussions have been very stimulating and the supportive nature of everyone in the group made the time fly by. In particular, I would like to extend my gratitude to Beenish Imtiaz, you have always listened when I was trying to rationalise my work out loud and provided critical and valuable feedback.

To the team at the Materials Characterisation and Fabrication Platform, specifically Dr Lauren Hyde, Dr Elena Taran, Dan Smith and Dr Tian Zheng, I am extremely grateful for the support you have given me, both when it came to using the instruments as part of

MCFP and providing opportunities for me to give back and help. The ability to use the instruments on the platform has been one of the key reasons this work has come together.

Dr Matthew Biviano, thank you for the insightful discussions surrounding the PFM technique and AFM in general, as well as stimulating discussions on science and technology as a whole. I hold our impromptu, long-winded and in-depth discussions in high regard.

I wish to thank the Research Project students who I had the pleasure of supervising, Miles Steffen, Yuze Wang, Xinxiu Bian and Georgia Tickle. Your experience and fresh ideas have made the time in the laboratory extremely enjoyable and your scientific contributions have provided significant insights.

To my mum, and in fact my entire family currently in Russia, it is your exemplary care and leadership that has led me to become the disciplined and determined person that I am today. Having experienced life in two completely different countries has helped me develop a comprehensive understanding on the type of person I am and has driven me to always better myself. To my partner, I wish to extend my special gratitude. You have continuously pushed me to aim high and stood by my side, even during the periods where my Ph.D. has consumed my waking hours. Thank you for your support throughout this time.

My Ph.D. has been a mixture of frustrating, stressful, enjoyable and triumphant. I have made many mistakes throughout this journey and made sure to learn something new from each mistake. This experience has resulted in tremendous personal development which I will treasure going forward in life.

TABLE OF CONTENTS

Abstract.....	III
Declaration.....	VI
Preface.....	VII
Acknowledgements.....	IX
Table of Contents	XII
List of Tables.....	XVI
List of Figures	XVII
List of Abbreviations and Acronyms.....	XXXIV
1 Introduction	1
1.1 Thesis structure	5
1.2 References	8
2 Fundamentals of piezoelectric phenomena in fluoropolymers	11
2.1 Abstract	12
2.2 Introduction	12
2.3 Metrics and definitions for piezoelectric materials	15
2.4 Properties of PVDF	21
2.4.1 <i>β phase as the preferred structural orientation and its electromechanical coupling properties</i>	<i>22</i>
2.4.2 <i>Thermal, mechanical and optical properties of PVDF.....</i>	<i>26</i>
2.4.3 <i>Comparison of PVDF properties with other piezoelectric materials</i>	<i>27</i>
2.5 Characterisation of PVDF	29
2.6 Control of parameters relating to piezoelectricity in fluoropolymers	35
2.6.1 <i>Polymerisation parameters and techniques</i>	<i>36</i>
2.6.2 <i>Co-monomer influences in fluorinated polymers</i>	<i>38</i>
2.6.3 <i>Fluoropolymer deposition and processing techniques.....</i>	<i>41</i>
2.6.4 <i>Poling techniques</i>	<i>52</i>
2.6.5 <i>Composites, additives and nanoscale fillers</i>	<i>56</i>
2.7 Flexible PVDF-based electric generators.....	61
2.7.1 <i>Wearable piezoelectric generators.....</i>	<i>61</i>
2.7.2 <i>Implanted piezoelectric generators</i>	<i>65</i>
2.7.3 <i>Piezoelectric generators driven by the environment.....</i>	<i>69</i>

2.8 Concluding remarks and future perspectives	76
2.9 References	80
3 Additive manufacturing of flexible and transparent piezoelectric generators...	102
3.1 Abstract	103
3.2 Introduction	103
3.3 Experimental	105
3.3.1 Materials	105
3.3.2 3D printing	105
3.3.3 Characterisation	106
3.4 Results and discussion.....	107
3.5 Conclusion.....	114
3.6 References	115
3.7 Supplementary Information.....	118
3.7.1 Supplementary References	124
4 Dipole templating of fluoropolymers from single-walled carbon nanotubes.....	125
4.1 Abstract	126
4.2 Introduction	126
4.3 Experimental	129
4.3.1 Ink preparation.....	129
4.3.2 Printing and PEG manufacture	130
4.3.3 Materials characterisation.....	131
4.3.4 PFM characterisation	132
4.3.5 Energy harvesting analysis	133
4.3.6 Molecular dynamics modelling.....	133
4.3.7 Recyclability testing	134
4.4 Results and discussion.....	135
4.4.1 Inks, printing and optical properties.....	135
4.4.2 Phase determination and materials properties	137
4.4.3 Nanoscale piezoelectric phenomena	141
4.4.4 Macroscale piezoelectric phenomena	144
4.4.5 Computational analysis of behaviour at the interface between SWCNT and PVDF-TrFE.....	148
4.4.6 Recyclability of extrusion printed films.....	152

4.5 Conclusion.....	156
4.6 References	158
4.7 Supplementary information.....	166
4.7.1 <i>Supplementary videos</i>	174
4.7.2 <i>References</i>	175
5 Polarisation locking in fluoropolymers at the interface with MXenes.....	176
5.1 Abstract	177
5.2 Introduction	177
5.3 Experimental	179
5.3.1 <i>Synthesis of $Ti_3C_2T_x$ dispersion</i>	179
5.3.2 <i>Molecular dynamics simulations</i>	179
5.3.3 <i>Extrusion printing ink preparation</i>	180
5.3.4 <i>Extrusion printing and PEG device fabrication</i>	181
5.3.5 <i>Materials characterisation</i>	181
5.4 Results and discussion.....	184
5.4.1 <i>Preparation of $Ti_3C_2T_x$/PVDF-TrFE composite SEA 3D printing inks</i>	184
5.4.2 <i>MD simulations of the $Ti_3C_2T_x$/PVDF-TrFE interface</i>	184
5.4.3 <i>Towards printing and net polarisation</i>	187
5.4.4 <i>SEA extrusion printed and mechanically robust $Ti_3C_2T_x$/PVDF-TrFE composite films</i>	190
5.4.5 <i>PVDF-TrFE phase dependence in $Ti_3C_2T_x$/PVDF-TrFE composites</i>	191
5.4.6 <i>Energy harvesting of the $Ti_3C_2T_x$/PVDF-TrFE composite films</i>	193
5.4.7 <i>Macro energy harvesting using $Ti_3C_2T_x$/PVDF-TrFE composite PEGs</i>	197
5.5 Conclusion.....	198
5.6 References	200
5.7 Supplementary information.....	205
5.7.1 <i>$Ti_3C_2T_x$ MXene nanosheets and properties</i>	205
5.7.2 <i>MD modelling of the interface between the $Ti_3C_2T_x$ nanosheets and the PVDF-TrFE co-polymer</i>	209
5.7.3 <i>Rheological printing optimisation of pristine PVDF-TrFE in acetone</i>	216
5.7.4 <i>Properties of the SEA extrusion printed $Ti_3C_2T_x$/PVDF-TrFE films</i>	221
5.7.5 <i>PFM of $Ti_3C_2T_x$/PVDF-TrFE films</i>	231
5.7.6 <i>PEG fabrication and macroscale energy harvesting</i>	238

5.7.7 <i>Supplementary videos</i>	246
5.7.8 <i>Supplementary references</i>	246
6 Concluding remarks	251
6.1 References	259
Scientific Contributions	261
Peer-reviewed publications	261
Non-peer-reviewed publications	262
Oral Presentations	262
Poster presentations.....	263

LIST OF TABLES

Table 2.1: Selected piezoelectric charge coefficients for PVDF	24
Table 2.2: Physical, dielectric and piezoelectric properties of selected piezoelectric materials, showing perovskites, bulk polymers and voided charged polymers.	28
Table 2.3: Comparison of the piezoelectric metrics and coefficients of various PVDF-based copolymers.	39
Table 2.4: Reported processing methods used to convert the non-polar α phase of fluorinated polymers to the electroactive β phase and pole the resultant fluoropolymer, outlining the advantages and disadvantages of each method. ^{11, 32, 43}	54
Table 3.S1: Solubility parameters of PVDF, and solvents acetone and DMF, as well as the difference in total solubility parameters between PVDF and solvent using the RMS method.	118
Table 4.1: Degree of crystallinity (χ_c) and the relative fractions of the electroactive phase (F_{EA}), β -phase (F_β) and γ -phase (F_γ) obtained <i>via</i> DSC, ATR-FTIR spectroscopy, Raman spectroscopy and XRD.	139
Table 4.S1: The CNT/fluoropolymer energy harvesting figures of merit found in recent literature and the materials and processes used to fabricate the PEGs.....	173
Table 5.S1: Experimentally determined width (w) and thickness (t) for each sample measured during the tensile mechanical testing. The S values designate the sample number.....	222
Table 5.S2: Experimentally determined Q_f for each PFM scan.	236
Table 5.S3: Values for the height (h) and the area under stress (A_σ) for energy harvesting experiments.	243

LIST OF FIGURES

Figure 2.1: Schematic of reference directions for piezoelectric materials.....	17
Figure 2.2: Experimental layout and verification of the piezoelectric FOM. (a) Schematic showing the layout of the purpose-built electrometer for precise mechanical deformation and the subsequent collection of data and (b) a photograph showing the experimental layout. (c) The stored energy plotted as a function of the FOM $g_{33}d_{33}$ for a range of piezoelectric materials including lead zirconate titanate (PZ27, PZT), PZT 1-3 fibre composite in epoxy (A), β phase PVDF (B), randomly distributed 0-3 particle composites from PZT (C, D) and lithium sodium potassium niobate in PDMS (E, KNLN), 1-3 dielectrophoretically aligned particle composites using PZT (F) and KNLN (E). (d) shows the dependence of U_{open} on the input force for the perovskite, fluoropolymer and perovskite-polymer composites and (e) shows the agreement between the model and experimental data for all samples. The modelled data is represented as the black dashed black line in (c-e). Reproduced with permission from ref 51. Copyright 2018, Royal Society of Chemistry.	21
Figure 2.3: Chemical structure of (a) alpha phase, (b) beta phase and (c) gamma phase conformations of PVDF, as well as the chemical structure of (d) PVDF-TrFE, (e) poly(vinylidene fluoride-co-hexafluoropropylene) and (f) poly(vinylidene fluoride-co-chlorotrifluoroethylene).	22
Figure 2.4: The temperature dependence of the directional (a) piezoelectric charge coefficients d_{ip} and (b) piezoelectric energy coupling coefficients k_{ip} . Reproduced with permission from ref 58. Copyright 1984, American Institute of Physics. Stress-strain response of PVDF in the (c) 1 direction and (d) 2 direction. Reproduced with permission from ref 69. Copyright 1999, Taylor and Francis.....	25
Figure 2.5: Typical fingerprints of α , β and γ phases of PVDF in common characterisation techniques, (a) XRD ($K_{\alpha 1}$, $\lambda = 1.5405600 \text{ \AA}$); (b) FTIR; (c) DSC, reproduced with permission from ref 43. Copyright 2014, Elsevier. (d) Raman spectroscopy ($\lambda = 532 \text{ nm}$), reproduced with permission from ref 78. Copyright 2014, SPIE. (e) Electric displacement-electric field (D - E) hysteresis loops, reproduced with permission from ref 79. Copyright 2010, American Institute of Physics.....	30

- Figure 2.6: Synopsis of the factors affecting the electrical output of a fluoropolymer PEG and the respective methods used for their characterisation.....35
- Figure 2.7: (a) Isomers of PVDF through polymerisation of vinylidene difluoride. Head-to-tail propagation (I) is the desired result, however head-to-head (II) and tail-to-tail (III) additions can occur as defects. (b) The fraction of α -phase polymorphs relative to the β -phase in PVDF synthesised with increasing head-to-head and tail-to-tail defect concentration. Reproduced with permission from ref 110. Copyright 1987, Elsevier.....37
- Figure 2.8: Pressure-temperature curves for the crystallisation of α and β phases, as well as the melting of α phase of PVDF. Grey lines represent the initial (a, b, and c) and final (a', b', and c') of pressure quenched PVDF for α , $\alpha+\beta$, and β phases, respectively. Reproduced with permission from ref 43. Copyright 2014, Elsevier.43
- Figure 2.9: Properties of electrospun fluoropolymer-based PEGs: (a) the β -phase fraction and the corresponding voltage and current outputs as a function of the concentration of PVDF in a solution of DMF and acetone (40:60 vol%) upon cyclic compression with 10 N force and 1 Hz frequency, with (b) the temporal evolution of the harvested voltage for the measured concentrations. Reproduced with permission from ref. 150. Copyright 2015, Royal Society of Chemistry. (c) The alignment of electrospun PVDF nanofibers with increasing rotational speed and (d) the electrical output of the resultant PEGs. Reproduced with permission from ref. 151. Copyright 2015, IEEE. (e) The crystallinity, β phase fraction, output voltage and current as a function of the applied voltage during electrospinning (left) and the rotational speed (right), as well as (f) the electrical generation characteristics for electrospun mats as a function of the content of electroactive phase. Reproduced with permission from ref. 152. Copyright 2018, Elsevier.46
- Figure 2.10: (a) Schematic of orientation of PVDF molecules on water surface and subsequent adsorption onto the substrate surface for the formation of a Langmuir-Blodgett film, (b) PFM images after applying a positive (left) and negative (right) voltage across the cantilever and the subsequent phase as a function of distance (bottom left), and (c) the change in amplitude measured as a function of applied voltage using PFM, whereby the slope of the line represents the thickness-axis

piezoelectric charge coefficient d_{33} . Reproduced with permission from ref 140. Copyright 2012, Elsevier. (d) image showing the colour of the PVDF/P3CPenT (23 wt%) stacked LB monolayers as a function of layer amount on a silicon substrate (left) and a 30-layer LB film on a PET substrate (right), (e) schematic outlining the switching process (top), and the resultant Kelvin probe force microscopy (KPM) images before (left) and after patterning (right), and (f) switching and reading properties for the non-volatile memory devices utilising PVDF. Reproduced with permission from ref 161. Copyright 2018, Royal Society of Chemistry.48

Figure 2.11: Recent progress in solvent-evaporation assisted 3D printing of fluoropolymer-based PEGs: (a) left, schematic outlining the printing process, right, optical image of the 70-layer composite 31-mode PEG consisting of 10 wt% BTO in PVDF and its respective voltage output upon tapping with a finger, (b) the specific charge output for printed 10 wt% BTO/PVDF composite film with increasing applied potential difference between the nozzle and the substrate, with the right hand panel showing the specific charge output of a single printed film after one year, (c) optical images showing a conformally-printed BTO/PVDF PEG on a copper substrate with a deposited silver paint top electrode and its electrical output upon finger tapping. Reproduced with permission from refs 32 and 168. Copyright 2017 and 2018, American Chemical Society. (d) Schematic showing the 3D printing technique for coextrusion of the silver-coated BTO/PVDF composite ink, with SEM micrographs showing the cross-section of the filament (red arrows indicate BTO agglomerates and dashed border indicates the silver electrode), (e) schematic showing the printing process for a wing-like composite PEG, along with the peak-to-peak voltage output as a function of input to an electromagnetic shaker (right) and the voltage signal over time as a function of frequency (bottom), and (f) a proof-of-concept PEG to harvest energy from the knee during exercise (top left) with the corresponding output voltage (top right) and energy harvesting from breathing, showing the generated voltage as a function of time for quick (bottom left) and deep (bottom right) breathing. Reproduced with permission from ref 169. Copyright 2018, Wiley.51

Figure 2.12: Schematic of poling systems for piezoelectric polymers, (a) electrode method and (b) corona poling method.53

Figure 2.13: The morphological structure and electrical output characteristics of recently reported woven fluoropolymer flexible PEGs. (a) the woven flexible PVDF fabric PEG with a schematic of the weave pattern on the right and (b) the voltage generated from the PEG upon cyclic compression. Reproduced with permission from ref 216. Copyright 2013, Wiley. (c) Photograph (top) demonstrating the flexibility of the PVDF-based 3D spacer textile PEG, cross-sectional SEM image (bottom) of the PEG, and (d) the electrical output characteristics including the voltage, current and power of the PEG under cyclic compression. Reproduced with permission from ref 30. Copyright 2014, Royal Society of Chemistry. (e) SEM images of the electrospun (E) and electrospun + film core-sheath (EF) yarns, with a schematic outlining the cross-sectional view, with optical images of the yarns. (f) output characteristics including the voltage and current from the EF yarn (top) and E yarn (bottom) under cyclic compression. Reproduced with permission from ref 219. Copyright 2018, Institute of Physics.64

Figure 2.14: The structure and electrical output characteristics of recently reported implanted fluoropolymer flexible PEGs. (a) Schematic (top) showing the working conditions for the implantable PEG and (bottom) implanted fluoropolymer PEG wrapped around the aorta of a Yorkshire porcine, both showing the ability to power a battery-less LCD display above a blood pressure of 120 mmHg *in-vitro* and 140 mmHg *in-vivo*. (b) The electrical output characteristics of the *in-vitro* experiment when wrapped around a latex tube mimicking the aortic artery and (c) the electrical output characteristics of the *in-vivo* experiments. Reproduced with permission from ref 226. Copyright 2016, Elsevier. (d) Image showing the structure of the implantable fluoropolymer PEG encapsulated in poly(dimethyl siloxane), (e) the electrical output characteristics during *in-vitro* experiments, showing the open circuit voltage and short circuit current, and (f) electrical output characteristics during the *in-vivo* experiment, showing the image of the PEG implanted in a mouse, the open circuit voltage and short circuit current when the leg of the mouse is deflected manually, as well as the output of the PEG as a function of implanted time. The bottom-right panel shows the *in-vitro* open circuit voltage before and after implantation. Reproduced with permission from ref 227. Copyright 2016, Elsevier. (g) *In-vivo* computed tomography images (top) of the PVDF PEGs encapsulated in PDMS and Parylene-C during the implantation period, as well as ultrasound images

of the devices implanted in mice. (h) Electrical output characteristics of the long-term implanted PVDF PEGs, showing (top) the voltage of both devices, (bottom left) average peak-to-peak voltage as a function of implantation period for both devices and (bottom right) the input and output currents during characterisation of the leakage current in the device encapsulated in poly(dimethyl siloxane) as a function of time. Reproduced with permission from ref 228. Copyright 2016, Elsevier.....67

Figure 2.15: The structure and electrical output characteristics of recently reported environment-driven fluoropolymer flexible PEGs. (a) Schematic and images showing the contents of the roadway unit harvester, as well as the ten-unit systems and 60-unit systems studied in this report. (b) The electrical output characteristics of the ten-unit systems, showing (top) V_{OC} and short circuit current, (middle) the resistance matching data, and (bottom) the voltage and current at the matched load resistance of 400 k Ω . (c) The electrical output characteristics of the 60-unit systems under simulated road conditions, showing (top) images of the experiments, (middle) resistance matching data and power across a 400 k Ω resistor and (bottom) V_{OC} and short circuit current as a function of the number of unit harvesters, as well as the matched load resistance and power output of the road-harvesting PEG as a function of the number of unit harvesters. Reproduced with permission from ref 22. Copyright 2017, Elsevier. (d) Schematic showing various geometries tested for the PVDF wind-harvesting PEG, (e) generated V_{OC} as a function of wind speed for the three geometries and (f) resistance matching data showing (top) the output power and (bottom) V_{OC} as a function of load resistance. Reproduced with permission from ref 238. Copyright 2014, American Institute of Physics. (g) Schematic showing the structure of the optimised vibration-excited PVDF PEG and (h) electrical output characteristics at an optimised of 34.4 Hz as a function of load resistance, based on simulated optimised geometry. Reproduced with permission from ref 239. Copyright 2017, Elsevier.71

Figure 3.1: Viscosity of PVDF-TrFE solutions as a function of shear rate for PVDF-TrFE loadings between 20 wt% and 40 wt%. Inset shows the viscosity at 1 s⁻¹ as a function of PVDF-TrFE loadings.108

Figure 3.2: Morphology of 3D printed PVDF-TrFE structures, showing (a) optical image of a 19-layer structure printed on top of a thin film, with the inset showing

transmittance and haze as a function of layers deposited, (b) cross-sectional HIM image of the thin film and subsequent layers deposited and (c) cross-sectional HIM image of the top of a 19-layer PVDF-TrFE structure.	110
Figure 3.3: ATR-FTIR characterisation of SEA 3D printed PVDF-TrFE materials, (a) the FTIR spectra in the fingerprint region as a function of the number of printed layers (offset for clarity) and (b) the calculated F_{EA} as a function of the number of printed layers.	112
Figure 3.4: (a) Representative open circuit voltage for SEA 3D printed PVDF-TrFE PEGs as a function of time under 5 Hz cyclic compression. The positive peaks represent increasing compressive force whereas negative peaks represent decreasing compressive force. Each division on the time axis represents 1 s. (b) Peak-to-peak voltage output of the PEGs as a function of the number of 3D printed structured layers of PVDF-TrFE. The first data point represents a 3D printed thin film. Error bars were obtained using the maxima and minima of 50 compression cycles, for three separate samples per data point.	114
Figure 3.S1: (a) Variation between the Hansen solubility parameters for PVDF and the solvent mixture and (b) RMS difference in solubility parameters for PVDF in a solution mixture consisting of acetone and DMF as a function of acetone volume fraction.	119
Figure 3.S2: Viscosity of PVDF-TrFE solutions as a function of shear rate for PVDF-TrFE loadings between 20 wt% and 40 wt%.	120
Figure 3.S3: Optical images showing the structures during optimisation of x-y speed of the 3D Bioplotter for the printing of PVDF-TrFE at 30 wt% in solution. The lamps in the background are used to demonstrate the transparency of the printed structures.	121
Figure 3.S4: Optical microscope images of the edge of the raster pattern during optimisation of x-y speed of the 3D Bioplotter for the printing of PVDF-TrFE at 30 wt% in solution.	122
Figure 3.S5: Optical images of PVDF-TrFE 3D printed onto a glass substrate, whereby the spacing of a raster pattern was investigated for the printing of a solid thin film.	

Printing conditions as follows: 178 kPa extrusion pressure, 30 mm/s x-y robot head speed, 5 °C cartridge temperature, 24 °C ambient temperature.....	123
Figure 3.S6: HIM image showing the cross section of an optimised SEA 3D printed PVDF-TrFE thin film with a 0.4 mm raster line width.....	123
Figure 4.1: (a) Optical images demonstrating the transparency of extrusion printed PVDF-TrFE films with increasing SWCNT concentration (0.000 wt% to 0.200 wt%) from left to right. Scale bar represents 5 mm. (b) Visible wavelength transmittance and haze as a function of SWCNT concentration (blue datapoints denote the PVDF-TrFE control). (c) HIM images showing the surface of the films for PVDF-TrFE (0.000 wt%) and SWCNT/PVDF-TrFE (0.005 wt% to 0.500 wt%). Scale bar represents 10 μ m.	136
Figure 4.2: Analysis of extrusion printed PVDF-TrFE films with SWCNT concentrations between 0.000 wt% and 0.500 wt%, showing (a) XRD spectra. (b) Raman spectra. (c) Ratio of the intensities of the G-band peak relative to the β phase peak from Raman spectra. (d) DSC heating traces. (e) ATR-FTIR spectra. (f) The relative phase ratios calculated from ATR-FTIR spectra (grey), Raman spectra (red) and XRD spectra (blue) for the electroactive ($\beta + \gamma$) phase (triangle), β phase (diamond) and γ phase (square).....	137
Figure 4.3: PFM characterisation of extrusion printed SWCNT/PVDF-TrFE (0.000 wt% to 0.200 wt%) films, (a) the pattern of the applied voltage to the cantilever during raster. (b) The piezoelectric amplitude response of the printed samples upon the application of voltage between the cantilever and the substrate and (c) the corresponding PFM phase response, showing representative slices for each sample. The scale bar represents 1 μ m. (d) The raw amplitude (A). (e) The raw phase (ϕ). (f) The resultant processed PFM amplitude ($A\cos(\phi)$) as a function of the applied voltage for the investigated SWCNT concentrations.....	142
Figure 4.4: Energy generation characteristics of the extrusion printed SWCNT/PVDF-TrFE (0.000 wt% to 0.500 wt%) PEGs, showing (a) the output voltage as a function of time arising from imparted cyclic compression of the samples at 5 Hz for the SWCNT concentrations between 0.000 wt% and 0.500 wt% using an Instron testing machine at a controlled strain rate. (b) The V_{pp} (grey), peak to peak current (I_{pp}) (red) and power density (P_D) (blue) for the 3D printed SWCNT/PVDF-TrFE (0.020 wt%)	

PEG as a function of the load resistance. The input impedance of measurement for the tests was 10 M Ω146

Figure 4.5: Volumetric power density P_D for PEGs containing CNTs as a function of CNT concentration for this study and previous publications reporting energy harvesting capabilities. Circles represent electrically poled PEGs and diamonds represent unpoled PEGs. Fluoropolymer PEGs without CNTs are presented where found in the literature for comparison.147

Figure 4.6: (a) The probability distribution of the angle, φ , between the vectors of the SWCNT axis of symmetry and the SWCNT/PVDF-TrFE dipole moment for the (8,8) (black line) and the (12,0) (red line) SWCNT configurations (insets). The probability distribution of the minimum distance, d , between fluoride (blue lines) or hydrogen atoms (red lines) of the TrFE units (inset of a faded VDF and a highlighted TrFE monomer) and the CNT with (b) (8,8) and (c) (12,0) chirality. The shaded regions represent the error bar obtained from three independent MD simulations. (d) Representative initial spatial arrangement at 0 ns (top) of two PVDF-TrFE chains (gold and blue) relative to SWCNTs (cyan) with (8,8) (left) and (12,0) (right) chiralities, the spatial arrangement after equilibration at 4 ns (middle) and the representative PVDF-TrFE dipole moment vector direction after equilibration at 4 ns (bottom).150

Figure 4.7: Recyclability of SWCNT/PVDF-TrFE films (extrusion printed from acetone and DMF, 60:40 vol%) in pure acetone, with (a) optical image demonstrating the transparency and mechanical flexibility of the initial extrusion printed SWCNT/PVDF-TrFE (0.020 wt%) film. (b) After 2 s of immersion in pure acetone. (c) After 9 s immersion in pure acetone. (d) SWCNT/PVDF-TrFE (0.020 wt%) film after recycling and reprinting from pure acetone. The 0.200 wt% sample is shown in (b) and (c) for visual clarity. (e) Top, HIM micrograph of SWCNT/PVDF-TrFE (0.020 wt%) film printed from acetone/DMF. Bottom, recycled and reprinted film from pure acetone. (f) Top, PFM amplitude trace after application of voltage to the SWCNT/PVDF-TrFE (0.020 wt%) film printed from acetone/DMF. Bottom, recycled and reprinted film. (g) Voltage output under cyclic compression for a recycled and reprinted SWCNT/PVDF-TrFE (0.020 wt%) PEG, obtained with an input impedance at 10 M Ω . Scale bars in (a) and (d) correspond to 10 mm, scale bar in (e) corresponds to 10 μ m and scale bar in (f) corresponds to 1 μ m.153

Figure 4.8: Energy harvesting characteristics of a PEG fabricated from a recycled extrusion printed SWCNT/PVDF-TrFE (0.020 wt%) film under low-force cyclic compression using finger pinching, showing (a) the generated voltage as a function of time with a load resistance between 100 k Ω and 20 M Ω . (b) The V_{pp} as a function of load resistance. (c) The I_{pp} as a function of load resistance. (d) The P_D as a function of load resistance. (e) The generated voltage at 20 M Ω as a function of time, where the PEG was compressed and held for approximately 1.7 s prior to release. (f) The generated voltage stability (red) and the V_{pp} (blue) as a function of the number of compression cycles under a load resistance of 20 M Ω . (g) The charging and discharging profiles of capacitors under 3.5 Hz cyclic compression *via* a bridge rectifier.155

Figure 4.S1: Images showing the SWCNTs dispersed in acetone (60 vol%) and DMF (40 vol%) after 30 min bath ultrasonication, showing concentrations between 0.000 mg mL⁻¹ and 0.727 mg mL⁻¹, corresponding to SWCNT concentrations of between 0.000 wt% and 0.200 wt% relative to PVDF-TrFE. (a) Directly after ultrasonication in a bath sonicator. (b) 16 h after ultrasonication. (c) 27 h after ultrasonication. (d) 3 weeks after ultrasonication.166

Figure 4.S2: The viscosity of SWCNT/PVDF-TrFE (0.000 wt% to 0.200 wt%) inks as a function of shear rate.166

Figure 4.S3: The visible wavelength (380 nm < λ < 780 nm) transmittance of the SWCNT/PVDF-TrFE (between 0.000 wt% and 0.200 wt%) films, shown as the total reflectance within the integrating sphere.167

Figure 4.S4: The visible wavelength (380 nm < λ < 780 nm) transmittance at angles >2° of the SWCNT/PVDF-TrFE (between 0.000 wt% and 0.200 wt%) films, shown as the scattered reflectance within the integrating sphere.167

Figure 4.S5: The d_{33} values calculated using PFM at +10 V for the initial 3D printed SWCNT/PVDF-TrFE (0.000 wt% to 0.200 wt%) films (shown in red) and the SWCNT/PVDF-TrFE (0.020 wt%) film recycled and reprinted from acetone (shown in blue).168

Figure 4.S6: PFM lithography (a) A and (b) ϕ plots showing the data obtained for the extrusion printed 0.020 wt% SWCNT/PVDF-TrFE film (red) and the commercially available poled PVDF film (grey) (Measurement Specialties).168

Figure 4.S7: The V_{pp} of SWCNT/PVDF-TrFE (0.000 wt% to 0.500 wt%) PEGs, with error presented for three separate samples at each data point.	169
Figure 4.S8: Cyclic voltammetry (CV) for 3D printed SWCNT/PVDF-TrFE (0.000 wt% and 0.500 wt%) films. Inset shows the y-axis expanded to a maximum of 5×10^{-6} mA.	169
Figure 4.S9: The measured mass for SWCNT/PVDF-TrFE (between 0.000 wt% and 0.200 wt%) films.	170
Figure 4.S10: The volume and thickness calculated from Supplementary Figure 4.S9 for SWCNT/PVDF-TrFE (between 0.000 wt% and 0.200 wt%) films. The length and width of the films was 3 cm and density was 1.49 g cm^{-3} (75 mol% VDF and 25 mol% TrFE, 420 kDa, Solvay).	170
Figure 4.S11: The probability distribution of the angle, θ , between the F – C (blue lines) or the C – H (red lines) of the TrFE units and the CNT axis of symmetry having (a) armchair (8,8) and (b) zig-zag (12,0) chirality. The F – C and the C – H branches are mostly perpendicular to the CNT surface. The shaded regions represent the error bar obtained from three different MD simulations.	171
Figure 4.S12: The Raman spectra for the initial 3D printed SWCNT/PVDF-TrFE (0.020 wt%) film (grey line) and SWCNT/PVDF-TrFE (0.020 wt%) recycled and reprinted from acetone (blue line).	171
Figure 4.S13: The XRD spectra for the initial 3D printed SWCNT/PVDF-TrFE (0.020 wt%) film (grey line) and SWCNT/PVDF-TrFE (0.020 wt%) recycled and reprinted from acetone (blue line).	172
Figure 4.S14: The voltage as a function of time for a PEG made from commercially available poled PVDF film (grey) and a PEG made using the extrusion printed 0.020 wt% SWCNT/PVDF-TrFE film (red). Low force cyclic compression using a finger pinch was used, with a load resistance of 20 M Ω	172
Figure 4.S15: The density of the PVDF-TrFE melt at 230 °C as function of the co-polymer molecular weight obtained by MD simulations (symbols). Increasing the molecular weight leads to a slight increase in the co-polymer density which attains asymptotically a value of about 1.57 g cm^{-3} for molecular weights bigger than about 10,000 g mol $^{-1}$. The MD-obtained density is in excellent agreement with the	

experimental value provided by the PVDF-TrFE manufacturer (Solvay, horizontal broken line).173

Figure 5.1: Comparative MD simulations of the PVDF-TrFE co-polymer film polarisation on $\text{Ti}_3\text{C}_2\text{T}_x$ and graphene substrates. (a, b) The top view (left column) and side view (right column) snapshots at $t = 0$ ns, 0.5 ns, 1 ns and 1.5 ns, with the resultant dipole moment vectors (right column) of the PVDF-TrFE co-polymer film (blue arrow) and the (a) $\text{Ti}_3\text{C}_2\text{T}_x$ substrate or (b) graphene substrate. The annotated s and θ in a represent the separation of the fluoropolymer from the substrate and the PVDF-TrFE co-polymer dipole angle relative to the substrate, respectively. (c, d) Probability distributions of the angle (θ) between the dipole moment vector of the PVDF-TrFE co-polymer film layers and the (c) $\text{Ti}_3\text{C}_2\text{T}_x$ or (d) graphene substrates as a function of separation (s), as calculated from the equilibrated region of the obtained MD simulation.....186

Figure 5.2: SEA extrusion printing of strengthened $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE films. (a) Oscillatory γ_s sweep ($\omega = 1$ Hz) and (b) oscillatory ω sweep ($\gamma_s = 1\%$) of the 40 wt% PVDF-TrFE ink with and without 0.20 wt% $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. (c) The temporal evolution of the G' and G'' during σ_s cycling between 1 Pa (white regions, representing the stationary state) and 5 kPa (grey regions, representing printing stress). (d) Photograph showing the SEA extrusion printing process for the $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE (0.50 wt%) ink, scale bar 10 mm. Inset shows a self-supporting single filament. (e) Photograph of the free-standing $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE films at various $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet loadings (from left to right: 0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt% 0.50 wt%). Inset shows HIM image of $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE (0.50 wt%) film surface, demonstrating the distribution of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets near the surface of the film. Scale bar represents 40 μm . (f) Photograph demonstrating an interdigitated structure of 0.50 wt% $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE composite printed onto a flexible poly(ethylene terephthalate) (PET) substrate. (g) Tensile strain (γ_t)-stress (σ_t) profiles of the printed $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE films (shaded region shows the error from replicates). (h) The elastic region of (g). (i) The Young's modulus (E_t) obtained from (h) (overlay represents a 95% confidence interval).....189

Figure 5.3: Material characteristics of $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE films. (a) Raman spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE composites (at various $\text{Ti}_3\text{C}_2\text{T}_x$ loadings) and $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. (b) The β/γ phase ratio, I_β/I_γ , calculated from the intensities of the β

phase (840 cm^{-1}) and γ phase (811 cm^{-1}) from Raman confocal mapping (Supplementary Figure 5.S15). The dashed line represents a visual guide. (c) The effect of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet loading on the PVDF-TrFE co-polymer crystallinity, as measured by DSC. The dashed line is a visual guide (d) The Raman I_β/I_γ map of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) film, where the dark point corresponds to a large $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet at the film surface (red circle). The inset shows a confocal microscope image of the area analysed using Raman confocal mapping. Both scale bars represent $5\text{ }\mu\text{m}$. (e) The representative Raman spectra for the area designated by the black circle and the red circle in d, showing the clear inhibition of β phase locally at the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet surface.192

Figure 5.4: Polarisation and energy harvesting of $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ composites. (a) DART-PFM of a $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet on a gold-coated silicon (Au@Si) substrate, showing the topography (top), piezoelectric amplitude (middle) and piezoelectric phase (bottom) traces. Scale bar represents 200 nm . (b) PFM of $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt% and 0.50 wt%) SEA extrusion printed films, showing the piezoresponse ($A\cos(\varphi)/Q_f$) under an applied voltage between -20 V and $+20\text{ V}$. Scale bar represents $1\text{ }\mu\text{m}$. (c) The effective piezoelectric charge coefficient (d_{33}) calculated from the PFM data, including for solvent-cast PVDF-TrFE and $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) films as controls. (d-f) The macroscale energy harvesting characterisation of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.00 wt% and 0.50 wt%) SEA extrusion printed PEGs with input force (ΔF) at 10 N following a sinusoidal input signal. (d) The generated surface charge as a function of time for 60 compression cycles at 2 Hz . The horizontal dashed line represents the charge generated from completely polarised ($d_{33} = -38\text{ pC N}^{-1}$) PVDF-TrFE co-polymer for a PEG with similar dimensions. (e) The stability of the generated charge as a function of cycle count over 10,000 cycles for the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) PEG at 10 Hz and (f) the expanded initial, middle and end regions of the charge stability data in (e) showing 1 s of data (10 cycles) in each panel.195

Figure 5.S1: $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheet characterisation. (a) XRD pattern and SEM images (insets) of Ti_3AlC_2 MAX phase and $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets after etching. Scale bar for SEM of Ti_3AlC_2 represents $5\text{ }\mu\text{m}$ and that of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets represents $1\text{ }\mu\text{m}$. (b) TEM image of single-layer 2D $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. Scale bar represents 500 nm . (c) The DLS result showing the hydrodynamic size of the $\text{Ti}_3\text{C}_2\text{T}_x$

nanosheets in water. (d) AFM image of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets deposited on a silicon wafer. Inset, represents the thickness profile along the line indicated. Deconvolution of high-resolution XPS spectra for the (e) Ti 2p, (f) C 1s and (g) O 1s orbitals, showing the surface termination and state of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets.	206
Figure 5.S2: Photographs of the 35 wt% (left column), 40 wt% (middle column) and 45 wt% (right column) PVDF-TrFE/acetone inks, demonstrating the viscosity of the inks before rotating the vial to 45° (top row, $t = 0$ s), 1 s after rotating the vial (middle row) and 5 s after rotating the vial (bottom row).	208
Figure 5.S3: Comparison of the stability of the PVDF-TrFE ink (left), $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE ink (middle) and SWCNT/PVDF-TrFE ink (right), five months after preparation of the ink.	209
Figure 5.S4: Evolution of the density of the PVDF-TrFE co-polymer melt as a function of the number of monomers.	210
Figure 5.S5: Distribution of the local density (ρ) of the PVDF-TrFE co-polymer film (14 chains) as a function of the distance from the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet (red line) and the graphene sheet (black line) substrates.	211
Figure 5.S6: Probability distribution ($P(d)$) of the number of F (squares) and H atoms (triangles) within the PVDF-TrFE co-polymer film (14 chains) as a function of the distance from the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate (d). The shaded areas represent the minimum and maximum number of F and H atoms over the entire simulation. ..	212
Figure 5.S7: Bond angle distributions of the PVDF-TrFE co-polymer on the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate. (a) Probability distribution ($P(\theta)$) of the dihedral angles (θ) averaged over 4 ns for a film of 14 PVDF-TrFE chains interacting with an immobile $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet. (b) Time evolution of the fraction of the <i>trans</i> (black line) and <i>gauche</i> angles (red line).	213
Figure 5.S8: The temporal evolution of the fraction of <i>trans</i> bond angles (black lines) and <i>gauche</i> bond angles (red lines) in the 70-chain PVDF-TrFE co-polymer film on a $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate (thick lines) and graphene substrate (thin lines).	214
Figure 5.S9: Time evolution of the angle (θ) between the total dipole vector (polarisation) in the PVDF-TrFE co-polymer film and the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet basal plane, for	

PVDF-TrFE co-polymer chains that are within 24 Å (green line), 29 Å (blue line), 34 Å (blue line) and 39 Å (grey line) from the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate.....215

Figure 5.S10: Steady-state rheology. (a) The shear rate sweeps for inks of PVDF-TrFE/(DMF:acetone, 40:60 vol%) and PVDF-TrFE/acetone, containing PVDF-TrFE (35 wt%). (b) The applied shear rate profile as a function of time and (c) the resultant viscosity (η) for PVDF-TrFE/acetone inks with PVDF-TrFE concentration at 35 wt% and 45 wt%.....217

Figure 5.S11: Oscillatory rheology measurements on PVDF-TrFE/acetone inks. (a-c) The oscillatory ω sweeps for (a) 35 wt%, (b) 40 wt% and (c) 45 wt% PVDF-TrFE/acetone inks, obtained at fixed shear strain ($\gamma_s = 1\%$). (d-f) The oscillatory γ_s sweeps for (d) 35 wt%, (e) 40 wt% and (f) 45 wt% PVDF-TrFE/acetone inks, obtained at fixed frequency ($\omega = 1 \text{ Hz} \approx 6.28 \text{ rad s}^{-1}$).218

Figure 5.S12: Time-dependent oscillatory σ_s cycling for the PVDF-TrFE/acetone (35 wt%, 40 wt% and 45 wt%) inks. (a) The applied σ_s with the high stress regions shaded grey. (b) The $\tan(\delta)$ response to the shear stress with the liquid-solid transition point ($\tan(\delta) = 1$) represented by a solid grey line. (c) The η^* response to the shear stress. (d-f) The G' and G'' response to the shear stress for (d) 35 wt% PVDF-TrFE/acetone ink, (e) 40 wt% PVDF-TrFE/acetone ink and (f) 45 wt% PVDF-TrFE ink, performed with ω at 1 Hz.....220

Figure 5.S13: The experimental layout of the mechanical testing. (a) Photograph of the geometry of the tested samples, with markings representing the position of the grips. (b) Photograph showing the sample inserted into the grips prior to extension. (c) Photograph showing the extent of extension required to break the SEA extrusion printed pristine PVDF-TrFE co-polymer film. (d) Photograph showing the dependence of transparency on the extension rate, shown for the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE (0.10 wt%) film (top) and SEA extrusion printed pristine PVDF-TrFE co-polymer film (bottom).....221

Figure 5.S14: Optical properties of SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE (0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt% and 0.50 wt%) films. (a) The total light transmittance (T_t). (b) The scattered light transmittance (T_d), inset shows the scattered transmittance below 7%. (c) The transmittance and haze as a function of

Ti ₃ C ₂ T _x nanosheet concentration. (d) Side by side photograph showing the colour and transmittance of the films.	224
Figure 5.S15: The confocal Raman microscopy maps of the surface of the films, showing the intensity ratio (I_{β}/I_{γ}) between the β phase peak (842 cm ⁻¹) and γ phase peak (811 cm ⁻¹). (a) The SEA extrusion printed pristine PVDF-TrFE co-polymer film. (b) The SEA extrusion printed Ti ₃ C ₂ T _x /PVDF-TrFE (0.02 wt%) film. (c) The SEA extrusion printed Ti ₃ C ₂ T _x /PVDF-TrFE (0.10 wt%) film. (d) The SEA extrusion printed Ti ₃ C ₂ T _x /PVDF-TrFE (0.20 wt%) film. (e) The SEA extrusion printed Ti ₃ C ₂ T _x /PVDF-TrFE (0.50 wt%) film. (f) The solvent cast Ti ₃ C ₂ T _x /PVDF-TrFE (0.50 wt%) film.	226
Figure 5.S16: ATR-FTIR spectroscopy characterisation of SEA extrusion printed Ti ₃ C ₂ T _x /PVDF-TrFE (0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt% and 0.50 wt%) films. (a) The FTIR spectra, offset for clarity. (b) The relative fractions of the electroactive ($\beta + \gamma$) phases and the α phase as a function of Ti ₃ C ₂ T _x concentration.	227
Figure 5.S17: XRD spectra of the SEA extrusion printed Ti ₃ C ₂ T _x /PVDF-TrFE films. (a) Survey scan. (b) Phase fingerprint region. Spectra offset for clarity.	229
Figure 5.S18: XRD deconvolution for the phases in SEA extrusion printed films. (a) Pristine PVDF-TrFE copolymer. (b) Ti ₃ C ₂ T _x /PVDF-TrFE (0.02 wt%). (c) Ti ₃ C ₂ T _x /PVDF-TrFE (0.10 wt%). (d) Ti ₃ C ₂ T _x /PVDF-TrFE (0.20 wt%). (e) Ti ₃ C ₂ T _x /PVDF-TrFE (0.50 wt%). (f) Phase fractions determined from XRD as a function of Ti ₃ C ₂ T _x nanosheet concentration.	229
Figure 5.S19: DSC thermograms of the SEA extrusion printed Ti ₃ C ₂ T _x /PVDF-TrFE films, offset for clarity.	231
Figure 5.S20: DART-PFM maps of Ti ₃ C ₂ T _x nanosheets adsorbed on an Au-coated Si wafer. (a-c) The topography traces. (d-f) The piezoelectric phase (φ) traces. (g-i) The piezoelectric amplitude (A) traces. (a, d, g) Field of view corresponding to 5 μ m. Scale bar represents 1 μ m. (b, e, h) Field of view corresponding to 2 μ m. Scale bar represents 500 nm. (c, f, i) Field of view corresponding to 1 μ m. Scale bar represents 250 nm. The arrow in each panel points to the location of the same Ti ₃ C ₂ T _x nanosheet.	232

Figure 5.S21: Applied bias characteristics during the PFM measurements on the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ films. (a) Map of applied bias. Scale bar represents 1 μm . (b) Bias as a function of the x coordinate for a single line in the scan direction, which is signified by the dashed line in a.	233
Figure 5.S22: Raw PFM data obtained for the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ films. (a-e) The topography. (f-j) The piezoelectric phase (φ). (k-o) The piezoelectric amplitude (A). The data was obtained for (a, f, k) pristine PVDF-TrFE (0.00 wt% $\text{Ti}_3\text{C}_2\text{T}_x$), (b, g, l) $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.02 wt%), (c, h, m) $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.10 wt%), (d, i, n) $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.20 wt%), (e, j, o) $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%). The scale bar represents 1 μm	234
Figure 5.S23: Raw PFM data obtained for the solvent cast (a-c) pristine PVDF-TrFE and (d-f) $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) films. (a, d) The topography. (b, e) The piezoelectric phase (φ). (c, f) The piezoelectric amplitude (A).	235
Figure 5.S24: Processed PFM results as a function of the input bias (V) for the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ films. (a) The phase (φ). (b) The amplitude (A). (c) The $A\cos(\varphi)$. (d) The $A\cos(\varphi)/Q_f$	236
Figure 5.S25: Piezoelectric generator layout. (a) Schematic showing the layout of the electrodes and the wire attachment tabs on both surfaces of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ films. (b) Photograph of the layout of the laser-cut shadow mask, with sputter-coated SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) films as the active layer of the PEGs. Scale bar represents 2 cm. (c) Photograph showing the final SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) PEG. Scale bar represents 3 cm.	239
Figure 5.S26: Representative mechanical excitation input. (a) The input force (F) over 30 s with frequency at 2 Hz and (b) the enlarged view of the final 1 s. (c) The input stress (σ_3), calculated from a, with (d) the enlarged view of the final 1 s.	241
Figure 5.S27: Schematic showing the layout of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ PEG for energy harvesting tests.	242
Figure 5.S28: Schematic showing the side view of the components of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ PEG during energy harvesting characterisation.	243

Figure 5.S29: The generated electric displacement field (∂D_3) as a function of the input stress ($\partial \sigma_3$) for the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) PEG. The solid line represents a linear fit to the data and the band represents a 95% confidence interval.244

LIST OF ABBREVIATIONS AND ACRONYMS

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
AFM	Atomic force microscopy
ATR	Attenuated total reflectance
BTO	Barium titanate, BaTiO ₃
CNT	Carbon nanotube
CTFE	Chlorotrifluoroethylene
CV	Cyclic voltammetry
DART	Dual AC resonance tracking
DFT	Density functional theory
DLS	Dynamic light scattering
DMAc	<i>N,N</i> -dimethylacetamide
DMF	<i>N,N</i> -dimethylformamide
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
FE	Ferroelectric
FOM	Figure of merit
FTIR	Fourier transform infrared (spectroscopy)
G	<i>Gauche</i>
GO	Graphene oxide
hBN	Hexagonal boron nitride
HFP	Hexafluoropropylene
HIM	Helium ion microscopy

ID	Internal diameter
IL	Ionic liquid
KNLN	Potassium sodium lithium niobate, $[\text{KNaLi}]\text{NbO}_3$
KPM	Kelvin probe force microscopy
LAMMPS	Large-scale atomic/molecular massively parallel simulator
LAOS	Large amplitude oscillatory shear
LB	Langmuir-Blodgett
LCD	Liquid crystal display
LED	Light emitting diode
MAPS	Materials and processes simulations
MD	Molecular dynamics
MILD	Minimally intensive layer delamination
MRI	Magnetic resonance imaging
MWCNT	Multi-walled carbon nanotube
MXene	Transition metal carbide
NP	Nanoparticle
NMR	Nuclear magnetic resonance
NVP	Constant number of particles, volume and temperature
NW	Nanowire
PA66	Polyamide-66, nylon-66
PCFF	Polymer consistent force field
PDMS	Poly(dimethylsiloxane)
PE	Paraelectric
PEG	Piezoelectric generator, piezoelectric energy harvester
PET	Poly(ethylene terephthalate)
PFM	Piezoresponse force microscopy

PP	Poly(propylene)
PVDF	Poly(vinylidene fluoride)
PVDF-CTFE	Poly(vinylidene fluoride- <i>co</i> -chlorotrifluoroethylene)
PVDF-HFP	Poly(vinylidene fluoride- <i>co</i> -hexafluoropropylene)
PVDF-TrFE	Poly(vinylidene fluoride- <i>co</i> -trifluoroethylene)
PZT	Lead zirconium titanate, $\text{Pb}[\text{ZrTi}]\text{O}_3$
RAFT	Reversible addition-fragmentation chain-transfer (polymerisation)
rGO	Reduced graphene oxide
RMS	Root mean square
SA/V	Surface area to volume ratio
SAOS	Small amplitude oscillatory shear
SEA	Solvent evaporation-assisted (printing)
SEM	Scanning electron microscopy
SWCNT	Single-walled carbon nanotube
T	<i>Trans</i>
TEAM-FF	Transferable, extensible, accurate and modular force field
TEM	Transmission electron microscopy
TrFE	Trifluoroethylene
VCP	Voided charged polymer
VDF	Vinylidene fluoride
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffractometry

1 INTRODUCTION

The availability of electricity has proven to be one of the key drivers of productivity and industrialisation in the world.¹ The discovery of steam-powered electricity generation, driven by a turbine, has fuelled the so-called “second industrial revolution” and enabled the modernisation of humanity.² Indeed, at this point it is difficult to imagine a world without electronic devices. Despite the decades that have passed since this discovery, coal remains the primary fuel source, generating steam upon combustion to drive a turbine generator, although it is recognised as unsustainable from an environmental perspective.^{3,4}

Thus, novel methods of converting chemical or kinetic energy to electricity have been pursued to overcome the non-renewable nature of coal-based electricity generation, such as those based on water flow (hydroelectric), wind flow, nuclear reactions and photon-electron interactions (photovoltaic).⁴⁻⁶ The former three examples utilise a turbine-based approach akin to the coal power technique, albeit through more sustainable methods, and all four operate by exploiting dynamic processes, with an inherent finite lifespan. Moreover, these techniques, to harvest energy into electricity, are suited for large- and medium-scale installations, with limited applicability in the emerging small-scale electronic devices sector.⁶ These two key limitations are a roadblock to the miniaturisation of electronic devices, such as those implemented as part of the next industrial revolution, the so-called “Internet of Things”, whereby always-on devices are used for sensing, monitoring and improving quality of life.⁷

In order to power these personal-scale devices, which includes portable, wearable and implantable electronics, it is evident that the human body can act as a source of energy.⁸ Indeed, the energy consumption for such devices is low, especially in the case of sensing or intermittent data transfer, enabling alternative energy harvesting technologies.⁶ Multiple techniques have been proposed to achieve this conversion of energy, either by the kinetic energy of movements or by the stress arising from movements of the body.⁹ The harvesting of kinetic energy has been the primary method of operation in automatic watches, whereby a rotor is attached to the winding mechanism, with the rotation providing potential energy to a spring in order to operate the timekeeping mechanisms.¹⁰ In fact, this technique has been present from the late 18th century, predating the formulation of the scientific foundation for electricity.¹¹ Following the rise of electrical theory, however,

the notion of converting between mechanical stress and electrical energy is experimentally observed, termed piezoelectricity.¹² This finding is of great importance: in contrast to the aforementioned energy conversion techniques, piezoelectricity forgoes kinetic or chemical processes in order to convert energy, resulting in a non-degradable method to harvest mechanical energy.¹³

The piezoelectric effect possesses the reversible capability to convert between mechanical and electrical energy.¹⁴ Historically, the conversion of an applied electric field to a mechanical stress (converse piezoelectric effect) has been the catalyst of research efforts on piezoelectric materials and has resulted in tremendous commercial demand.¹⁵ During the manufacture of the piezoelectric materials, one of the key processing steps involves the application of a large electric field to the material, called electrical poling, which maximises the energy conversion efficiency of the material.^{16,17} Evidently, for the purposes of the converse piezoelectric effect, where an electric field will be applied to the material during the general course of use, this processing step is considered necessary and does not pose any drawbacks to the operation of the device. However, for the conversion of applied mechanical stress to electrical energy (direct piezoelectric effect), the requirement for electrical poling is a distinct limitation. In applications using the direct piezoelectric effect for energy harvesting, the piezoelectric device must take significantly less energy to produce than it is able to harvest over the device lifetime. As the poling process requires a tremendous amount of electrical energy, the ability of a piezoelectric device to harvest more energy than consumed during its fabrication is limited.¹⁶ Furthermore, this process is susceptible to dielectric breakdown at a high electric field, which forms conductive channels through the material between electrodes.¹⁸ Dielectric breakdown limits the maximum possible energy conversion efficiency in piezoelectric materials and leads to the failure of the piezoelectric device.¹⁹ Therefore, the process of maximising the energy conversion efficiency in piezoelectric materials must be revisited for the use as energy harvesting devices.

Piezoelectric polymers offer inherent advantages relative to ceramic materials for the purposes of personal-scale energy harvesting. Namely, fluoropolymers possess the highest piezoelectric energy conversion coefficients,²⁰ along with biocompatibility,²¹ optical transparency²² and mechanical flexibility. These semi-crystalline¹⁶ polymers can be

processed from the melt or solution,²³ allowing for facile deposition routes. The most common fluoropolymer, poly(vinylidene fluoride) (PVDF), has one major drawback when considered for energy harvesting applications: the solvent-based deposition method commonly results in a symmetric conformation of the polymer after solvent evaporation.¹⁷ Two separate methods have been employed to overcome this limitation, which involve either uniaxial stretching following deposition or the introduction of an additional monomer during the polymerisation step.²⁴ The former applies mechanical energy to transform the conformation of the polymer, while the latter displaces the symmetric conformation at the molecular scale.¹⁶ The copolymer technique to achieve piezoelectricity in fluoropolymers is beneficial, as it reduces the number of processing steps to produce an energy harvesting device, such as in the case of PVDF-TrFE. Therefore, in the case of PVDF-TrFE energy harvesters, the elimination of electrical poling can reduce the manufacturing pathway by two steps. These changes are anticipated to have profound effects in lowering the cost of manufacture and presenting a completely sustainable energy harvesting device for the purposes of powering personal-scale electronic devices.

Analogous to the second industrial revolution, which has resulted in new inventions based on the discovery of electricity, the ability to efficiently and sustainably harvest mechanical energy provides an opportunity to transform current technologies, as well as unlock new, unforeseen applications across a multitude of sectors. For example, obvious extensions of current technologies include the powering of portable and wearable electronics based on the mechanical stress imparted on the sole of a shoe or in the strap of a backpack while walking; the powering of medical electronic devices such as pacemakers from the beating motion of the heart or the movements of muscle tissue; and sensors possessing the inherent ability to deliver power to a logging or transmitting device, especially in enclosed environments such as within the human body.²⁴ The possible applications for this technology are rapidly evolving, with recent examples encompassing the fields of separation membranes,²⁵ catalysis,²⁶ photonics²⁷ and human-machine interfaces.²⁸ Thus, piezoelectric energy conversion, especially in polymeric materials, is a critical platform for the advancement of technology.

1.1 Thesis structure

This thesis focuses on the improvement of energy conversion efficiency in fluoropolymers towards the elimination of electrical poling. The parameters influencing the efficiency of fluoropolymer energy conversion materials are investigated and pathways to maximise the energy conversion efficiency are developed by facile mechanisms with a low input energy.

The second chapter of this thesis provides a thorough overview of piezoelectric theory and a critical review of literature on the aspects influencing the piezoelectricity in fluoropolymers, additionally elaborating on the progress in translating fluoropolymer energy conversion devices for applications in energy harvesting. The piezoelectric theory is derived from constitutive equations for elastic and dielectric materials, providing a physical origin for the piezoelectric coefficients. The physical and chemical properties of PVDF are detailed and compared to conventional piezoelectric materials, demonstrating the necessity for the use of fluoropolymers in emerging applications. The complete manufacture process for fluoropolymers is investigated, from polymerisation to packaging, in order to understand how the parameters of each step influence the energy conversion capabilities. In each step of manufacture, alternative techniques are analysed, such as copolymerisation, introduction of additives and alternative deposition and processing techniques. Finally, the possible applications are detailed in the wearable, implantable and environmental energy harvesting sectors.

The third chapter follows one particular emerging deposition technique briefly mentioned in chapter two, SEA 3D printing, as a low-temperature method to deposit PVDF-TrFE and induce energy conversion capabilities without poling. This chapter details the first report of a fluoropolymer printed from solution in the absence of additives and investigates the structure-property relationship in 3D printed PVDF-TrFE for energy harvesting applications. Here, the parameters surrounding the 3D printing technique are optimised *via* a systematic process. The PVDF-TrFE solution is printed to form a thin film as a substrate layer, with subsequent layers deposited in a raster pattern to achieve a high aspect ratio, investigating the optical, conformational and piezoelectric properties as a function of the layer number. The 3D printed PVDF-TrFE, which undergoes shear stress during the pressure driven extrusion process, is observed to convert mechanical energy to

electricity without poling, confirming the shear stress induces partial alignment of the dipoles within the polymer and gives rise to a net polarisation.

The fourth chapter introduces a nanoscale, non-piezoelectric additive to the process detailed in chapter three, in order to enhance the piezoelectric energy harvesting capabilities of PVDF-TrFE and understand the role of non-piezoelectric additives in the enhancement of piezoelectric coefficients. This chapter utilises SWCNTs as the model for a one-dimensional additive, which align parallel to the nozzle under shear. Furthermore, the conductivity of SWCNTs is hypothesised to reduce the piezoelectric efficiency in fluoropolymers; however, all prior research claims the carbon nanotubes act to increase the piezoelectric conformation fraction. The SWCNTs are incorporated into the PVDF-TrFE solution and 3D printed as free-standing films to reduce complexity. The optical, morphological, physical and piezoelectric properties are probed with varying SWCNT concentration in the PVDF-TrFE, finding negligible variation in the polymer crystallinity and conformation of PVDF-TrFE at concentrations below the percolation threshold of SWCNTs, contrary to the majority of prior literature. The piezoelectric properties, measured at the nanoscale by PFM and macroscale by imparting mechanical stress, were found to increase with increasing SWCNT loading up to 0.02 wt%. Notably, in the absence of crystallinity and conformation changes, the sole mechanism of piezoelectricity enhancement is the alignment of the dipoles in PVDF-TrFE, as the SWCNTs lack piezoelectricity. This phenomenon, referred to as dipole templating, is evident in both nanoscale and macroscale polarisation testing, and is confirmed by molecular dynamics simulations, observing a polarisation vector parallel to the length of the SWCNT. Furthermore, the PVDF-TrFE is discovered to be recyclable in acetone, eliminating the toxic and high boiling point solvent *N,N*-dimethylformamide (DMF), and allowing the composites to be recycled with no decrease in the polarisation of the polymer. These recycled films perform better than most electrically poled carbon nanotube-fluoropolymer composites reported in literature, exhibiting a generated power density of $70 \mu\text{W cm}^{-3}$ upon light finger tapping, with stable energy conversion characteristics for a minimum of 10,000 finger tapping cycles.

The fifth chapter extends the phenomenon of dipole templating and elucidates the origin of this observation *via* the substitution of SWCNTs for a tailored 2D additive. In this

study, the additive is chosen from the evolving class of MXene nanosheets, in particular $\text{Ti}_3\text{C}_2\text{T}_x$, due to its well understood surface chemistry, rigidity, out of plane polarisability and the lack of out of plane piezoelectricity. These $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE composites are 3D printed following the protocol set out in chapter three, albeit without DMF in the solvent. The PVDF-TrFE is found to form a stable physical gel at high concentrations in acetone and this solution prevents the restacking of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. The 3D printed composite films are flexible and robust, with a lower Young's modulus in comparison to previously reported PVDF-TrFE films, however an exceptional elongation at break $>1,000\%$. Importantly, a polarisation locking phenomenon is observed in PVDF-TrFE on a $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet during molecular dynamics simulations, attributed to strong electrostatic interactions at the interface. The polarisation vector of the PVDF-TrFE is locked perpendicular to the basal plane of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet during the initial femto-seconds and remains locked for the duration of the simulation. In contrast, a modelled graphene/PVDF-TrFE interface exhibits a time-dependent polarisation vector. The crystallinity and the piezoelectric conformation fraction of the prepared $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE composites are investigated, observing decreases at a low concentration of $\text{Ti}_3\text{C}_2\text{T}_x$, driven by densification of the polymer at the interface with the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet. Interestingly, the polarisation is found to increase at the nanoscale despite the suppression of the crystallinity and the piezoelectric conformation fraction, experimentally confirming the polarisation locking phenomenon. Furthermore, nanoscale polarisation measurements on solution cast composites result in an equal polarisation to the 3D printed films, implying the polarisation locking occurs in solution prior to printing and can be used with either deposition method. The macroscale polarisation measurements, which directly measure the generated surface charge from induced mechanical stress, find the composite films with 0.5 wt% $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets exhibit an approximately two-fold increase in the piezoelectric coefficient relative to 3D printed PVDF-TrFE films. Moreover, the piezoelectric charge coefficient of the composite film is greater than that of electrically poled PVDF-TrFE films, implying the polarisation locking technique is a viable alternative to electrical poling and that the dielectric breakdown limitation on the upper limit of the polarisation can be overcome by the interfacial templating and locking technique.

1.2 References

1. J. Chow, R. J. Kopp and P. R. Portney, Energy Resources and Global Development, *Science*, **302**, 1528–1531 (2003).
2. S. Chu and A. Majumdar, Opportunities and challenges for a sustainable energy future, *Nature*, **488**, 294–303 (2012).
3. P. C. Stern, K. B. Janda, M. A. Brown, L. Steg, E. L. Vine and L. Lutzenhiser, Opportunities and insights for reducing fossil fuel consumption by households and organizations, *Nature Energy*, **1**, 16043 (2016).
4. M. S. Dresselhaus and I. L. Thomas, Alternative energy technologies, *Nature*, **414**, 332–337 (2001).
5. M. Grätzel, Photoelectrochemical cells, *Nature*, **414**, 338–344 (2001).
6. Y. Bai, H. Jantunen and J. Juuti, Energy Harvesting Research: The Road From Single Source to Multisource, *Advanced Materials*, **30**, 1707271 (2018).
7. Y. Khan, A. E. Ostfeld, C. M. Lochner, A. Pierre and A. C. Arias, Monitoring of Vital Signs with Flexible and Wearable Medical Devices, *Advanced Materials*, **28**, 4373–4395 (2016).
8. J. M. Donelan, Q. Li, V. Naing, J. A. Hoffer, D. J. Weber and A. D. Kuo, Biomechanical energy harvesting: Generating electricity during walking with minimal user effort, *Science*, **319**, 807–810 (2008).
9. S. Roundy and S. Troler-Mckinstry, Materials and approaches for on-body energy harvesting, *MRS Bulletin*, **43**, 206–213 (2018).
10. D. Georges and L. Felipe, Self-winding watch movement, *US Patent*, US3412550A (1968).
11. A. Chapuis and E. Jaquet, *The History of the Self-Winding Watch 1770-1931*, Editions du Griffon, Neuchatel (1956).
12. J. Curie and P. Curie, Développement par compression de l'électricité polaire dans les cristaux hémiedres à faces inclinées, *Bulletin de la Société Française de Minéralogie et de Crystallographie*, **3**, 90–93 (1880).
13. Z. L. Wang, On Maxwell's displacement current for energy and sensors: the origin of nanogenerators, *Materials Today*, **20**, 74–82 (2017).
14. H. Fu and R. E. Cohen, Polarization rotation mechanism for ultrahigh electromechanical response in single-crystal piezoelectrics, *Nature*, **403**, 281–283 (2000).
15. W. Heywang, K. Lubitz and W. Wersing, *Piezoelectricity*, Springer, Berlin,

Heidelberg (2008).

16. A. J. Lovinger, Ferroelectric polymers, *Science*, **220**, 1115–1121 (1983).
17. M. M. D. Ramos, H. M. G. Correia and S. Lanceros-Méndez, Atomistic modelling of processes involved in poling of PVDF, *Computational Materials Science*, **33**, 230–236 (2005).
18. I. Souza, J. Íñiguez and D. Vanderbilt, First-Principles Approach to Insulators in Finite Electric Fields, *Physical Review Letters*, **89**, 117602 (2002).
19. Z. Suo, Models for breakdown-resistant dielectric and ferroelectric ceramics, *Journal of the Mechanics and Physics of Solids*, **41**, 1155–1176 (1993).
20. D. B. Deutz, J. A. Pascoe, B. Schelen, S. van der Zwaag, D. M. de Leeuw and P. Groen, Analysis and experimental validation of the figure of merit for piezoelectric energy harvesters, *Materials Horizons*, **5**, 444–453 (2018).
21. J. Li, L. Kang, Y. Yu, Y. Long, J. J. Jeffery, W. Cai and X. Wang, Study of long-term biocompatibility and bio-safety of implantable nanogenerators, *Nano Energy*, **51**, 728–735 (2018).
22. M. Li, I. Katsouras, C. Piliego, G. Glasser, I. Lieberwirth, P. W. M. Blom and D. M. de Leeuw, Controlling the microstructure of poly(vinylidene-fluoride) (PVDF) thin films for microelectronics, *Journal of Materials Chemistry C*, **1**, 7695–7702 (2013).
23. P. Martins, A. C. Lopes and S. Lanceros-Mendez, Electroactive phases of poly(vinylidene fluoride): Determination, processing and applications, *Progress in Polymer Science*, **39**, 683–706 (2014).
24. N. A. Shepelin, A. M. Glushenkov, V. C. Lussini, P. J. Fox, G. W. Dicinoski, J. G. Shapter and A. V. Ellis, New developments in composites, copolymer technologies and processing techniques for flexible fluoropolymer piezoelectric generators for efficient energy harvesting, *Energy & Environmental Science*, **12**, 1143–1176 (2019).
25. M. T. Darestani, H. G. L. Coster and T. C. Chilcott, Piezoelectric membranes for separation processes: Operating conditions and filtration performance, *Journal of Membrane Science*, **435**, 226–232 (2013).
26. Y. Wang, X. Wen, Y. Jia, M. Huang, F. Wang, X. Zhang, Y. Bai, G. Yuan and Y. Wang, Piezo-catalysis for nondestructive tooth whitening, *Nature Communications*, **11**, 1328 (2020).
27. J. Hao and C. N. Xu, Piezophotonics: From fundamentals and materials to applications, *MRS Bulletin*, **43**, 965–969 (2018).

28. M. Han, H. Wang, Y. Yang, C. Liang, W. Bai, Z. Yan, H. Li, Y. Xue, X. Wang, B. Akar, H. Zhao, H. Luan, J. Lim, I. Kandela, G. A. Ameer, Y. Zhang, Y. Huang and J. A. Rogers, Three-dimensional piezoelectric polymer microsystems for vibrational energy harvesting, robotic interfaces and biomedical implants, *Nature Electronics*, **2**, 26–35 (2019).

2 FUNDAMENTALS OF PIEZOELECTRIC PHENOMENA IN FLUOROPOLYMERS

The information presented in this chapter has been published as:

Nick A. Shepelin, Alexey M. Glushenkov, Vanessa C. Lussini, Phillip J. Fox, Greg W. Dicinoski, Joseph G. Shapter and Amanda V. Ellis, New developments in composites, copolymer technologies for flexible fluoropolymer piezoelectric generators for efficient energy harvesting, *Energy & Environmental Science*, **12**, 1143-1176 (2019).

2.1 Abstract

Flexible piezoelectric generators (PEGs) have recently attracted significant interest, as they are able to harvest mechanical energy and convert it to electricity, decreasing reliance on conventional energy sources. These devices enable innovative applications including smart clothing, wearable electronics, on-skin and implantable sensors, as well as harvesting energy from the movement of vehicles, water and wind. PVDF and related fluoropolymers are the most common flexible piezoelectric materials, widely utilised for their high electromechanical conversion efficiencies, optimal mechanical flexibility, processability and biocompatibility. This critical review covers the processing of fluoropolymers towards the maximisation of piezoelectric conversion parameters. Particular emphasis is placed on the correlation between synthetic routes, inclusion of further co-monomers, addition of additives and nanomaterials, as well as processing techniques and the optimised electricity generation in the resultant PEGs, providing an important analysis to complement existing literature. The importance of novel polymer deposition techniques, which reduce reliance on the conventional, highly energetic post-processing steps, are highlighted. Recent advances in fluoropolymer-based flexible PEGs open an array of exciting applications, which rapidly progress towards commercialisation. This review provides a timely analysis of this increasingly important field to the cross-disciplinary community of polymer chemists, materials scientists, nanotechnologists, engineers, and industry practitioners.

2.2 Introduction

Harvesting energy into a usable form through sustainable methods is gaining importance for portable and wearable electronics and sensors. According to the requirements of portable electronic devices and in-line with the trend of miniaturisation of wearable electronics, conversion of energy to electricity from a number of sources is possible.^{1, 2} Sustainable electrical generators have been proposed which utilise solar, thermal and mechanical energies. Photovoltaic generators produce useable energy from sunlight, with experimental power conversion efficiencies up to 13% in flexible and organic solar cells; however, they are limited to daytime operation for conversion and require large areas continuously exposed to direct sunlight.^{3, 4} Commercialisation of photovoltaics as electrical

generators has occurred, and solar cells are currently regarded as the most prominent source of small-scale sustainable energy in industry.⁵

Pyroelectric generators that harvest electricity from changes in temperature have been proposed. The power efficiency of these devices is typically below 3% at temperatures near 25 °C and they possess a slow electrical output response.⁶ The advantage of these types of harvesters is that they can be used in environments where significant and frequent temperature changes occur. Bowen *et al.*⁷ provide a recent in-depth review of pyroelectric generators.

Scavenging mechanical energy through piezoelectricity is a prospective solution due to high energy conversion efficiencies up to 75% in inorganic materials and 37% in fluoropolymers.⁸⁻¹¹ These systems are broadly referred to as PEGs and are the topic of this review.

Piezoelectricity occurs in crystalline dielectric materials possessing a dipole moment. The concept of electromechanical coupling through piezoelectricity has been proposed and experimentally verified in the nineteenth century by Curie *et al.*^{12, 13} and Lippmann¹⁴. During the first half of the twentieth century, piezoelectric materials have found limited industrial uses in sensors and actuators.¹⁵⁻¹⁷ However, in 1961 Sonus Corporation patented the first energy harvesters using PEGs.¹⁸ The electric output from the induced strain through stretching, bending or compression of piezoelectric materials has been shown to power electrical items, such as light emitting diodes (LEDs), liquid crystal displays (LCDs), MP3 players, and sensors.¹⁹⁻²⁴ This ability to generate electricity through the use of PEGs has the potential to supplement the use of batteries or remove them in some applications where only intermittent power is required.

Piezoelectric materials span from naturally-found crystals to synthetic ceramics, polymers and nanostructured metal oxides.²⁵ Early literature has focused solely on the transduction mechanism in quartz, Rochelle salt, and other naturally-occurring anisotropic crystals.^{12, 26}

The ability to fabricate advanced inorganic structures led to the development of perovskites showing enhanced piezoelectricity due to the polarisation of the central atom within the unit cell.^{27, 28} A class of synthetic polymers with a dipole moment perpendicular to the backbone have since gained attention as flexible piezoelectric materials, enabling the utilisation of flexible and biocompatible PEGs in wearable electronics and *in-vivo* sensors.^{29, 30} Recent advances have incorporated into these polymers nanostructured perovskites and inorganic oxides in the form of nanoparticles and nanowires. The incorporation of these nanofillers has shown promise in increasing the electrical output of flexible PEGs.³¹⁻³⁵

Polymers, in comparison to ceramic materials, tend to exhibit a variety of properties beneficial for uses as PEGs. The 2014 review by Ramadan *et al.*¹¹ has comparatively analysed the benefits of piezoelectric polymers and their composites relative to common inorganic materials, suggesting their enhanced mechanical flexibility, lower costs and increased ease of production, as well as biocompatibility for uses such as implantable or wearable sensors. Through tailored processing parameters, piezoelectric polymers have shown high optical transparency and low haze, leading to potential applications in capacitive touch sensors as a top layer on LED displays.³⁶⁻³⁸ Recent utilisation of nanomaterials and fillers has been reported to increase electromechanical coupling efficiencies of piezoelectric polymers, with the potential of retaining optical transparency, leading to highly efficient flexible and transparent PEGs.^{39, 40}

PVDF and related fluoropolymers are the most common commercialised piezoelectric polymers.^{41, 42} These polymers are stable at room temperature, simple to process using conventional solvent casting and melt-extrusion techniques, chemically inert, biocompatible and exhibit conversion efficiencies higher than those of other piezoelectric polymers.^{11, 43} These properties make fluoropolymers ideal for use as sustainable electrical generators for powering portable, wearable and implantable sensors and electrical devices, with or without an integrated energy storage solution.

This review is focused on the factors influencing the electrical output in flexible piezoelectric PVDF-based fluoropolymers and how these factors can be controlled to maximise energy conversion, providing a critical analysis of the recent literature on polymerisation

and processing techniques and parameters, as well as device geometries. The theory of piezoelectricity in materials and the operating principles of PEGs are introduced first. The synthesis of PVDF and related fluoropolymers is subsequently discussed with reference to literature and a special focus on decreasing defects, increasing the electroactive phase fractions and the optimisation of electromechanical conversion efficiencies. The latest developments in processing of fluoropolymers, such as 3D printing and electrospinning, are reviewed next, and their potential in manufacturing PEGs is discussed and compared to conventional techniques including solvent casting, melt extrusion, and melt-drawing. The inclusion of nanofillers and additives into the polymers is presented as a preferred single-step method to reorient polymer chains, superior to conventional, high-energy multi-step processes. This review highlights the on-going evolution of the field and aims to identify future directions towards the development of commercially relevant low-energy processing methods to produce PVDF-based PEGs.

2.3 Metrics and definitions for piezoelectric materials

This first section looks at the phenomena in piezoelectric materials and the mathematical toolkit used to describe them. Unlike non-piezoelectric dielectrics, a net dipole moment is present in piezoelectric materials in the absence of external stimuli. When a force is applied, an instantaneous electric field is generated parallel to the direction of the polarisation vector. Under finite load resistance conditions, this electric field is proportional to the time-differential of applied mechanical stress and leads to separation of positive and negative surface charges on the opposite surfaces of the material, with a fast response time. When an external load is connected to electrodes deposited on the opposing surfaces, the surface charges force electron migration across the load to neutralise the potential difference between the electrodes. The behaviour of piezoelectric materials and the aforementioned transient phenomena are described by directional coefficients and a number of mathematical equations. This part will focus on the discussion of the mathematical foundation of piezoelectricity in materials.

It is widely accepted that all linear elastic materials exhibit a displacement (x) with applied force (F), related by a spring constant (k). This relationship is known as Hooke's law.^{44, 45} This equation is given for the simplest one-dimensional scenario in Equation (2.1).

$$F = kx \quad (2.1)$$

Strain (S) and stress (T) are related by a similar equation with elastic compliance (s) as a proportionality coefficient. In the simplest, one-dimensional case, Equation (2.2) applies.

$$S = sT \quad (2.2)$$

Furthermore, dielectric elastic materials are polarisable when placed under an external electric field. The constitutive equation for such materials is given in Equation (2.3).

$$D = \varepsilon E \quad (2.3)$$

In this equation, the electric displacement (D) depends on the permittivity (ε) of the material and the applied electric field (E). In piezoelectric materials, the properties described in Equation (2.2) and Equation (2.3) are interrelated and the following Equation (2.4) and Equation (2.5) can be written in a one-dimensional situation.

$$S = s^E T + d^t E \quad (2.4)$$

$$D = dT + \varepsilon^T E \quad (2.5)$$

Here, the relationship coefficient (d) is termed as the piezoelectric charge coefficient, d^t is the piezoelectric charge coefficient for the case of the inverse piezoelectric effect, and superscripts E and T refer to constant electric field and stress, respectively.

In reality, to describe piezoelectric phenomena, one should consider the descriptions of the processes in three dimensions. In particular, the requirement for piezoelectricity is a net dipole moment oriented along one direction of the material in question. To aid understanding, the directionality used in defining piezoelectric properties is shown in Figure 2.1. Note that rotational directions 4, 5, and 6 are also introduced when directionality is considered in three dimensions. For the clarity of presentation, let us assume that this direction coincides with the z axis (Figure 2.1, direction 3). In such a case, piezoelectric properties in x (1) and y (2) directions (Figure 2.1, directions 1 and 2) can be considered identical and that of the 3 direction is non-equivalent relative to the others. Taking into account the anisotropy of piezoelectric materials, Equation (2.4) and Equation (2.5) take on the form shown in Equation (2.6) and Equation (2.7), where the constituents are replaced with their tensor analogues.

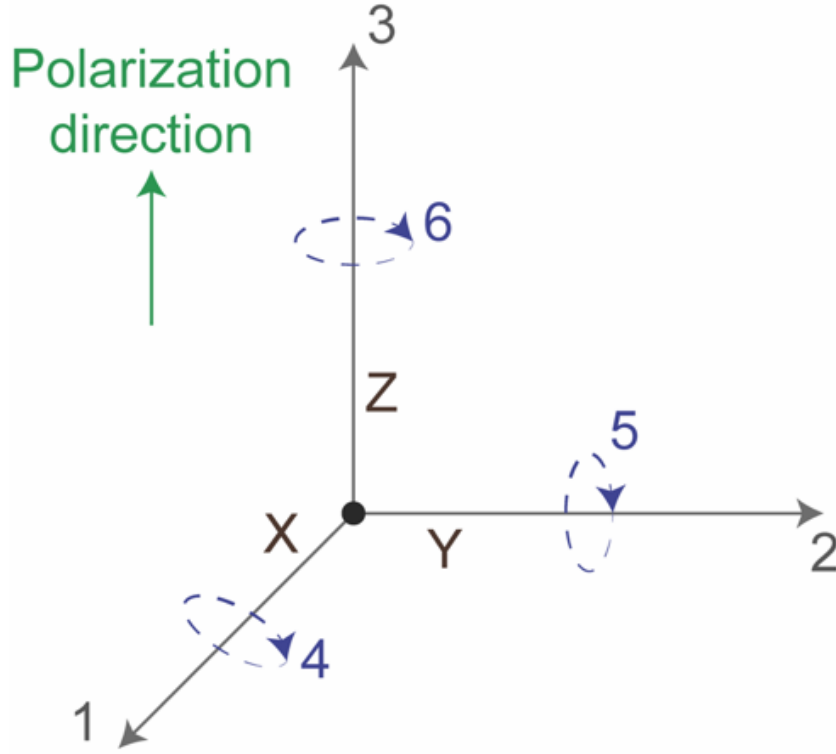


Figure 2.1: Schematic of reference directions for piezoelectric materials.

$$S_p = s_{pq}^E T_q + d_{ip} E_i \quad (2.6)$$

$$D_i = d_{iq} T_q + \varepsilon_{ik}^T E_k \quad (2.7)$$

In this form, subscripts i and k represent directions 1, 2 or 3, and p and q represent directions 1, 2, 3, 4, 5 or 6. When expanded, the equations form a matrix relating strain, stress, electric displacement and electric field, as shown in Equation (2.8).

$$\begin{pmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \\ D_1 \\ D_2 \\ D_3 \end{pmatrix} = \begin{pmatrix} S_{11} \\ S_{22} \\ S_{33} \\ 2S_{23} \\ 2S_{13} \\ 2S_{12} \\ D_1 \\ D_2 \\ D_3 \end{pmatrix} = \begin{pmatrix} s_{11}^E & s_{12}^E & s_{13}^E & 0 & 0 & 0 & 0 & 0 & d_{31} \\ s_{21}^E & s_{22}^E & s_{23}^E & 0 & 0 & 0 & 0 & 0 & d_{32} \\ s_{31}^E & s_{32}^E & s_{33}^E & 0 & 0 & 0 & 0 & 0 & d_{33} \\ 0 & 0 & 0 & s_{44}^E & 0 & 0 & 0 & d_{24} & 0 \\ 0 & 0 & 0 & 0 & s_{55}^E & 0 & d_{15} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & s_{66}^E & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{15} & 0 & \varepsilon_{11}^T & 0 & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 & 0 & \varepsilon_{22}^T & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 & 0 & 0 & \varepsilon_{33}^T \end{pmatrix} \begin{pmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \\ E_1 \\ E_2 \\ E_3 \end{pmatrix} \quad (2.8)$$

Here, the values for p and q are used to simplify indices according to the following rules: $1 \Rightarrow 11$, $2 \Rightarrow 22$, $3 \Rightarrow 33$, $4 \Rightarrow 23 \equiv 32$, $5 \Rightarrow 13 \equiv 31$ and $6 \Rightarrow 12 \equiv 21$.⁴⁶⁻⁴⁸ One of the alternate forms

of the constitutive equations is given using the piezoelectric voltage coefficient (g) (as opposed to the piezoelectric charge coefficient), shown in Equation (2.9) and Equation (2.10).

$$S_p = s_{pq}^D T_q + g_{ip} D_i \quad (2.9)$$

$$E_i = -g_{iq} T_q + \beta_{ik}^T D_k \quad (2.10)$$

Here, the mechanical compliance (s^D) at constant electric displacement is related to s^E by $s^D = s^E - d^2/\epsilon^T$ and the impermeability at constant stress (β^T) is the inverse of ϵ^T . Furthermore, it should be noted that g and d are related via $g = d/\epsilon^T$.⁴⁷

The equations for displacement current (J_D), open circuit voltage (V_{OC}) and current transport were discussed in a recent review by Wang⁴⁹ based on Ampere's circuital law with Maxwell's addition. The displacement current as postulated by Maxwell is shown in Equation (2.11), formulated to supplement Ampere's law for magnetic fields with regards to contribution from electric charges. This equation is a differential form of Equation (2.3) for dielectric materials with respect to time.

$$J_D = \frac{\partial D}{\partial t} = \epsilon \frac{\partial E}{\partial t} + \frac{\partial P}{\partial t} \quad (2.11)$$

The displacement current is noted to be a time-dependent electric field for either vacuum (utilising $\epsilon = \epsilon_0$, the permittivity of vacuum) or alternate media such as a dielectric material, rather than the conventional definition of current utilising the movement of charges. The reason for this distinction arises from the second term in Equation (2.11), the time-dependent dielectric polarisation within the material ($\partial P/\partial t$). Since $P_i = d_{iq} T_q$ (rearranged from Equation (2.7)), the displacement current arising from polarisation of the material is shown in Equation (2.12).

$$J_D = \frac{\partial P_i}{\partial t} = d_{iq} \left(\frac{\partial T}{\partial t} \right)_q = h_{iq} \left(\frac{\partial S}{\partial t} \right)_q \quad (2.12)$$

Here, the piezoelectric coefficient is $h_{iq} = d_{iq}/(s_{pq}^E \epsilon_{ik}^T)$. Equation (2.12) suggests that the output arises from a time-dependent variation of strain, proportional to a time-dependent variation of the polarisation vector. Furthermore, the equations for V_{OC} and the current

transport for piezoelectric materials with electrodes attached across the thickness axis are given in Equation (2.13) and Equation (2.14), respectively.

$$V_{OC} = \frac{l_3 \sigma_m(l_3)}{\epsilon_{33}} \quad (2.13)$$

$$RA \left(\frac{d\sigma}{dt} \right) = \frac{l_3 (\sigma_m(l_3) - \sigma_e(l_3))}{\epsilon_{33}} \quad (2.14)$$

Here, l_3 represents thickness of the piezoelectric material (also the distance between electrodes), ϵ_{33} represents permittivity of the piezoelectric material, $\sigma_m(l_3)$ is the density of piezoelectric charges on the surface of the material, $\sigma_e(l_3)$ is the charge density of mobile electrons within the electrodes, A is the surface area of electrodes and R is the resistance of the attached external load. Equation (2.13) suggests a direct relationship between V_{OC} and thickness, as well as an inverse relationship with the dielectric constant—implying a material with lower ϵ_{33} such as a fluoropolymer can exhibit higher open circuit voltage relative to ceramic materials. Furthermore, Equation (2.14) implies dependence of the time-dependent current transport on the load resistance and electrode properties.

The transport phenomena in Equation (2.12), Equation (2.13) and Equation (2.14) explain the operational principles in PEGs, whereby factors such as strain, time-dependent strain rate, directionality of strain, thickness of material, dipolar strength, anisotropic dielectric permittivity of the piezoelectric material, quality and surface area of the electrode can all play a role in the development of efficient PEGs.

For the indiscriminate comparative analysis of piezoelectric materials used in PEGs, a figure of merit (FOM) is required. For a long time, the electromechanical coupling coefficient k^2 has been considered as the non-biased FOM, as shown for the 33 directionality in Equation (2.15).⁵⁰

$$k_{33}^2 = \frac{\text{stored electrical energy}}{\text{input mechanical energy}} = \frac{d_{33}^2}{s_{33}^E \epsilon_{33}^T} \quad (2.15)$$

The relationship between the piezoelectric charge (d) and voltage (g) coefficients, as shown above, is $d_{33} = g_{33} / \epsilon_{33}^T$, allowing Equation (2.15) to be expressed as a function of both coefficients. Furthermore, the Young's modulus of a material, defined as the ratio

of stress and strain (T/S) from Equation (2.2), is inversely proportional to the mechanical compliance at constant electric field (s^E). Hence, the coupling coefficient relationship from Equation (2.15) then takes on the form shown in Equation (2.16).

$$k_{33}^2 = d_{33}g_{33}Y_3 \quad (2.16)$$

Recently, Deutz *et al.*⁵¹ have investigated the FOM for a variety of piezoelectric materials, suggesting that the k^2 value does not consistently represent the stored electrical energy per unit volume (U_{open}) in the sample. They have proposed that U_{open} scales linearly with the product of the charge and the voltage coefficients, shown in Equation (2.17) and Figure 2.2.

$$U_{open} = \frac{1}{2}d_{33}g_{33}\left(\frac{\Delta F}{A_e}\right)^2 \quad (2.17)$$

Here, the ΔF denotes the input force amplitude and A_e stands for the electrode area. This research has verified the proposed model using a purpose-built electrometer (Figure 2.2a, b) and measuring U_{open} as a function of $d_{33}g_{33}$ (Figure 2.2c) for a range of piezoelectric materials including perovskites, fluoropolymers and perovskite-polymer composites. The study has shown good agreement for varying materials (Figure 2.2c-e), varying $g_{33}d_{33}$ (Figure 2.2c) and varying applied force (Figure 2.2d). The relationship in Equation (2.17) has been argued to describe the electromechanical conversion in all piezoelectric materials irrespective of their composition, morphology or geometry. It is also noted to be independent of the elastic compliance, unlike the equation for the k^2 coefficient. In previous literature, the piezoelectric ceramics have been reported with significantly higher k^2 relative to flexible polymeric materials. The use of $d_{33}g_{33}$ as an unbiased FOM suggests that flexible materials are highly effective in their use as PEGs.

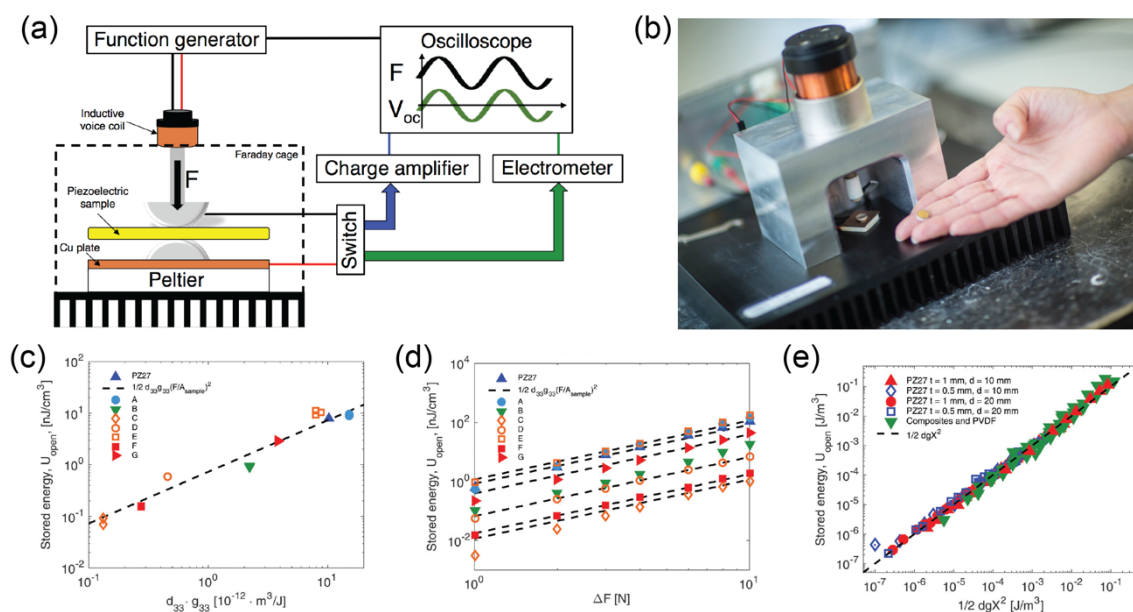


Figure 2.2: Experimental layout and verification of the piezoelectric FOM. (a) Schematic showing the layout of the purpose-built electrometer for precise mechanical deformation and the subsequent collection of data and (b) a photograph showing the experimental layout. (c) The stored energy plotted as a function of the FOM $g_{33}d_{33}$ for a range of piezoelectric materials including lead zirconate titanate (PZ27, PZT), PZT 1-3 fibre composite in epoxy (A), β phase PVDF (B), randomly distributed 0-3 particle composites from PZT (C, D) and lithium sodium potassium niobate in PDMS (E, KNLN), 1-3 dielectrophoretically aligned particle composites using PZT (F) and KNLN (E). (d) shows the dependence of U_{open} on the input force for the perovskite, fluoropolymer and perovskite-polymer composites and (e) shows the agreement between the model and experimental data for all samples. The modelled data is represented as the black dashed black line in (c-e). Reproduced with permission from ref 51. Copyright 2018, Royal Society of Chemistry.

2.4 Properties of PVDF

Among the variety of materials exhibiting piezoelectricity, polymers are of interest due to several enhanced properties desirable in flexible PEGs, such as the ability to deform, ease of processing and low dielectric constant. In particular, polymers possessing a dipole moment perpendicular to the backbone have been found to exhibit piezoelectric properties.⁵² This phenomenon is particularly evident in fluorinated polymers such as PVDF, whereby two fluorine atoms are attached to every second carbon atom along a vinyl

backbone (Figure 2.3a-c). If the fluorine atoms are arranged a certain way, the chain substituents orient in a manner that shows an effective dipole perpendicular to the chain.⁹ This is described further in the following section. PVDF and its co-polymers remain the most interesting and widely researched polymeric materials for flexible PEGs.

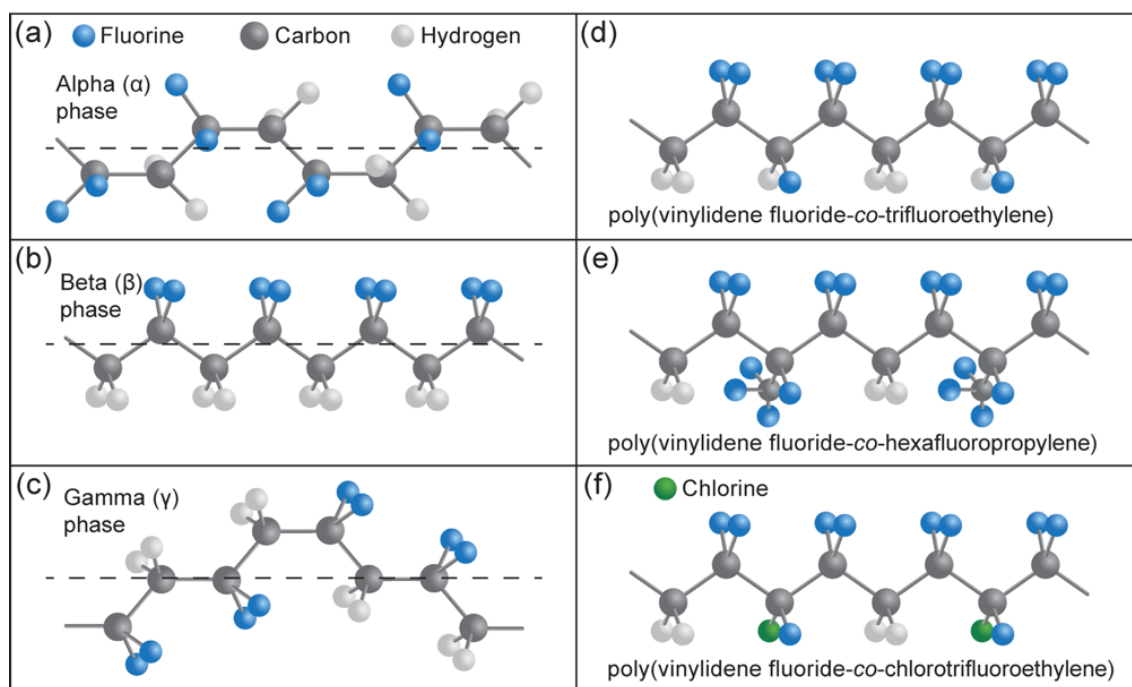


Figure 2.3: Chemical structure of (a) alpha phase, (b) beta phase and (c) gamma phase conformations of PVDF, as well as the chemical structure of (d) PVDF-TrFE, (e) poly(vinylidene fluoride-co-hexafluoropropylene) and (f) poly(vinylidene fluoride-co-chlorotrifluoroethylene).

2.4.1 β phase as the preferred structural orientation and its electromechanical coupling properties

The properties of PVDF are influenced directly by its structure. It is a semi-crystalline polymer with properties dependent on the phase.⁵³ The polymer has been found in five distinct phases, known as α , β , γ , δ and ϵ .^{54, 55} Of those, the α and β phases are the most commonly found. The γ phase is a transitional state between α and β and therefore not as common.⁴³ The other phases, δ and ϵ , are more difficult to isolate and not generally found through conventional processing techniques.⁵⁵

The α phase of PVDF has a *trans-gauche* conformation (TGTG') (Figure 2.3a), and hence is non-polar. The β phase consists of all-*trans* conformation (TTTT) (Figure 2.3b) meaning the majority of fluorine atoms are separated from hydrogen atoms and hence it possesses a dipole moment perpendicular to the polymer chain (7.0×10^{-30} C m).⁵⁶ The third type of chain orientation is the γ phase (Figure 2.3c). This orientation is a transitional structure between the α and β phases and hence shows a smaller dipole moment than that of the β phase.⁵⁷ This can be explained by its structure, taking on a *trans-gauche* conformation with a higher *trans* fraction (TTTGTTTG'). Thus, of all the chain orientations in PDVF, the β phase shows the highest net dipole moment, suggesting the necessity to increase its proportion within the material to maximise the electrical output of a PVDF-based PEG.

The presence of a dipole moment in the 3 direction of β -PVDF, in combination with the material acting as a dielectric material, allows this fluoropolymer to exhibit electromechanical coupling. As shown in Equation (2.8) in the previous section, the contribution of surface charge to electromechanical coupling is dependent on the d_{ip} coefficients, which have been reported in literature for β -PVDF for all three directions of strain. However, discrepancies between the magnitude of values in literature are observed, generally attributed to a varying degree of β phase purity within the polymer, the temperature at which values were obtained and the thickness of the measured film.

Table 2.1 shows the reported values for d_{ip} in β -PVDF for $i = 3$ and $p = 1, 2, 3$. Here, it is assumed that the polarisation vector is parallel to the 3 direction, the electrodes are attached across the 3 direction, i.e., along the surfaces of the films with the highest area, and p accounts for the compressive and longitudinal strains along directions 1, 2 and 3. It has been shown that the d_{33} charge coefficient is the largest due to the compression of the dipole vector directly, whereas d_{31} is smaller as the stretching occurs along the polymer chain orientation axis (indirectly compressing the distance between dipoles). The smallest values are observed for d_{32} because it corresponds to the increase of the distance between polymer chains with low compressibility of the dipole.⁴⁵

Table 2.1: Selected piezoelectric charge coefficients for PVDF

Piezoelectric charge coefficient	Experimentally obtained values (pC N ⁻¹)	References
d_{31}	6-20	45, 58
d_{32}	1-4	45, 58
d_{33}	13-28	11, 59-61

The charge coefficient is further dependent on the temperature of the sample, which affects the compressibility of the dipole. Figure 2.4a shows the relationship of the coefficient and temperature. The study by Destruel *et al.*⁵⁸ has found a direct relationship between d_{ip} and temperature, which can be attributed to the chain mobility of the polymer, allowing for a greater net dipole moment change. It is further accepted that the coefficients reduce to zero at the Curie temperature (T_C); therefore, at ambient conditions, PVDF exhibits piezoelectric properties in all deformation directions. This attribute is essential, as the strain cannot be isolated to a single direction in applications related to portable and implantable electronics.

The electromechanical energy coupling coefficients k_{ip} for $i = 3$ and their temperature dependence are shown in Figure 2.4b.⁵⁸ Experiments have suggested the coupling factor remains constant between -20 °C and 60 °C when strain is applied in directions 2 and 3. Conversely, an increase in the coupling factor has been observed for the case of strain applied in direction 1 as a function of increasing temperature, deviating from the other directions.

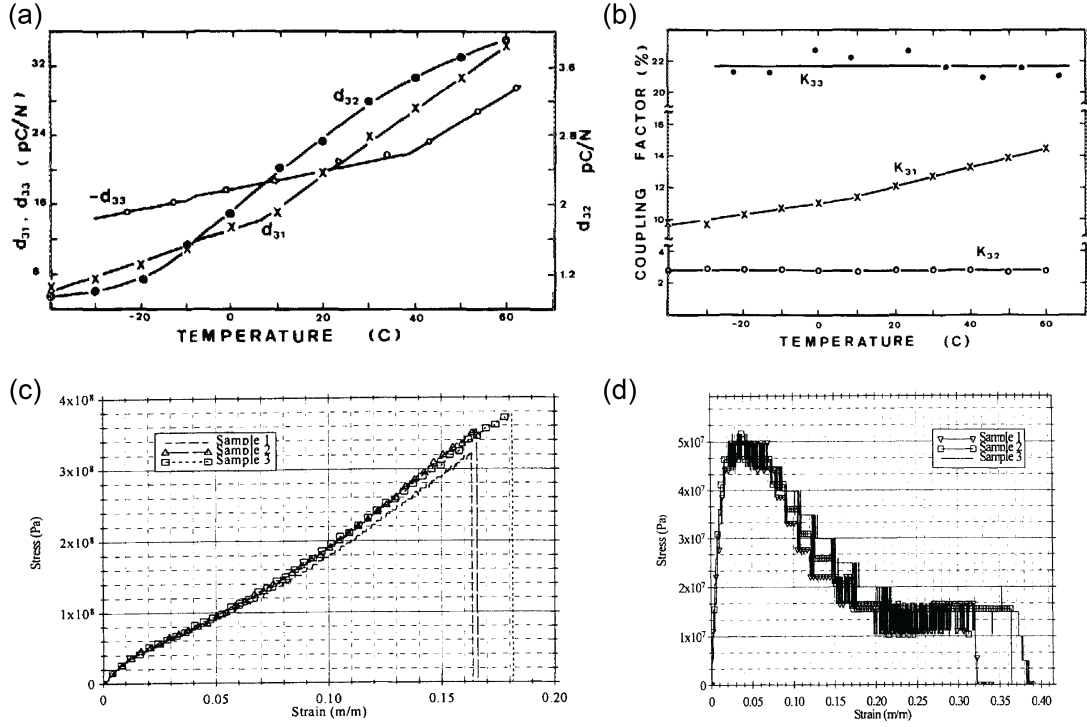


Figure 2.4: The temperature dependence of the directional (a) piezoelectric charge coefficients d_{ip} and (b) piezoelectric energy coupling coefficients k_{ip} . Reproduced with permission from ref 58. Copyright 1984, American Institute of Physics. Stress-strain response of PVDF in the (c) 1 direction and (d) 2 direction. Reproduced with permission from ref 69. Copyright 1999, Taylor and Francis.

The dielectric constant of PVDF, with a value of $\epsilon = 12$, is significantly lower than that of conventional piezoelectric materials (i.e., perovskites such as lead zirconate titanate ($\text{Pb}[\text{Zr}_x\text{Ti}_{1-x}]\text{O}_3$, PZT, $\epsilon = 2400$) and barium titanate (BaTiO_3 , BTO, $\epsilon = 2479$)).^{11, 45, 60, 62} Additionally, the spontaneous polarisation of pure β -PVDF has been experimentally reported as $P_s = 1.32 \times 10^{-2} \text{ C m}^{-2}$. The remnant polarisation (P_r) of PVDF has further been linked to the thickness of the material, with experiments suggesting an increase in P_r as a function of an increase in thickness. This phenomenon is attributed to a change in the aspect ratio of the material, where the potential difference on a 33-form PEG is given by Equation (2.18).

$$V_{Q=0} = \frac{a}{bc} g_{33} F \quad (2.18)$$

Here, a is the thickness of the material, b and c are the length and width of the material, respectively, and F is the applied force.^{63, 64} Hence, as the thickness increases, higher

voltage can be observed. The recent review by Uchino⁶⁵ has discussed the influence of PEG geometry on the resultant electricity generation, as well as the optimal circuitry on how to measure the electrical output of PEGs.

2.4.2 Thermal, mechanical and optical properties of PVDF

While the electromechanical coupling is the most interesting property of PVDF, especially within the β phase, other properties are important for its application. For example, requirements of optical transparency, thermal and chemical stability, as well as mechanical flexibility and biocompatibility can play a key role in enabling applications.

PVDF is a thermoplastic polymer, with the electroactive phase melting at approximately 170 °C. The β orientation of PVDF has an increased density ($\rho = 1.97 \text{ g mL}^{-1}$) compared to the amorphous PVDF ($\rho = 1.78 \text{ g mL}^{-1}$) due to a higher degree of crystallinity and hence higher packing density. The lattice parameters have been determined experimentally for the orthorhombic β -PVDF unit cell, given as $a = 8.47 \text{ \AA}$, $b = 4.90 \text{ \AA}$, $c = 2.56 \text{ \AA}$.⁵⁴ As the glass transition temperature (T_g) of PVDF is between -60 °C and -20 °C, PVDF is a rubbery polymer at all temperatures above 0 °C, irrespective of the phase.^{45, 57} Furthermore, all phases of the polymer melt at similar temperatures (T_m), although minor differences in the T_m have been suggested to be influenced by the phase. Hence, the value of T_m has been proposed as a characterisation tool to discern various crystalline phases and will be discussed this in greater detail in the next section. The T_C of PVDF has been widely debated, however most data suggests it to be above the T_m , between 195 °C and 197 °C.^{66, 67} The T_C is regarded as the point when the material loses spontaneous polarisation. Therefore, in PVDF this means the polymer chains rotate to reduce the net energy and hence randomise the polarisation vector.

In regard to mechanical properties the Young's moduli (Y_i) in various directions i of strain for PVDF are similar, where $Y_1 = 2.56 \times 10^9 \text{ Pa}$ for direction 1 (along the axis of the polymer backbone) and $Y_2 = 2.6 \times 10^9 \text{ Pa}$ for direction 2 (perpendicular to the polymer chain orientation and the thickness axis). However, the similarity is only at the initial region of the strain-stress curve, shown in Figure 2.4c, d. Past the initial region in the direction 1, the stress-strain curves exhibit behaviour typically found in brittle materials

(Figure 2.4c) — a linear increase in stress as a function of strain up to a maximum, whereby the material fails. Conversely, PVDF shows properties representative of ductile materials in direction 2 (Figure 2.4d).⁴⁵ Studies on the anisotropic mechanical properties of PVDF suggest that there is a difference of approximately one order of magnitude between maximum stresses ($\sigma_{max,i}$) between directions 1 and 2: $\sigma_{max,1} = 3.5 \times 10^8$ Pa and $\sigma_{max,2} = 5.1 \times 10^7$ Pa.^{68, 69}

The optical properties of PVDF are also important. Ideally, the control over transparency, haze and clarity is required depending on the use of the material. The major reason for low visible-wavelength transmittance and high haze in PVDF is surface roughness. Although limited efforts have been made in isolating optical properties and optimal conditions for transparency of β -PVDF, several researchers have studied α - and δ -PVDF.

Li *et al.*³⁷ have proposed a relationship between the root mean square (RMS) roughness and the optical transparency, clarity and lack of haze in δ -PVDF. The films have been deposited *via* both Meyer bar coating and spin coating methods at elevated temperatures to decrease surface roughness. Here, post-processing includes applying a short electrical pulse across the attached electrodes to convert the α phase into the δ phase. Further work by the researchers, Li *et al.*³⁸, suggests the presence of humidity as the main factor for the presence of haze in films of solvent cast α -PVDF. Further, they report vapor-induced phase transition as the primary cause of high haze and low clarity in solvent evaporation-assisted PVDF deposition methods. Hence, the authors have been able to produce thin films of PVDF with approximately 0% haze, approximately 100% clarity and visible wavelength absorbances below $<10^{-2}$ at 0% relative humidity and 40 °C deposition temperature.

2.4.3 Comparison of PVDF properties with other piezoelectric materials

It is useful to compare the properties of PVDF to other well-known piezoelectric materials, in order to highlight its suitability for applications in flexible PEGs. Table 2.2 shows a selected list of properties for PVDF compared to alternative piezoelectric materials. Materials such as PZT and BTO are perovskite structures, whereby the titanium atom arranges itself in the centre of the unit cell and induces spontaneous polarisation below

the T_C . The d_{33} coefficient in PZT and BTO is one order of magnitude higher than polymer-based piezoelectric materials. These materials are dense in nature ($>5 \text{ g mL}^{-1}$) with a high Young's modulus, suggesting their brittleness and limiting their use in applications requiring flexible materials without significant processing.⁷⁰⁻⁷³ The presence of lead in PZT and similar perovskites further limits applications in medical devices due to its toxicity.³⁹ On the other hand, voided charged polymers (VCPs) such as cellular poly(propylene) (PP) have a comparable d_{33} to perovskite materials. Conversely, VCPs generally have a lower maximum operating temperature, a low conversion from mechanical to electrical energy (k_{33}), low structural integrity and low dielectric constant, limiting their utilisation in real-world applications as mechanoelectrical conversion devices.⁵⁹

Table 2.2: Physical, dielectric and piezoelectric properties of selected piezoelectric materials, showing perovskites, bulk polymers and voided charged polymers.

Material		PZT ^{a)}	BTO ^{a)}	PVDF ^{c)}	Cellular PP ^{c)}
References		11, 80	60, 62, 80	11, 59-61	11, 59, 81
Density ρ	g mL^{-1}	7.80	5.72	1.78	0.33
Young's modulus Y	GPa	50-60	116-128	2.5-3.2	0.002
Dielectric constant ϵ		2400	3279	7.6-12	1.12-1.23
Charge coefficient d_{33}	pC N^{-1} , pm V^{-1}	289-500	105-460	13-28	80-800
Voltage coefficient g_{33}	V m N^{-1}	0.026	0.013	0.320	30
FOM ^{d)}	$\text{pm}^2 \text{N}^{-1}$	8-13	1-6	4-9	2400-24000
Coupling factor k_{33}		0.69	0.49	0.20-0.27	0.06
Maximum operating temperature	$^{\circ}\text{C}$	250	120	90	50

^{a)} perovskite; ^{b)} solid polymer; ^{c)} voided charged polymer; ^{e)} given as $d_{33}g_{33}$, from Equation (2.17).

In contrast to perovskite structures and VCPs, PVDF and related fluoropolymers exhibit a moderate electromechanical conversion efficiency; importantly, they possess an acoustic impedance similar to that of human tissue, making them more suitable for biomedical applications relative to perovskites and VCPs.^{74, 75} It is biocompatible as it does not contain toxic lead, unlike many perovskites, in particular PZT.¹¹ Furthermore, PVDF is flexible with a high Young's modulus relative to that of VCPs, suggesting its improved mechanical strength.⁶⁹ Additionally, it can be processed to show high transparency in the visible wavelength region with high clarity and low haze.^{37, 38}

2.5 Characterisation of PVDF

To understand the properties of PVDF, and quantify the phase composition, several characterisation techniques have been commonly utilised, including x-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC) and polarity switching measurements are then used to measure the total polarisation in the material. More recently Raman spectroscopy has also been employed. This section will highlight these techniques.

XRD, FTIR and DSC are commonly used together to develop an understanding of the contributions of various phases to the microstructure of PVDF. Representative fingerprints of α , β and γ phases can be obtained by these techniques and are shown in Figure 2.5a-c, for XRD, FTIR and DSC, respectively.^{56, 68, 76-79}

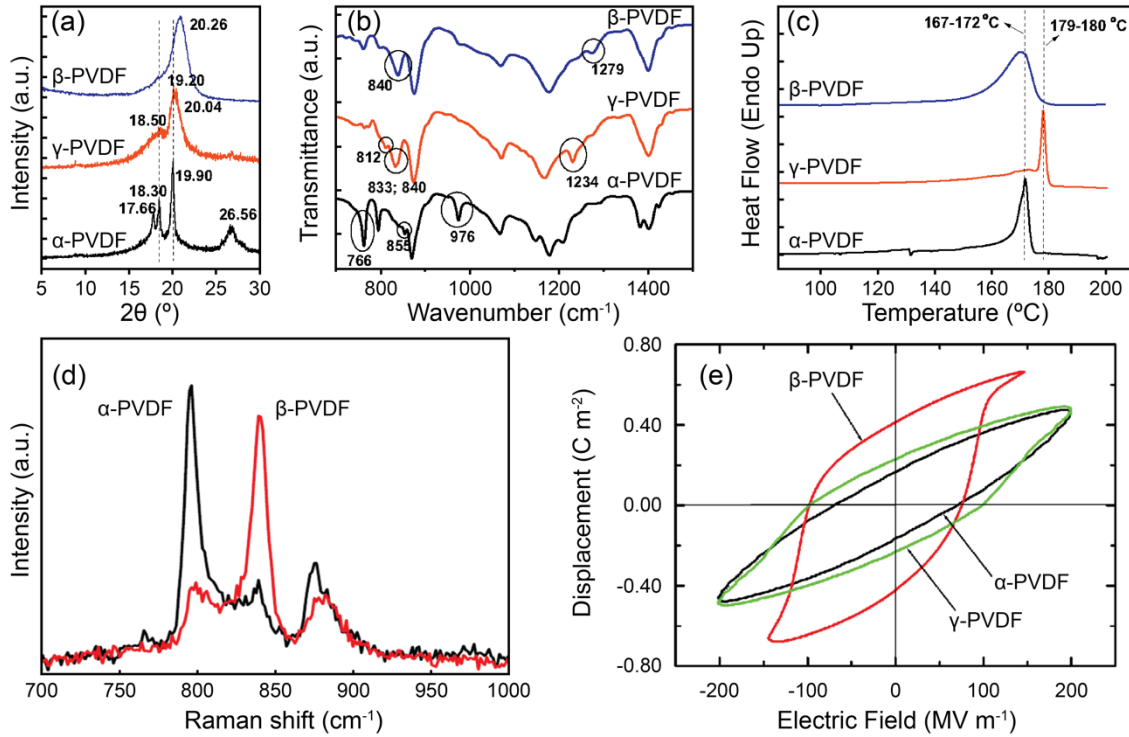


Figure 2.5: Typical fingerprints of α , β and γ phases of PVDF in common characterisation techniques, (a) XRD ($K_{\alpha 1}$, $\lambda = 1.5405600 \text{ \AA}$); (b) FTIR; (c) DSC, reproduced with permission from ref 43. Copyright 2014, Elsevier. (d) Raman spectroscopy ($\lambda = 532 \text{ nm}$), reproduced with permission from ref 78. Copyright 2014, SPIE. (e) Electric displacement-electric field (D - E) hysteresis loops, reproduced with permission from ref 79. Copyright 2010, American Institute of Physics.

XRD is commonly used to fingerprint the phases of the polymer.⁴³ As shown in Figure 2.5a, the XRD pattern for β phase shows the combination of a broadened peak at 20.26° (2θ) and a weakened shoulder at lower angles. In contrast, the XRD patterns of α and γ phases are noticeably different. The α phase of PVDF displays a sharp peak at 19.90° , an additional pair of easily resolvable peaks at 17.66° and 18.30° , as well as a feature at 26.56° . In the XRD pattern of γ phase PVDF, peak broadening occurs and the main characteristic peak shifts to a higher 2θ angle of 20.04° , while the pair of sharp peaks found in α PVDF transforms into a single broad feature located at approximately 18.50° . The features between 17.66° and 18.50° in α and γ phases have been attributed to the *gauche* conformation in the structure of PVDF, which is not found in β phase.⁸² The XRD method can serve as a qualitative analysis for confirming the presence of pure β phase and distinguishing it from other commonly found phases.

The FTIR characterisation is most widely used to determine β phase fraction of PVDF (Figure 2.5b). It involves the quantitative comparison of absorbance at 766 cm^{-1} (attributed to α phase) and that at 840 cm^{-1} (attributed to β phase) through Equation (2.19).

$$F(\beta) = \frac{A_\beta}{(K_\beta/K_\alpha)A_\alpha + A_\beta} \quad (2.19)$$

Here, $F(\beta)$ represents the fraction of β phase PVDF, A_α and A_β represent the absorbances at 766 cm^{-1} and 840 cm^{-1} , respectively, and K_α and K_β are the absorption coefficients at the respective wavenumbers with the values given as $6.1 \times 10^4\text{ cm}^2\text{ mol}^{-1}$ and $7.7 \times 10^4\text{ cm}^2\text{ mol}^{-1}$, respectively.⁸³ However, it should be noted that FTIR cannot be used alone to quantify the presence and relative proportions of the phases, due to the peak at 833 cm^{-1} from γ phase PVDF overlapping with the peak at 840 cm^{-1} for β phase PVDF.⁸⁴ Many authors suggest that Equation (2.19) should be used to determine the total fraction of electroactive phases (β and γ phases combined), as shown in Equation (2.20).⁸⁵ In this modification, F_{EA} is the total electroactive fraction and I_{EA} is the absorbance at 840 cm^{-1} .

$$F_{EA} = \frac{I_{EA}}{(K_\beta/K_\alpha)I_\alpha + I_{EA}} \quad (2.20)$$

Furthermore, to separate the contribution from the distinct electroactive phases, a peak-to-valley height ratio approach has been proposed, whereby the absorbances reflecting the β phase peak at 1275 cm^{-1} and the γ phase peak at 1235 cm^{-1} are used, shown in Equation (2.21) and Equation (2.22).

$$F(\beta) = F_{EA} \times \left(\frac{\Delta I_{\beta'}}{\Delta I_{\beta'} + \Delta I_{\gamma'}} \right) \quad (2.21)$$

$$F(\gamma) = F_{EA} \times \left(\frac{\Delta I_{\gamma'}}{\Delta I_{\beta'} + \Delta I_{\gamma'}} \right) \quad (2.22)$$

In this instance, $\Delta I_{\beta'}$ is attributed to the difference in intensity between the β phase peak at 1275 cm^{-1} and the preceding “valley” at approximately 1260 cm^{-1} , and $\Delta I_{\gamma'}$ is attributed to the difference in intensity between the γ phase peak at 1234 cm^{-1} and its preceding “valley” at approximately 1225 cm^{-1} . This method of quantification has been increasingly utilised since its initial reports.⁸⁶⁻⁸⁸ It should be noted that the peaks for the various phases tend to overlap in FTIR, making quantitative fingerprinting of the phases difficult. Hence,

XRD should be used as a secondary characterisation method to confirm the presence of β phase and, more importantly, rule out the presence of α and γ phases in PVDF and related fluoropolymers.

In addition, DSC is an alternative method to qualitatively distinguish relatively pure phases from each other, shown in Figure 2.5c. Depending on the phase of the material, the endothermic peak related to the relaxation in the polymer chain conformation upon melting shifts to a different position and changes its relative width. Moreover, DSC can be applied as a quantitative technique to measure the enthalpy of melting within the sample, and hence calculate the relative crystallinity using the reference value for the enthalpy of completely crystalline PVDF.⁸⁹ In this method, the temperature of melting has been suggested to shift based on the conformation, as shown in Figure 2.5c.⁴³ The enthalpy of melting (ΔH_m) can be calculated from the area under the melting peak on the thermogram and is given as a mass-normalised value with units J g^{-1} . The total crystallinity percentage can then be calculated using Equation (2.23).³⁹

$$\chi_c = \frac{\Delta H_m}{\Delta H_0} \times 100 \quad (2.23)$$

Here, χ_c is the crystallinity fraction and ΔH_0 is the literature melting enthalpy the completely crystalline PVDF material with a value of 103.4 J g^{-1} .^{68, 89, 90}

In recent times, Raman spectroscopy has been suggested as an alternative method to fingerprint the phases in fluoropolymers. This method was first utilised by Constantino *et al.*^{91, 92}. Subsequent work by Riosbaas *et al.*⁷⁸ has further popularised this method for discriminative characterisation of α and β phases in PVDF. The representative spectra for the samples with predominantly α and β phases are shown in Figure 2.5d, and clear differences can be seen between the typical Raman signatures. This publication has attributed the peak at 839 cm^{-1} to the growing amount of β phase upon mechanical stretching of the PVDF films and have suggested the decreasing intensity at 794 cm^{-1} is due to the α phase. Raman spectroscopy has since been used in an increased number of studies.⁹³⁻⁹⁹ The main fingerprinting region in Raman is found between 700 cm^{-1} and 900 cm^{-1} . The peak at 794 cm^{-1} has been suggested to result from the rocking of CH_2 in the α phase and that at 839 cm^{-1} attributed to the rocking of the β phase CH_2 .⁹¹ Furthermore, an additional peak at 812 cm^{-1} has been reported recently due to the influence of γ phase of the

polymer.¹⁰⁰ The quantitative analysis of the fraction of β phase relative to that of α phase has been proposed using Equation (2.24).⁷⁸

$$\frac{\beta}{\alpha} = \frac{I(\beta)}{I(\alpha)} = \frac{I_{839 \text{ cm}^{-1}}}{I_{794 \text{ cm}^{-1}}} \quad (2.24)$$

Here, $I(\beta)$ corresponds to the intensity of the peak at 839 cm^{-1} and $I(\alpha)$ to that of 794 cm^{-1} . A β/α ratio of greater than 1 suggests majority β phase content and below 1 suggests predominantly α phase. Due to the strong and sharp signals in Raman spectroscopy, the peaks do not tend to overlap, hence this technique may be useful in quantifying the relative proportions of the various phases in fluoropolymers.

The presence of a dipole moment in the β phase in the fluoropolymer is a requirement for it to exhibit electromechanical coupling; however, it is not the only requirement. For example, a sample of highly crystalline PVDF with predominantly β phase can exhibit no electrical output if the dipoles are arranged in a random manner, such that the dipole vectors cancel each other (Figure 2.6).¹⁰¹ In this context, a specialised bulk fingerprinting technique for the quantification of a total dipole moment, polarity switching spectroscopy, is used. The measurement generates electrical displacement-electrical field (D - E) or polarisation-electrical field (P - E) hysteresis loops as shown in Figure 2.5e.⁷⁹

Piezoelectric polymers such as β -PVDF are a special case of dielectric materials, whereby their dipoles remain polarised after an external influence is removed. This gives rise to several critical parameters necessary to quantify the polarisability of fluoropolymers, described in great detail by Damjanovic⁴⁴. The first parameter is spontaneous polarisation P_s , which is denoted by the y-intercept of the extrapolation of the final linear region in the hysteresis loop of a piezoelectric material (Figure 2.5e), and this parameter quantifies the total possible polarisation. Hence, a larger P_s correlates with a higher electrical output of the polymer. The second important parameter, introduced as the y intercept of the hysteresis loop, is called remnant polarisation P_r and represents polarisation due to oriented dipoles which remain aligned with no external field in the material. For the piezoelectric material to be considered stable, P_r should be comparative to that of P_s . In most real-world scenarios, P_r tends to be lower than P_s due to factors such as temperature and electromagnetic interferences.

The final parameter used in measuring polarisation in fluoropolymers is the x-intercept of the hysteresis loop and is generally referred to as coercive field E_C . The physical meaning of this parameter is the electric field required to instantaneously depolarise the material. Measuring these parameters is quite important for optimising the conditions for post-deposition processing (poling—refer to section 2.6.4) as well as understanding and enhancing electromechanical properties in PEGs.

The characterisation techniques outlined in this section form a basis for understanding the conformational properties of PVDF and its related copolymers. The ability to pinpoint the amount of total crystallinity (Figure 2.6a) is important, as it encompasses all non-amorphous phases, which include α , β and γ . Investigation using FTIR, XRD and Raman spectroscopy assists in quantifying the relative proportions of the crystalline phases (Figure 2.6b). As outlined previously, the main purpose of the research into PVDF as a piezoelectric polymer able to generate electricity is to increase the fraction of total crystallinity, whereby the β phase within the crystalline portion is maximised. Therefore, these spectroscopic methods are critical for understanding the material. However, to optimise the electrical signal obtained from mechanical deformation of the polymer, the dipole moment direction of all the polymer chains must be oriented in a single direction. Polarity switching measurements are then used to measure the total polarisation in the material (Figure 2.6c). Thus, the methods outlined in this section are necessary to understand the various properties of PVDF and related fluoropolymers, in order to tailor the materials for greatest electromechanical conversion appropriate for their uses in PEGs.

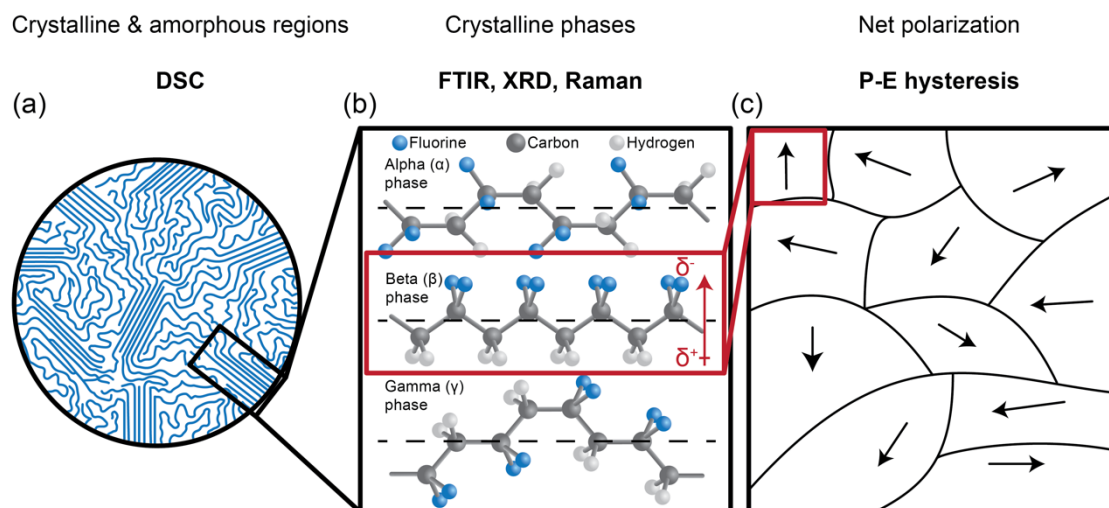


Figure 2.6: Synopsis of the factors affecting the electrical output of a fluoropolymer PEG and the respective methods used for their characterisation.

2.6 Control of parameters relating to piezoelectricity in fluoropolymers

For the purposes of translating PVDF-based PEGs into the aforementioned applications, the electrical output of the devices should be maximised. In fluoropolymers, a range of variables can be controlled to either directly or indirectly affect the electrical output of the resultant PEGs. Namely, the choice of polymerisation parameters and techniques can increase the purity of the polymer and aid preferential nucleation into the electroactive β phase during later stages of processing. Different polymer deposition techniques also exist and can significantly affect the electrical output of flexible PEGs.

The electrical characteristics of PEGs can be altered by post-deposition processing methods, also commonly known as poling, aimed at increasing polarisation within the polymers. Also, the inclusion of various co-monomers can influence the processability and electromechanical coupling effects in resulting copolymers. Lastly, the incorporation of nanomaterials and fillers to make fluoropolymer composites can vary the magnitude of the electrical output due to a range of effects. The following sections discuss each of these in detail.

2.6.1 Polymerisation parameters and techniques

The synthesis route of PVDF plays an important role in the enhancement of the polymer's electroactivity, allowing for increased energy conversion efficiencies. PVDF is a linear chain fluoropolymer consisting of a linear vinyl chain with a difluorine functionality on every second carbon.¹⁰² The polymer is generally synthesised *via* either a free-radical polymerisation or a more controlled method such as reversible addition-fragmentation chain-transfer (RAFT) polymerisation from the monomer, vinyl difluoride.^{57, 103}

The monomer itself is gaseous at standard atmospheric conditions, hence the polymerisation is typically undertaken in an emulsion or in a suspension to maximise yield.¹⁰³ The former utilises water soluble initiators, whereas the latter uses organosoluble initiators coupled with water soluble polymers such as poly(vinyl alcohol) acting as stabilisers for the monomer. It should be noted that the emulsion polymerisation is undertaken in a medium with a high heat capacity such as water, which is able to dissipate the heat produced by the polymerisation reaction.¹⁰⁴ The documented method of termination of the PVDF polymerisation reaction is described as either recombination, through the combination of two active polymer chains, or alternatively hydrogen abstraction from a proton donor solvent if available.^{53, 105}

Several works have extensively documented the parameters of PVDF polymerisation, including assessments of quality of polymer based on parameter sets.^{57, 106} Ameduri⁵⁷ and Soulestin *et al.*¹⁰⁷ have written several extensive reviews on the various polymerisation techniques and pathways for PVDF and other fluoropolymers, as well as the influence of key parameters during the polymerisation on the properties of the resulting polymers. These reviews can be used as a guide for literature surrounding the polymerisation parameters.

Due to the nature of radical-initiated polymerisation processes, defects have been found in the products, deviating from the desired head-to-tail propagation (Figure 2.7a, I).⁵³ The presence of head-to-head (Figure 2.7a, II) and tail-to-tail (Figure 2.7a, III) defects has been attributed to polymerisation conditions and temperature.⁵⁷

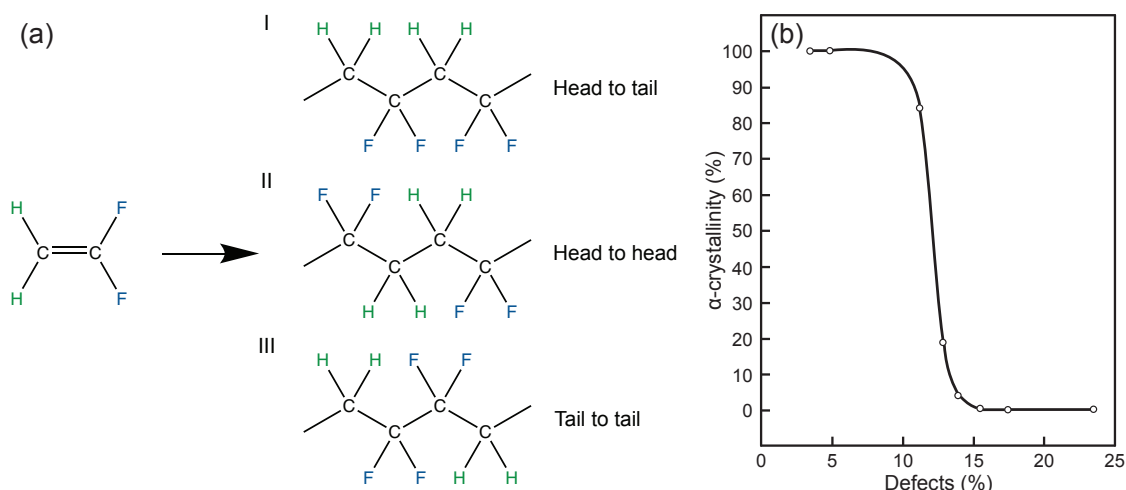


Figure 2.7: (a) Isomers of PVDF through polymerisation of vinylidene difluoride. Head-to-tail propagation (I) is the desired result, however head-to-head (II) and tail-to-tail (III) additions can occur as defects. (b) The fraction of α -phase polymorphs relative to the β -phase in PVDF synthesised with increasing head-to-head and tail-to-tail defect concentration. Reproduced with permission from ref 110. Copyright 1987, Elsevier.

Emulsion-polymerised PVDF has been found to contain a higher proportion of head-to-head defects relative to suspension, with a 3-7 mol% defect proportion in commercially produced PVDF. It has been proposed that decreasing the proportion of defects within the polymer will increase crystallinity, with researchers claiming a low degree of defects (0.73 mol%) in vinylidene fluoride telomers results in a well-organised β phase structure.¹⁰⁸ This data suggests an increased β phase fraction can be obtained with a decrease in the molecular weight of the polymer. However, in PVDF with higher molecular weights, the opposite has been found to occur. In one of the few experiments linking polymerisation parameters to the major polymorphic phase in PVDF, Cais *et al.*¹⁰⁹ have studied the effects of induced defects in the polymer during synthesis and correlated their values to the major phase (Figure 2.7b). The authors report the α phase to be the most stable at 11% head-to-head additions and below. However, the β phase of PVDF becomes more stable than the α phase at 15% defects and remains the dominant phase for all analysed data up to 23% defects.¹⁰⁹ It has been further noted that the melting temperature of PVDF decreases from 180 °C at 3.5% defects (inherent to polymerisation of VDF) to 122 °C at 15% defects, with further increases up to 140 °C at 23% defects.¹¹⁰

As discussed in section 2.4.3, the preferential β phase formation of PVDF is one of the parameters to be maximised for the increased electrical output of fluoropolymers. Hence, the high head-to-head defect fraction at 23% is linked to enhancements of the electrical output of PVDF-based flexible PEGs. In the current state, it is difficult to examine polymerisation parameters and their effects on the electromechanical coupling of the fluoropolymers due to a lack of relevant literature. The research in this area is expected to evolve in the near future and will be one of the key areas in enabling commercialisation of fluoropolymer-based flexible PEGs.

2.6.2 Co-monomer influences in fluorinated polymers

One of the main downsides of PVDF is low electromechanical coupling relative to perovskites, manifested in its moderate piezoelectric charge coefficient d_{33} , as well as difficulty to process it into the β phase.^{43, 111} To counteract these shortcomings, various polymer blends have been developed utilising alternative fluorinated co-monomers.⁵⁷ The commonly studied copolymers of PVDF are presented in this section, and Table 2.3 lists their electromechanical and dielectric properties for optimised molar fractions of comonomers.

It is clear that variation of these polymers leads to variation in the electrical output of the PEGs based on these blends (Table 2.3). Maximisation of d_{33} and g_{33} is required for increased conversion efficiencies in these copolymers.

Table 2.3: Comparison of the piezoelectric metrics and coefficients of various PVDF-based copolymers.

Electroactivity coefficient	PVDF	PVDF-TrFE 30 mol% TrFE	PVDF-HFP 10 mol% HFP	PVDF-CTFE 12 mol% CTFE
Refs	10, 11, 60, 112, 113	80, 112	114, 115	113, 116
P_r (mC m ⁻²)	80	80-110	26-30	28
P_s (mC m ⁻²)	120	120-130	26	80
E_C (MV m ⁻¹)	80-100	50-70	52	100
g_{33} (V m N ⁻¹)	0.32	0.38	-	0.40
d_{33} (pC N ⁻¹)	13-28	38	5.4-32	140
k_{33}	0.20-0.27	0.29	0.14-0.36	0.39
FOM ^{a)} (pm ² N ⁻¹)	4.2-9.0	14.4	-	56.0

^{a)} given as $d_{33}g_{33}$, from Equation (2.17).

A wide variety of copolymers have been synthesised by incorporating vinylidene difluoride with TrFE, hexafluoropropylene (HFP) and chlorotrifluoroethylene (CTFE) co-monomers.⁴³ The choice of co-monomer, as well as relative ratios of each, leads to tailoring of properties such as T_m , T_g , Young's modulus, dielectric constant, stability and crystallinity, amongst others.⁵⁷ Copolymers, with optimised co-monomer ratios, have been shown to deposit as an electroactive phase due to steric effects and dipole-dipole interactions. The reason for changes in the polymer properties is the modification of the symmetry of the polymer and varying the intramolecular and intermolecular forces.

A review by Soulestin *et al.*¹⁰⁷ reports on the effects of the copolymer chemistry on the properties of fluoropolymer copolymers and readers are directed towards their publication for an in-depth discussion on the topic.

The most studied copolymer is PVDF-TrFE (structure shown in Figure 2.3d). In this system, the relative molar ratio of VDF has been experimentally varied in free radical polymerisations.¹¹⁷ Previous works have suggested successful conversion at all ratios, however only ones containing between 93 mol% and 50 mol% VDF have been produced on a commercial scale.⁵⁷

The addition of the third fluoride atom into the vinyl backbone has been shown to enhance crystallinity in the resultant polymer due to its large steric hindrance relative to the hydrogen it replaces.¹¹⁸ The favoured conformation is all-*trans* and therefore the β phase is the most prevalent in PVDF-TrFE when the VDF is in the range of 50 mol% and 80 mol%.^{119, 120} In this range, the T_m of the PVDF-TrFE is lower than that of PVDF, with a T_C between 55 °C and 128 °C (compared to PVDF at 196 °C).¹²¹ The introduction of the TrFE monomer in molar ratios between 25 mol% and 30 mol% has been shown to selectively obtain thin films with high β phase fractions.¹⁰⁷ In terms of the electroactive properties of PVDF-TrFE, the remnant polarisation has been determined to be $P_r = 110 \text{ mC m}^{-2}$, much higher than that of PVDF ($P_r = 80 \text{ mC m}^{-2}$), leading to a higher k_{33} .^{9, 112}

The copolymer incorporating the hexafluoropropylene functional group as a co-monomer, poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP), has also been reported to exhibit electromechanical coupling properties (shown in Figure 2.3e).^{114, 122-124} The HFP group is significantly larger than the TrFE group, hence lower HFP molar ratios are required for the manufacture of semi-crystalline copolymers, induced by steric hindrance.

PVDF-HFP shows semi-crystalline properties at HFP ratios below 20 mol% relative to the VDF monomer.^{125, 126} The optimal ratio for the utilisation as flexible PEGs has been shown to be between 5 mol% and 15 mol% HFP.¹²⁷ Interestingly, PVDF-HFP has been reported to exhibit a larger longitudinal piezoelectric charge coefficient ($d_{31} = 43.1 \text{ pC N}^{-1}$) than its thickness piezoelectric charge coefficient ($|d_{31} / d_{33}| > 1$).

Of all the copolymers highlighted in this review, PVDF-HFP has the lowest remnant polarisation ($P_r \approx 30 \text{ mC m}^{-2}$), however the d_{33} coefficient has been reported as up to -32 pC

N^{-1} , higher than that of pure PVDF.¹¹⁵ To the best of the author's knowledge, no value for the g_{33} coefficient has been presented in prior literature, hence the FOM for the 33 direction cannot be calculated. The 31 directionality of PVDF-HFP with 10 mol% HFP has been analysed for its electromechanical coupling properties by Sukwisute *et al.*¹²⁸, suggesting a FOM of $8.8 \text{ pm}^2 \text{ N}^{-1}$ with a d_{31} of 28.7 pC N^{-1} . These values are similar to those of pure PVDF in the 33 directionality, although significantly lower for the use of this copolymer in flexible PEGs.

Another copolymer with reports of enhanced piezoelectric activity is poly(vinylidene fluoride-*co*-chlorotrifluoroethylene) (PVDF-CTFE), the structure for which is shown in Figure 2.3f. In this structure the co-monomer replaces a hydrogen atom along the vinyl backbone with a chlorine atom, which provides steric hindrance at specific monomer ratios in the polymer, between 70 mol% and 93.4 mol% VDF.¹²⁹ Between these molar ratios, the copolymer is predominantly crystalline. PVDF-CTFE exhibits a T_g between that of PVDF (approximately -40°C) and PCTFE (approximately 45°C), based on monomer ratios⁵⁷ and is a thermoplastic at VDF fractions above 70 mol%.¹³⁰

One previous study has reported the highest electromechanical efficiency of PVDF-CTFE between 91 mol% and 88 mol% VDF, with the piezoelectric charge coefficient as high as $d_{33} = -140 \text{ pC N}^{-1}$. This is significantly higher than any previously reported fluoropolymer.¹¹⁶ Based on the report of the extraordinarily high d_{33} in this polymer, the electromechanical properties of PVDF-CTFE make it potentially very attractive as an alternative to low-output piezoelectric polymers such as PVDF. However, to date there is limited literature on this polymer; therefore, there is scope for broader studies on this system going forward. Of particular interest are studies on the piezoelectric properties of PVDF-CTFE, as well as studies on PEGs fabricated from this copolymeric system.

2.6.3 Fluoropolymer deposition and processing techniques

The properties of PEGs are highly dependent on the processing technique of their fluoropolymer components. An overview of the processing techniques and the various applications of PVDF has been recently published elsewhere.^{43, 54} Here, a more specialised discussion of deposition and processing techniques is provided in the context of flexible

PEGs. Conventionally, PVDF is deposited in a non-polarised manner due to thermodynamic minimisation of energy. This randomly oriented polymer needs to be processed post-deposition through the process called poling, whereby the randomly oriented dipoles of the β phase are rotated and aligned in a single direction through the application of an external electric field. The poling process will be discussed further in the review. Firstly, let us consider suitable deposition techniques for fluorinated polymers.

The most common starting conditions for processing and deposition of PVDF into a predominantly β phase material are (1) the melt, (2) solution, (3) α phase solid and (4) composite systems (discussed separately in section 2.6.5).⁴³ Melt extrusion of PVDF is a well-defined process and the most viable in commercial settings. This is evidenced by current commercial availability of materials from Measurement Specialities Inc., Kureha and Arkema Inc. in the form of thin films with thickness between 9 μm and 250 μm .⁴¹

PVDF films produced from the melt tend to exhibit low β phase fraction.¹³¹ The β phase can be maximised through either a quenching and annealing treatment, stretching and annealing, poling of the α phase films, or a combination of the above.^{132, 133} Uniaxial drawing as a processing technique has been reported to yield high fractions of β phase, however further studies have suggested the need for poling as the drawn films are not polarised.¹³⁴ The β phase is prevalent in the produced films, although it is not oriented and hence the polarisation vector parallel to the thickness axis has low magnitude.

The method of extrusion coupled with immediate uniaxial drawing has been commercialised by Measurement Specialities⁴¹, whereby the films show a piezoelectric charge constant $d_{33} = -33 \text{ pC N}^{-1}$, an attractive value for pure PVDF, after the polarisation process. However, the coupling factor for the films is low relative to literature values, $k_{33} = 0.14$ (with respect to typical values between 0.20 and 0.27 in PVDF).⁴¹

High pressure, high temperature quenching has been previously suggested as a viable alternative to uniaxial drawing, undertaking the treatment at 500 MPa and 280 °C, respectively.¹³⁵ This method has resulted in the deposition of a mixture of α and β phases; however, more recent studies at higher pressures show the formation of pure β phase¹³⁶,

and a mixture of β and γ phases¹³¹. A study of the dependence of increasing pressure on the fraction of β phase suggests that an enhancement in the β phase fraction occurs with increasing pressure, from 0% at 200 MPa to 85% at 700 MPa.¹³⁷ Furthermore, these authors have established temperature-pressure dependence curves for the melting and crystallisation of the various phases of PVDF, as shown in Figure 2.8. However, for the produced films to show piezoelectricity, and thus be used in PEGs, they are still required to be poled by the application of high voltages, in the range between 100 MV m⁻¹ and 400 MV m⁻¹, which is an undesirable post-processing step.¹³⁸

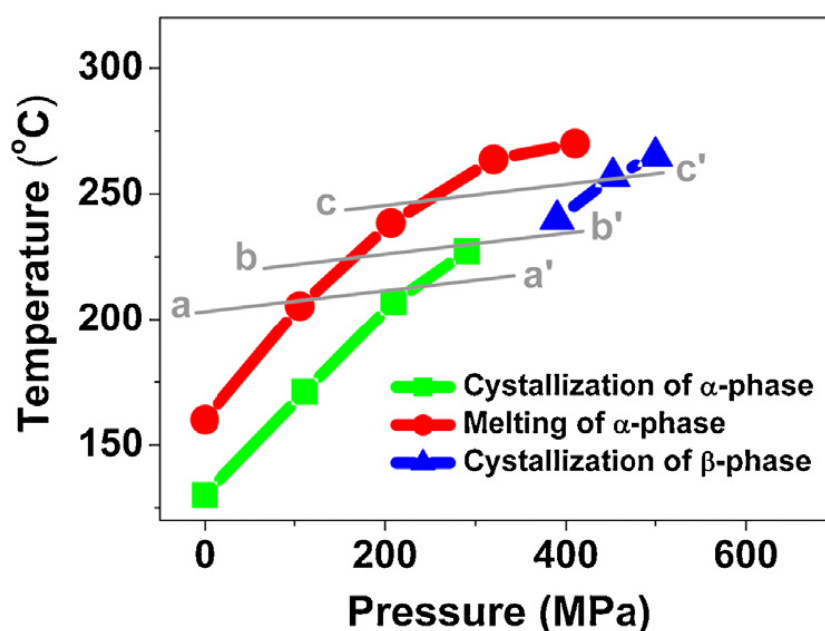


Figure 2.8: Pressure-temperature curves for the crystallisation of α and β phases, as well as the melting of α phase of PVDF. Grey lines represent the initial (a, b, and c) and final (a', b', and c') of pressure quenched PVDF for α , $\alpha+\beta$, and β phases, respectively. Reproduced with permission from ref 43. Copyright 2014, Elsevier.

A variety of methods of processing PVDF into the β phase from solution have been proposed, including solvent casting, spin coating, electrospinning and Langmuir-Blodgett technique.^{43, 54} Recent progress in 3D printing techniques has also allowed for 3D micro-printing; however, this technique has led to limited reports to date.³²

Solvent casting and spin coating have been found to produce films consisting primarily of α phase at near-ambient temperatures, which then require post-processing to convert

to β phase.^{11, 139, 140} Alternatively, electrospinning and Langmuir-Blodgett techniques yield β phase directly under optimised conditions. These techniques use solvents that can readily dissolve fluoropolymers, such as *N,N*-dimethyl formamide (DMF), *N,N*-dimethylacetamide (DMAc) or dimethyl sulfoxide (DMSO).³⁸ The boiling points for these solvents are high (>150 °C) and are therefore unsuitable for processing large quantities of polymer solutions at low temperatures.^{141, 142} Due to this, swelling agents of PVDF with high volatility such as acetone have been utilised as co-solvents to decrease the drying time of the polymer and improve scalability of the final devices.³² Solvent systems with boiling points below 100 °C and relatively low toxicity have been reported to dissolve fluoropolymers, which hold potential in utilisation where polymer solutions are required for processing.¹⁴³

Solvent casting is the conventional method for the deposition of freestanding polymer films and has been widely utilised and characterised in the field of water-filtration membranes.¹⁴⁴ It is a low energy technique and has potential for commercial roll-to-roll production. The films prepared from this technique show high fractions of α phase and exhibit low piezoelectric properties. They are required to be converted into the β phase through uniaxial drawing (described previously) and reoriented for increased polarisation through electrical poling.¹¹

Similarly, spin coating allows for materials to be deposited without heating; however, the deposition occurs in the α phase requiring further processing. Spin coating also shows low potential for scalability.

The formation of β phase has been reported on silicon wafers through spin coating, whereby the spin speed and relative humidity were claimed to affect the β phase formation.¹⁴² Secondary effects from the substrate crystallinity could have aided to the crystalline nature of the films.

Electrospinning has been proposed as an alternative technique, whereby a PVDF solution is extruded through a fine nozzle onto a substrate.¹⁰² During the process, a high potential difference of approximately 15 kV is applied between the nozzle and the substrate.¹⁴⁵ The

resulting material consists of nano- to micro-scale fibres of PVDF deposited randomly to form low density mats.⁷⁴ This technique combines the deposition and poling processes into a single step, with β phase fractions of up to 86%.¹⁴⁶ A rotating collector is commonly used in order to increase the β phase content. The rotation of the collector acts in a similar manner to uniaxial drawing, and the effect depends on the speed of rotation. For example, Ribeiro *et al.*¹⁴⁷ have shown that an increase of the drum speed from 500 rpm to 740 rpm results in a β fraction content between 45% and 85%. Increased spin speeds of the collectors have shown little change in the β fraction.

Electrospinning is limited by the flow rates of the solution, which are commonly between $1 \mu\text{L min}^{-1}$ and $100 \mu\text{L min}^{-1}$.¹⁴⁵ This represents a potential weakness for scalability in fabricating β phase of PVDF; however, other recent reviews have expressed alternative views, describing pilot-scale equipment with possible commercial uses.¹⁴⁸

Mokhtari *et al.*¹⁴⁹ have reviewed in-depth the literature on the topics of electrospinning and electrospraying of PVDF PEGs, providing an overview of literature up until 2014. Since then, further progress has been made in the optimisation of parameters and maximising electrical generation based on electrospinning fluoropolymers and this review will focus on that literature.

Shao *et al.*¹⁵⁰ have reported on the electrospinning of a nanofibrous PVDF mat with a high β phase content, able to generate a voltage of 2.2 V and current of 2.3 μA under a load of 10 N (Figure 2.9a, b). However, the authors have not stated whether the values were collected at a load resistance or at open circuit voltage and short circuit current conditions.

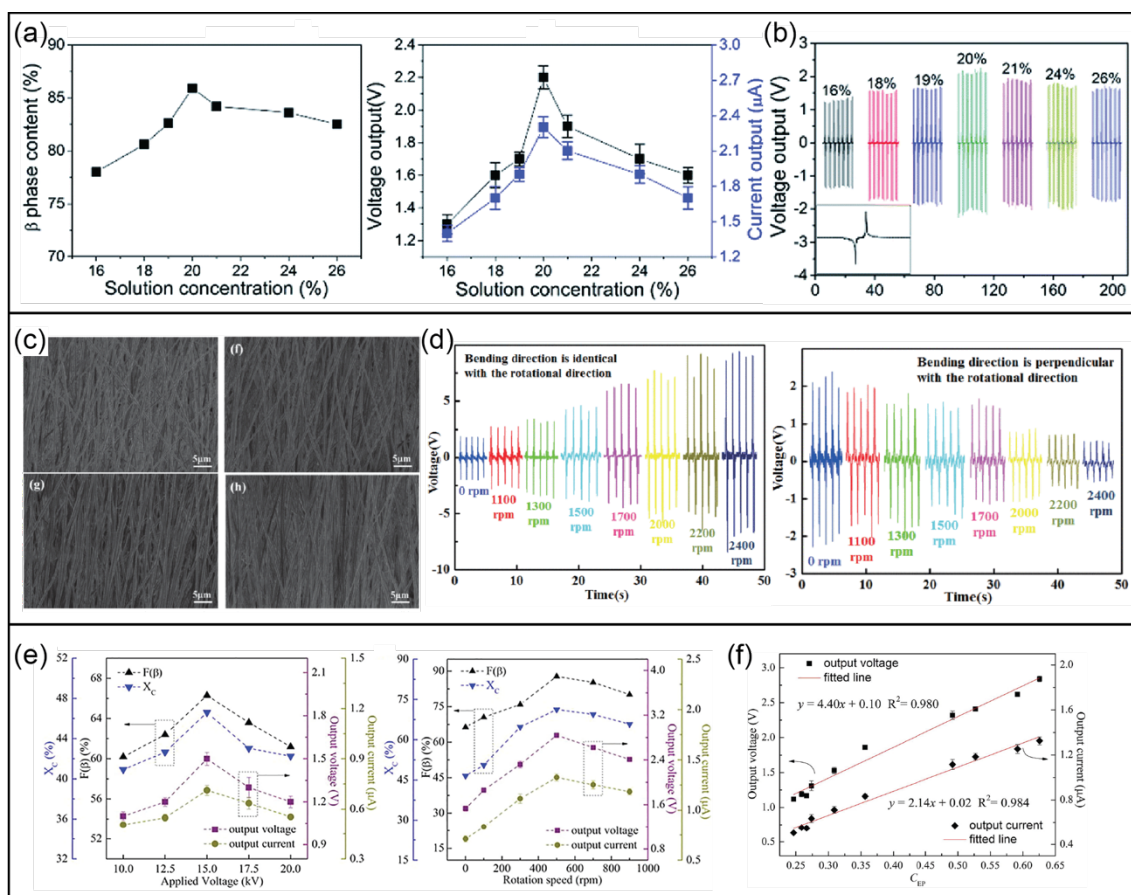


Figure 2.9: Properties of electrospun fluoropolymer-based PEGs: (a) the β -phase fraction and the corresponding voltage and current outputs as a function of the concentration of PVDF in a solution of DMF and acetone (40:60 vol%) upon cyclic compression with 10 N force and 1 Hz frequency, with (b) the temporal evolution of the harvested voltage for the measured concentrations. Reproduced with permission from ref. 150. Copyright 2015, Royal Society of Chemistry. (c) The alignment of electrospun PVDF nanofibers with increasing rotational speed and (d) the electrical output of the resultant PEGs. Reproduced with permission from ref. 151. Copyright 2015, IEEE. (e) The crystallinity, β phase fraction, output voltage and current as a function of the applied voltage during electrospinning (left) and the rotational speed (right), as well as (f) the electrical generation characteristics for electrospun mats as a function of the content of electroactive phase. Reproduced with permission from ref. 152. Copyright 2018, Elsevier.

Bin *et al.*¹⁵¹ have shown that high drum collector rotating speeds can improve the V_{OC} of electrospun PVDF due to highly aligned nanofibers (Figure 2.9c). The study reports an increase in V_{OC} from 2 V in mats collected on a stationary drum to 9 V (Figure 2.9d) in

mats collected at 2400 rpm (754 m min^{-1}), whereby the β phase fraction and the crystallinity have not been found to change.

Hu *et al.*¹⁵² have reported a linear correlation between the “content of effective piezo-phase” (the product of the beta phase fraction from Equation (2.19) and the crystallinity from Equation (2.23), the $F(\beta) \times \chi_c$) and the electrical output of electrospun PVDF mats (Figure 2.9e, f). This study shows that the optimal conditions for the maximisation of the content of effective piezo-phase are for a 15 kV needle-to-collector voltage and a collector rotation of 500 rpm (157 m min^{-1}), shown in Figure 2.9e. Here, the β phase fraction and the crystallinity are shown to be 87.8% and 71.3%, respectively. The corresponding maximum voltage is reported as 2.8 V with a current of 1.32 μA (Figure 2.9f), compared to approximately 1.6 V and 0.75 μA obtained from a PEG deposited onto a stationary collector.¹⁵⁴ With a piezoelectric layer dimensions of 3 cm^2 area and 50 μm thickness, the maximum volumetric power density in this study corresponds to 154 $\mu\text{W cm}^{-3}$. Clearly, there is scope to utilise this technique for the production of highly effective flexible PEGs with low volume. Further improvements in the scalability of this method could potentially see it being utilised on a commercial scale.

Thin films have also been made using the Langmuir-Blodgett (LB) technique.^{153, 154} In this method, a monolayer of PVDF is floated on the surface of ultrapure water with the help of an amphiphilic stabiliser such as poly(*N*-dodecylacrylamide), forming hydrogen bonds between the fluorine groups in PVDF and the hydrogens in water (Figure 2.10a).¹⁵⁵ The monolayer is then adsorbed onto the surface of a substrate by immersing the substrate in water. This technique can be repeated until a desired thickness is obtained, it also removes the need for poling.¹⁵⁶

The LB method has found to produce nanoscale films of pure and oriented β phase PVDF and PVDF-TrFE.^{154, 155} These films have been well-characterised in terms of their compositional¹⁵⁷, optical¹⁵⁴, morphological^{154, 158, 159} and piezoelectric^{154, 159} properties. PVDF-TrFE thin films produced by the LB technique show a quasi-monolayer formation behaviour, approximately 3.5 nm in thickness and a RMS roughness of 3.1 nm for one layer.¹⁵⁴ The thickness of a PVDF LB single-layer film is approximately 2.3 nm.¹⁵⁵ The thickness of a PVDF-TrFE layer is therefore 35% higher than that of PVDF, which has

been justified by the steric hindrance of the additional fluoride atom in the TrFE co-monomer and hence the larger unit cell structure.¹⁵⁴

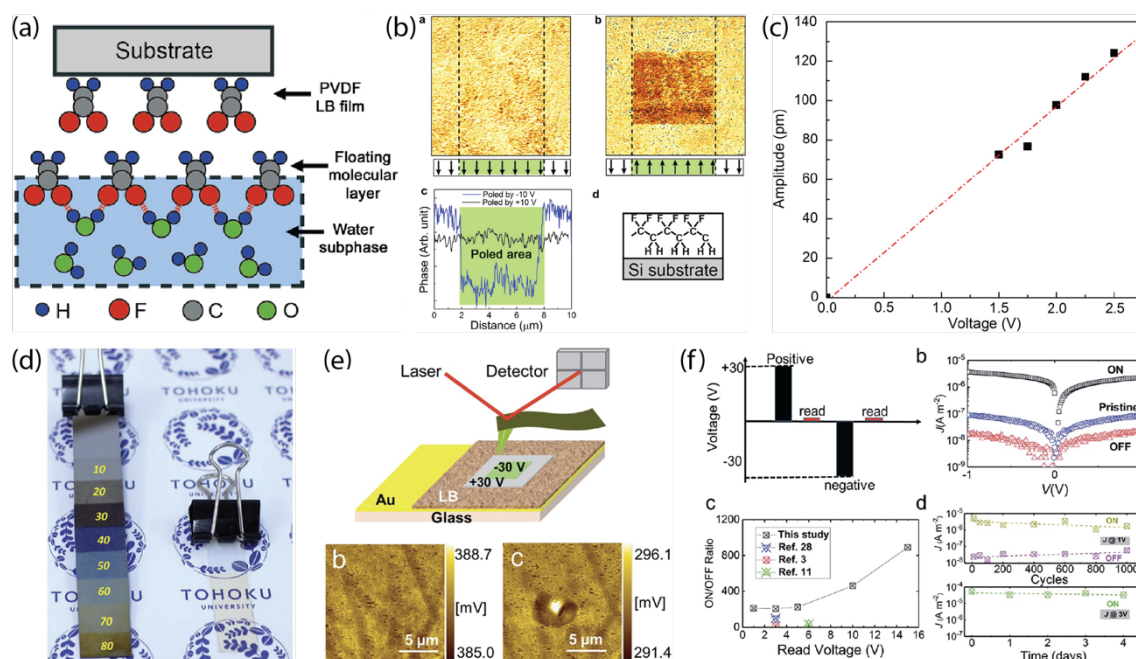


Figure 2.10: (a) Schematic of orientation of PVDF molecules on water surface and subsequent adsorption onto the substrate surface for the formation of a Langmuir-Blodgett film, (b) PFM images after applying a positive (left) and negative (right) voltage across the cantilever and the subsequent phase as a function of distance (bottom left), and (c) the change in amplitude measured as a function of applied voltage using PFM, whereby the slope of the line represents the thickness-axis piezoelectric charge coefficient d_{33} . Reproduced with permission from ref 140. Copyright 2012, Elsevier. (d) image showing the colour of the PVDF/P3CPenT (23 wt%) stacked LB monolayers as a function of layer amount on a silicon substrate (left) and a 30-layer LB film on a PET substrate (right), (e) schematic outlining the switching process (top), and the resultant Kelvin probe force microscopy (KPM) images before (left) and after patterning (right), and (f) switching and reading properties for the non-volatile memory devices utilising PVDF. Reproduced with permission from ref 161. Copyright 2018, Royal Society of Chemistry.

The remnant polarisation of PVDF 30-layer LB film (35 nm thickness) is 60 mC m^{-2} , whereas that of 5-layer (18 nm thickness) PVDF-TrFE is slightly lower at 50 mC m^{-2} . It should be noted that the values for E_C increase drastically with a decreasing thickness,

between 500 MV m^{-1} and 2.5 GV m^{-1} in single layer PVDF films.¹⁶⁰ The voltage required to switch the polarity of the fluoropolymers are nonetheless low, as the thickness is on the order of nanometres. This is evidenced by piezoresponse force microscopy (PFM) images of a LB surface with an area patterned by applying a voltage to the cantilever, shown in Figure 2.10b. The piezoelectric charge coefficient for 20-layer (29 nm thickness) PVDF LB films is $d_{33} = -49.4 \text{ pC N}^{-1}$ (Figure 2.10c), higher than reported elsewhere in literature.¹⁴⁰ Despite the high charge coefficient, these properties are achieved in ultra-thin films ($< 30 \text{ nm}$) after the deposition of 20 layers, implying limitations in scalable production of the LB technique, hence it can be used only in special nanotechnology applications.

For example, Zhu *et al.*¹⁶¹ have utilised PVDF in a blend with a semiconductive polymer, P3CPenT, for a nanoscale non-volatile memory device deposited via the LB technique (Figure 2.10d-f). The polarity switching properties of PVDF are utilised for the writing aspect, undertaken by applying a potential difference $+30 \text{ V}$ for the “ON” state and -30 V for the “OFF” state (Figure 2.10e). The two states have been patterned into the 40-layer (104 nm thickness) LB films and the authors report an ON/OFF ratio of approximately 200 when read at 1 V , increasing to 891 at 15 V (Figure 2.10f), suggesting a high potential for the use of such polymer blends in flexible nanoscale electronics. Obtaining films with micron scale thicknesses, required for generating electricity in practical PEGs, becomes a tedious process and difficult for scale-up to commercial quantities using this technique.

Recent progress in 3D printing technologies has allowed for smaller extrusion nozzles, able to deposit polymers with high precision and resolution.^{162, 163} 3D printing utilises two main modes of operation: melt-extrusion mode, whereby a polymer filament is heated past its melting temperature and pushed through a fine nozzle, and solvent-evaporation mode, where a piston extrudes a concentrated polymer solution through a fine nozzle and the solvent subsequently evaporates.

Melt-extrusion has now been utilised for a multitude of polymeric materials and there is obviously scope and opportunity for printing PVDF structures using this technique.^{164, 165} At the time of writing, several companies have released PVDF-based filaments using melt-extrusion 3D printing; however, these tend to be used where chemical resistance is

needed, as opposed to for PEG applications. The filaments produced are rigid and opaque in nature.

To date, solvent evaporation-assisted 3D printing for the production of piezoelectric materials for PEGs, has only been undertaken by one research group.³¹ Here, they utilise a nanocomposite matrix of BTO in PVDF.³² In this technique, the solution is extruded using pressure, inducing high shear at the walls of the nozzle. Increased shear forces have previously been shown to produce β phase PVDF.¹⁶⁶ Hence, this process shows potential in regards to fabrication of piezoelectric structures and is scalable as a part of the fast-growing additive manufacturing industry.^{74, 167}

The initial work utilising solvent evaporation-assisted 3D printing, undertaken by Bodkhe *et al.*³², has printed up to 70 layers of the material from a mixture of DMF and acetone (Figure 2.11a). The nozzle has an internal diameter of 100 μm , which is used to deposit a cylindrical structure with a piezoelectric charge coefficient $d_{31} = 18 \text{ pC N}^{-1}$ without the use of poling (described in the next section). This group has additionally reported the re-orientation of the polymer chains in the material during printing by applying a potential difference up to 1 MV m^{-1} between the nozzle and the substrate (Figure 2.11b).¹⁶⁸ In the printing of single-layer structures, increasing the electric field did not show significant changes in the β phase fraction; however, the specific charge output has been reported to increase both in the PVDF and in the PVDF-BTO samples with the highest at 1 MV m^{-1} for both materials. The study has further demonstrated the 3D printing of patterns and more advanced structures, such as circular and square spirals up to 40 layers and mesh scaffolds up to 9 layers, although their electromechanical properties were not presented. Additionally, a conformal composite printed PEG has been placed onto a hemispherical substrate and upon pressing with a finger has generated a peak voltage of approximately 6.5 V (Figure 2.11c).

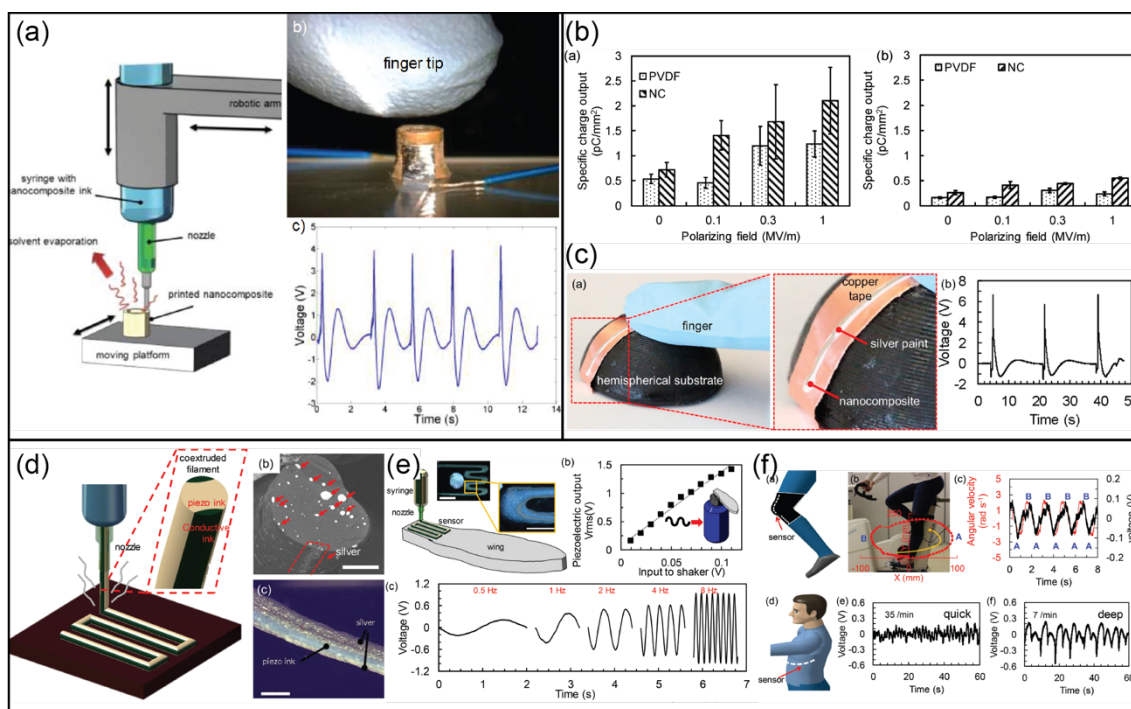


Figure 2.11: Recent progress in solvent-evaporation assisted 3D printing of fluoropolymer-based PEGs: (a) left, schematic outlining the printing process, right, optical image of the 70-layer composite 31-mode PEG consisting of 10 wt% BTO in PVDF and its respective voltage output upon tapping with a finger, (b) the specific charge output for printed 10 wt% BTO/PVDF composite film with increasing applied potential difference between the nozzle and the substrate, with the right hand panel showing the specific charge output of a single printed film after one year, (c) optical images showing a conformally-printed BTO/PVDF PEG on a copper substrate with a deposited silver paint top electrode and its electrical output upon finger tapping. Reproduced with permission from refs 32 and 168. Copyright 2017 and 2018, American Chemical Society. (d) Schematic showing the 3D printing technique for coextrusion of the silver-coated BTO/PVDF composite ink, with SEM micrographs showing the cross-section of the filament (red arrows indicate BTO agglomerates and dashed border indicates the silver electrode), (e) schematic showing the printing process for a wing-like composite PEG, along with the peak-to-peak voltage output as a function of input to an electromagnetic shaker (right) and the voltage signal over time as a function of frequency (bottom), and (f) a proof-of-concept PEG to harvest energy from the knee during exercise (top left) with the corresponding output voltage (top right) and energy harvesting from breathing, showing the generated voltage as a function of time for quick (bottom left) and deep (bottom right) breathing. Reproduced with permission from ref 169. Copyright 2018, Wiley.

The latest study by Bodkhe *et al.*¹⁶⁹ has introduced the single-step printing of a one-dimensional PEG *via* co-extrusion of the previously reported PVDF-BTO composites with a commercially available silver ink on two opposite sides of the piezoelectric material (Figure 2.11d). This type of PEG has been reported to generate a voltage of up to approximately 1.5 V when it is attached to a polymer substrate and strain is induced by an electromagnetic shaker (Figure 2.11e). Furthermore, this study has shown the generated voltage of 100 mV from the movement of a knee while operating an exercise bike when the flexible filament PEG is incorporated into a knee brace (Figure 2.11f, top). Lastly, the work has demonstrated the feasibility of electrical generation from cyclic chest movement due to deep breathing. The authors show that 0.6 V is generated when the PEG is incorporated into the chest portion of a t-shirt (Figure 2.11f, bottom).

The recent advances in the deposition and processing methods for fluoropolymers show a variety of facile preparation techniques for the manufacture of PEGs. The controlled additive techniques such as 3D printing show great promise for the *in-situ* alignment of the polymer chains, preferential re-orientation into a polarised state, and potentially even electrode deposition. Furthermore, fabrication of new geometries opens up a variety of new parameters to enhance the electrical output of the flexible PEG, arising from a higher induced strain applied to each part of the PEG.

2.6.4 Poling techniques

The majority of deposition methods for PVDF result in a material with either a high fraction of α phase or β phase with a low degree of dipolar orientation and hence insufficient polarisation vector for applications in PEGs.^{43, 70, 167, 170} As a consequence, the material is required to be converted to oriented β phase to enable piezoelectric properties. Poling is a group of widely used techniques to reorient the polymer with the aim of increasing the net polarisation vector in the 3 direction. Conventionally, poling is undertaken using an electric field applied along the thickness axis of the piezoelectric material at elevated temperatures.¹¹ The two most common methods of poling are electrode and corona techniques, which are shown schematically in Figure 2.12a, b).

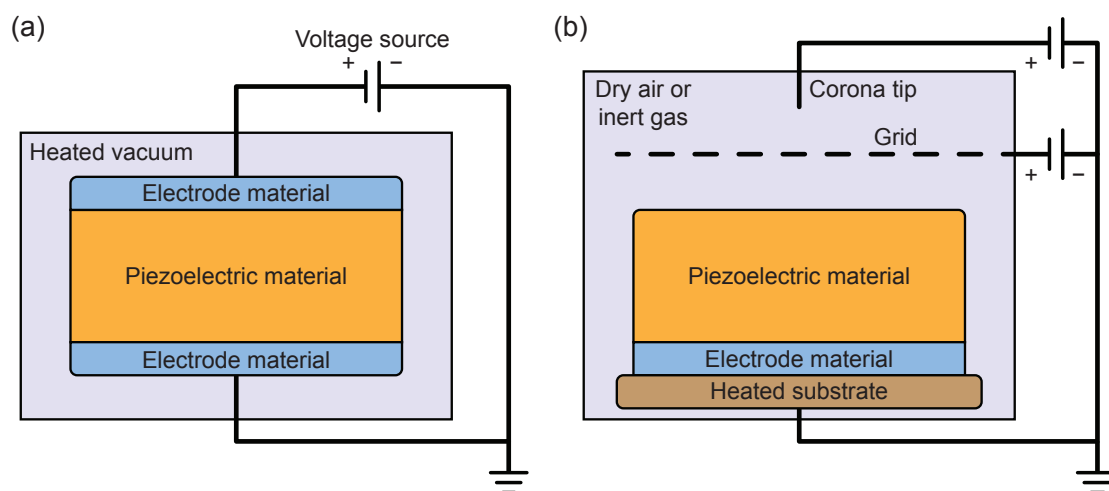


Figure 2.12: Schematic of poling systems for piezoelectric polymers, (a) electrode method and (b) corona poling method.

Electrode poling is the least complicated method out of the two, as it only requires electrodes to be placed on both sides of the film, as shown in Figure 2.12a. The system is encapsulated into an enclosure and air is evacuated from the chamber to avoid breakdown of the polymer through arcing between the electrodes.¹⁷¹ Alternatively, the enclosure can be filled with an insulating fluid for the same purpose. In order to polarise the fluoropolymer material, an electric field between 5 MV m^{-1} and 100 MV m^{-1} is applied.^{171, 172} Intimate contact between the polymer surfaces and the electrodes is required to achieve the desired effect of enhancing the polarisation of the dipoles in the β phase of PVDF.¹¹

Corona poling does not require vacuum conditions as opposed to electrode poling; however, the relative humidity needs to be minimised through circulation of dry gas, as shown in Figure 2.12b. In this technique, only one electrode has intimate contact with the polymer film, allowing for the presence of patterned features on the other side.¹¹ The corona tip is subjected to a high voltage (10^4 V) and placed on top of a conductive grid with a much lower voltage, ionising the gas between them and accelerating it towards the polymer, which in turn poles the material.^{171, 173}

Alternative methods have been proposed to pole PVDF films into the β phase, such as electron beam poling.¹⁷⁴ This technique utilises a focused electron beam, whereby the polymer is irradiated locally by electrons to overcome the energy barrier required to

reorient into the β phase. This electron beam technique is quite effective at patterning small areas of material with β phase, however is not effective on a large scale.^{11, 175}

The majority of flexible PEGs utilising fluoropolymers have undertaken poling *via* the electrode method, with a select few opting towards the corona technique. One of the emerging trends is the deposition of electrodes onto the fluoropolymer prior to the poling, therefore using the PEGs own electrodes to pole the material.^{176, 177}

Table 2.4 compares poling methods discussed in this review as well as their advantages and disadvantages. For scalable production of highly electroactive and efficient PVDF polymers, the poling of the polymer should be a low-energy method and be integrated as part of the deposition process, as opposed to undertaking a separate processing step to pole the material. Indeed, a topic of increasing interest in the community is the fabrication of self-poled flexible PEGs.¹⁷⁸⁻¹⁸³ This type of energy harvester is able to be polarised in a single step of operation, which can arise from one of many factors, i.e., the processing technique itself, the conditions of the deposition such as temperature, pressure and humidity, or alternatively the careful use of additives into the polymer matrix. The utilisation of additives to induce preferential nucleation will be discussed in section 2.6.5.

Table 2.4: Reported processing methods used to convert the non-polar α phase of fluorinated polymers to the electroactive β phase and pole the resultant fluoropolymer, outlining the advantages and disadvantages of each method. ^{11, 32, 43}

Technique	Opportunities	Limitations
Electrode poling ^{a)}	- High d_{33} coefficient - Reproducible	- High electric field required - Use of heat - Limited scope for structures and patterns - Undertaken in vacuum (difficult to scale up)
Corona poling ^{a)}	- High d_{33} coefficient	- High voltage required

	- Requires only one electrode for poling - Allows for structures on one side of the material	- Requires heating - Undertaken in vacuum (difficult to scale up)
Electron beam poling ^{a)}	- Allows for patterning of highly piezoelectric regions - High resolution	- Slow and lengthy process, difficult to upscale - Unwanted chemical modification of material - Degradation of polymer - High cost process - Undertaken in vacuum
Mechanical drawing ^{a)}	- Highly reproducible - Simple process - Scalable	- Extrusion methods provide low scope for patterning and structuring the material - Tends to be used in conjunction with electrode or corona poling
Electrospinning	- Suitable for preparation of micro- and nano- scale fibres - Low temperature method - High degree of crystallinity can be obtained - Eliminates need for further poling	- High electric field required - Low reproducibility - Extraction of micro- and nano- fibres at low feed rates suggests low potential for scalability - Fibrous structure shows low Young's modulus and tensile properties
Additive manufacturing	- Low temperature method - High degree of crystallinity can be obtained <i>via</i> shear stresses at the nozzle - Scope for patterning of 3D features	- Requires solvent-based system at low temperatures - Shortage of available literature

-
- Simple adaptation of designs
 - Reduces need for further poling
-

^{a)} denotes methods commonly used for post-processing as a second step in the manufacture of electroactive fluorinated polymers

By taking advantage of electric fields (used in the electrospinning technique)¹⁵², or shear stresses (in 3D printing), nucleation of PVDF into the electroactive phases can be achieved, showing the generation of electricity without the requirement of poling. However, of all the poling techniques, the additive technologies have recently shown the greatest promise relative to the conventional post-processing methods.

2.6.5 Composites, additives and nanoscale fillers

Co-polymerising several fluorocarbon-based monomers together has demonstrated the altering of fluoropolymer properties (see section 2.6.2). However, the scope for such modifications is limited. The integration of additives and nanoscale fillers into the polymer matrix has been proposed as an alternative method to achieve enhanced electromechanical properties in PVDF-based polymers. The electrical output in the resulting PEGs has been evaluated, and will be discussed in this section.

A vast range of literature exists on incorporation of fillers into the polymer matrix of PVDF and its copolymers, processed using several of the techniques outlined previously. For example, researchers have attempted to integrate piezoelectric nanoparticles (NPs), nanorods (CNTs) and nanowires (NWs) into the PVDF matrix, showing increased electrical output due to synergetic effects between the piezoelectric NPs and the piezoelectric polymer matrix.⁴³ Conductive NPs, nanorods and NWs show enhanced orientation of PVDF into the desired β phase due to electrostatic interactions between the nanofiller and the surrounding polymer.³¹ Furthermore, insulating and dielectric nanomaterials, such as graphene oxide and DNA, have also been shown to increase the β phase fractions of PVDF.^{39, 43, 184}

Piezoelectric perovskite NPs are a primary candidate as nanofillers with the goal of increasing piezoelectric output, as they tend to show a higher piezoelectric charge coefficient ($d_{33} > 100 \text{ pC N}^{-1}$) and a higher energy conversion efficiency ($k_{33} > 0.5$).¹¹ Indeed, the incorporation of BTO NPs with PVDF has been reported to increase the β phase fraction of the fluoropolymer matrix, scaling as a function of decreasing NP size and increasing filler content.¹⁸⁵ The findings suggest selective nucleation of the β phase from the BTO surface. Additionally, the formation of β phase of PVDF is promoted by an increased surface area/volume (SA/V) ratio of the smaller particles and an increased local electric field around the BTO.¹⁸⁶ The maximum β fraction is determined to be 82% at a 5 wt% concentration of 10 nm diameter BTO relative to PVDF, decreasing to 70% at 10 wt% and further to 42% in 5 wt% of 500 nm BTO.¹⁸⁶ Recent studies have further proposed the interactions of the Ti^{4+} ion in BTO to preferentially nucleate the β phase through interactions with the fluorine atoms on the PVDF.¹⁸⁷

Ferrite NPs have been added to PVDF in the form of NiFe_2O_4 and CoFe_2O_4 , with an increase of β phase to 90% being reported.^{188, 189} Two separate mechanisms have been previously proposed to explain the findings; (1) the epitaxial nucleation of β phase PVDF from the surfaces of the ferrite NPs and (2) the interruption of chain mobility during crystallisation into the α phase which causes the polymer to crystallise into the β phase.¹⁸⁸ Sebastian *et al.*¹⁹⁰ have reported the preferential nucleation of β -PVDF in a mixture containing 1 wt% Fe_3O_4 nanorods (diameter $\approx 75 \text{ nm}$). This composite shows a β phase fraction of 75%, relative to 10% β phase in 1 wt% Fe_3O_4 NPs (using Equation (2.19)). The authors have suggested that the increase of the β phase content is dependent upon the aspect ratio of the material. Recently, Samadi *et al.*¹⁹¹ have studied the electrical output of PVDF with the incorporation of Fe_3O_4 -graphene oxide hybrid nanofillers. The study shows a generated voltage of 1.75 V per N of force at 2 wt% nanofiller, whereas the pure PVDF produces 0.24 V N^{-1} .

Titanium dioxide (TiO_2) NPs with average diameter of 21 nm have been incorporated into PVDF in a solvent mixture of DMF (30 vol%) and acetone (70 vol%).¹⁹² The study has found improved mechanical strength in the composite as well as significant increases in dielectric constant below 1 Hz ($\epsilon = 20$ at 0.1 Hz compared to $\epsilon = 10$ in PVDF), attributed

to the increase in β phase content. It should be noted the study does not measure the β phase fraction and only postulates their findings based on the dielectric constant measurements. Lastly, the composite material shows improved strength under an applied electric field, where the breakdown voltage is $150 \text{ V } \mu\text{m}^{-1}$, compared to $50 \text{ V } \mu\text{m}^{-1}$ in PVDF.

Metallic NPs have also been studied as fillers. Palladium and gold NPs integrated *via* solvent systems show increased β phase fractions.^{193, 194} These effects have been attributed to surface charge interactions of the NPs with the dipoles of PVDF.

A variety of carbon-based nanofillers have been integrated into the matrices of fluoropolymers. The use of CNTs has been extensively studied for their effects on the formation of the crystalline β phase of PVDF, with a recent review publication on processing and characterisation of composites by Kabir *et al.*³¹. More recent literature is highlighted in the following.

The incorporation of 1 wt% multi-walled CNTs (MWCNTs) has been found to increase the β fraction of PVDF from 30% to almost 50% in melt moulded samples and from 0% to 40% in electrospun mats.¹⁰² Further processing through uniaxial drawing produces β phase fractions of approximately 90% for all loadings of MWCNTs up to 1 wt%. However, the data in this study shows similar results in pure PVDF, suggesting that the effects observed here, after incorporation of CNTs, should be studied further.

The use of ultrasonication during the solution-based preparation of MWCNT/PVDF composites has been shown to induce β phase.¹⁹⁵ Samples are prepared *via* two methods, mechanical mixing (as a method with low energy input) and sonication (high energy input). The former technique produces purely α phase PVDF, while the latter technique produces predominantly β phase.¹⁹⁵ This phenomenon has been examined *via* density functional theory (DFT) calculations and is explained by the very large energy barrier required to convert the α phase PVDF to β phase.¹⁹⁵

A number of studies have shown that the incorporation of ionic liquids (ILs) into the PVDF matrices is a simple method to significantly enhance the β phase fraction in PVDF.

For example, Xing *et al.*¹⁹⁶ have used 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF₆]) and MWCNTs functionalised with the same IL to make composites with PVDF. Complete conversion of PVDF to β phase has been reported in all samples containing both MWCNTs and excess amounts of IL relative to MWCNTs by weight.¹⁹⁶

Maity *et al.*¹⁹⁷ have investigated the effects of the incorporation of IL-functionalised GO sheets into the PVDF matrix. This study reports an increase in the β phase content (through FTIR analysis and wide-angle x-ray scattering), the enthalpy of melting due to the β phase (through DSC analysis at 171.7 °C) and the mechanical properties with increasing IL-functionalised GO loading. Most of the desired metrics have shown to improve with the addition of GO; however, the study does not examine the electromechanical conversion of the resultant composite.

Dias *et al.*¹⁹⁸ investigated the incorporation of the IL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim][TFSI]) into the matrix of PVDF at loading rates up to 40 wt%. Through the use of FTIR and Equation (2.19), the study reports improved β phase content of 93% at 25 wt% IL relative to 0% in pure PVDF. Deviating from the reports by Maity *et al.*¹⁹⁷, the DSC study shows a decrease in T_m from 173 °C in the PVDF to 160 °C in the 40 wt% IL/PVDF sample. This decrease can potentially be attributed to the use of IL without GO. Furthermore, the crystallinity has been reported to decrease in these samples from 44% to 25%, respectively, in agreement with the reports of Xing *et al.*⁴⁰ however opposite to the reports of Maity *et al.*¹⁹⁷.

In a later publication, Dias *et al.*¹⁹⁹ explored the same IL incorporated into PVDF for its biocompatibility with the aim of utilising fluoropolymer-based PEGs for the purposes of implantable mechanical energy harvesting devices. In this work, the authors incorporate 10 wt% IL relative to PVDF with deposition *via* electrospinning. Results show the lack of significant decrease in cell viability of C2C12 mouse myoblast cells on the electrospun IL/PVDF materials, suggesting that fluoropolymer-based PEGs with IL additives are biocompatible.

Recently, Lopes *et al.*³⁹ have used IL 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF₄]) with PVDF. The study has found a linear increase in the β phase of PVDF as the IL content increases from 0% to 10%, leading to a maximum β phase content of 60%, in agreement with previous reports.^{40, 197, 198} Interestingly, by washing the composite with water at 70 °C the IL is removed from the polymer resulting in 100% β phase PVDF.³⁸ These findings demonstrate a low-temperature and low-energy processing pathway to the preparation of pure β phase PVDF. This study further reports a d_{33} coefficient of -27 pC N⁻¹ after corona poling. The d_{33} value of the unpoled IL/PVDF system has not been measured and hence cannot be directly compared.

Fukagawa *et al.*²⁰⁰ have recently investigated the piezoelectric properties of the IL [Emim][TFSI] upon incorporation into PVDF-TrFE. This study utilised a three-layer PEG, where a gel layer of 79 wt% IL in PVDF-TrFE is sandwiched between two annealed films of PVDF-TrFE, with Al electrodes on the top and bottom of the resultant structure. Through polarisation switching experiments on this device, the authors report a coercive field E_C of below 10 MV m⁻¹, significantly lower than 53 MV m⁻¹ obtained for the polymer without the IL. These values suggest that the required poling field strength is significantly reduced relative to pure polymer, hence decreasing the energy required to fabricate electroactive PEGs. Furthermore, the remnant polarisation of this device is reported to be 64.3 mC m⁻², slightly lower than that of the pure PVDF-TrFE film.²⁰⁰

On the other hand, the d_{33} value for the same device is measured at 129 pC N⁻¹, increasing to 381 pC N⁻¹ for a device where the active layer consists of 87 wt% IL.²⁰⁰ These values are approximately an order of magnitude higher than those of a PVDF-TrFE film and hence suggest that highly efficient flexible PEGs can be fabricated from these devices.

Interestingly, Tiwari *et al.*²⁰¹ have shown the formation of the γ phase in PVDF upon the incorporation of a poly(ionic liquid), poly(2-(dimethylamino)ethyl methacrylate) methyl chloride quaternary salt. Here, the poly(ionic liquid) is added to the PVDF in solution at loadings up to 50 wt% and thin films are then solvent cast. The amount of γ phase has been reported from FTIR using Equation (2.19), where the authors justify the use of the equation by the lack of β phase (at 1275 cm⁻¹) in the sample. The fraction of the γ phase has been shown to increase from 0% in pure PVDF to approximately 50% in the sample

containing 40 wt% poly(ionic liquid) in PVDF. The P - E analysis of the materials indicates a significant increase in the P_r from 14 mC m⁻² for PVDF to 60 mC m⁻² for the sample containing 25 wt% poly(ionic liquid). A further increase in the amount of poly(ionic liquid) results in leakage, although the P_r values are given as 62 mC m⁻² and 66 mC m⁻² for 30 wt% and 40 wt% poly(ionic liquid), respectively.

The utilisation of ILs, due to their structure, has been suggested to aid preferential nucleation in fluoropolymers *via* ion-dipole interactions.²⁰² The effects of various ILs on the resultant crystallinity, conformation and polarisation are required to be studied for greater understanding of the underlying chemistry and hence the tailoring of the electromechanical properties of these systems. Nonetheless, the current literature suggests that ILs enhance the piezoelectric properties of fluoropolymers towards efficient flexible PEGs.

Overall, the incorporation of fillers and additives in fluoropolymers shows great promise. In particular, the inclusion of nanomaterials for enhancement of electromechanical conversion is very exciting.

2.7 Flexible PVDF-based electric generators

PVDF is a versatile material, with properties allowing it to generate charges when mechanically deformed. Widespread efforts have been made by researchers to develop PVDF-based PEGs on both a lab scale and towards commercial applications. The following sections will discuss some of the applications of PVDF-based PEGs.

2.7.1 Wearable piezoelectric generators

The majority of research in fluoropolymer-based PEGs has been around applications in wearable electronics, either on-skin or as part of clothing. In fact, the first flexible polymeric PEG has been embedded in part of the shoe, allowing the wearer to generate electricity from walking.²⁰³ Here, Kymissis *et al.*²⁰³ have reported a shoe-embedded laminate of 16 layers of PVDF film (each 28 µm thick) bonded with epoxy, able to generate a maximum voltage and power of approximately 60 V and 20 mW per step, respectively. Due to the time-dependent nature of the electrical signal, the average power generated

from this device is 1.1 mW at a frequency of approximately 1 Hz. Since then, many researchers have investigated the possibility of integrating fluoropolymers into shoe-mounted PEGs.²⁰⁴⁻²⁰⁷ A comprehensive review on this topic can be found by Xin *et al.*²⁰⁸.

A further mechanism for harvesting mechanical energy from human movement has been found in backpack straps. Granstrom *et al.*²⁰⁹ have reported a PVDF PEG working in the 31 mode for conversion of the mechanical strain of walking with a backpack into electricity by placing PVDF into the straps. This form of PEG shows a maximum power output of 3.75 mW for a single strap with a thickness of 28 μm .²⁰⁹

More recently, PEGs integrated into textiles have become a topic of great interest. A variety of publications have proposed the use of fluoropolymer fibres in woven textiles utilising electrospinning and mechanical drawing techniques.²¹⁰⁻²¹⁴ The fabrication of PVDF fibres towards utilisation in energy harvesting textiles has been initially reported by Hadimani *et al.*²¹⁵. This study shows a maximum generated voltage of 2 V when a 1.02 kg mass is dropped from a height of 5 cm onto several fibres sandwiched between two copper plates, indicating prospects for the use of PVDF fibres as a textile PEG.

Magniez *et al.*²¹⁶ have presented initial reports on 2D woven PVDF textile generators using melt-extruded and drawn piezoelectric fibres, along with silver-coated nylon fibrous electrodes and non-conductive nylon as a spacer, shown in Figure 2.13a. This 2D woven device has an average voltage between 3 V and 4 V, with a maximum of 6 V under cyclic compression with a force of 70 N (shown in Figure 2.13b). In another study, the group has analysed the impacts of the electrode materials on the output voltage, finding that silver-coated copper electrodes show the highest generated voltage under sine wave shaped vibration. Here, the work has analysed metal-wire electrodes consisting entirely of aluminium, titanium or steel, as well as coaxial fibres composed of either nylon or copper core with a silver coating external layer. It is noted that the various materials used in the study are not consistent in their geometry and hence are difficult to compare directly.²¹⁷

The work of Soin *et al.*³⁰ has demonstrated a 3D spacer textile, woven using silver-coated polyamide-66 (PA66) yarn as electrodes, with melt-spun and poled PVDF fibres as the piezoelectric yarn between them, shown in Figure 2.13c. This PA66-PVDF-PA66 system, which feels just like standard fabric, is able to generate a voltage up to approximately 14 V, with a power density of $5.10 \mu\text{W cm}^{-2}$ at an impact pressure of 0.1 MPa (Figure 2.13d). Similarly, Talbourdet *et al.*²¹⁸ have reported on a 3D interlocked woven PVDF textile, generating a maximum voltage of 2.3 V (average 1.29 V) with an overall energy of $10.5 \mu\text{J m}^{-2}$ (at a resistance of 1 M Ω). These values have been achieved through cyclic compression of the textile at a frequency of 100 Hz and a force of 5 N. The authors have reported a power output density on the order of $10^{-12} \text{ W cm}^{-2}$, significantly lower than the values reported in the work of Soin *et al.*³⁰. It should be noted that in this study the electrodes are not woven into the textile; instead, bulk copper electrodes are used, which results in measured voltage losses upon decompression. All of the aforementioned PVDF-based textile PEGs have utilised melt-spinning to obtain fibres, with mechanical drawing and dual-electrode electrical poling of the fibres used during spinning to increase the amount of β phase and polarisation within the fibres, respectively.

More recently, Gao *et al.*²¹⁹ have produced a piezoelectric yarn by electrospinning of a PVDF solution onto a silver-coated nylon yarn, followed by coating with PVDF by passing the resultant yarn through a solution of PVDF to produce an electrospun + film core-sheath yarn (Figure 2.13e). An external silver electrode has been deposited onto the outer surface of the yarn *via* electron beam evaporation. A single yarn with a length of 3 cm has been reported to produce a voltage and current of 0.52 V and 18.76 nA, respectively (Figure 2.13f). The volumetric power density has been reported as $5.54 \mu\text{W cm}^{-3}$ when exposed to cyclic compressions at 0.02 MPa pressure at a frequency of 1.85 Hz.

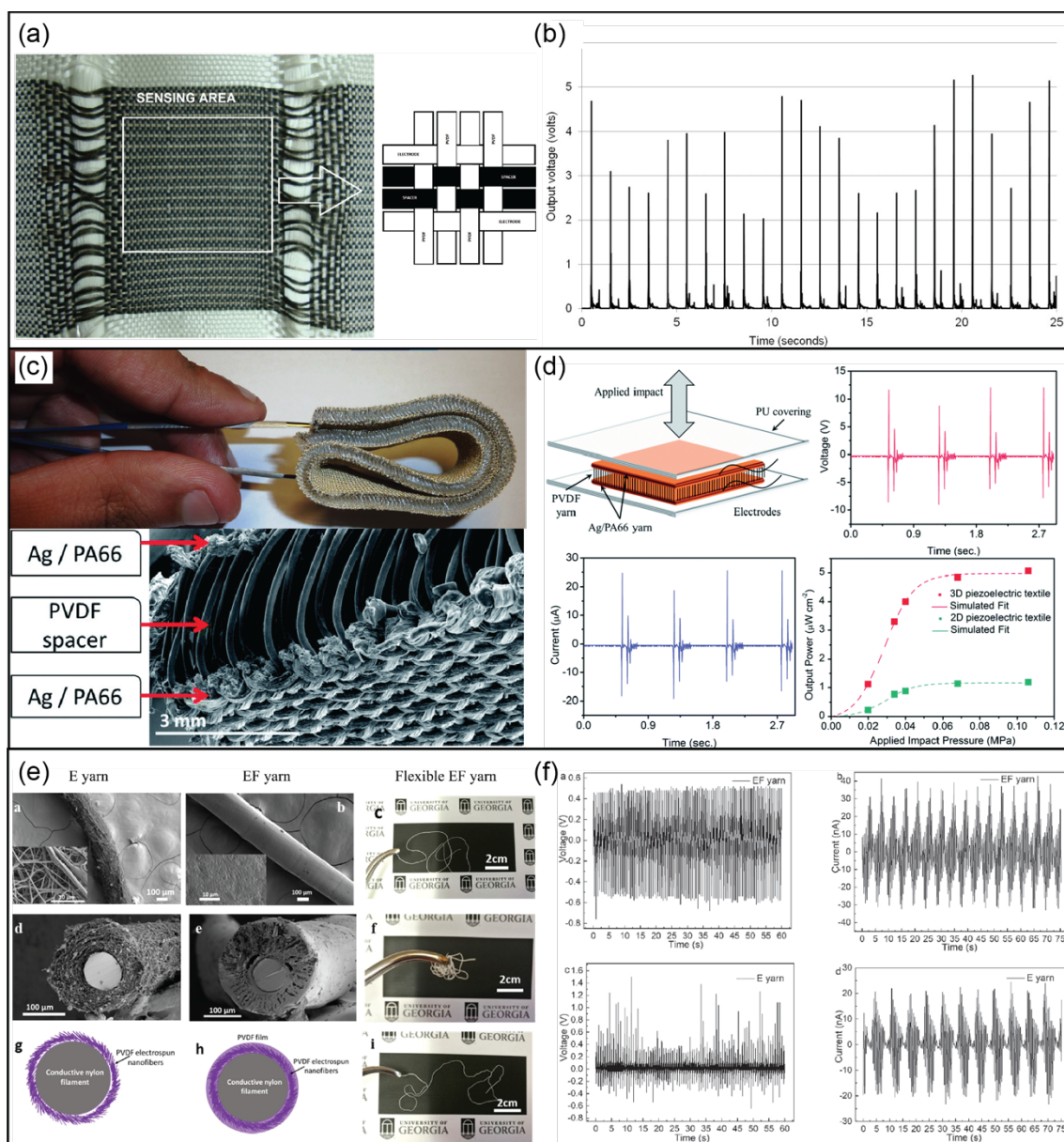


Figure 2.13: The morphological structure and electrical output characteristics of recently reported woven fluoropolymer flexible PEGs. (a) the woven flexible PVDF fabric PEG with a schematic of the weave pattern on the right and (b) the voltage generated from the PEG upon cyclic compression. Reproduced with permission from ref 216. Copyright 2013, Wiley. (c) Photograph (top) demonstrating the flexibility of the PVDF-based 3D spacer textile PEG, cross-sectional SEM image (bottom) of the PEG, and (d) the electrical output characteristics including the voltage, current and power of the PEG under cyclic compression. Reproduced with permission from ref 30. Copyright 2014, Royal Society of Chemistry. (e) SEM images of the electrospun (E) and electrospun + film core-sheath (EF) yarns, with a schematic outlining the cross-sectional view, with optical images of the yarns. (f) output characteristics including the voltage and current from the EF yarn (top) and E yarn

(bottom) under cyclic compression. Reproduced with permission from ref 219. Copyright 2018, Institute of Physics.

Similarly, Lund *et al.*²⁹ have fabricated a coaxial fibre PEG, which has been woven *via* plain weave and twill patterns into a textile. This work has used a melt-spinning mechanism to simultaneously co-extrude a fibre with a conductive core consisting of 10 wt% carbon black in polyethylene and an outer piezoelectric layer consisting of PVDF. Polyamide yarns coated with Ag have been utilised as the outer electrodes. To demonstrate the applicability of these flexible PEG textiles, they have been incorporated into the shoulder strap of a bag. During walking, with the strap carried by hand, the PEG is reported to generate $1.9 \mu\text{W cm}^{-3}$ volumetric power density. This power density is notably lower than the work of Gao *et al.*²¹⁹, even though this report has poled the material *via* the corona method. This type of PEG has additionally been shown to provide enough electrical energy to power a commercial LED after 15 sec of charging a 22 μF capacitor, resulting in continuous blinking of the LED with an average frequency of 0.13 Hz.

PVDF-based flexible yarn PEGs certainly have been shown to have the potential to be woven into textiles for the scavenging of energy from human movements into electricity. Furthermore, the proof-of-concept textile PEGs mentioned in this section show the potential of transformation into industrial products such as smart clothing with the ability to power portable electronic devices in a sustainable manner, through the scavenging of the wearer's movements.

2.7.2 Implanted piezoelectric generators

Another promising use of fluoropolymer-based flexible PEGs is harvesting biomechanical energy to power implantable electronic devices, such as permanent pacemakers, implantable cardioverter-defibrillators, cardiac resynchronisation therapy devices, and long-term implantable wireless sensors among others. The main drawback of current generation devices lies in the lifespan of the batteries; consequently, implanted devices are required to be removed from the body for the replacement of their power sources. Thus, using flexible PEGs to harvest biomechanical energy can be advantageous for the purposes of powering such devices, as has been reported recently by several authors.²²⁰⁻²²⁴

The first reports of an implanted fluoropolymer PEG have been published by Hausler *et al.*²²⁵. This study investigates the *in-vivo* operation of a PEG, with PVDF as the active material, attached to a rib of a dog in order to harvest energy from respiration. The *in-vivo* experiments have shown a maximum voltage of 18 V, corresponding to a power of 17 μ W, with no loss in durability over the three hours of the experiment.

Cheng *et al.*²²⁶ have fabricated an implantable self-powered PVDF blood pressure sensor, based on the principles of PEGs (Figure 2.14a). This device has been found to generate a maximum instantaneous power of 2.3 μ W during *in-vitro* experiments, whereby the thin film PEG is wrapped around a tubular latex artery analogue filled with saline (Figure 2.14b). Here, the deformation is induced using an intra-aortic balloon pump to mimic the pumping action of the heart. The *in-vivo* studies in this work have been found to generate a maximum instantaneous power output of 40 nW with the device wrapped around the aorta of a Yorkshire porcine (Figure 2.14c). Here, the generated power is found to scale linearly with systolic blood pressure, whereby the maximum is obtained at 220 mmHg. Although no voltage or power data has been presented for blood pressure below 160 mmHg, the study further reports a liquid crystal display to be powered directly by the cyclic expansion and contraction of the aorta at blood pressures at, and above, 140 mmHg with no additional electrical signal conditioning or electrical energy storage connected (Figure 2.14a).

Yu *et al.*²²⁷ have reported an implanted sponge-like PVDF-based thin film PEG (Figure 2.14d) inserted under the skin of living mice and rats. During *in-vitro* testing of the PEG in the mode of cantilever-like deflection under an applied strain of approximately 0.1%, the device has been found to generate a maximum voltage and current of 3.8 V and 3.5 μ A, respectively, corresponding to an instantaneous power of 13.3 μ W (Figure 2.14e). The PEG has been further inserted beneath the skin of the right leg of a mouse and its electrical output has been measured during manual deflection of the leg (Figure 2.14f). Similar to the work of Cheng *et al.*²²⁶ discussed above, both the voltage and current, 0.26 V and 0.17 μ A, respectively, are lower than during *in-vitro* tests, corresponding to 44.2 nW instantaneous power (Figure 2.14f).

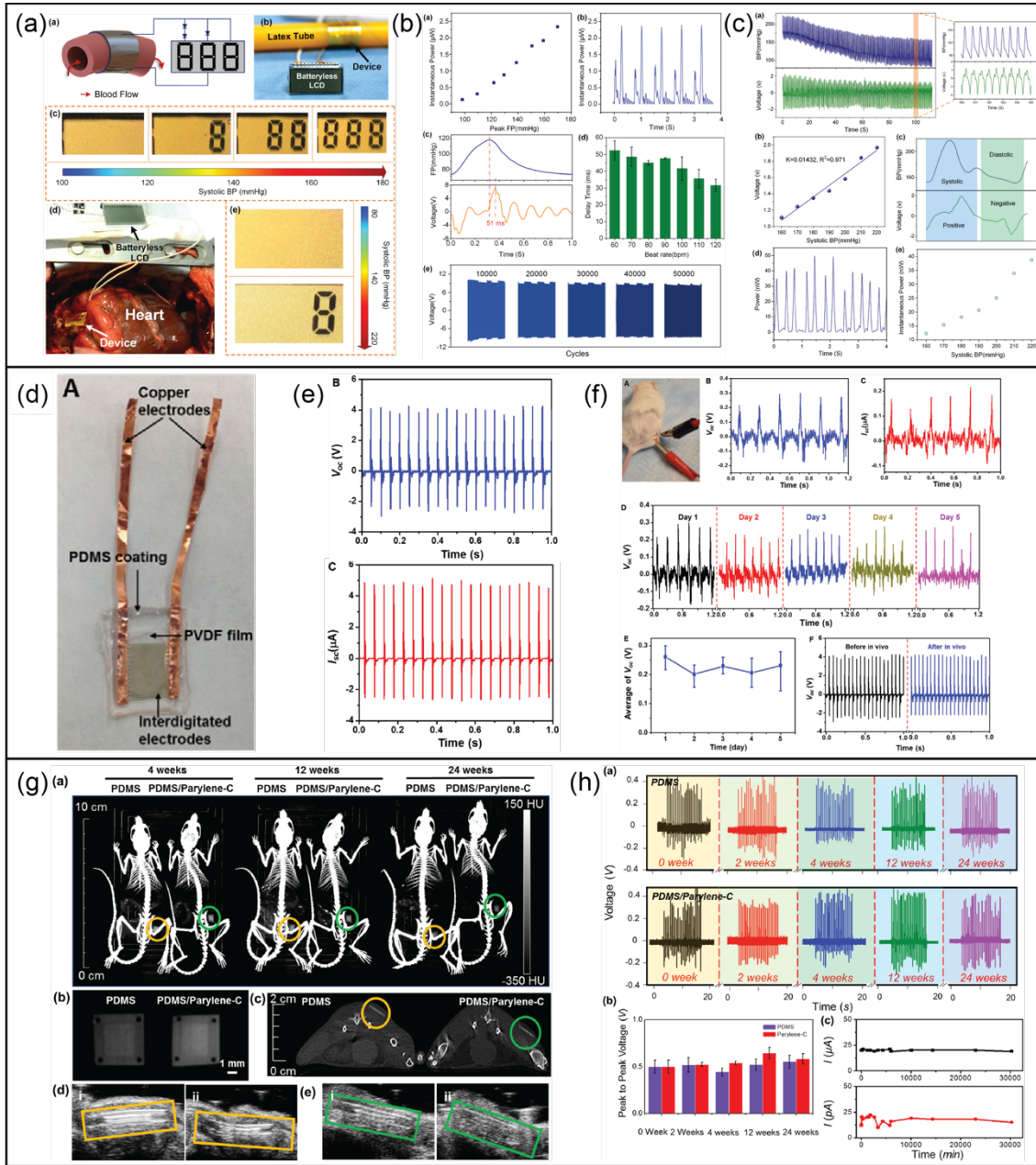


Figure 2.14: The structure and electrical output characteristics of recently reported implanted fluoropolymer flexible PEGs. (a) Schematic (top) showing the working conditions for the implantable PEG and (bottom) implanted fluoropolymer PEG wrapped around the aorta of a Yorkshire porcine, both showing the ability to power a battery-less LCD display above a blood pressure of 120 mmHg *in-vitro* and 140 mmHg *in-vivo*. (b) The electrical output characteristics of the *in-vitro* experiment when wrapped around a latex tube mimicking the aortic artery and (c) the electrical output characteristics of the *in-vivo* experiments. Reproduced with permission from ref 226. Copyright 2016, Elsevier. (d) Image showing the structure of the implantable fluoropolymer PEG encapsulated in poly(dimethyl siloxane), (e) the electrical output characteristics during *in-vitro* experiments, showing the open circuit voltage

and short circuit current, and (f) electrical output characteristics during the *in-vivo* experiment, showing the image of the PEG implanted in a mouse, the open circuit voltage and short circuit current when the leg of the mouse is deflected manually, as well as the output of the PEG as a function of implanted time. The bottom-right panel shows the *in-vitro* open circuit voltage before and after implantation. Reproduced with permission from ref 227. Copyright 2016, Elsevier. (g) *In-vivo* computed tomography images (top) of the PVDF PEGs encapsulated in PDMS and Parylene-C during the implantation period, as well as ultrasound images of the devices implanted in mice. (h) Electrical output characteristics of the long-term implanted PVDF PEGs, showing (top) the voltage of both devices, (bottom left) average peak-to-peak voltage as a function of implantation period for both devices and (bottom right) the input and output currents during characterisation of the leakage current in the device encapsulated in poly(dimethyl siloxane) as a function of time. Reproduced with permission from ref 228. Copyright 2016, Elsevier.

Although it is difficult to directly compare the two studies, the values of the maximum instantaneous power generated are similar. Of note is the biocompatibility study performed in the work of Yu *et al.*²²⁷, which suggests no signs of toxicity or incompatibility under the skin of the mice after six weeks. As a proof-of-concept, this study demonstrates the utilisation of a miniaturised energy storage package attached externally to the back of the mouse (in a backpack-like manner), consisting of a rectification circuit and a 1 μF capacitor, able to store the harvested electricity from the implanted PEG, with a steady open circuit voltage of 0.052 V.

More recently, Li *et al.*²²⁸ have undertaken a follow-up study on the long-term *in-vivo* biocompatibility of a PVDF-based PEG. Their research examines the safety of encapsulated PVDF-based PEGs under *in-vivo* conditions for up to six months post-implantation, namely for the presence of inflammatory infiltration, fibrosis, muscle degeneration and cellular anomalies (Figure 2.14g).²²⁸ Additionally, the electrical output of the PEGs has been studied *in-vitro*, after the implantation for up to six months (Figure 2.14h). In this set of experiments, each device has been initially implanted into a mouse for a set period and extracted for *in-vitro* tests.

This extensive study has shown that the implantation of fluoropolymer-based PEGs does not show signs of cytotoxicity *in-vivo* throughout long-term implantation. Relative to the previous study by Yu *et al.*²²⁷ (same group), this study reports a lower *in-vitro* electrical power value of 13.5 nW, based on 0.3 V potential difference and 45 nA current (when the PEG is deflected by an electromagnetic shaker with a force of 6 N and a frequency of 2 Hz). Notably, a different frequency has been applied between the two studies, which makes it difficult to compare the relevant results. Similar to the previous study,¹¹⁶ the voltage generation of the PEG has been tested *in-vivo* through stretching of the leg muscle of the mouse, as the PEG has been implanted subcutaneously onto the leg muscle.¹¹⁷ A peak-to-peak voltage of 0.05 V at a leg-stretching frequency of 1 Hz and 0.1 V at 2 Hz has been reported. Lastly, the implanted PEGs removed from the mice after six months for voltage testing show no long-term degradation of piezoelectric properties due to implantation of the device.¹¹⁷

These studies have been the first to provide insights into the stability and durability of fluoropolymer-based PEGs in the body, suggesting their suitability for commercial applications in the field of powering implanted electronic devices. In the current state of the field, more work needs to be undertaken on *in-vivo* studies and utilising more powerful fluoropolymer PEG systems reported elsewhere. Fluoropolymer PEGs are fully expected to contribute significantly to future applications in the healthcare sector.

2.7.3 Piezoelectric generators driven by the environment

Harvesting energy from the urban and natural environments (external mechanical stimuli such as road deformation under passing vehicles, vibration, wind and water flow) has been previously shown as a viable option for building sustainable electricity generators towards reducing the reliance on fossil fuels. Of these, wind-based energy harvesting has seen the greatest commercial acceptance.

External mechanical forces are present and abundant throughout the environment, implying that energy harvesters based on the principles of piezoelectricity are suitable candidates to generate electricity from these sources. A variety of innovative applications have been both proposed and validated at a laboratory scale. Among these, is the harvesting of

mechanical energy from the movement of vehicles on a road, previously proposed as one of the technologies enabling “smart roads”.^{22, 229, 230} PEGs are anticipated to be capable of powering street lamps and nearby buildings, in addition to acting as sensors for monitoring the ongoing traffic density and the condition of the road itself.²³¹ Employing PEGs as sensors is forecasted to optimise traffic signal timing for the reduction of roadway congestion and to assist in the efficient allocation of road maintenance resources.²³²

Initially, piezoelectric ceramic materials have been utilised for this purpose and have shown significant promise. In fact, attempts have been made to commercialise this technology using PZT as the active piezoelectric component, and pilot-scale studies to validate the viability of the roadway PEGs have been undertaken.²³³

For efficient and long-term use of this technology, flexible materials are highly desirable to prevent cracking when integrated under the pavement surface of the road. In this instance, polymeric materials with a much lower Young’s modulus are more suitable relative to their brittle, ceramic counterparts. The first report of a PEG, with PVDF as the active material, embedded into a road is from Jung *et al.*²², shown in Figure 2.15a-c. This study utilised a commercial PVDF film with a thickness of 110 μm to create laminated stacks of up to 60 piezoelectric films with an optimised initial radius of curvature for use in the 31 mode of operation. Each harvester in this study consists of two PVDF films immobilised on the front and back sides of a polyimide substrate (300 μm thickness, predetermined radius of curvature) by using nickel-based fabric tape, which acts as the electrode (Figure 2.15a). The electrical output for the unit harvester has been reported to result in an open circuit voltage of 61.2 V and a short circuit current of 18.4 μA under a strain rate of 1.5% s^{-1} .²²

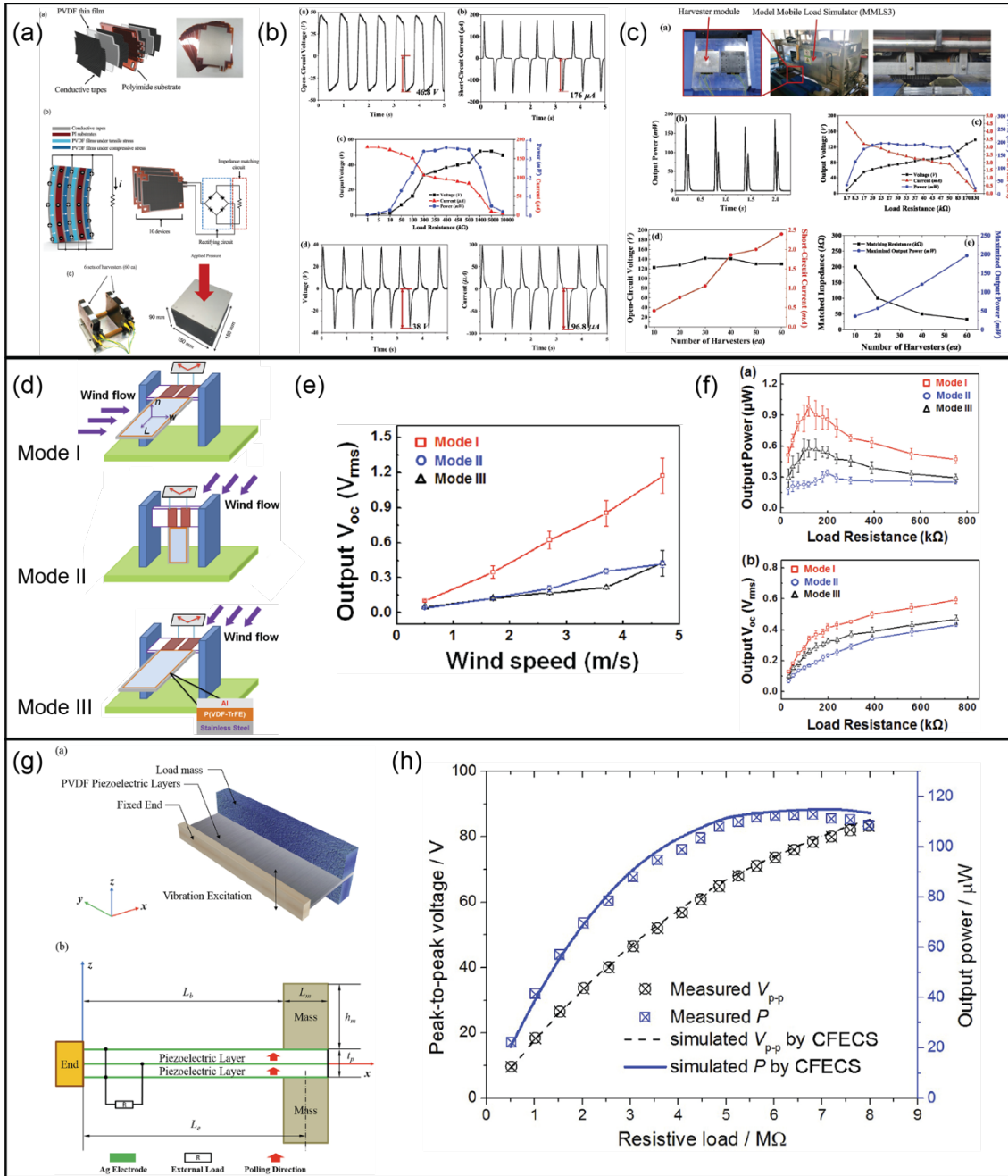


Figure 2.15: The structure and electrical output characteristics of recently reported environment-driven fluoropolymer flexible PEGs. (a) Schematic and images showing the contents of the roadway unit harvester, as well as the ten-unit systems and 60-unit systems studied in this report. (b) The electrical output characteristics of the ten-unit systems, showing (top) V_{OC} and short circuit current, (middle) the resistance matching data, and (bottom) the voltage and current at the matched load resistance of 400 kΩ. (c) The electrical output characteristics of the 60-unit systems under simulated road conditions, showing (top) images of the experiments, (middle) resistance matching data and power across a 400 kΩ resistor and (bottom) V_{OC} and short circuit current as a function of the number of unit harvesters, as well as the

matched load resistance and power output of the road-harvesting PEG as a function of the number of unit harvesters. Reproduced with permission from ref 22. Copyright 2017, Elsevier. (d) Schematic showing various geometries tested for the PVDF wind-harvesting PEG, (e) generated V_{OC} as a function of wind speed for the three geometries and (f) resistance matching data showing (top) the output power and (bottom) V_{OC} as a function of load resistance. Reproduced with permission from ref 238. Copyright 2014, American Institute of Physics. (g) Schematic showing the structure of the optimised vibration-excited PVDF PEG and (h) electrical output characteristics at an optimised of 34.4 Hz as a function of load resistance, based on simulated optimised geometry. Reproduced with permission from ref 239. Copyright 2017, Elsevier.

Through optimisation of the initial radius of curvature to 300 mm, the study has claimed an increase in the open circuit voltage of 75 V, justified by an increase in the maximum induced stress. A set of ten unit harvesters have been connected in parallel, and consequently attached to a suitable resistor *via* a rectifying bridge. Under similar strain conditions, this set has been reported to output 3.6 mW, corresponding to 38 V and 96.8 μ A at the impedance-matched resistive load of 400 k Ω (Figure 2.15b).²² Jung *et al.*²² have further investigated the energy harvesting characteristics of a PEG consisting of six sets of harvesters, with a total of 60 unit harvesters (or 120 PVDF thin films) in parallel, which is tested under a simulated load of a passing vehicle (using a model mobile load simulator, shown in Figure 2.15c). The reported maximum instantaneous power output due to the equivalent of a personal vehicle moving at 8 km h⁻¹ (with a reported force of 2.5 kN) is 200 mW, corresponding to 88.9 V and 2.25 mA at an impedance-matched resistance of 40 k Ω (Figure 2.15c). The authors have further claimed a calculated power density of 8.9 W m⁻² for the roadway PEG, acceptable for large-scale energy harvesting under the pavement in roads.

An alternative approach has recently been proposed for harvesting energy in high-speed railway applications.²³⁴ This technique utilises PVDF films acting as cantilevers placed inside Helmholtz resonators to harvest energy from the vibrations induced by moving trains, while providing a secondary function as a noise-reducing barrier. At the experimentally-optimised resonant frequency of 447 Hz and impedance-matched resistance of

6 k Ω , the PVDF film PEG (thickness = 200 μm) has been reported to produce a maximum power of 1.24 μW , corresponding to a voltage and current of 74.6 mV and 16.6 μA , respectively. This value is obtained at a sound pressure level of 110 dB. Interestingly, the power output noticeably decreases to 0.59 μW (52.2 mV, 11.3 μA) when the sound pressure level dropped to 100 dB. This is an interesting innovative application for flexible PEGs and this group appears to be progressing towards large-scale installations consisting of 480 Helmholtz resonator PEG devices per module.

The harvesting of energy from natural environments using flexible PVDF-based PEGs has also been previously reported. For example, Vatansever *et al.*²³⁵ have fabricated a PVDF cantilever PEG, with half of the length secured to the support and the other half suspended in air. This study investigates the ability of the PEG to generate electricity from falling raindrops and wind under dynamic conditions. Two lengths of 28 μm thick PVDF film were used for the experiment, 41 mm and 171 mm, each sandwiched between two Cu-coated polyester laminates. The raindrop experiment has reported that the 41 mm-long PVDF PEG generates an open circuit voltage of approximately 2.3 V when a droplet weighing 7.5 mg is dropped from a releasing height of 100 cm, increasing to approximately 12 V for a droplet weighing 50 mg.¹²¹ Furthermore, the authors report the open circuit voltage of a short PVDF cantilever PEG to be significantly higher than that of a composite consisting of uniaxially aligned PZT fibres in an epoxy matrix under similar experimental conditions.¹²¹

Vatansever *et al.*²³⁵ have further characterised the power generated for the aforementioned flexible cantilever-type PVDF PEGs, suggesting that the short PVDF strip generates an electrical power on the order of nanowatts, whereas the longer sample generates 93.6 μW at a wind speed of 10 m s^{-1} . Comparatively, the same study has reported a PZT composite, generating 6.5 μW for a single layer PEG and 3.6 μW for a bimorph.²³⁵ The authors further reported a volumetric power density of 16.2 $\mu\text{W cm}^{-3}$ at 5 m s^{-1} and 157.9 $\mu\text{W cm}^{-3}$ at 10 m s^{-1} wind speed, the latter showing an increase over the PZT composite by a factor of 16.

Work by Li *et al.*²³⁶ has investigated the effects on the positioning of a flexible cantilever-type PVDF wind-driven PEG relative to the direction of the wind and correlating it to the

electrical generation capability. Two directions have been investigated, using a parallel-flow device and a cross-flow device, positioned parallel and perpendicular to the wind flow direction, respectively. The study reported an enhanced power density from the cross-flow device relative to the parallel-flow device, with maximum values of approximately $14 \mu\text{W}$ and $3.5 \mu\text{W}$, respectively, at a wind speed of 6.5 m s^{-1} and a load resistance of $1 \text{ M}\Omega$. Increasing the load resistance to $10 \text{ M}\Omega$, the maximum power output increases to $296 \mu\text{W}$ in the cross-flow device at a wind speed of 8 m s^{-1} . The maximum volumetric power density at a moderate wind speed of 5 m s^{-1} has been reported at $68.5 \mu\text{W cm}^{-3}$.

Further work by the same research group has investigated similar PEGs with varying dimensions, the long cantilever (72 mm length and 16 mm width), the short cantilever (41 mm length and 16 mm width) and a narrow short cantilever (41 mm length and 8 mm width).²³⁷ The varying devices have been immobilised in a wind tunnel with cross-sectional dimensions of 25 cm in height and 25 cm in width in the cross-flow orientation, whereby the induced wind speed ranged from 0 m s^{-1} to 8 m s^{-1} . The generated volumetric power density has been investigated with varying wind speed, showing that the long cantilever-type PEG has the highest values at wind speeds below 4 m s^{-1} . Results also indicate that the narrow short cantilever-type PEG generates the highest power densities between 4 m s^{-1} and 7.5 m s^{-1} , whereas at 8 m s^{-1} the short cantilever generates the highest volumetric power density at approximately 1.5 mW cm^{-3} .¹²³ The study further reports that a maximum generated volumetric power density of 2.0 mW cm^{-3} is obtained for the narrow short cantilever with a load resistance of $30 \text{ M}\Omega$. However, no data is shown for the influence of the variation of load resistance on the electrical output of the wind-powered PEGs.

Li *et al.*²³⁸ have utilised a PVDF-TrFE copolymer thin film as the piezoelectric layer in flexible wind-powered PEGs and have investigated the electricity generated from three geometries, shown in Figure 2.15d-f. Mode I and mode III correspond to cross-flow and parallel-flow devices as outlined above, whereas mode II corresponds to the wind flow perpendicular to the PEG in a manner where the wind impacts the surface of the PEG (Figure 2.15d). In this work, the PVDF-TrFE layer has a thickness of $4 \mu\text{m}$ and is deposited onto an $8 \mu\text{m}$ thick stainless steel foil acting as the bottom electrode. The resulting structure is then annealed at $130 \text{ }^\circ\text{C}$ for 2 h . The top electrode consists of a 100 nm

thermally evaporated layer of Al, and post-processing is undertaken to polarise the piezoelectric layer. This work, compared to the aforementioned studies, has investigated wind speeds below 4.7 m s^{-1} , as those speeds are more comparable to those found in nature. However, the wind tunnel in Li *et al.*'s²³⁸ study has a circular cross-section with a diameter of 8.5 cm. The comparative study of the three modes suggests a linear increase in the generated open circuit voltage as a function of wind speed, whereby the cross-flow (mode I) device shows the highest open circuit voltage of the investigated harvesting modes at approximately 1.2 V (Figure 2.15e). This is four times higher than those of modes II and III. Through resistance matching experiments at a wind flow of 3.9 m s^{-1} , the output power for the mode I device has been reported as $0.98 \text{ }\mu\text{W}$ for a resistive load of $120 \text{ k}\Omega$ (Figure 2.15f). This value corresponds to a volumetric power density of $233 \text{ }\mu\text{W cm}^{-3}$ based on top electrode dimensions of 7 cm length and 1.5 cm width. This value is lower than the previously reported volumetric power output; however, it should be noted that differences in design could have contributed to the changes in output values.

More recently, Song *et al.*²³⁹ have investigated a generalised case of off-resonance vibration-based excitation of a flexible PVDF bimorph PEG in the shape of a cantilever with a fixed mass at the end (Figure 2.15g). The work utilises a coupled finite-element-circuit approach to optimise the parameters of the PEG, and the results of modelling are verified in experimental studies. The maximum volumetric power density for two $50 \text{ }\mu\text{m}$ thick PVDF layers bonded together with thin Ag electrodes has been reported as 8.61 mW cm^{-3} with an optimised load resistance of $6.81 \text{ M}\Omega$ (Figure 2.15h). The excitation acceleration has been reported as 0.5 g at the optimised frequency at 34.4 Hz, corresponding to 25.5 MPa maximum stress.

These examples are intended to provide an overview of the possible applications where flexible polymeric PEGs have been previously utilised. These promising proof-of-concept devices are expected to encourage further growth of prospective applications in this field, both in laboratories and in commercial settings.

2.8 Concluding remarks and future perspectives

Flexible fluoropolymer-based PEGs have attracted increasing attention as a promising energy harvesting solution due to their mechanical flexibility, transparency, operating temperatures suitable for widespread use, high compatibility with straightforward deposition and processing methods, biocompatibility and high piezoelectric energy conversion efficiencies. This type of PEGs has been demonstrated for applicability in either directly powering a range of electronic devices or providing an additional source of electricity for their operation. This all assists in decreasing the reliance on the outdated conventional electricity generation and storage technologies.

Despite the advancement of flexible PEGs in the recent years, challenges remain before the commercial adoption of these devices can occur. These challenges arise largely from a lack of clear understanding of the connection between the various aspects of this complex field. Currently, the field appears heavily segmented into largely independent studies undertaken by polymer chemists exploring novel synthetic routes, and material scientists and engineers processing and depositing the polymers into useful devices, with mechanical engineers optimising the physical parameters for enhanced energy conversion, and electrical engineers efficiently integrating the PEG into usable devices. It is, therefore, important that these fields work together to successfully produce devices with the required parameters to maximise the energy conversion from mechanical force to electricity and the production of commercially relevant devices.

Moreover, the characterisation techniques utilised by each of these disciplines, generally, do not provide a complete description of the flexible fluoropolymer PEG systems, reducing the ability to directly and quantitatively compare the results obtained. Therefore, the development of cross-disciplinary collaborations between the disciplines holds great potential in facilitating the in-depth understanding of complex connections between the chemistry of fluoropolymers, their processing, and the properties of the resulting flexible PEGs.

Aside from the shift towards multidisciplinary studies, optimisations of the current methods in each discipline is also crucial. For example, the current spectroscopic techniques used to fingerprint the phases of PVDF, and related polymers, show clear limitations. The

FTIR technique, commonly used in the characterisation of these polymers, often results in complex spectra with overlapping peaks for the β and γ phases. Recent literature has attempted to overcome this constraint; however, further efforts are required. The utilisation of Raman spectroscopy leads to characteristic peaks for the various phases with higher resolution relative to FTIR; however, is currently underutilised in literature. Simultaneous DSC-Raman can also provide a fingerprint both of the relative phase content and the overall crystallinity.

Additionally, the currently accepted methods for measuring the net polarisation vector are limited in their scope—the P - E hysteresis technique utilises an electric field which has the parasitic effect of poling the material and therefore generally provides only the maximum polarisation that can be obtained in the fluoropolymer. Characterising the net polarisation within the sample without affecting it will provide insight into the net dipole vector in the fluoropolymers without influencing the system. Researchers within this field are strongly encouraged to pay appropriate attention to developing a suitable characterisation method for polarisation measurements.

Currently, poling is commonly used as an additional step to polarise the fluoropolymers in PEGs; however, as will be discussed in section 2.6.4, this step is undesirable because it utilises high temperatures and high electric fields. Therefore, methods to produce suitable fluoropolymers for PEGs without poling are extremely interesting. It is very exciting that scalable solvent-assisted extrusion technologies such as 3D printing and electrospinning have been recently shown to be able to provide *in-situ* poling (without the need for the post-processing *via* electric fields) through either shear stresses or induced electric fields, respectively. The ability to fabricate flexible PEGs in a shorter number of fabrication steps and with less energy input is expected to be a key contributor in driving the commercialisation of the PEG and further increase the prospects of sustainable energy harvesting methods.

The emergence of additive manufacturing technologies such as 3D printing and electrospinning has opened the door for advanced fluoropolymer structures, which have been difficult to explore previously. In particular, preliminary research in the fabrication of high aspect ratio structures has reported drastic improvements in the energy conversion

efficiency of fluoropolymers. It is expected that various new 3D printing technologies, such as fused deposition modelling, solvent-evaporation assisted printing and melt electrowriting (among others), will enable layer-by-layer and true 3D extrusion of the fluoropolymers and lead to the increase of energy conversion efficiency in flexible PEGs. In addition, multi-material printing shows great potential for complete end-to-end production of PEGs through the controlled deposition of electrode materials, reducing waste and providing a true single-step fabrication technique.

Another exciting developing area to emphasise is the incorporation of additives into piezoelectric fluoropolymers. Preferential reorientation of the crystalline phases of the polymer into the β phase has been proposed as the standard mechanism of increasing the electromechanical conversion, due to either steric or electrostatic interactions. However, the optimisation of crystallinity and polarisation using additives has not been systematically explored to date. These factors influence the electrical output from electromechanical conversion in flexible PEGs and hence it will be critical to investigate the influences and the underlying mechanisms of nanomaterials and other additives on the enhancement of these properties.

In general, the new developments in understanding how the properties of fluoropolymers enable future flexible PEG applications has led to a significant push in research efforts in recent years. Future fluoropolymer-based PEG research is anticipated to provide further insights into the understanding of the open questions posed in this review. Several key open questions remain unanswered, some of which are as follows: (1) the literature on process-dependent polarisation enhancement is currently limited in its scope, attributing enhancements of energy conversion efficiency to increases in either the β phase or the total polymer crystallinity. The understanding of how processing techniques affect (and more importantly enhance) the polarisation is critical to progressing the field; (2) there is large scope to move away from electrical fields for poling to enhance polarisation to study shear-induced polarisation through various techniques such as 3D printing; (3) there needs to be a stronger fundamental understanding of how the properties of the fluoropolymers influence the electrical output which ties into fully characterising the materials and not just focusing on single properties of the material such as β phase or output, as this is a multi-parametric system; (4) the use of non-destructive techniques are expected to

provide new and valuable information such as confocal Raman microscopy, PFM and 3D magnetic resonance imaging (MRI), among others.

The future for low-energy, always-on electronic devices and wireless sensors is emerging fast. Flexible polymeric PEGs have great potential in these devices and pose a unique opportunity for the sustainable energy harvesting from mechanical energy, which is abundant in daily life. This type of energy harvesting will act to reduce the reliance on powering electronic devices from the grid, opening up new possibilities for personal and wearable electronics, as well as long-term implantable medical diagnostics and cardiac devices. More and more inspirational developments are expected in the applications of flexible fluoropolymer PEGs in the near future.

2.9 References

1. Z. L. Wang, G. Zhu, Y. Yang, S. H. Wang and C. F. Pan, Progress in nanogenerators for portable electronics, *Materials Today*, **15**, 532-543 (2012).
2. P. Satyavolu, S. J. Cherian and S. Rajagopalan, *Wearable Technology: Automotive's Next Digital Frontier*, Cognizant (2015).
3. Y. Zheng, J. Huang, G. Wang, J. Kong, D. Huang, M. M. Beromi, N. Hazari, A. D. Taylor and J. Yu, A highly efficient polymer non-fullerene organic solar cell enhanced by introducing a small molecule as a crystallizing-agent, *Materials Today*, **21**, 79-87 (2018).
4. X. Peng, T. W. Root and C. T. Maravelias, Storing solar energy with chemistry: the role of thermochemical storage in concentrating solar power, *Green Chemistry*, **19**, 2427-2438 (2017).
5. *Clean Energy Australia Report 2018*, Clean Energy Council (2018).
6. E. Fatuzzo, H. Kiess and R. Nitsche, Theoretical Efficiency of Pyroelectric Power Converters, *Journal of Applied Physics*, **37**, 510-516 (1966).
7. C. R. Bowen, J. Taylor, E. LeBoulbar, D. Zabek, A. Chauhan and R. Vaish, Pyroelectric materials and devices for energy harvesting applications, *Energy & Environmental Science*, **7**, 3836-3856 (2014).
8. H. Ohigashi and K. Koga, Ferroelectric Copolymers of Vinylidenefluoride and Trifluoroethylene with a Large Electromechanical Coupling Factor, *Japanese Journal of Applied Physics*, **21**, L455-L457 (1982).
9. K. Koga and H. Ohigashi, Piezoelectricity and related properties of vinylidene fluoride and trifluoroethylene copolymers, *Journal of Applied Physics*, **59**, 2142-2150 (1986).
10. C. Jean-Mistral, S. Basrour and J. J. Chaillout, Comparison of electroactive polymers for energy harvesting, *Smart Materials and Structures*, **19**, 085012 (2010).
11. K. S. Ramadan, D. Sameoto and S. Evoy, A review of piezoelectric polymers as functional materials for electromechanical transducers, *Smart Materials and Structures*, **23**, 033001 (2014).
12. J. Curie and P. Curie, Développement par compression de l'électricité polaire dans les cristaux hémiedres à faces inclinées, *Bulletin de la Société Française de Minéralogie et de Crystallographie*, **3**, 90-93 (1880).

13. J. Curie and P. Curie, Contractions et dilatations produites par des tensions électriques dans les cristaux hémihédres à faces inclinées, *Comptes Rendus*, **T.XCII(26)**, 1137-1140 (1881).
14. M. G. Lippmann, Sur le principe de la conservation de l'électricité, *Comptes Rendus*, **T.XCII(18)**, 151-154 (1881).
15. A.M. Nicholson, Piezophony, *US Patent*, US1495429A (1924).
16. C. Chilowsky, Method and means for the observation and measurement of the speed of a vessel by directed beams of ultra-audible waves, *US Patent*, US1864638A (1932).
17. P. Langevin, Piezoelectric signaling apparatus, *US Patent*, US2248870A (1941).
18. C. Kolm and P.H. Fowler, Piezoelectric power system, *US Patent*, US3239678A (1966).
19. S. Jana, S. Garain, S. Sen and D. Mandal, The influence of hydrogen bonding on the dielectric constant and the piezoelectric energy harvesting performance of hydrated metal salt mediated PVDF films, *Physical Chemistry Chemical Physics*, **17**, 17429-17436 (2015).
20. Y. Imai, D. Tadaki, T. Ma, Y. Kimura, A. Hirano-Iwata and M. Niwano, Response characteristics of hydrogen gas sensor with porous piezoelectric poly(vinylidene fluoride) film, *Sensors and Actuators B: Chemical*, **247**, 479-489 (2017).
21. X. Chen, X. Li, J. Shao, N. An, H. Tian, C. Wang, T. Han, L. Wang and B. Lu, High-Performance Piezoelectric Nanogenerators with Imprinted P(VDF-TrFE)/BaTiO₃ Nanocomposite Micropillars for Self-Powered Flexible Sensors, *Small*, **13**, 1604245 (2017).
22. I. Jung, Y. H. Shin, S. Kim, J. Y. Choi and C. Y. Kang, Flexible piezoelectric polymer-based energy harvesting system for roadway applications, *Applied Energy*, **197**, 222-229 (2017).
23. B. Saravanakumar, S. Soyoon and S. J. Kim, Self-Powered pH Sensor Based on a Flexible Organic-Inorganic Hybrid Composite Nanogenerator, *ACS Applied Materials & Interfaces*, **6**, 13716-13723 (2014).
24. Y. Zi, L. Lin, J. Wang, S. Wang, J. Chen, X. Fan, P. K. Yang, F. Yi and Z. L. Wang, Triboelectris-Pyroelectric-Piezoelectric Hybrid Cell for High-Efficiency Energy-Harvesting and Self-Powered Sensing, *Advanced Materials*, **27**, 2340-2347 (2015).

25. P. Dineva, D. Gross, R. Muller and T. Rangelov, *Dynamic Fracture of Piezoelectric Materials*, Springer, Cham (2014).
26. W. Voigt, *Lehrbuch der Kristallphysik: mit Ausschluß der Kristalloptik*, Vieweg + Teubner Verlag, Wiesbaden (1910).
27. A. S. Bhalla, R. Y. Guo and R. Roy, The perovskite structure – a review of its role in ceramic science and technology, *Material Research Innovations*, **4**, 3-26 (2000).
28. D. Y. Park, D. J. Joe, D. H. Kim, H. Park, J. H. Han, C. K. Jeong, H. Park, J. G. Park, B. Joung and K. J. Lee, Self-Powered Real-Time Arterial Pulse Monitoring Using Ultrathin Epidermal Piezoelectric Sensors, *Advanced Materials*, **29**, 1702308 (2017).
29. A. Lund, K. Rundqvist, E. Nilsson, L. Yu, B. Hagström and C. Müller, Energy harvesting textiles for a rainy day: woven piezoelectrics based on melt-spun PVDF microfibres with a conducting core, *npj Flexible Electronics*, **2**, 9 (2018).
30. N. Soin, T. H. Shah, S. C. Anand, J. F. Geng, W. Pornwannachai, P. Mandal, D. Reid, S. Sharma, R. L. Hadimani, D. V. Bayramol and E. Siores, Novel “3-D spacer” all fibre piezoelectric textiles for energy harvesting applications, *Energy & Environmental Science*, **7**, 1670-1679 (2014).
31. E. Kabir, M. Khatun, L. Nasrin, M. J. Raihan and M. Rahman Pure β -phase formation in polyvinylidene fluoride (PVDF)-carbon nanotube composites, *Journal of Physics D: Applied Physics*, **50**, 163002 (2017).
32. S. Bodkhe, G. Turcot, F. P. Gosselin and D. Therriault, One-Step Solvent Evaporation-Assisted 3D Printing of Piezoelectric PVDF Nanocomposite Structures, *ACS Applied Materials & Interfaces*, **9**, 20833-20842 (2017).
33. D. Singh, A. Choudhary and A. Garg, Flexible and Robust Piezoelectric Polymer Nanocomposites Based Energy Harvesters, *ACS Applied Materials & Interfaces*, **10**, 2793-2800 (2018).
34. A. S. ELmezayyen, F. M. Reicha, I. M. El-Sherbiny, J. Zheng and C. Xu, Significantly enhanced electroactive β phase crystallization and UV shielding properties in PVDF nanocomposites flexible films through loading of ATO nanoparticles: Synthesis and formation mechanism, *European Polymer Journal*, **90**, 195-208 (2017).
35. C. K. Jeong, C. Baek, A. I. Kingon, K. I. Park and S. H. Kim, Lead-Free Perovskite Nanowire-Employed Piezopolymer for Highly Efficient Flexible Nanocomposite Energy Harvester, *Small*, **14**, 1704022 (2018).

36. J. H. Lee, K. Y. Lee, B. Kumar, N. T. Tien, N. E. Lee and S. W. Kim, Highly sensitive stretchable transparent piezoelectric nanogenerators, *Energy & Environmental Science*, **6**, 169-175 (2013).
37. M. Li, H. J. Wondergem, M. J. Spijkman, K. Asadi, I. Katsouras, P. W. M. Blom and D. M. de Leeuw, Revisiting the δ -phase of poly(vinylidene fluoride) for solution-processed ferroelectric thin films, *Nature Materials*, **12**, 433-438 (2013).
38. M. Li, I. Katsouras, C. Piliego, G. Glasser, I. Lieberwirth, P. W. M. Blom and D. M. de Leeuw, Controlling the microstructure of poly(vinylidene-fluoride) (PVDF) thin films for microelectronics, *Journal of Materials Chemistry C*, **1**, 7695-7702 (2013).
39. A. C. Lopes, J. Gutierrez and J. M. Barandiaran, Direct fabrication of a 3D-shape film of polyvinylidene fluoride (PVDF) in the piezoelectric β -phase for sensor and actuator applications, *European Polymer Journal*, **99**, 111-116 (2018).
40. C. Xing, L. Zhao, J. You, W. Dong, X. Cao and Y. Li, Impact of Ionic Liquid-Modified Multiwalled Carbon Nanotubes on the Crystallization Behavior of Poly(vinylidene fluoride), *Journal of Physical Chemistry B*, **116**, 8312-8320 (2012).
41. Measurement Specialities, Inc., *Piezo Film Sensors: Technical Manual*, Sensor Products Division, USA (1999).
42. Kureha Corporation, Piezo Films by Kureha, <http://www.piezofilms.com>, (accessed July, 2018).
43. P. Martins, A. C. Lopes and S. Lanceros-Mendez, Electroactive phases of poly(vinylidene fluoride): Determination, processing and applications, *Progress in Polymer Science*, **39**, 683-706 (2014).
44. D. Damjanovic, Hysteresis in Piezoelectric and Ferroelectric Materials, in *The Science of Hysteresis, Volume III*, eds. G. Bertotti and I. D. Mayergoyz, Academic Press (2006).
45. A. Vinogradov, Piezoelectricity in Polymers, in *Encyclopedia of Smart Materials*, ed. M. Schwartz, Wiley, New York (2002).
46. C. K. Lee, Theory of laminated piezoelectric plates for the design of distributed sensors/actuators. Part I: Governing equations and reciprocal relationships, *Journal of the Acoustical Society of America*, **87**, 1144-1158 (1990).

47. Publication and Proposed Revision of ANSI/IEEE Standard 176-1987 “ANSI/IEEE Standard on Piezoelectricity”, *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*, **43**, 717 (1996).
48. A. Erturk and D. J. Inman, *Piezoelectric Energy Harvesting*, Wiley, Chichester (2011).
49. Z. L. Wang, On Maxwell’s displacement current for energy and sensors: the origin of nanogenerators, *Materials Today*, **20**, 74-82 (2017).
50. G. G. Yaralioglu, A. S. Ergun, B. Bayram, E. Haeggstrom and B. T. Khuri-Yakub, Calculation and measurement of electromechanical coupling coefficient of capacitive micromachines ultrasonic transducers, *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*, **50**, 449-456 (2003).
51. D. B. Deutz, J. A. Pascoe, B. Schelen, S. van der Zwaag, D. M. de Leeuw and P. Groen, Analysis and experimental validation of the figure of merit for piezoelectric energy harvesters, *Materials Horizons*, **5**, 444-453 (2018).
52. M. Broadhurst, G. Davis, J. McKinney and R. Collins, Piezoelectricity and pyroelectricity in polyvinylidene fluoride—A model, *Journal of Applied Physics*, **49**, 4992-4997 (1978).
53. Q. M. Zhang, V. Bharti and G. Kavarnos, Poly(Vinylidene Fluoride) (PVDF) and its Copolymers, in *Encyclopedia of Smart Materials*, ed. M. Schwartz, Wiley, New York (2002).
54. L. Ruan, X. Yao, Y. Chang, L. Zhou, G. Qin and X. Zhang, Properties and Applications of the β Phase Poly(vinylidene fluoride), *Polymers*, **10**, 228 (2018).
55. J. Martin, D. Zhao, T. Lenz, I. Katsouras, D. M. de Leeuw and N. Stingelin, Solid-state-processing of δ -PVDF, *Materials Horizons*, **4**, 408-414 (2017).
56. V. Sencadas, S. Lanceros-Méndez and J. F. Mano, Characterization of poled and non-poled β -PVDF films using thermal analysis techniques, *Thermochimica Acta*, **424**, 201-207 (2004).
57. B. Ameduri, From Vinylidene Fluoride (VDF) to the Applications of VFD-Containing Polymers and Copolymers: Recent Developments and Future Trends, *Chemical Reviews*, **109**, 6632-6686 (2009).
58. P. Destruel, F. S. Rojas, D. Tougne and Hoang-The-Giam, Pressure and temperature dependence of the electromechanical properties of polarized polyvinylidene fluoride films, *Journal of Applied Physics*, **56**, 3298-3303 (1984).

59. J. Döring, V. Bovtun, J. Bartusch, U. Beck and M. Kreutzbruck, Cellular Polypropylene Ferroelectret Film: Piezoelectric Material for Non-Contact Ultrasonic Transducers, *17th World Conference of Nondestructive Testing*, Shanghai, China (2008).
60. S. Crossley, R. A. Whiter and S. Kar-Narayan, Polymer-based nanopiezoelectric generators for energy harvesting applications, *Materials Science and Technology*, **30**, 1613-1624 (2014).
61. C. Jean-Mistral, S. Basrour and J. J. Chaillout, Comparison of electroactive polymers for energy scavenging applications, *Smart Materials and Structures*, **19**, 085012 (2010).
62. R. Calio, U. B. Rongala, D. Camboni, M. Milazzo, C. Stefanini, G. de Petris and C. M. Oddo, Piezoelectric Energy Harvesting Solutions, *Sensors*, **14**, 4755-4790 (2014).
63. C. R. Bowen, H. A. Kim, P. M. Weaver and S. Dunn, Piezoelectric and ferroelectric materials and structure for energy harvesting applications, *Energy & Environmental Science*, **7**, 25-44 (2014).
64. C. Li, P. M. Wu, S. Lee, A. Gorton, M. J. Schulz and C. H. Ahn, Flexible Dome and Bump Shape Piezoelectric Tactile Sensors Using PVDF-TrFE Copolymer, *Journal of Microelectromechanical Systems*, **17**, 334-341 (2008).
65. K. Uchino, Piezoelectric Energy Harvesting Systems—Essentials to Successful Developments, *Energy Technology*, **6**, 829-848 (2017).
66. A. J. Lovinger, D. D. Davis, R. E. Cais and J. M. Kometani, On the Curie temperature of poly(vinylidene fluoride), *Macromolecules*, **19**, 1491-1494 (1986).
67. Y. Murata and N. Koizumi, Curie Transition in Copolymers of Vinylidene Fluoride and Tetrafluoroethylene, *Polymer Journal*, **17**, 1071-1074 (1985).
68. S. Lanceros-Méndez, J. F. Mano, A. M. Costa and V. H. Schmidt, FTIR and DSC studies of mechanically deformed β -PVDF films, *Journal of Macromolecular Science, Part B: Physics*, **40**, 517-527 (2001).
69. A. Vinogradov and F. Holloway, Electro-mechanical properties of the piezoelectric polymer PVDF, *Ferroelectrics*, **226**, 169-181 (1991).
70. F. R. Fan, W. Tang and Z. L. Wang, Flexible Nanogenerators for Energy Harvesting and Self-Powered Electronics, *Advanced Materials*, **28**, 4283-4305 (2016).

71. C. Dagdeviren, B. D. Yang, Y. Su, P. L. Tran, P. Joe, E. Anderson, J. Xia, V. Doraiswamy, B. Dehdashti, X. Feng, B. Lu, R. Poston, Z. Khalpey, R. Ghaffari, Y. Huang, M. J. Slepian and J. A. Rogers, Conformal piezoelectric energy harvesting and storage from motions of the heart, lung, and diaphragm, *Proceedings of the National Academy of Sciences*, **111**, 1927-1932 (2014).
72. C. Dagdeviren, P. Joe, O. L. Tuzman, K.-I. Park, K. J. Lee, Y. Shi, Y. Huang and J. A. Rogers, Recent progress in flexible and stretchable piezoelectric devices for mechanical energy harvesting, sensing and actuation, *Extreme Mechanics Letters*, **9**, 269-281 (2016).
73. G. T. Hwang, Y. Kim, J. H. Lee, S. Oh, C. K. Jeong, D. Y. Park, J. Ryu, H. Kwon, S. G. Lee, B. Joung, D. Kim and K. J. Lee, Self-powered deep brain stimulation via a flexible PIMNT energy harvester, *Energy & Environmental Science*, **8**, 2677-2684 (2015).
74. V. F. Cardoso, D. M. Correia, C. Ribeiro, M. M. Fernandes and S. Lanceros-Méndez, Fluorinated Polymers as Smart Materials for Advanced Biomedical Applications, *Polymers*, **10**, 161 (2018).
75. C. Chandrana, J. Talman, T. Pan, S. Roy and A. Fleischman, Design and Analysis of MEMS Based PVDF Ultrasonic Transducers for Vascular Imaging, *Sensors*, **10**, 8740 (2010).
76. M. A. Bachmann, W. L. Gordon, J. L. Koenig and J. B. Lando, An infrared study of phase-III poly(vinylidene fluoride), *Journal of Applied Physics*, **50**, 6106-6112 (1979).
77. W. M. Prest and D. J. Luca, The formation of the γ phase from the α and β polymorphs of polyvinylidene fluoride, *Journal of Applied Physics*, **49**, 5042-5047 (1978).
78. M. T. Riosbaas, K. J. Loh, G. O'Bryan and B. R. Loyola, In Situ Phase Change Characterization of PVDF Thin Films using Raman Spectroscopy, *SPIE Smart Structures and Materials + Nondestructive Evaluation and Health Monitoring*, San Diego, USA (2014).
79. W. Li, Q. Meng, Y. Zheng, Z. Zhang, W. Xia and Z. Xu, Electric energy storage properties of poly(vinylidene fluoride), *Applied Physics Letters*, **96**, 192905 (2010).
80. K. Uchino, *Introduction to Piezoelectric Actuators and Transducers*, Pennsylvania State University (2003).

81. A. Mohebbi and D. Rodrigue, Energy absorption capacity of ferroelectrets based on porous polypropylene, *Polymer Engineering & Science*, **58**, 300-309 (2017).
82. D. M. Esterly and B. J. Love, Phase transformation to β -poly(vinylidene fluoride) by milling, *Journal of Polymer Science, Part B: Polymer Physics*, **42**, 91-97 (2004).
83. R. Gregorio Jr. and M. Cestari, Effect of crystallization temperature on the crystalline phase content and morphology of poly(vinylidene fluoride), *Journal of Polymer Science, Part B: Polymer Physics*, **32**, 859-870 (1994).
84. B. S. Ince-Gunduz, K. Burke, M. Koplitz, M. Meleski, A. Sagiv and P. Cebe, Impact of Nanosilicates on Poly(vinylidene fluoride) Crystal Polymorphism: Part 2. Melt-crystallization at Low Supercooling, *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, **47**, 1208-1219 (2010).
85. X. Cai, T. Lei, D. Sun and L. Lin, A critical analysis of the α , β and γ phases in poly(vinylidene fluoride) using FTIR, *RSC Advances*, **7**, 15382-15389 (2017).
86. S. Barrau, A. Ferri, A. Da Costa, J. Defebvin, S. Leroy, R. Desfeux and J. M. Lefebvre, Nanoscale Investigations of α - and γ -Crystal Phases in PVDF-Based Nanocomposites, *ACS Applied Materials & Interfaces*, **10**, 13092-13099 (2018).
87. H. Kim, T. Fernando, M. Li, Y. Lin and T. L. B. Tseng, Fabrication and characterization of 3D printed BaTiO₃/PVDF nanocomposites, *Journal of Composite Materials*, **52**, 197-206 (2018).
88. J. E. Lee and S. N. Leung, Multi-stage crystallization mechanism of electroactive phase polyvinylidene fluoride induced by thermal and supercritical carbon dioxide processing, *CrystEngComm*, **20**, 4080-4089 (2018).
89. A. J. Lovinger, Poly(Vinylidene Fluoride), in *Developments in Crystalline Polymers*, ed. D. C. Bassett, Springer, Dordrecht (1982).
90. G. Teyssedre, A. Bernes and C. Lacabanne, Influence of the crystalline phase on the molecular mobility of PVDF, *Journal of Polymer Science, Part B: Polymer Physics*, **31**, 2027-2034 (1993).
91. C. J. L. Constantino, A. E. Job, R. D. Simões, J. A. Giacometti, V. Zucolotto, O. N. Oliveira Jr., G. Gozzi and D. L. Chinaglia, Phase Transition in Poly(Vinylidene Fluoride) Investigated with Micro-Raman Spectroscopy, *Applied Spectroscopy*, **59**, 275-279 (2005).
92. C. J. L. Constantino, A. E. Job, R. D. Simões, J. A. Giacometti, V. Zucolotto, O. N. Oliveira Jr., G. Gozzi and D. L. Chinaglia, The Investigation of $\alpha \rightarrow \beta$ Phase

- Transition in Poly(Vinylidene Fluoride) (PVDF), *12th International Symposium on Electrets*, Salvador, Brazil (2005).
93. O. García-Zaldívar, T. Escamilla-Díaz, M. Ramírez-Cardona, M. A. Hernández-Landaverde, R. Ramírez-Bon, J. M. Yañez-Limón and F. Calderón-Piñar, Ferroelectric-Paraelectric Transition In A Membrane With Quenched-Induced δ -Phase Of PVDF, *Scientific Reports*, **7**, 5566 (2017).
 94. S. K. Pradhan, A. Kumar, A. N. Sinha, P. Kour, R. Pandey, P. Kumar and M. Kar, Study of ferroelectric properties on PVDF-PZT nanocomposite, *Ferroelectrics*, **516**, 18-27 (2017).
 95. D. Sengupta, A. G. P. Kottapalli, S. H. Chen, J. M. Miao, C. Y. Kwok, M. S. Triantafyllou, M. E. Warkiani and M. Asadnia, Characterization of single polyvinylidene fluoride (PVDF) nanofiber for flow sensing applications, *AIP Advances*, **7**, 105205 (2017).
 96. F. Xu, K. Zhang, Y. Zhou, Z. Qu, H. Wang, Y. Zhang, H. Zhou and C. Yan, Facile preparation of highly oriented poly(vinylidene fluoride) ununiform films and their ferro- and piezoelectric properties, *RSC Advances*, **7**, 17038-17043 (2017).
 97. M. H. Ghajar, M. M. Mashhadi, M. Irannejad, S. Jebril, M. Yavuz and E. Abdel-Rahman, Degree of Crystallinity and β Phase Fraction of Polyvinylidene Fluoride Nanocomposites Containing Ionic Liquid and Graphene/Carbon Nanotube, *Polymer Composites*, **39**, E1208-E1215 (2018).
 98. M. H. Ghajar, M. M. Mashhadi, M. Irannejad, M. Yavuz and E. Abdel-Rahman, Effects of static electricity and fabrication parameters on PVDF film properties, *Bulletin of Materials Science*, **41**, 43 (2018).
 99. J. Ma, Q. Zhang, K. Lin, L. Zhou and Z. Ni, Piezoelectric and optoelectric properties of electrospinning hybrid PVDF and ZnO nanofibers, *Materials Research Express*, **5**, 035057 (2018).
 100. S. Zhang, H. Wang, D. Xu, W. Yang, P. Tang and Y. Bin, Study of crystallization behavior of neat poly(vinylidene fluoride) and transcrystallization of carbon fiber/poly(vinylidene fluoride) composite under a temperature gradient, *Journal of Applied Polymer Science*, **133**, 43605 (2016).
 101. V. Bhavanasi, V. Kumar, K. Parida, J. Wang and P. S. Lee, Enhanced Piezoelectric Energy Harvesting Performance of Flexible PVDF-TrFE Bilayer Films with Graphene Oxide, *ACS Applied Materials & Interfaces*, **8**, 521-529 (2016).

102. J. Y. Lim, S. Kim and Y. Seo, Enhancement of β -phase in PVDF by electrospinning, *AIP Conference Proceedings*, **1664**, 070006 (2015).
103. M. Guerre, G. Lopez, T. Soulestin, C. Totée, B. Améduri, G. Silly and V. Ladmiral, A journey into the Microstructure of PVDF Made by RAFT, *Macromolecular Chemistry and Physics*, **217**, 2275-2285 (2016).
104. R. A. Ferren, Synthesis of poly(vinylidene fluoride) and its copolymers, in *The Applications of Ferroelectric Polymers*, ed. T. T. Wang, J. M. Herbert and A. M. Glass, Blackie, Glasgow (1988).
105. R. Timmerman and W. Greyson, The predominant reaction of some fluorinated polymers to ionizing radiation, *Journal of Applied Polymer Science*, **6**, 456-460 (1962).
106. D. A. Seiler, PVDF in the Chemical Process Industry, in *Modern Fluoropolymers: High Performance Polymers for Diverse Applications*, ed. J. E. Scheirs, Wiley, Chichester (1997).
107. T. Soulestin, V. Ladmiral, F. D. Dos Santos and B. Améduri, Vinylidene fluoride- and trifluoroethylene-containing fluorinated electroactive copolymers. How does chemistry impact properties?, *Progress in Polymer Science*, **72**, 16-60 (2017).
108. B. Ameduri, C. Ladavière, F. Delolme and B. Boutevin, First MALDI-TOF Mass Spectrometry of Vinylidene Fluoride Telomers Endowed with Low Defect Chaining, *Macromolecules*, **37**, 7602-7609 (2004).
109. R. E. Cais and J. M. Kometani, Synthesis and two-dimensional NMR of highly atactic poly(vinylidene fluoride), *Macromolecules*, **18**, 1354-1357 (1985).
110. A. J. Lovinger, D. D. Davis, R. E. Cais and J. M. Kometani, The role of molecular defects on the structure and phase transitions of poly(vinylidene fluoride), *Polymer*, **28**, 617-626 (1987).
111. T. Wang, M. Farajollahi, Y. S. Choi, I. T. Lin, J. E. Marshall, N. M. Thompson, S. Kar-Narayan, J. D. W. Madden and S. K. Smoukov, Electroactive polymers for sensing, *Interface Focus*, **6**, 19 (2016).
112. Z. Li, J. Wang, X. Wang, Q. Yang and Z. Zhang, Ferro- and piezo-electric properties of a poly(vinyl fluoride) film with high ferro- to para-electric phase transition temperature, *RSC Advances*, **5**, 80950-80955 (2015).
113. E. Klimiec, W. Zaraska, K. Zaraska, A. Cichocki, K. Gąsiorwski, T. Sadowski and M. Pajda, Electroactive polymers: investigation of piezoelectric properties, *Elektronika*, **47**, 11-13 (2006).

114. F. Wang, P. Frubing, W. Wirges, R. Gerhard and M. Wegener, Enhanced polarization in melt-quenched and stretched poly(vinylidene fluoride-hexafluoropropylene) films, *IEEE Transactions on Dielectrics and Electrical Insulation*, **17**, 1088-1095 (2010).
115. Y. Wang, B. Neese, Q. Zhang, C. Huang and J. West, High Piezoelectric Responses in P(VDF-HFP) Copolymers for Sensors and Transducers, *IEEE Ultrasonics Symposium Proceedings*, New York, USA (2007).
116. Z. Li, Y. Wang and Z. Y. Cheng, Electromechanical properties of poly(vinylidene-fluoride-chlorotrifluoroethylene) copolymer, *Applied Physics Letters*, **88**, 062904 (2006).
117. T. Yagi and M. Tatemoto, A Fluorine-19 NMR Study of the Microstructure of Vinylidene Fluoride-Trifluoroethylene Copolymers, *Polymer Journal*, **11**, 429-436 (1979).
118. A. J. Lovinger, Ferroelectric Polymers, *Science*, **220**, 1115-1121 (1983).
119. E. Fukada, History and recent progress in piezoelectric polymers, *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*, **47**, 1277-1290 (2000).
120. T. Furukawa, Ferroelectric properties of vinylidene fluoride copolymers, *Phase Transitions*, **18**, 143-211 (1989).
121. K. Tashiro, H. Tadokoro and M. Kobayashi, Structure and piezoelectricity of poly(vinylidene fluoride), *Ferroelectrics*, **32**, 167-175 (1981).
122. B. Neese, Y. Wang, B. Chu, K. Ren, S. Liu and Q. M. Zhang, Piezoelectric responses in poly(vinylidene fluoride/hexafluoropropylene) copolymers, *Applied Physics Letters*, **90**, 242917 (2007).
123. B. Hu, N. Hu, L. Wu, F. Liu, Y. Liu, H. Ning, S. Atobe and H. Fukunaga, Effects of initial crystallization process on piezoelectricity of PVDF-HFP films, *Journal of Polymer Engineering*, **35**, 451-461 (2015).
124. R. E. Sousa, J. Nunes-Pereira, J. C. C. Ferreira, C. M. Costa, A. V. Machado, M. M. Silva and S. Lanceros-Mendez, Microstructural variations of poly(vinylidene fluoride co-hexafluoropropylene) and their influence on the thermal, dielectric and piezoelectric properties, *Polymer Testing*, **40**, 245-255 (2014).
125. B. Améduri, B. Boutevin and G. Kostov, Fluoroelastomers: synthesis, properties and applications, *Progress in Polymer Science*, **26**, 105-187 (2001).
126. T. S. Ahmed, J. M. DeSimone and G. W. Roberts, Continuous Copolymerization of Vinylidene Fluoride with Hexafluoropropylene in Supercritical Carbon

- Dioxide: Low Hexafluoropropylene Content Semicrystalline Polymers, *Macromolecules*, **40**, 9322-9331 (2007).
127. X. Lu, A. Schirokauer and J. Scheinbeim, Giant electrostrictive response in poly(vinylidene fluoride-hexafluoropropylene) copolymers, *IEEE Transactions on Ultrasonics, Ferroelectrics and Frequency Control*, **47**, 1291-1295 (2000).
 128. P. Sukwisute, N. Muensit, S. Soontaranon and S. Rugmai, Micropower energy harvesting using poly(vinylidene fluoride hexafluoropropylene), *Applied Physics Letters*, **103**, 063905 (2013).
 129. N. K. Kalfoglou and H. L. Williams, Mechanical relaxations of poly(vinylidene fluoride) and some of its copolymers, *Journal of Applied Polymer Science*, **17**, 3367-3373 (1973).
 130. M. Latour and H. A. Dorra, Structural study of a vinylidene fluoride chlorotrifluoroethylene copolymer by x ray and infrared spectroscopy, *Ferroelectrics*, **44**, 197-203 (1982).
 131. T. Hattori, M. Hikosaka and H. Ohigashi, The crystallization behavior and phase diagram of extended-chain crystals of poly(vinylidene fluoride) under high pressure, *Polymer*, **37**, 85-91 (1996).
 132. D. Yang and Y. Chen, β -phase formation of poly(vinylidene fluoride) from the melt induced by quenching, *Journal of Materials Science Letters*, **6**, 599-603 (1987).
 133. J. P. Luongo, Far-infrared spectra of piezoelectric polyvinylidene fluoride, *Journal of Polymer Science, Part A: Polymer Physics*, **10**, 1119-1123 (1972).
 134. H. Kawai, The Piezoelectricity of Poly(vinylidene Fluoride), *Japanese Journal of Applied Physics*, **8**, 975-976 (1969).
 135. W. W. Doll and J. B. Lando, Polymorphism of poly(vinylidene fluoride). III. The crystal structure of phase II, *Journal of Macromolecular Science, Part B: Physics*, **4**, 309-329 (1970).
 136. W. W. Doll and J. B. Lando, The polymorphism of poly(vinylidene fluoride) IV. The structure of high-pressure-crystallized poly(vinylidene fluoride), *Journal of Macromolecular Science, Part B: Physics*, **4**, 889-896 (1970).
 137. J. Scheinbeim, C. Nakafuku, B. A. Newman and K. D. Pae, High-pressure crystallization of poly(vinylidene fluoride), *Journal of Applied Physics*, **50**, 4399-4405 (1979).

138. M. M. D. Ramos, H. M. G. Correia and S. Lanceros-Méndez, Atomistic modelling of processes involved in poling of PVDF, *Computational Materials Science*, **33**, 230-236 (2005).
139. S. Ramasundaram, S. Yoon, K. J. Kim and J. S. Lee, Direct Preparation of Nanoscale Thin Films of Poly(vinylidene fluoride) Containing β -Crystalline Phase by Heat-Controlled Spin Coating, *Macromolecular Chemistry and Physics*, **209**, 2516-2526 (2008).
140. S. Chen, X. Li, K. Yao, F. E. H. Tay, A. Kumar and K. Zeng, Self-polarized ferroelectric PVDF homopolymer ultra-thin films derived from Langmuir-Blodgett deposition, *Polymer*, **53**, 1404-1408 (2012).
141. J. R. Gregorio and C. Marcelo, Effect of crystallization temperature on the crystalline phase content and morphology of poly(vinylidene fluoride), *Journal of Polymer Science, Part B: Polymer Physics*, **32**, 859-870 (1994).
142. M. Benz, W. B. Euler and O. J. Gregory, The Role of Solution Phase Water on the Deposition of Thin Films of Poly(vinylidene fluoride), *Macromolecules*, **35**, 2682-2688 (2002).
143. J. Nunes-Pereira, P. Martins, V. F. Cardoso, C. M. Costa and S. Lanceros-Méndez, A green solvent strategy for the development of piezoelectric poly(vinylidene fluoride-trifluoroethylene) films for sensors and actuators applications, *Materials & Design*, **104**, 183-189 (2016).
144. S. S. Madeni and A. H. Taheri, Effect of Casting Solution on Morphology and Performance of PVDF Microfiltration Membranes, *Chemical Engineering & Technology*, **34**, 1328-1334 (2011).
145. Z. M. Huang, Y. Z. Zhang, M. Kotaki and S. Ramakrishna, A review on polymer nanofibers by electrospinning and their applications in nanocomposites, *Composites Science and Technology*, **63**, 2223-2253 (2003).
146. C. Ribeiro, V. Sencadas, J. L. G. Ribelles and S. Lanceros-Méndez, Influence of Processing Conditions on Polymorphism and Nanofiber Morphology of Electroactive Poly(vinylidene fluoride) Electrospun Membranes, *Soft Materials*, **8**, 274-287 (2010).
147. C. Ribeiro, D. M. Correia, S. Ribeiro, V. Sencadas, G. Botelho and S. Lanceros-Méndez, Piezoelectric poly(vinylidene fluoride) microstructure and poling state in active tissue engineering, *Engineering in Life Sciences*, **15**, 351-356 (2015).

148. L. Persano, A. Camposeo, C. Tekmen and D. Pisignano, Industrial Upscaling of Electrospinning and Applications of Polymer Nanofibers: A Review, *Macromolecular Materials and Engineering*, **298**, 504-520 (2013).
149. F. Mokhtari, M. Latifi and M. Shamshirsaz, Electrospinning/electrospray of polyvinylidene fluoride (PVDF): piezoelectric nanofibers, *Journal of the Textile Institute*, **107**, 1037-1055 (2016).
150. H. Shao, J. Fang, H. Wang and T. Lin, Effect of electrospinning and polymer concentration on mechanical-to-electrical energy conversion of randomly-oriented electrospun poly(vinyliden fluoride) nanofiber mats, *RSC Advances*, **5**, 14345-14350 (2015).
151. Y. Bin, Y. Hao, M. Mengye, W. Hongzhi and Z. Meifang, Enhanced output power polyvinylidene fluoride (PVDF) electrospun nanogenerator with high fiber alignment, *IEEE 15th International Conference on Nanotechnology*, Rome, Italy (2015).
152. P. Hu, D. Zheng, C. Zhao, Y. Zhang and J. Niu, Linear dependence between content of effective piezo-phase and mechanical-to-electrical conversion in electrospun poly(vinylidene fluoride) fibrous membrane, *Materials Letters*, **218**, 71-75 (2018).
153. M.C. Petty and W.A. Barlow, Film Deposition, in *Langmuir-Blodgett Films*, ed. G. Roberts, Springer, Boston (1990).
154. H. Zhu, S. Yamamoto, J. Matsui, T. Miyashita and M. Mitsuishi, Highly oriented poly(vinylidene fluoride-co-trifluoroethylene) ultrathin films with improved ferroelectricity, *RSC Advances*, **6**, 32007-32012 (2016).
155. H. Zhu, M. Mitsuishi and T. Miyashita, Facile Preparation of Highly Oriented Poly(vinylidene fluoride) Langmuir-Blodgett Nanofilms Assisted by Amphiphilic Polymer Nanosheets, *Macromolecules*, **45**, 9076-9084 (2012).
156. Y. Jiang, Y. Ye, J. Yu, Y. Yang, J. Xu and Z. Wu, A study on ferroelectric PVDF ultrathin films prepared by LB technique, *Integrated Ferroelectrics*, **88**, 21-26 (2007).
157. H. Zhu, G. Yu, Y. Shunsuke, M. Tokuji and M. Masaya, Angle-resolved X-ray photoelectron spectroscopy study of poly(vinylidene fluoride)/poly(*N*-dodecylacrylamide) Langmuir-Blodgett nanofilms, *Japanese Journal of Applied Physics*, **55**, 03DD11 (2016).
158. W. Y. Kim, D. S. Song, G. J. Jeon, I. K. Kang, H. B. Shim, D. K. Kim, H. C. Lee, H. Park, S. W. Kang and J. H. Bae, Characterisation of ferroelectric

- poly(vinylidene fluoride-trifluoroethylene) film prepared by Langmuir-Blodgett deposition, *Micro & Nano Letters*, **10**, 384-388 (2015).
159. Y. Y. Choi, P. Sharma, C. Phatak, D. J. Gosztola, Y. Liu, J. Lee, B. Lee, J. Li, A. Gruverman, S. Ducharme and S. Hong, Enhancement of Local Piezoresponse in Polymer Ferroelectrics *via* Nanoscale Control of Microstructure, *ACS Nano*, **9**, 1809-1819 (2015).
 160. E. V. Paramonova, S. V. Filippov, V. E. Gevorkyan, L. A. Avakyan, X. J. Meng, B. B. Tian, J. L. Wang and V. S. Bystrov, Polarization switching in ultrathin polyvinylidene fluoride homopolymer ferroelectric films, *Ferroelectrics*, **509**, 143-157 (2017).
 161. H. Zhu, S. Yamamoto, J. Matsui, T. Miyashita and M. Mitsuishi, Resistive non-volatile memories fabricated with poly(vinylidene fluoride)/poly(thiophene) blend nanosheets, *RSC Advances*, **8**, 7963-7968 (2018).
 162. Tecdia Inc, *ARQUE catalog*, Campbell, USA (2017).
 163. K. Kim, W. Zhu, X. Qu, C. Aaronson, W. R. McCall, S. Chen and D. J. Sirbuly, 3D Optical Printing of Piezoelectric Nanoparticle-Polymer Composite Materials, *ACS Nano*, **8**, 9799-9806 (2014).
 164. H. Kim, F. Torres, Y. Wu, D. Villagran, Y. Lin and T. L. Tseng, Integrated 3D printing and corona poling process of PVDF piezoelectric films for pressure sensor application, *Smart Materials and Structures*, **26**, 085027 (2017).
 165. C. Lee and J. A. Tarbutton, Electric poling-assisted additive manufacturing process for PVDF polymer-based piezoelectric device applications, *Smart Materials and Structures*, **23**, 7 (2014).
 166. J. H. Yang, T. Ryu, Y. Lansac, Y. H. Jang and B. H. Lee, Shear stress-induced enhancement of the piezoelectric properties of PVDF-TrFE thin films, *Organic Electronics*, **28**, 67-72 (2016).
 167. J. Oliveira, V. Correia, H. Castro, P. Martins and S. Lanceros-Mendez, Polymer-based smart materials by printing technologies: Improving application and integration, *Additive Manufacturing*, **21**, 269-283 (2018).
 168. S. Bodkhe, P. S. M. Rajesh, F. P. Gosselin and D. Therriault, Simultaneous 3D Printing and Poling of PVDF and Its Nanocomposites, *ACS Applied Energy Materials*, **1**, 2474-2482 (2018).
 169. S. Bodkhe, C. Noonan, F. P. Gosselin and D. Therriault, Coextrusion of Multifunctional Smart Sensors, *Advanced Engineering Materials*, **20**, 1800206 (2018).

170. A. H. Rajabi, M. Jaffe and T. L. Arinze, Piezoelectric materials for tissue regeneration: A review, *Acta Biomaterialia*, **24**, 12-23 (2015).
171. C. Park, Z. Ounaies, K. E. Wise and J. S. Harrison, In situ poling and imidization of amorphous piezoelectric polyimides, *Polymer*, **45**, 5417-5425 (2004).
172. C. Li, P. M. Wu, S. Lee, A. Gorton, M. J. Schulz and C. H. Ahn, Flexible Dome and Bump Shape Piezoelectric Tactile Sensors Using PVDF-TrFE Copolymer, *Journal of Microelectromechanical Systems*, **17**, 334-341 (2008).
173. S. K. Mahadeva, J. Berring, K. Walus and B. Stoeber, Effect of poling time and grid voltage on phase transition and piezoelectricity of poly(vinylidene fluoride) thin films using corona poling, *Journal of Physics D: Applied Physics*, **46**, 285305 (2013).
174. B. Gross, R. Gerhard-Multhaupt, A. Berraisoul and G. M. Sessler, Electron-beam poling of piezoelectric polymer electrets, *Journal of Applied Physics*, **62**, 1429-1432 (1987).
175. R. Gerhard, Piezoelectricity and Electrostriction, in *Electromechanically Active Polymers*, ed. F. Carpi, Springer, Cham (2016).
176. P. H. Ducrot, I. Dufour and C. Ayela, Optimization Of PVDF-TrFE Processing Conditions For The Fabrication Of Organic MEMS Resonators, *Scientific Reports*, **6**, 19426 (2016).
177. S. Rajala, M. Schouten, G. Krijnen and S. Tuukkanen, High Bending-Mode Sensitivity of Printed Piezoelectric Poly(vinylidene fluoride-co-trifluoroethylene) Sensors, *ACS Omega*, **3**, 8067-8073 (2018).
178. S. K. Ghosh, A. Biswas, S. Sen, C. Das, K. Henkel, D. Schmeisser and D. Mandal, Yb³⁺ assisted self-polarized PVDF based ferroelectric nanogenerator: A facile strategy of highly efficient mechanical energy harvester fabrication, *Nano Energy*, **30**, 621-629 (2016).
179. P. Thakur, A. Kool, N. A. Hoque, B. Bagchi, F. Khatun, P. Biswas, D. Brahma, S. Roy, S. Banerjee and S. Das, Superior performances of *in situ* synthesized ZnO/PVDF thin film based self-poled piezoelectric nanogenerator and self-charger photo-power bank with high durability, *Nano Energy*, **44**, 456-467 (2018).
180. K. Maity and D. Mandal, The nucleation of self-poled electroactive β -phase in Eu³⁺ doped PVDF nanocomposite film for optoelectronic devices, *AIP Conference Proceedings*, **1942**, 050088 (2018).

181. M. Pusty, A. Sharma, L. Sinha, A. Chaudhary and P. Shirage, Comparative Study with a Unique Arrangement to Tap Piezoelectric Output to Realize a Self Poled PVDF Based Nanocomposite for Energy Harvesting Applications, *ChemistrySelect*, **2**, 2774-2782 (2017).
182. S. K. Karan, R. Bera, S. Paria, A. K. Das, S. Maiti, A. Maitra and B. B. Khatua, An Approach to Design Highly Durable Piezoelectric Nanogenerator Based on Self-Poled PVDF/AlO-rGO Flexible Nanocomposite with High Power Density and Energy Conversion Efficiency, *Advanced Energy Materials*, **6**, 1601016 (2016).
183. R. A. Whiter, V. Narayan and S. Kar-Narayan, A Scalable Nanogenerator Based on Self-Poled Piezoelectric Polymer Nanowires with High Energy Conversion Efficiency, *Advanced Energy Materials*, **4**, 1400519 (2014).
184. A. Tamang, S. K. Ghosh, S. Garain, M. M. Alam, J. Haeberle, K. Henkel, D. Schmeisser and D. Mandal, DNA-Assisted β -phase Nucleation and Alignment of Molecular Dipoles in PVDF Film: A Realization of Self-Poled Bioinspired Flexible Polymer Nanogenerator for Portable Electronic Devices, *ACS Applied Materials & Interfaces*, **7**, 16143-16147 (2015).
185. H. J. Ye, W. Z. Shao and L. Zhen, Crystallization kinetics and phase transformation of poly(vinylidene fluoride) films incorporated with functionalized BaTiO_3 nanoparticles, *Journal of Applied Polymer Science*, **129**, 2940-2949 (2013).
186. S. F. Mendes, C. M. Costa, C. Caparros, V. Sencadas and S. Lanceros-Méndez, Effect of filler size and concentration on the structure and properties of poly(vinylidene fluoride)/ BaTiO_3 nanocomposites, *Journal of Materials Science*, **47**, 1378-1388 (2012).
187. M. Sharma, J. K. Quamara and A. Gaur, Behaviour of multiphase PVDF in $(1-x)\text{PVDF}/(x)\text{BaTiO}_3$ nanocomposite films: structural, optical, dielectric and ferroelectric properties, *Journal of Materials Science: Materials in Electronics*, **29**, 10875-10884 (2018).
188. P. Martins, C. M. Costa and S. Lanceros-Mendez, Nucleation of electroactive β -phase poly(vinylidene fluoride) with CoFe_2O_4 and NiFe_2O_4 nanofillers: a new method for the preparation of multiferroic nanocomposites, *Applied Physics A*, **103**, 233-237 (2011).

189. L. M. S. Medina and R. M. Negri, Dielectric Behavior and Electro-Magnetic Coupling at Room Temperature in BiFeO₃/PVDF and CoFe₂O₄/PVDF Composites, *Journal of Physical Chemistry C*, **121**, 27683-27692 (2017).
190. M. S. Sebastian, A. Larrea, R. Gonçalves, T. Alejo, J. L. Vilas, V. Sebastian, P. Martins and S. Lanceros-Mendez, Understanding nucleation of the electroactive β -phase of poly(vinylidene fluoride) by nanostructures, *RSC Advances*, **6**, 113007-113015 (2016).
191. A. Samadi, S. M. Hosseini and M. Mohseni, Investigation of the electromagnetic microwaves absorption and piezoelectric properties of electrospun Fe₃O₄-GO/PVDF hybrid nanocomposites, *Organic Electronics*, **59**, 149-155 (2018).
192. N. An, H. Liu, Y. Ding, M. Zhang and Y. Tang, Preparation and electroactive properties of a PVDF/nano-TiO₂ composite film, *Applied Surface Science*, **257**, 3831-3835 (2011).
193. D. Mandal, K. J. Kim and J. S. Lee, Simple Synthesis of Palladium Nanoparticles, β -Phase Formation, and the Control of Chain and Dipole Orientations in Palladium-Doped Poly(vinylidene fluoride) Thin Films, *Langmuir*, **28**, 10310-10317 (2012).
194. W. Wang, S. Zhang, L. o. Srisombat, T. R. Lee and R. C. Advincula, Gold-Nanoparticle- and Gold-Nanoshell-Induced Polymorphism in Poly(vinylidene fluoride), *Macromolecular Materials and Engineering*, **296**, 178-184 (2011).
195. S. Yu, W. Zheng, W. Yu, Y. Zhang, Q. Jiang and Z. Zhao, Formation Mechanism of β -Phase in PVDF/CNT Composite Prepared by the Sonication Method, *Macromolecules*, **42**, 8870-8874 (2009).
196. C. Xing, L. Zhao, J. You, W. Dong, X. Cao and Y. Li, Impact of Ionic Liquid-Modified Multiwalled Carbon Nanotubes on the Crystallization Behavior of Poly(vinylidene fluoride), *Journal of Physical Chemistry B*, **116**, 8312-8320 (2012).
197. N. Maity, A. Mandal and A. K. Nandi, Interface engineering of ionic liquid integrated graphene in poly(vinylidene fluoride) matrix yielding magnificent improvement in mechanical, electrical and dielectric properties, *Polymer*, **65**, 154-167 (2015).
198. J. C. Dias, A. C. Lopes, B. Magalhães, G. Botelho, M. M. Silva, J. M. S. S. Esperança and S. Lanceros-Mendez, High performance electromechanical actuators based on ionic liquid/poly(vinylidene fluoride), *Polymer Testing*, **48**, 199-205 (2015).

199. J. C. Dias, D. C. Correia, A. C. Lopes, S. Ribeiro, C. Ribeiro, V. Sencadas, G. Botelho, J. M. S. S. Esperança, J. M. Laza, J. L. Vilas, L. M. León and S. Lanceros-Méndez Development of poly(vinylidene fluoride)/ionic liquid electrospun fibers for tissue engineering applications, *Journal of Materials Science*, **51**, 4442-4450 (2016).
200. M. Fukagawa, Y. Koshiha, T. Fukushima, M. Morimoto and K. Ishida, Anomalous piezoelectric properties of poly(vinylidene fluoride-trifluoroethylene)/ionic liquid gels, *Japanese Journal of Applied Physics*, **57**, 04FL06 (2018).
201. V. K. Tiwari, Y. Lee, G. Song, K. L. Kim, Y. J. Park and C. Park, Thin poly(ionic liquid) and poly(vinylidene fluoride) blend films with ferro- and piezo-electric polar γ -crystals, *Journal of Polymer Science, Part B: Polymer Physics*, **56**, 795-802 (2018).
202. Y. Zhu, C. Li, B. Na, R. Lv, B. Chen and J. Zhu, Polar phase formation and competition in the melt crystallization of poly(vinylidene fluoride) containing an ionic liquid, *Materials Chemistry and Physics*, **144**, 194-198 (2014).
203. J. Kyrmis, C. Kendall, J. Paradiso and N. Gershenfeld, Parasitic power harvesting in shoes, *Second International Symposium on Wearable Computers*, Pittsburgh, USA (1998).
204. S. Singh, V. K. Gupta and S. Mukherjee, Piezoelectric based energy harvester embedded in shoe for wearable electronics, *Materials Physics and Mechanics*, **37**, 159-167 (2018).
205. E. Klimiec, K. Zaraska, W. Zaraska and S. Kuczyński, Micropower generators and sensors based on piezoelectric polypropylene PP and polyvinylidene fluoride PVDF films - energy harvesting from walking, *Applied Mechanics and Materials*, **110**, 1245-1251 (2012).
206. J. Zhao and Z. You, A Shoe-Embedded Piezoelectric Energy Harvester for Wearable Sensors, *Sensors*, **14**, 12497-12510 (2014).
207. Y. Cha, Energy harvesting using flexible piezoelectric materials from human walking motion: Theoretical analysis, *Journal of Intelligent Material Systems and Structures*, **28**, 3006-3015 (2017).
208. Y. Xin, X. Li, H. Tian, C. Guo, C. Qian, S. Wang and C. Wang, Shoes-equipped piezoelectric transducer for energy harvesting: A brief review, *Ferroelectrics*, **493**, 12-24 (2016).

209. J. Granstrom, J. Feenstra, H. A. Sodano and K. Farinholt, Energy harvesting from a backpack instrumented with piezoelectric shoulder straps, *Smart Materials and Structures*, **16**, 1810-1820 (2007).
210. A. Gheibi, M. Latifi, A. A. Merati and R. Bagherzadeh, Piezoelectric electrospun nanofibrous materials for self-powering wearable electronic textiles applications, *Journal of Polymer Research*, **21**, 469 (2014).
211. H. J. Sim, C. Choi, C. J. Lee, Y. T. Kim and S. J. Kim, Flexible Two-ply Piezoelectric Yarn Energy Harvester, *Current Nanoscience*, **11**, 539-544 (2015).
212. J. H. Yang, H. S. Cho, S. H. Park, S. H. Song, K. S. Yun and J. H. Lee, Effect of garment design on piezoelectricity harvesting from joint movement, *Smart Materials and Structures*, **25**, 035012 (2016).
213. B. Li, F. Zhang, S. Guan, J. Zheng and C. Xu, Wearable piezoelectric device assembled by one-step continuous electrospinning, *Journal of Materials Chemistry C*, **4**, 6988-6995 (2016).
214. A. Atalay, O. Atalay, M. D. Husain, A. Fernando and P. Potluri, Piezofilm yarn sensor-integrated knitted fabric for healthcare applications, *Journal of Industrial Textiles*, **47**, 505-521 (2017).
215. R. L. Hadimani, D. V. Bayramol, N. Sion, T. Shah, L. Qian, S. Shi and E. Siores, Continuous production of piezoelectric PVDF fibre for e-textile applications, *Smart Materials and Structures*, **22**, 075017 (2013).
216. K. Magniez, A. Krajewski, M. Neuenhofer and R. Helmer, Effect of drawing on the molecular orientation and polymorphism of melt-spun polyvinylidene fluoride fibers: Toward the development of piezoelectric force sensors, *Journal of Applied Polymer Science*, **129**, 2699-2706 (2013).
217. A. S. Krajewski, K. Magniez, R. J. N. Helmer and V. Schrank, Piezoelectric Force Response of Novel 2D Textile Based PVDF Sensors, *IEEE Sensors Journal*, **13**, 4743-4748 (2013).
218. A. Talbourdet, F. Rault, G. Lemort, C. Cochrane, E. Devaux and C. Campagne, 3D interlock design 100% PVDF piezoelectric to improve energy harvesting, *Smart Materials and Structures*, **27**, 075010 (2018).
219. H. Gao, P. T. Minh, H. Wang, S. Minko, J. Locklin, T. Nguyen and S. Sharma, High-performance flexible yarn for wearable piezoelectric nanogenerators, *Smart Materials and Structures*, **27**, 095018 (2018).
220. L. Engel, K. R. Van Volkinburg, M. Ben-David, G. N. Washington, S. Krylov and Y. Shacham-Diamand, Fabrication of a self-sensing electroactive polymer

- bimorph actuator based on polyvinylidene fluoride and its electrostrictive terpolymer, *SPIE Smart Structures and Materials + Nondestructive Evaluation and Health Monitoring*, Las Vegas, USA (2016).
221. C. Lee, D. Wood, D. Edmondson, D. Yao, A. E. Erickson, C. T. Tsao, R. A. Revia, H. Kim and M. Zhang, Electrospun uniaxially-aligned composite nanofibers as highly-efficient piezoelectric material, *Ceramics International*, **42**, 2734-2740 (2016).
 222. Z. Zhang, C. Yao, Y. Yu, Z. Hong, M. Zhi and X. Wang, Mesoporous Piezoelectric Polymer Composite Films with Tunable Mechanical Modulus for Harvesting Energy from Liquid Pressure Fluctuation, *Advanced Functional Materials*, **26**, 6760-6765 (2016).
 223. J. W. Tsai, J. J. Wang and Y. C. Su, Piezoelectric rubber films for human physiological monitoring and energy harvesting, *IEEE 26th International Conference on Micro Electro Mechanical Systems (MEMS)*, Taipei, Taiwan (2013).
 224. D. H. Kim, H. J. Shin, H. Lee, C. K. Jeong, H. Park, G. T. Hwang, H. Y. Lee, D. J. Joe, J. H. Han, S. H. Lee, J. Kim, B. Joung and K. J. Lee, In Vivo Self-Powered Wireless Transmission Using Biocompatible Flexible Energy Harvesters, *Advanced Functional Materials*, **27**, 1700341 (2017).
 225. E. Häslér, L. Stein and G. Harbauer, Implantable physiological power supply with PVDF film, *Ferroelectrics*, **60**, 277-282 (1984).
 226. X. Cheng, X. Xue, Y. Ma, M. Han, W. Zhang, Z. Xu, H. Zhang and H. Zhang, Implantable and self-powered blood pressure monitoring based on a piezoelectric thinfilm: Simulated, *in vitro* and *in vivo* studies, *Nano Energy*, **22**, 453-460 (2016).
 227. Y. Yu, H. Sun, H. Orbay, F. Chen, C. G. England, W. Cai and X. Wang, Biocompatibility and in vivo operation of implantable mesoporous PVDF-based nanogenerators, *Nano Energy*, **27**, 275-281 (2016).
 228. J. Li, L. Kang, Y. Yu, Y. Long, J. J. Jeffery, W. Cai and X. Wang, Study of long-term biocompatibility and bio-safety of implantable nanogenerators, *Nano Energy*, **51**, 728-735 (2018).
 229. J. H. Ahn, W. S. Hwang, J. Y. Cho, S. Y. Jeong, G. J. Song, S. D. Hong, T. H. Sung, S. Jeong and H. H. Yoo, A Bending-Type Piezoelectric Energy Harvester with a Displacement-Amplifying Mechanism for Smart Highways, *Journal of the Korean Physical Society*, **73**, 330-337 (2018).

230. Y. Song, C. H. Yang, S. K. Hong, S. J. Hwang, J. H. Kim, J. Y. Choi, S. K. Ryu and T. H. Sung, Road energy harvester designed as a macro-power source using the piezoelectric effect, *International Journal of Hydrogen Energy*, **41**, 12563-12568 (2016).
231. R. Abinaya, V. Varsha and K. Hariharan, An intelligent street light system based on piezoelectric sensor networks, *Indian Journal of Science and Technology*, **9**, 1-6 (2017).
232. C. H. Yang, Y. Song, M. S. Woo, J. H. Eom, G. J. Song, J. H. Kim, J. Kim, T. H. Lee, J. Y. Choi and T. H. Sung, Feasibility study of impact-based piezoelectric road energy harvester for wireless sensor networks in smart highways, *Sensors and Actuators A: Physical*, **261**, 317-324 (2017).
233. H. Abramovich, E. Harash, C. Milgrom, U. Amit and L.E. Azulay, Power harvesting apparatus, system and method, *US Patent*, US7830071B2 (2010).
234. Y. Wang, X. Zhu, T. Zhang, S. Bano, H. Pan, L. Qi, Z. Zhang and Y. Yuan, A renewable low-frequency acoustic energy harvesting noise barrier for high-speed railways using a Helmholtz resonator and a PVDF film, *Applied Energy*, **230**, 52-61 (2018).
235. D. Vatansever, R. L. Hadimani, T. Shah and E. Siores, An investigation of energy harvesting from renewable sources with PVDF and PZT, *Smart Materials and Structures*, **20**, 055019 (2011).
236. S. Li and H. Lipson, Vertical-Stalk Flapping-Leaf Generator for Wind Energy Harvesting, *ASME 2009 Conference on Smart Materials, Adaptive Structure and Intelligent Systems*, Oxnard, USA (2009).
237. S. Li, J. Yuan and H. Lipson, Ambient wind energy harvesting using cross-flow fluttering, *Journal of Applied Physics*, **109**, 026104 (2011).
238. D. J. Li, S. Hong, S. Gu, Y. Choi, S. Nakhmanson, O. Heinonen, D. Karpeev and K. No, Polymer piezoelectric energy harvesters for low wind speed, *Applied Physics Letters*, **104**, 012902 (2014).
239. J. Song, G. Zhao, B. Li and J. Wang, Design optimization of PVDF-based piezoelectric energy harvesters, *Heliyon*, **3**, e00377 (2017).

3 ADDITIVE MANUFACTURING OF FLEXIBLE AND TRANSPARENT PIEZOELECTRIC GENERATORS

The information presented in this chapter has been published as:

Nick A. Shepelin, Vanessa C. Lussini, Phillip J. Fox, Greg W. Dicinoski, Alexey M. Glushenkov, Joseph G. Shapter and Amanda V. Ellis, 3D printing of poly(vinylidene fluoride-trifluoroethylene): a poling-free technique to manufacture flexible and transparent piezoelectric generators, *MRS Communications*, **9**, 159-164 (2019).

3.1 Abstract

Flexible PEGs present a unique opportunity for renewable and sustainable energy harvesting. Here, a low-temperature and low-energy deposition method is presented, using solvent evaporation-assisted 3D printing to deposit electroactive PVDF-TrFE up to 19 structured layers. Visible-wavelength transmittance was above 92%, while ATR-FTIR spectroscopy showed little change in the electroactive phase fraction between layer depositions. Electroactivity from the fabricated PVDF-TrFE PEGs showed that a single structured layer gave the greatest output at 289.3 mV peak-to-peak voltage. This was proposed to be due to shear-induced polarisation affording the alignment of the fluoropolymer dipoles without an electric field or high temperature.

3.2 Introduction

Renewable energy harvesting is gaining importance for reducing reliance on conventional fossil fuel-based techniques. While large-scale installations are currently the main focus of the renewable energy sector, the trends in portable, wearable and implantable electronic devices have opened up new opportunities in personal-scale energy harvesting. A variety of energy harvesting mechanisms have been proposed for this purpose, such as triboelectricity (energy harvesting from frictional contact), pyroelectricity (energy harvesting through changes in temperature) and piezoelectricity (harvesting energy through mechanical forces), among others.¹⁻³ Of the piezoelectric materials, polymers such as PVDF have been previously reported to show high electromechanical coupling, biocompatibility,^{4,5} processability,^{6,7} optical transparency⁸ and mechanical flexibility,⁹ showing great promise in their utilisation as flexible PEGs.

PVDF is a semi-crystalline polymer, which is generally deposited into the symmetric and non-electroactive α phase using conventional polymer-compatible methods.^{7, 10} In this case, post-processing is undertaken to convert the α phase into the polar and highly electroactive β phase.^{6,9}

In order to increase the β phase content in the polymer the TrFE co-monomer can be introduced, which enables β phase formation due to the steric hindrance arising from the

additional fluorine in the resultant PVDF-TrFE.^{11, 12} The copolymer, with monomer ratios at 75 mol% VDF and 25 mol% TrFE, exhibits greater electromechanical coupling properties than the PVDF homopolymer.^{7, 10} PVDF-TrFE has been reported to show a thickness-axis piezoelectric charge coefficient $d_{33} = 38 \text{ pC N}^{-1}$ (higher than PVDF $d_{33} = 28 \text{ pC N}^{-1}$) and a thickness-axis piezoelectric voltage coefficient $g_{33} = 380 \text{ mV m N}^{-1}$ (PVDF $g_{33} = 320 \text{ mV m N}^{-1}$).^{6, 7, 13, 14}

Under low-energy deposition conditions, the dipolar orientations in the β phase PVDF-TrFE are randomised, leading to a minimal net polarisation vector. For the polymer to be utilised in PEGs, the dipoles are required to be aligned, or polarised, *via* a process referred to as poling.⁶ This method utilises high temperatures coupled with high electric fields to preferentially align the dipole vector in a single direction. The harsh conditions of poling introduce several limitations, including the increased cost of manufacture, the lack of scalability and the potential for electrical breakdown of the polymer.^{6, 15} Hence, for the commercialisation and scalable production of flexible fluoropolymer PEGs, the poling step should ultimately be a low-energy step, integrated into the deposition process. Previous reports have utilised electrospinning to simultaneously deposit and pole the PVDF-TrFE, however the process still requires high electric fields and the intrinsic low feed volumes limit the scalability of this technique.¹⁶

More recently, 3D printing has been reported for the fabrication of electroactive fluoropolymer PEGs. Lee and Tarbutton¹⁷ have reported the use of electric poling-assisted melt 3D printing to simultaneously deposit and pole the PVDF homopolymer by applying an electric field up to 2 MV m^{-1} , generating 12 nC charge from the bending of the structure. Kim *et al.*¹⁸ have utilised a similar method with electric fields up to 13 MV m^{-1} during 3D printing, generating 0.033 nC charge, which corresponds to $d_{33} = 0.048 \text{ pC N}^{-1}$.

Bodkhe *et al.*¹⁹ have reported a poling-free solvent evaporation-assisted (SEA) 3D printed PVDF composite with a piezoelectric ceramic barium titanate nanoparticle filler (10 wt%) in the form of a 70-layer cylinder printed through a $100 \text{ }\mu\text{m}$ internal diameter (ID) nozzle. The composite cylinder, printed at 20 mm s^{-1} x-y speed at 1 MPa pressure, is shown to generate up to 4 V from finger tapping in the 31-mode (electrodes deposited on the

cylinder walls), with a calculated $d_{31} = 18 \text{ pC N}^{-1}$. This composite material is reported to fracture below 2 N of peak-to-peak force, an undesirable trait for a sustainable generator.

In the present work, SEA 3D printing was utilised to manufacture highly flexible and transparent PEGs from PVDF-TrFE under low-energy conditions. The shear-induced nozzle effects were investigated for the purpose of piezoelectric polymer polarisation, and the effects of structured layer height on the resultant electrical output were analysed.

3.3 Experimental

3.3.1 Materials

PVDF-TrFE powder (75 mol% VDF and 25 mol% TrFE, Solvay, Italy), acetone (AR grade, Chem-Supply Pty Ltd, Australia) and DMF (ACS Reagent, Sigma-Aldrich, USA) were used without further purification.

3.3.2 3D printing

PVDF-TrFE powder was added to a solvent mixture consisting of acetone (60 vol%) and DMF (40 vol%) and magnetically stirred at 23 °C for the complete dissolution of the polymer into solution. For viscosity measurements, the PVDF-TrFE solutions were made at 20 wt%, 25 wt%, 30 wt%, 35 wt% and 40 wt%. For 3D printing experiments, the 30 wt% solution was used. The PVDF-TrFE solution was transferred into a 30 mL dispensing barrel (Optimum, Nordson EFD, USA) through a 0.24 µm Teflon syringe filter (Milipore, USA).

The PVDF-TrFE solutions were 3D printed on a pneumatically controlled dispensing system (3D-Bioplotter, EnvisionTEC, Germany) through a 204 µm internal diameter (ID) nozzle (SmoothFlow Tapered, Nordson EFD, USA) at 5 °C barrel temperature. The x-y speed was investigated between 5 mm s⁻¹ and 45 mm s⁻¹. The extrusion pressure was set at 178 kPa.

A thin film layer acting as a substrate (layer zero) was first printed onto a clean glass substrate with total height and width set at 3 cm to obtain a total material area of 9 cm², using a raster pattern with the width between lines at 400 μm . Consecutive layers (up to 19 layers) were then printed on top of the substrate thin film layer using a raster pattern with the width between lines set at 2 mm.

3.3.3 Characterisation

Viscosity (η) characterisation was carried out using a rheometer (MCR-702, Anton Paar, Austria) with cone-plate geometry (25 mm diameter, 2 ° angle). The measurements were taken at 5 °C by a continuous upwards ramp of the shear rate.

Optical properties of the 3D-printed PVDF-TrFE were measured using an ultraviolet, visible and near-infrared spectrophotometry (UV-Vis-NIR) system (Lambda 950, Perkin Elmer, USA) with an integrating sphere (150 mm diameter) at wavelengths between 780 nm and 380 nm with a resolution of 5 nm. Total luminous transmittance was reported as an average of the spectrum. Haze was measured in accordance with ASTM D1003 standard. The values reported were an average of measurements on three separate 3D-printed samples.

Helium ion beam microscopy (HIM) was utilised to characterise the cross-sectional morphology of the SEA 3D printed PVDF-TrFE thin films and layered structures. The HIM micrographs were obtained using the Orion NanoFab (Carl Zeiss AG, Germany), whereby the samples were sliced and adhered onto double-sided Cu tape on a cross-sectional holder.

For the determination of total electroactive ($\beta + \gamma$) phase fraction and confirming the absence of the non-electroactive α phase, ATR-FTIR spectroscopy was used (Frontier, Perkin Elmer, USA). The absorbance was taken between 4000 cm⁻¹ and 600 cm⁻¹ with a resolution of 0.5 cm⁻¹. The values reported for the fraction of electroactive phase ($\beta + \gamma$) were an average of measurements on three separate 3D-printed samples.

To measure the electrical output, PVDF-TrFE PEGs were fabricated by sputter coating (Q150T ES, Quorum, UK) electrodes onto the top and bottom surfaces of the 3D printed PVDF-TrFE. Sputtering consisted of a 2 nm coating of Cr to enhance adhesion, followed by a 10 nm coating of Au, masked to deposit a total electrode area of 2.8 cm². Cu tape with attached wires was physically adhered onto each electrode. The voltage output of the 3D-printed PVDF-TrFE PEGs was measured using an oscilloscope (TDS 2002B, Tektronix, USA) under cyclic compression (5943, Instron, USA) with a frequency of 5 Hz (parameters set at 400 mm min⁻¹ speed and 50 N maximum force).

3.4 Results and discussion

The initial part of this study investigated suitable parameters for SEA 3D printing of PVDF-TrFE. For a fast setting material, the solvent must be volatile.²⁰ Fluoropolymers such as PVDF and PVDF-TrFE are generally soluble in solvents with boiling point greater than 100 °C, limiting their applications in SEA systems.²¹ Acetone, a swelling agent of PVDF-TrFE, was added as a co-solvent with DMF, which can readily dissolve fluoropolymers. Conventionally, fluoropolymers are dissolved at a ratio of 80 vol% DMF and 20 vol% acetone, requiring high temperatures or long processing times to evaporate the solvent.^{19, 22} In the work presented here, a volume ratio of 60 vol% acetone relative to 40 vol% DMF was used after analysis of the solubility parameters, described in Supplementary Figure 3.S1.

The flow behaviour of PVDF-TrFE solutions was investigated *via* rheological characterisation. Figure 3.1 shows the dependence of the viscosity on the applied shear rate for the solutions with varying PVDF-TrFE loadings in acetone:DMF (60:40 vol%). A shear-thinning behaviour was observed for all samples and the effect of PVDF-TrFE loading was significant. The viscosity of the PVDF-TrFE solutions was found to decrease with increasing shear rate, indicative of a non-Newtonian fluid.²³ This type of rheological behaviour is ideal for 3D printing, as the solutions must be free-flowing (low viscosity) under the high shear stresses of the extrusion nozzle and consequently retain their shape (high viscosity) following extrusion.²⁴

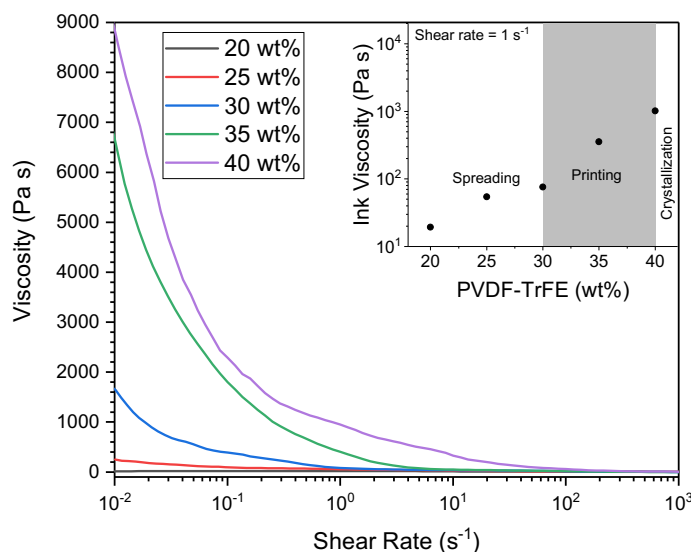


Figure 3.1: Viscosity of PVDF-TrFE solutions as a function of shear rate for PVDF-TrFE loadings between 20 wt% and 40 wt%. Inset shows the viscosity at 1 s^{-1} as a function of PVDF-TrFE loadings.

The viscosity at shear rates below 1 s^{-1} was found to increase with increasing PVDF-TrFE loading, desirable for the printed structures to retain their shape post-deposition. The viscosity of the 20 wt% PVDF-TrFE solution (Figure 3.1, black line) was relatively constant, between 20 Pa s and 10 Pa s up to a shear rate of 10 s^{-1} , decreasing past 1 Pa s above 500 s^{-1} shear rates (Supplementary Figure 3.S2). The 25 wt% PVDF-TrFE solution (Figure 3.1, red line) was found to exhibit shear thinning behaviour throughout the investigated region. The viscosity at 0.01 s^{-1} shear rate was 20 times higher than that of the 20 wt% solution, indicating greater shape retention and therefore higher printing resolution. Conversely, the viscosity was not found to decrease below 1 Pa s at up to 1000 s^{-1} . The 30 wt% (Figure 3.1, blue line) and 35 wt% (Figure 3.1, green line) PVDF-TrFE solutions showed enhanced rheological properties optimal for SEA 3D printing. The PVDF-TrFE solution containing 30 wt% exhibited an increase in viscosity of one order of magnitude over the 25 wt% solution at 0.01 s^{-1} , decreasing to 0.11 Pa s at 1000 s^{-1} shear rate. A more pronounced effect was seen in the 35 wt% PVDF-TrFE solution, however it was noted that magnetic stirring alone was insufficient to completely dissolve the polymer. Therefore, the 30 wt% PVDF-TrFE in acetone:DMF (60:40 vol%) was used for further SEA 3D printing experiments.

The PVDF-TrFE solutions were subsequently 3D printed onto a clean glass substrate, consisting initially of a thin film layer as the substrate layer and consecutive structured layers. The temperature of the polymer solution was kept at 5 °C and the substrate at 23 °C.

The x-y speed of the robot head was optimised for greatest lateral resolution during printing, with the resulting structures shown optically in Supplementary Figure 3.S3 and under an optical microscope in Supplementary Figure 3.S4. At low speeds below 25 mm s⁻¹, the structures were found to be significantly wider than the nozzle ID, indicating low resolution of printing. Robot head speeds above 35 mm s⁻¹ deposited structures with significantly lower width, however loss of resolution at the squared corners was observed (Supplementary Figure 3.S4). The structures with low width and high reproduction of desired shape were obtained at 30 mm s⁻¹ printing and hence this speed was utilised for further printing.

The substrate thin film layer was printed into a square with 3 cm width and height, following a raster pattern. The formation of the thin film was dependent upon successful binding of adjacent raster lines, hence the distance between the lines was varied to obtain a solid film with minimal thickness. The optimisation of the initial thin film layer is shown in Supplementary Figure 3.S5. At distances between raster lines greater than 500 µm, the final structure resembled the input pattern. When the distance was set to 500 µm, a thin film was obtained, however the structure of the film was inconsistent. The formation of a thin film with no gaps is necessary for the fabrication of flexible PEGs, to ensure no short circuiting occurs between the electrodes. Consistent thin films were formed at a raster line distance of 400 µm, which resulted in films with approximately 40 µm thickness (Supplementary Figure 3.S6). The SEA 3D printed PVDF-TrFE thin films were transparent, with 94% total luminous transmittance (Figure 3.2, inset).

Following the printing of the initial PVDF-TrFE thin film layer, structures were deposited in a layer-by-layer manner up to 19 layers. Figure 3.2a shows an optical image of a 19-layer PVDF-TrFE raster structure on top of a printed thin film layer. The structures are free-standing and self-supporting, retaining their shape when removed from the glass

substrate. The 3D printed PVDF-TrFE structures were found to be transparent at up to 19 layers (Figure 3.2a, inset), with total luminous transmittance above 92% and haze below 58% in all samples.

The cross-sectional HIM analysis of the thin film and the initial structured layers is shown in Figure 3.2b. The image shows the solid internal nature of the structures, confirming the complete evaporation of the solvents. Furthermore, the initial layers printed on top of the PVDF-TrFE thin film exhibited broadening of the structures, likely explained by enhanced compatibility of the PVDF-TrFE solution and the previous deposited layer, as well as the minimisation of liquid-air interfacial surface area. Figure 3.2c shows the cross-sectional HIM image of the top of a 19-layer 3D printed PVDF-TrFE structure. The maximum width of the structures was found to be 260 μm , corresponding to 27% broadening relative to the nozzle ID. The final layer had a width of 225 μm , corresponding to 10% broadening and suggesting near-optimal printability of the 30 wt% PVDF-TrFE solutions in acetone:DMF (60:40 vol%).

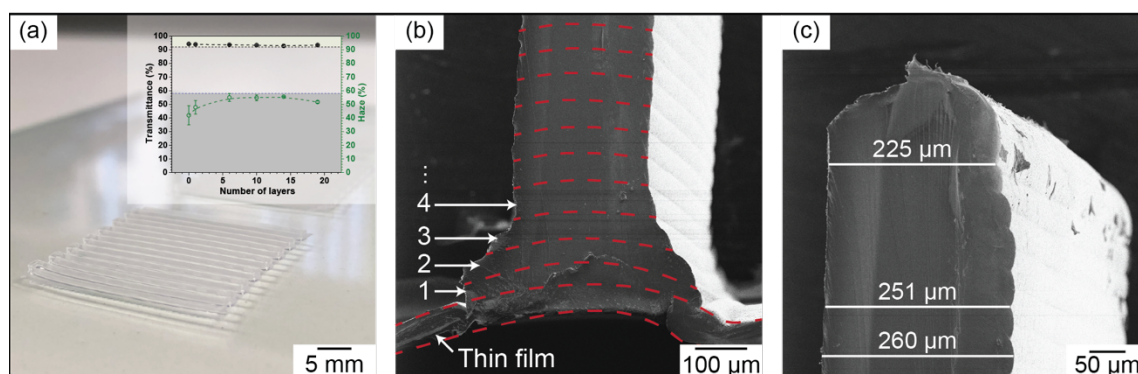


Figure 3.2: Morphology of 3D printed PVDF-TrFE structures, showing (a) optical image of a 19-layer structure printed on top of a thin film, with the inset showing transmittance and haze as a function of layers deposited, (b) cross-sectional HIM image of the thin film and subsequent layers deposited and (c) cross-sectional HIM image of the top of a 19-layer PVDF-TrFE structure.

In order to obtain highly efficient fluoropolymer PEGs it is necessary to maximise the content of electroactive phases (consisting of the highly polar β phase and semi-polar γ phase), which is often characterised using FTIR.²⁵ Figure 3.3a shows the ATR-FTIR

spectra in the region of interest between 1500 cm^{-1} and 600 cm^{-1} for the SEA 3D printed PVDF-TrFE structures on printed thin films as a function of the number of layers. The peak at 840 cm^{-1} in all samples is indicative of the presence of the electroactive phase consisting of the β and γ phases.⁷ The secondary contributing peaks at 1280 cm^{-1} and 1240 cm^{-1} were representative of the presence of the β and γ phases, respectively.²⁶ The prominent presence of the secondary β phase peak was found in all samples, whereas the secondary γ peak was found as a shoulder. Moreover, the absence of pronounced peaks at 766 cm^{-1} , generally correlated to the non-polar crystalline α phase in fluoropolymers, indicates that the SEA 3D printed PVDF-TrFE structures were deposited directly into the electroactive phases through low-temperature printing.

The fraction of total electroactive phase F_{EA} was quantified through Equation (3.1), shown as a function of the number of layers in Figure 3.3b.^{25, 26} Here, I_{EA} corresponds to the intensity of the peak at 840 cm^{-1} , I_{α} corresponds to the intensity of the peak at 766 cm^{-1} , and K_{EA} and K_{α} correspond to the absorption coefficients at the respective wave-numbers, given as $6.1 \times 10^4\text{ cm}^2\text{ mol}^{-1}$ and $7.7 \times 10^4\text{ cm}^2\text{ mol}^{-1}$, respectively.²⁷

$$F_{EA} = \frac{I_{EA}}{(K_{EA}/K_{\alpha})I_{\alpha} + I_{EA}} \quad (3.1)$$

The F_{EA} (shown in Figure 3.3b) of the 3D printed PVDF-TrFE thin films was 81.7%, which is significantly higher than that of the PVDF homopolymer when processed using low-energy methods.²⁶ 3D printing of PVDF-TrFE structures on top of the printed thin film layer resulted in a slight decrease of F_{EA} to 79.0%, attributed to the increasing interfacial area between the solution and surrounding air. Additional layer-by-layer deposition of structures decreased the F_{EA} to a minimum 76.8% at 19 3D printed layers of PVDF-TrFE. These decreases were not considered significant, as the contributions in Figure 3.3a from β (1280 cm^{-1}) and γ (1240 cm^{-1}) were present throughout the entire printing process.

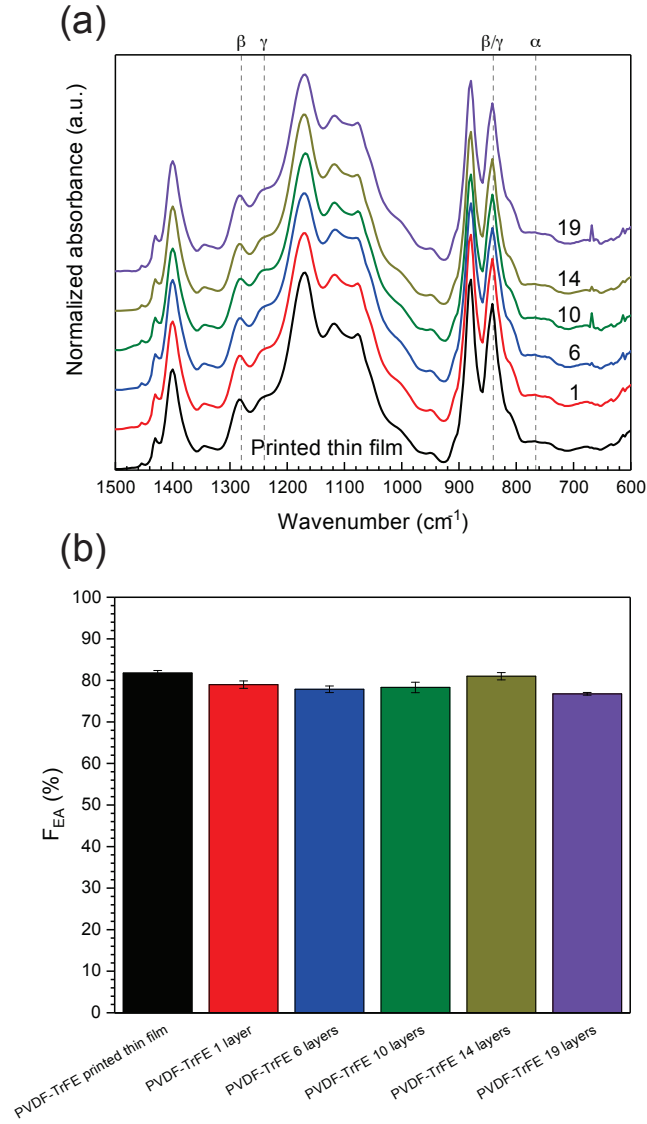


Figure 3.3: ATR-FTIR characterisation of SEA 3D printed PVDF-TrFE materials, (a) the FTIR spectra in the fingerprint region as a function of the number of printed layers (offset for clarity) and (b) the calculated F_{EA} as a function of the number of printed layers.

The energy harvesting capability was quantified for PEGs fabricated using the SEA 3D printed PVDF-TrFE. In general, PVDF-TrFE PEGs prepared *via* solvent evaporation techniques such as drop casting and solvent casting show a randomised directionality for the polarisation vector, inhibiting electromechanical conversion and showing no electrical output upon deformation without poling.⁹ Hence, to be electroactive, the piezoelectric polymer is generally required to be poled *via* highly energetic methods. However, in this work, the electrical output of the 3D printed layers was investigated, which have not been

exposed to any conventional poling techniques in order to ascertain if shear alone would enhance the output, building on previous modelling²⁸ and rheology²⁹ studies.

Here, the SEA 3D printed PVDF-TrFE samples were coated with two conductive materials on each side through a shadow mask, consisting of a 2 nm Cr layer, acting as a seeding and adhesion layer, and a 10 nm Au layer. The sputter-coated electrode covered the entire surface on each side, both the bottom of the substrate layer and the top of the structure and substrate, including the walls of the structures. Wires were soldered to Cu tape and physically adhered to the coated electrodes. The PVDF-TrFE with electrodes was then encapsulated with insulating polyimide (Kapton) tape to prevent external influences on the electrical output. The resulting SEA 3D printed PVDF-TrFE PEGs with a varying number of layers were investigated for their electroactivity upon mechanical compression. An Instron was used in cyclic compression mode to induce deformation. The V_{OC} was measured concurrently by an oscilloscope.

Figure 3.4a shows the representative V_{OC} as a function of time for the increasing number of layers in the SEA 3D printed PVDF-TrFE PEGs. Initially, it was found that the 3D printed thin film was able to generate electricity upon cyclic deformation, which does not occur in other low-energy deposition techniques.⁹ The 3D printed PVDF-TrFE thin film PEG generated an average peak-to-peak voltage (V_{pp}) of 69.6 ± 49.6 mV (Figure 3.4b), exhibiting electroactivity.

The PEG samples consisting of one structured layer 3D printed onto the printed thin film layer were found to generate the highest voltage. The average V_{pp} of the one-layer samples was 289.3 ± 27.6 mV, a four-fold increase over that of the thin film printed PEG. This was attributed to the increased aspect ratio and surface area of the material compared to the printed thin film PEG. As noted in the ATR-FTIR results there is not a great change in the F_{EA} %, therefore it is proposed that this increase in electrical output for the one layer is primarily due to shear-induced polarisation at the 3D printing nozzle walls.^{28, 29}

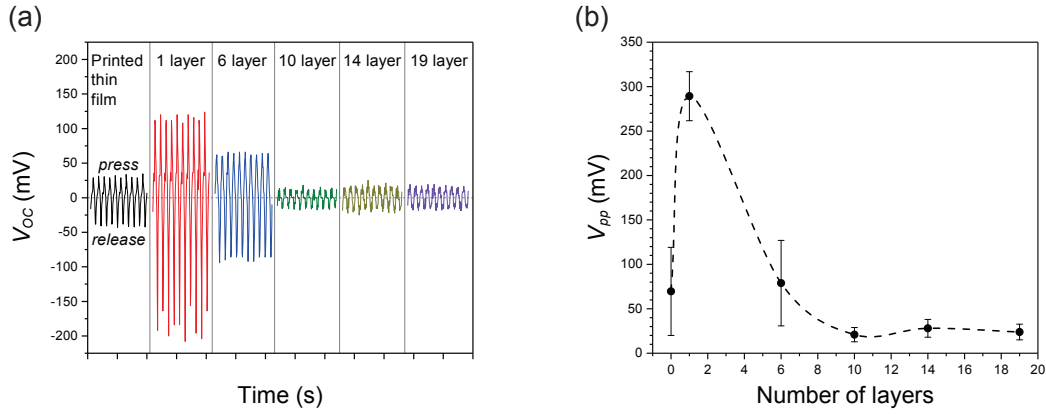


Figure 3.4: (a) Representative open circuit voltage for SEA 3D printed PVDF-TrFE PEGs as a function of time under 5 Hz cyclic compression. The positive peaks represent increasing compressive force whereas negative peaks represent decreasing compressive force. Each division on the time axis represents 1 s. (b) Peak-to-peak voltage output of the PEGs as a function of the number of 3D printed structured layers of PVDF-TrFE. The first data point represents a 3D printed thin film. Error bars were obtained using the maxima and minima of 50 compression cycles, for three separate samples per data point.

By further increasing the number of layers that were 3D printed on top of the thin film a decrease in the V_{pp} output from cyclic compression to background levels was observed. This phenomenon was attributed to the spatial distribution of the electrode. The sputter coating technique deposits the electrode on the walls of the 3D printed PVDF-TrFE structures, negating further enhancements in electroactivity at higher layer numbers.

3.5 Conclusion

In summary, SEA 3D printing was used to manufacture flexible and transparent PVDF-TrFE PEGs and the effects of utilising a shear-enhanced deposition technique were investigated. The visible-wavelength transmittance for the 3D printed PVDF-TrFE was above 92% for all samples, up to 19 layers on a thin film. The electroactive ($\beta + \gamma$) phase fraction showed values between 75% and 80% for all samples. The 3D printed thin film PVDF-TrFE piezoelectric generator exhibited 69.6 mV peak-to-peak voltage, increasing to a maximum of 289.3 mV in the generator consisting of one structured layer printed on top of the thin film. This increased output was proposed to be due to shear-induced

polarisation—not related to an increase in β phase. Overall, the SEA 3D printing technique shows great promise in producing enhanced electrical output from fluoropolymer-based piezoelectric generators through low-temperature and low-energy deposition methods.

3.6 References

1. Z. L. Wang, G. Zhu, Y. Yang, S. Wang and C. Pan, Progress in nanogenerators for portable electronics, *Materials Today*, **15**, 532-543 (2012).
2. C. R. Bowen, J. Taylor, E. LeBoulbar, D. Zabek, A. Chauhan and R. Vaish, Pyroelectric materials and devices for energy harvesting applications, *Energy & Environmental Science*, **7**, 3836-3856 (2014).
3. C. R. Bowen, H. A. Kim, P. M. Weaver and S. Dunn, Piezoelectric and ferroelectric materials and structures for energy harvesting applications, *Energy & Environmental Science*, **7**, 25-44 (2014).
4. J. Li, L. Kang, Y. Yu, Y. Long, J. J. Jeffery, W. Cai and X. Wang, Study of long-term biocompatibility and bio-safety of implantable nanogenerators, *Nano Energy*, **51**, 728-735 (2018).
5. Y. Yu, H. Sun, H. Orbay, F. Chen, C. G. England, W. Cai and X. Wang, Biocompatibility and in vivo operation of implantable mesoporous PVDF-based nanogenerators, *Nano Energy*, **27**, 275-281 (2016).
6. K. S. Ramadan, D. Sameoto and S. Evoy, A review of piezoelectric polymers as functional materials for electromechanical transducers, *Smart Materials and Structures*, **23**, 033001 (2014).
7. P. Martins, A. C. Lopes and S. Lanceros-Mendez, Electroactive phases of poly(vinylidene fluoride): Determination, processing and applications, *Progress in Polymer Science*, **39**, 683-706 (2014).
8. M. Li, I. Katsouras, C. Piliego, G. Glasser, I. Lieberwirth, P. W. M. Blom and D. M. de Leeuw, Controlling the microstructure of poly(vinylidene-fluoride) (PVDF) thin films for microelectronics, *Journal of Materials Chemistry C*, **1**, 7695-7702 (2013).
9. V. Bhavanasi, V. Kumar, K. Parida, J. Wang and P. S. Lee, Enhanced Piezoelectric Energy Harvesting Performance of Flexible PVDF-TrFE Bilayer

- Films with Graphene Oxide, *ACS Applies Materials & Interfaces*, **8**, 521-529 (2016).
10. S. Rajala, M. Schouten, G. Krijnen and S. Tuukkanen, High Bending-Mode Sensitivity of Printed Piezoelectric Poly(vinylidene fluoride-co-trifluoroethylene) Sensors, *ACS Omega*, **3**, 8067-8073 (2018).
 11. G. Eberle, H. Schmidt and W. Eisenmenger, Piezoelectric polymer electrets, *IEEE Transactions on Dielectrics and Electrical Insulation*, **3**, 624-646 (1996).
 12. T. Soulestin, V. Ladmiral, F. D. Dos Santos and B. Ameduri: Vinylidene fluoride- and trifluoroethylene-containing fluorinated electroactive copolymers. How does chemistry impact properties?, *Progress in Polymer Science*, **72**, 16-60 (2017).
 13. Y. Ito and K. Uchino, Piezoelectricity, in *Encyclopedia of RF and Microwave Engineering*, ed. K. Chang, Wiley, Hoboken (2005).
 14. X. Chen, H. O. T. Ware, E. Baker, W. Chu, J. Hu and C. Sun, The Development of an All-polymer-based Piezoelectric Photocurable Resin for Additive Manufacturing, *Procedia CIRP*, **65**, 157-162 (2017).
 15. M. Fortunato, R. C. Chandraiahgari, G. De Bellis, P. Ballirano, F. Sarto, A. Tamburrano and S. M. Sarto, Piezoelectric Effect and Electroactive Phase Nucleation in Self-Standing Films of Unpoled PVDF Nanocomposite Films, *Nanomaterials*, **8**, 743 (2018).
 16. S. K. Ghosh and D. Mandal, Synergistically enhanced piezoelectric output in highly aligned 1D polymer nanofibers integrated all-fiber nanogenerator for wearable nano-tactile sensor, *Nano Energy*, **53**, 245-257 (2018).
 17. C. Lee and J. A. Tarbutton, Electric poling-assisted additive manufacturing process for PVDF polymer-based piezoelectric device applications, *Smart Materials and Structures*, **23**, 095044 (2014).
 18. H. Kim, F. Torres, Y. Wu, D. Villagran, Y. Lin and T. L. Tseng, Integrated 3D printing and corona poling process of PVDF piezoelectric films for pressure sensor application, *Smart Materials and Structures*, **26**, 085027 (2017).
 19. S. Bodkhe, G. Turcot, F. P. Gosselin and D. Therriault, One-Step Solvent Evaporation-Assisted 3D Printing of Piezoelectric PVDF Nanocomposite Structures, *ACS Applied Materials & Interfaces*, **9**, 20833-20842 (2017).
 20. G. Postiglione, G. Natale, G. Griffini, M. Levi and S. Turri, Conductive 3D microstructures by direct 3D printing of polymer/carbon nanotube

- nanocomposites via liquid deposition modeling, *Composites Part A: Applied Science and Manufacturing*, **76**, 110-114 (2015).
21. A. Bottino, G. Capannelli, S. Munari and A. Turturro, Solubility parameters of poly(vinylidene fluoride), *Journal of Polymer Science, Part B: Polymer Physics*, **26**, 785-794 (1988).
 22. L. Yu and P. Cebe, Crystal polymorphism in electrospun composite nanofibers of poly(vinylidene fluoride) with nanoclay, *Polymer*, **50**, 2133-2141 (2009).
 23. S. V. Murphy and A. Atala, 3D bioprinting of tissues and organs, *Nature Biotechnology*, **32**, 773-785 (2014).
 24. S. C. Ligon, R. Liska, J. Stampfl, M. Gurr and R. Mülhaupt, Polymers for 3D Printing and Customized Additive Manufacturing, *Chemical Reviews*, **117**, 10212-10290 (2017).
 25. X. Cai, T. Lei, D. Sun and L. Lin, A critical analysis of the alpha, beta and gamma phases in poly(vinylidene fluoride) using FTIR, *RSC Advances*, **7**, 15382-15389 (2017).
 26. S. Barrau, A. Ferri, A. Da Costa, J. Defebvin, S. Leroy, R. Desfeux and J. M. Lefebvre, Nanoscale Investigations of α - and γ -Crystal Phases in PVDF-Based Nanocomposites, *ACS Applied Materials & Interfaces*, **10**, 13092-13099 (2018).
 27. R. Gregorio and M. Cestari, Effect of crystallization temperature on the crystalline phase content and morphology of poly(vinylidene fluoride), *Journal of Polymer Science, Part B: Polymer Physics*, **32**, 859-870 (1994).
 28. J.H. Yang, T. Ryu, Y. Lansac, Y.H. Jang and B.H. Lee, Shear stress-induced enhancement of the piezoelectric properties of PVDF-TrFE thin films, *Organic Electronics*, **28**, 67-72 (2016).
 29. A. Gebrekrstos, M. Sharma, G. Madras and S. Bose, Critical Insights into the Effect of Shear, Shear History, and the Concentration of a Diluent on the Polymorphism in Poly(vinylidene fluoride), *Crystal Growth & Design*, **17**, 1957-1965 (2017).

3.7 Supplementary Information

The solubility of PVDF in a solvent mixture consisting of DMF and acetone was modelled using Hansen¹ solubility parameters reported by Bottino *et al.*² as a function of solvent ratios. This was achieved through the use of the RMS error method of the variation in solubility parameters of each solvent and the polymer (shown in Supplementary Table 3.S1). The distance between the Hansen solubility parameters for PVDF and the solvent mixture with varying acetone volume fraction is shown in Supplementary Figure 3.S1a, whereby the dashed line at the origin represents the optimal value for the dissolution of PVDF. To the best knowledge of the authors, the solubility parameters of PVDF-TrFE have not been determined, hence PVDF was used to determine the optimal solvent ratios.

Table 3.S1: Solubility parameters of PVDF, and solvents acetone and DMF, as well as the difference in total solubility parameters between PVDF and solvent using the RMS method.

Influence of parameter	δ_d Dispersion	δ_p Dipolar intermolecular	δ_h Hydrogen	δ difference (RMS) $\sqrt{\frac{\sum_{i=d}^h (\delta_{i,s} - \delta_{i,PVDF})^2}{N_i}}$
PVDF	17.2	12.5	9.2	0.0
Acetone	15.5	10.4	7.0	2.01
DMF	17.4	13.7	11.3	1.4

The RMS variation in solubility parameter ($\delta_{difference}$) was then calculated by Supplementary Equation (3.S1) for ratios of acetone and DMF in the solvent mixture ranging from 100 vol% DMF to 100 vol% acetone.

$$\delta_{difference} = \sqrt{\frac{\sum_{i=d}^h ([a\delta_{i,DMF} + (1-a)\delta_{i,acetone}] - \delta_{i,PVDF})^2}{N_i}} \quad (3.S1)$$

Here, a was the relative volume fraction of DMF in the solution mixture and $\delta_{i, DMF}$ and $\delta_{i, acetone}$ were the parameters given in Supplementary Table 3.S1 for each solvent. The $\delta_{difference}$, the RMS distance of the three solubility parameters, was then plotted as a function of the relative volume fraction resulting in the plot shown in Supplementary Figure 3.S1b. The dashed line represents the total RMS variation in the solubility parameters between PVDF and the solvent mixture at the commonly used volume fractions of DMF (80 vol%) and acetone (20 vol%).³ It was noted that the dashed line additionally intercepts the curve at 61 vol% acetone, therefore the range of solvent ratios between 20 vol% and 61 vol% acetone was determined to successfully dissolve the fluoropolymer. Acetone has a significantly higher volatility relative to DMF, hence the solvent ratio used for this work maximised the acetone volume fraction to 60 vol% to decrease the drying time of the polymer upon printing.⁴

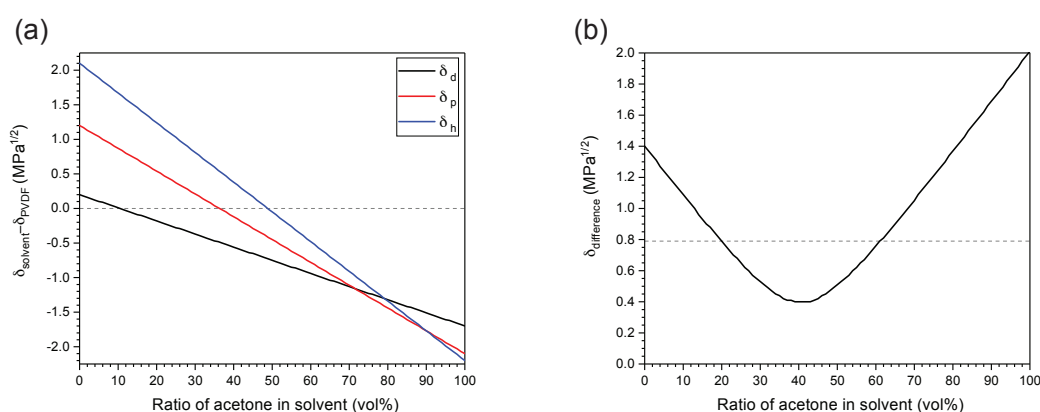


Figure 3.S1: (a) Variation between the Hansen solubility parameters for PVDF and the solvent mixture and (b) RMS difference in solubility parameters for PVDF in a solution mixture consisting of acetone and DMF as a function of acetone volume fraction.

The viscosity of the PVDF-TrFE solutions at concentrations between 20 wt% and 40 wt% in a solvent mixture containing 60 vol% acetone and 40 vol% DMF was measured at shear rates between 0.01 s⁻¹ and 1000 s⁻¹, shown in Supplementary Figure 3.S2.

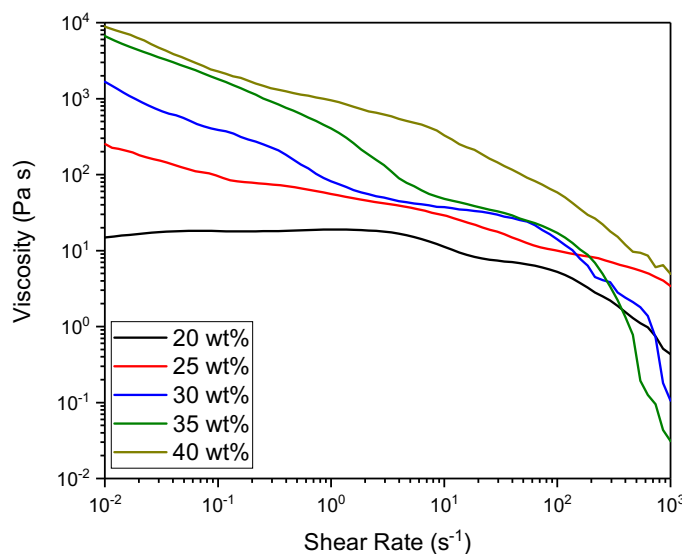


Figure 3.S2: Viscosity of PVDF-TrFE solutions as a function of shear rate for PVDF-TrFE loadings between 20 wt% and 40 wt%.

The optimal printing parameters were investigated experimentally. Supplementary Figure 3.S3 shows an optical image of structures deposited onto a glass substrate at x-y robot head speeds between 5 mm s^{-1} and 45 mm s^{-1} using a raster pattern with a line spacing of 2 mm. Here, the lamps in the background were used to demonstrate the transparency of the printed structures after drying. Supplementary Figure 3.S4 shows the optical micrographs of the corner sections of the structures, highlighting the resolution of printing at various speeds.

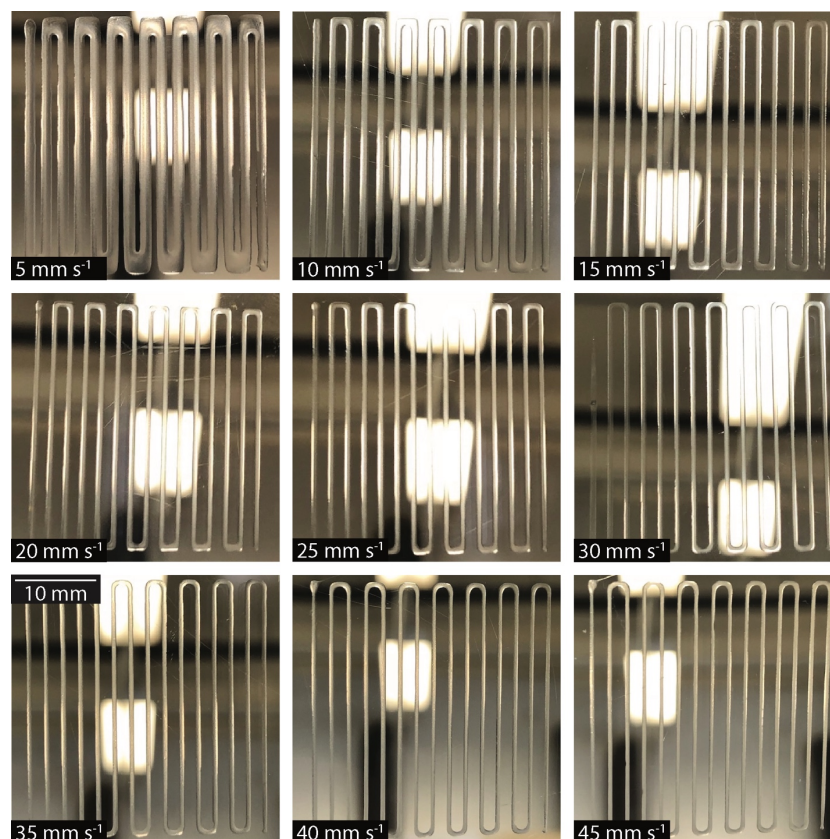


Figure 3.S3: Optical images showing the structures during optimisation of x-y speed of the 3D Bioplotter for the printing of PVDF-TrFE at 30 wt% in solution. The lamps in the background are used to demonstrate the transparency of the printed structures.

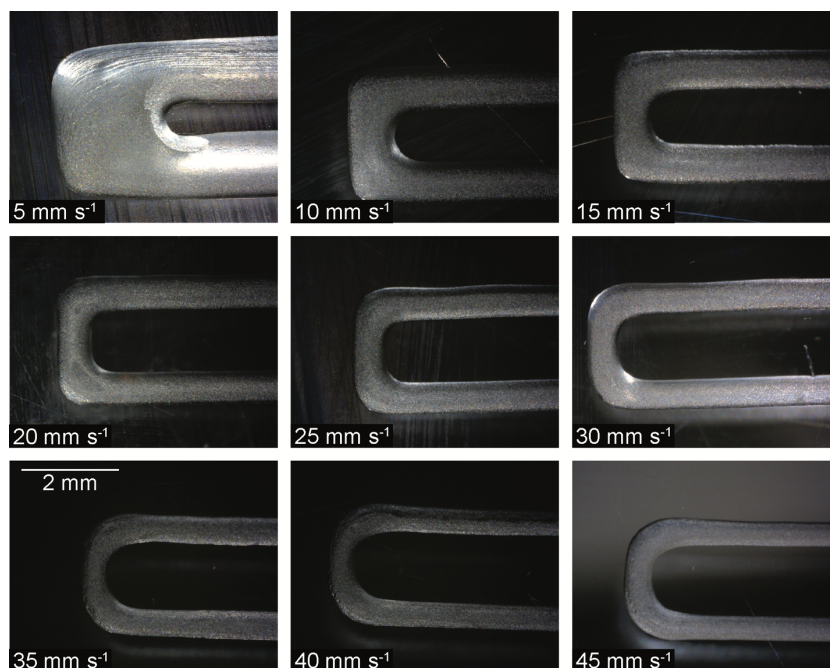


Figure 3.S4: Optical microscope images of the edge of the raster pattern during optimisation of x-y speed of the 3D Bioplotter for the printing of PVDF-TrFE at 30 wt% in solution.

Supplementary Figure 3.S5 shows the results of the thin film optimisation. In this study, the width between lines in the raster pattern was controlled between 1.2 mm (top left) and 0.4 mm (bottom right). The cross-sectional HIM micrograph is shown in Supplementary Figure 3.S6 for the thin film printed using a 0.4 mm line width for the raster pattern. Here, the thickness was found to be below 40 μm .

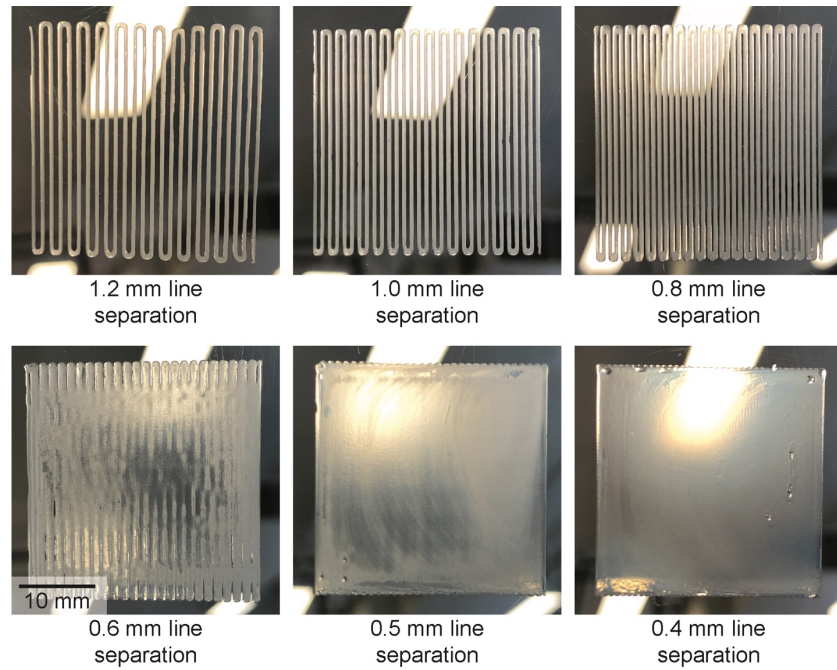


Figure 3.S5: Optical images of PVDF-TrFE 3D printed onto a glass substrate, whereby the spacing of a raster pattern was investigated for the printing of a solid thin film. Printing conditions as follows: 178 kPa extrusion pressure, 30 mm/s x-y robot head speed, 5 °C cartridge temperature, 24 °C ambient temperature.

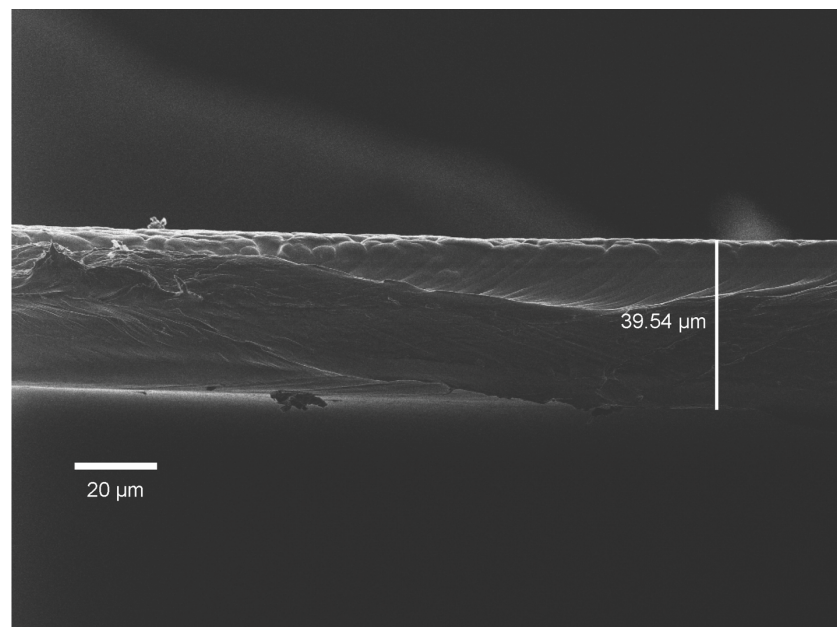


Figure 3.S6: HIM image showing the cross section of an optimised SEA 3D printed PVDF-TrFE thin film with a 0.4 mm raster line width.

3.7.1 Supplementary References

1. C. M. Hansen, *Hansen Solubility Parameters: A User's Handbook*, CRC Press, Boca Raton (2007).
2. A. Bottino, G. Capannelli, S. Munari and A. Turturro, Solubility parameters of poly(vinylidene fluoride), *Journal of Polymer Science, Part B: Polymer Physics*, **26**, 785-794 (1988).
3. L. Yu and P. Cebe, Crystal polymorphism in electrospun composite nanofibers of poly(vinylidene fluoride) with nanoclay, *Polymer*, **50**, 2133-2141 (2009).
4. M. Baqeri, M. M. Abolhasani, M. R. Mozdianfard, Q. Guo, A. Oroumei and M. Naebe, Influence of processing conditions on polymorphic behavior, crystallinity and morphology of electrospun poly(vinylidene fluoride) nanofibers, *Journal of Applied Polymer Science*, **132**, 42304 (2015).

4 DIPOLE TEMPLATING OF FLUOROPOLYMERS FROM SINGLE-WALLED CARBON NANOTUBES

The information presented in this chapter has been published as:

Nick A. Shepelin, Peter C. Sherrell, Eirini Goudeli, Emmanuel N. Skountzos, Vanessa C. Lussini, Greg W. Dicinoski, Joseph G. Shapter and Amanda V. Ellis, Printed recyclable and self-poled polymer piezoelectric generators through single-walled carbon nanotube templating, *Energy & Environmental Science*, **13**, 868-883 (2020).

4.1 Abstract

With an increasing global energy demand, along with a rising uptake of portable electronic devices, it is of great importance to investigate the viability of alternative energy harvesting technologies. Flexible PEGs are able to convert mechanical energy to electricity, making them an ideal candidate to decrease reliance on conventional energy sources and to power flexible, portable and implantable electronics. In this study, a low-energy production pathway is demonstrated for transparent PEGs based on PVDF-TrFE *via* shear-induced alignment of its dipoles through extrusion printing, complemented by spatial dipolar templating onto SWCNTs at low concentrations (<0.05 wt%). The resulting composite PEGs show up to a 500% enhancement in the piezoelectric charge coefficient d_{33} relative to extrusion printed pristine PVDF-TrFE, with similar enhancements in energy harvesting, exhibiting a power density of up to $20 \mu\text{W cm}^{-3}$ at 0.02 wt% SWCNTs. The extrusion printed composite PEGs showed recyclability using only a green solvent (acetone) and were found to exhibit piezoelectric energy harvesting with a power density of up to $71 \mu\text{W cm}^{-3}$ upon reprinting, overcoming two of the most significant hurdles towards commercial production of flexible PEGs.

4.2 Introduction

Wearable electronic devices are ubiquitous in modern society, providing personalised information and sensing to an estimated 22% of US adults in 2019 and growing year on year.¹ Similar to trends over the last 20 years in smartphone technology, there is a desire for the next generation of wearable electronics to be lighter and smaller, with longer lifetimes. A major bottleneck toward achieving miniaturisation in electronic devices is the power supply, conventionally based on electrochemical devices, which require the incorporation of fluid electrolytes and manual recharging.² Therefore, finding lightweight and low footprint alternatives for power delivery is crucial in the development of next generation wearable electronics.³ Many sustainable technologies have been proposed as alternative energy sources, including photovoltaic, thermo-, pyro-, and mechano-electric technologies.⁴⁻⁷ However, for devices with low power requirements, flexible PEGs have emerged as ideal candidates, requiring no manual recharge, being completely solid-state, and being relatively lightweight.

While piezoelectricity as a means of harvesting energy has been found in literature as early as 1961, the desire for renewable and independent energy generators has provoked a great revival of interest within the academic community over the past several years.⁸ For the purposes of energy harvesting, ceramic and polymer materials have shown the highest promise, however ceramic devices are rigid, brittle, and often lack biocompatibility.^{7,9,10} Conversely, polymeric materials are flexible and biocompatible, with the potential for transparency, thus increasing their scope for reliable commercial use.^{9,11,12} In particular, fluoropolymers have shown the highest piezoelectric energy harvesting capability of all flexible polymer PEGs due to their high dipole polarisation, on the order of 131 mC m^{-2} , between their hydrogen and fluorine atoms perpendicular to the carbon backbone.¹³ The piezoelectric FOM for thin films, corresponding to the product of the piezoelectric charge (d_{33}) and voltage (g_{33}) coefficients, $d_{33}g_{33}$, has been experimentally validated to show similar values for both ceramic materials and polymers.¹⁴ Piezoelectric polymers, dominated largely by fluoropolymers, have shown lower values for the harvested d_{33} and volumetric power density (P_D); however, the reports of the g_{33} have shown significantly higher values relative to the ceramic materials.⁷ Similar FOM values, coupled with their ease of use in flexible, wearable and implantable electronic devices, make fluoropolymers an attractive option for energy harvesting applications. For wearable electronics, flexible, transparent and light weight devices are paramount. Polymer-based PEGs are far superior in these requirements compared to their ceramic counterparts.

However, one of the major challenges currently preventing widespread use of fluoropolymers in energy harvesting is the cost to process the polymers into the piezoelectric phase and subsequently align their inherent dipoles, which is also a requirement for efficient PEGs.^{7,9}

Polycrystalline dielectric fluoropolymers such as PVDF can be deposited into the non-polar and non-piezoelectric α phase (*trans-gauche-trans-gauche'* polymorph, TGTG') when low energy techniques such as solvent-casting are employed.¹⁵ The conversion of the α phase to the polar phases, including the highly piezoelectric β phase (TTTT polymorph) and the partially piezoelectric γ phase (TTTGT'TTG' polymorph), has become a widespread research area, whereby multiple authors have claimed to achieve β phase fractions as high as 100%.^{7,16,17} The utilisation of a co-monomer during the polymerisation

process, such as TrFE, has been further reported to enhance the nucleation of fluoropolymers into the piezoelectric phases during deposition.¹⁵ At TrFE fractions between 25 mol% and 30 mol% relative to VDF, the copolymer films have been demonstrated to contain a higher β phase fraction relative to equivalent PVDF films, arising from the steric interactions between the third fluoride atom in the TrFE.⁹ Nonetheless, an additional processing step called poling is required to spatially align the dipoles of the piezoelectric phases for high energy conversion efficiencies.^{9,18} In the poling process, generally undertaken under vacuum and at temperatures between the T_C and T_m (90 °C and 110 °C, respectively), electric fields between 2 MV m⁻¹ and 400 MV m⁻¹ are applied across the material.^{7,9,19} Each part of this step utilises a significant amount of energy and is difficult to scale to roll-to-roll processes, currently only undertaken by Measurement Specialties, Inc.²⁰

In order to improve piezoelectric outputs from fluoropolymers, researchers have incorporated various conducting, semiconducting, insulating and piezoelectric additives into fluoropolymers.^{7,15} Additionally, a range of additive morphologies have been trialled such as nanoparticles,^{21–25} nanowires/nanotubes^{26–36} and planar nanomaterials.^{37,38} The majority of the studies have reported enhancements in the β -phase fraction, crystallinity or both.^{22–25,28,32,37–39} One-dimensional (1D) CNT additives are of increasing interest due to their decreased toxicity relative to their inorganic counterparts and provide mechanical reinforcement while remaining flexible at concentrations <1 wt%, important for both wearable and implantable energy harvesters.^{40–42} CNTs have been shown to potentially aid β phase nucleation.^{32,39,43} Fabrication methods including solvent casting (poling at 60 MV m⁻¹ electric field), electrospinning (7 MV m⁻¹) and spray coating have been used to produce CNT/PVDF composites, with the highest energy harvesting enhancements found at approximately 0.1 wt% CNTs.^{30,44} More recently, Lee *et al.*³⁹ have investigated the energy harvesting characteristics of spray coated MWCNT/PVDF composites without poling. The unpoled MWCNT/PVDF PEGs produced a maximum open circuit voltage at 1.2 V and short circuit current at 3.8 nA, approximately 30% of the voltage output and 1% of the current output, respectively, of poled MWCNT/PVDF composites.

To fabricate electroactive fluoropolymers without poling, extrusion printing has been performed, albeit with significantly lower piezoelectric FOM. Bodkhe *et al.*^{45,46} have 3D

printed a composite containing piezoelectric BTO NPs and PVDF. More recently, PVDF-TrFE has been 3D printed with no additives, showing partial shear-induced polarisation in PVDF-TrFE for unpoled PEGs.⁴⁷ In addition to inducing polarisation of the fluoropolymers, the 3D printing technique allows for PEGs to be fabricated into complex shapes and structures. Recent advances in 3D printing have demonstrated printing on moving, rough and uneven surfaces, enabling conformal printing directly onto skin.⁴⁸

This work presents significant advances in the design and manufacturing of flexible piezoelectric energy harvesters. Through the combination of molecular dynamics (MD) modelling of the dipole direction, solvent evaporation-assisted extrusion printing, and the selected use of SWCNTs as additives, this study demonstrates efficient, low voltage switching, and high power density PVDF-TrFE piezoelectric energy harvesters that can be used as produced. The use of this intelligent design and bespoke processing enables a preferential dipole alignment which leads to the complete elimination of the electrical poling process, an expensive and arduous process that is unavoidable in the current manufacture of polymer-based piezoelectric generators. The printed devices show no significant change in the piezoelectric β -phase through SWCNT addition; however, exhibit dramatic increases in the d_{33} and P_D at the optimal SWCNT concentration, confirming the increased performance arises from the theoretically predicted dipole alignment. The printed piezoelectric generators are transparent and flexible with figures of merit comparable to commercially available poled PVDF. These piezoelectric PVDF-TrFE energy harvesters are shown to be recyclable in green solvents such as acetone, a never before observed phenomenon, and can be reprocessed into new piezoelectric materials without loss of properties. These key points provide a fundamental breakthrough in the design and fabrication of low cost and recyclable flexible PEGs, opening up a path to their broad application for low power flexible electronics.

4.3 Experimental

4.3.1 Ink preparation

PVDF-TrFE powder (75 mol% VDF and 25 mol% TrFE, M_w at 420 kDa, ρ at 1.49 g cm⁻³, Solvay, Italy), acetone (AR grade, Chem-Supply Pty Ltd, Australia) and DMF (ACS Reagent, Sigma-Aldrich, USA) were used without further purification. SWCNTs with a

conductivity of $>100 \text{ S cm}^{-1}$, outer diameter between 1 nm and 2 nm, and length between 3 μm and 30 μm (99% purity, Cheap Tubes Inc., USA) were dispersed *via* ultrasonication (Elmasonic S 30 H, Elma Schmidbauer, Germany) for 30 min in a solution consisting of acetone (60 vol%) and DMF (40 vol%) at 0.727 mg mL^{-1} to make a stock solution (corresponding to 0.200 wt% SWCNT/PVDF-TrFE solution). Further dilutions were then prepared from the stock solution at 0.363 mg mL^{-1} , 0.182 mg mL^{-1} , 0.073 mg mL^{-1} , 0.036 mg mL^{-1} and 0.018 mg mL^{-1} , corresponding to the relevant SWCNT concentration relative to PVDF-TrFE at 0.100 wt%, 0.050 wt%, 0.020 wt%, 0.010 wt% and 0.005 wt%, respectively. The diluted solutions were further ultrasonicated for 5 min. Subsequently, PVDF-TrFE powder (4 g) was added to each of the solutions (9.333 g) at 23 °C and magnetically stirred to dissolve the PVDF-TrFE. This made inks containing 30 wt% PVDF-TrFE relative to the solvent mixture with varying SWCNT concentrations (0.000 wt% to 0.200 wt%) relative to PVDF-TrFE.

4.3.2 Printing and PEG manufacture

The SWCNT/PVDF-TrFE (0.000 wt% to 0.200 wt%) inks were transferred into 30 mL dispensing barrels (Optimum, Nordson EFD, USA) and stored at -5 °C prior to printing. The printing was carried out on a piston-driven 3D extrusion system (Bioplotter, EnvisionTEC, USA) through a nozzle with 0.20 mm internal diameter (SmoothFlow, Nordson EFD, USA) onto a clean glass substrate. Throughout printing, the barrel was kept at a temperature of 5 °C and the stage at 23 °C. A one-layer film was printed following a raster pattern with 400 μm spacing at 30 mm s^{-1} x-y speed under 1.7 Bar extrusion pressure with total dimensions of 30 mm in width and length. Subsequently, the films were placed under vacuum with an absolute pressure below 253 mbar for 10 min.

Post printing, the samples were stored in a sealed desiccator. For fabrication of the PEGs, electrodes were adhered to the extrusion printed films *via* sputter coating deposition (Q150T ES, Quorumtech, UK), consisting of a 2 nm Cr layer and a 10 nm Au layer through a shadow mask with active area of 2.1 cm^2 on both sides of the material. Wires, soldered to Cu foil tape with conductive adhesive (1181, 3M, USA), were adhered to both surfaces of the printed films, ensuring strong contact between the Cu tape and Cr/Au coating. The films were finally encapsulated in insulating Kapton polyimide tape on both surfaces to complete the PEGs.

4.3.3 Materials characterisation

Viscosity of the inks was confirmed using a rheometer (MCR-702, Anton Paar, Austria) with cone-plate geometry, with a cone diameter of 25 mm and angle at 2°. The measurements were obtained at a temperature of 5 °C in accordance with the printing barrel temperature by an upwards logarithmic ramp of shear rate from 0.01 s⁻¹ to 200 s⁻¹.

Optical properties, including transmittance and haze measurements of the printed PVDF-TrFE and SWCNT/PVDF-TrFE films were performed on an UV-vis-NIR spectrophotometer (Lambda 950, Perkin Elmer, USA). The films were placed on the entry port of a 25 cm diameter integrating sphere accessory to capture the total light not absorbed by the material, as well as the proportion of light scattered at angles greater than 2° from the beam direction.

The surface of the films was imaged using HIM (Orion NanoFab, Zeiss, Germany) to show representative distributions of the SWCNTs in the PVDF-TrFE. The micrographs were obtained with a 75 µm field of view using a dwell time of 2 µs and acceleration voltage of 25 kV.

XRD patterns were obtained for the printed films using Bragg-Brentano geometry (D8 Advance, Bruker, Germany) using Cu-K α radiation ($\lambda = 1.54060$ Å). The Bragg angle, 2θ , was varied between 5° and 70° with a step size of 0.02° and 1 s per step, with the sample rotated at 15 rpm. The films were placed on silicon low background holders for the measurements.

Raman spectroscopy (inVia, Renishaw, UK) was undertaken on the printed films, adhered to glass microscope slides using a 532 nm laser with an 1800 line mm⁻¹ grating and a 50x objective. Each spectrum was centred at 1300 cm⁻¹ and obtained using a laser power of 1.68 mW with an exposure time of 0.15 s accumulated over 1000 scans. Confocal images were obtained 0.5 s before scanning and 0.5 s after the scan was finished in order to ensure the sample remained stable under laser irradiation.

DSC traces were obtained using a simultaneous thermal analyser (STA 8000, Perkin Elmer, USA). Samples weighing between 10 mg and 15 mg were placed into a ceramic pan and heated to 180 °C at a ramp rate of 10 °C min⁻¹. The furnace was continuously purged with nitrogen of ultra-high purity at a rate of 20 mL min⁻¹, and equilibrated for 30 min between scans.

FTIR analysis (ALPHA II, Bruker, USA) was performed on the printed films in ATR mode. The absorbance was taken as an average of 128 individual scans with a resolution of 2 cm⁻¹ between 600 cm⁻¹ and 4000 cm⁻¹.

The thickness, and consequently the volume of the printed films was determined from the final dry mass using the density of PVDF-TrFE as 1.49 g cm⁻³. The mass was determined as an average of a minimum of three printed films for each SWCNT concentration and the length and width were taken as 3 cm to obtain the thickness.

4.3.4 PFM characterisation

PFM was undertaken (Cypher ES, Asylum Research, USA) at 23 °C on the printed films for the determination of nanoscale polarisation characteristics. Cantilevers (Econo-SCM-PIC, Asylum Research, USA) with Cr/Pt conductive coating, tip radius below 25 nm and spring constant of 0.2 N m⁻¹ were used for the PFM measurements. The scans were completed on an area of 5 µm × 5 µm at 256 pixels per line, corresponding to approximately 20 nm per pixel.

The PFM was carried out in contact lithography mode, whereby a potential was applied to the sample in pre-defined patterns and the amplitude and phase changes relative to the unbiased areas were observed. The voltage was swept in increments of approximately 2 V from 20 V to -20 V on each scan line, with a scan rate of 0.2 Hz. Each voltage step was applied to an area of 195 nm in the x direction and 3.906 µm in the y direction.

The resultant piezoelectric amplitude and phase data, collected during the application of voltage, were then correlated to the corresponding voltage for each pixel on the scan. The

on-voltage measurements were collected at voltages below the electrical poling voltage for the extrusion printed films in order to measure the effective d_{33} from the resultant strain. Dual AC resonance tracking (DART) PFM was then undertaken at 1 Hz scan rate to ensure the stability of the material.

4.3.5 Energy harvesting analysis

Energy harvesting characterisation was completed to determine the macroscale polarisation and ultimate energy harvesting potential of the PVDF-TrFE and SWCNT/PVDF-TrFE PEGs. The voltage output of the PEGs was measured using an oscilloscope with 10 M Ω input impedance (TDS2002B, Tektronix, USA) under cyclic compression (5963, Instron, USA) with a constant frequency of approximately 5 Hz and controlled strain rate. The load cell was rated at 1 kN. The speed was set at 10 mm s⁻¹, with a 50 N maximum set force. Rubber mats were placed between the PEG and the instrument for the measurement, with a thickness of $\sim$ 1 mm each.

Further characterisation of the power and power density was carried out in a similar manner, while resistive loads were attached in parallel and the voltage output was measured under cyclic compression.

4.3.6 Molecular dynamics modelling

All-atom MD simulations were employed to investigate the preferred conformation of the PVDF-TrFE chains on various SWCNTs. SWCNTs with two chiralities were simulated, a (8,8) and a (12,0) CNT corresponding to the armchair and the zig-zag configuration, respectively. The SWCNT systems had a length of 10 nm each and diameters of 1.084 nm and 0.993 for the (8,8) and (12,0) chiralities, respectively. For each SWCNT, two PVDF-TrFE chains containing 21 VDF and 9 TrFE monomers were introduced in the simulation cell, corresponding to molar concentrations of 70 mol% VDF and 30 mol% TrFE.

The SWCNT and co-polymer systems were simulated in the NVT (constant number of particles, volume, and temperature) ensemble at 300 K for at least 4 ns under vacuum.

For statistically relevant results three simulations of the same system were carried out at the same conditions with different initial configurations, meaning that new positions and velocities were assigned to each atom. The equations of motion were integrated using the velocity-Verlet algorithm⁷⁹ with a time step of 1 fs using the polymer consistent force field (PCFF) for both the CNT and the co-polymers. Partial charges were assigned to each atom of the CNT and the PVDF-TrFE using the bond increments method. The PCFF interatomic potential was validated with the density of bulk PVDF-TrFE melts at 230 °C. Supplementary Figure 4.S15 shows the monotonic increase of the PVDF-TrFE density ρ with the molecular weight M_w , attaining a plateau at approximately 1.57 g cm⁻³ for PVDF-TrFE melts with M_w greater than 10,000 g mol⁻¹. The MD-obtained density was found to be in accordance (deviation below 5.5 %) with the experimental value ($\rho_{bulk} = 1.49$ gr cm⁻³) of the bulk PVDF-TrFE copolymer with the same composition (70 mol% VDF and 30 mol% TrFE), validating the interatomic potential used in the present simulations. The MD simulations were performed on the University of Melbourne's High-Performance Computing system using the LAMMPS MD code.⁸⁰

4.3.7 Recyclability testing

Four printed SWCNT/PVDF-TrFE (0.020 wt%) films, with a total mass of 0.214 g were placed into a dispensing barrel. Acetone, with a total volume of 0.905 mL was added to the barrel, corresponding to 23 wt% polymer loading. The barrel was sealed, gently shaken and subsequently held at -5 °C for 12 h, to ensure a homogeneous mixture of the ink. Printing of the resulting ink was undertaken in similar conditions to the initial printing cycle with the exception of the extrusion pressure, which was decreased to 0.3 Bar.

The energy harvesting experiment for the recycled and reprinted SWCNT/PVDF-TrFE (0.020 wt%) PEG used low-force cyclic finger pinching as input force. The load resistance was set using a resistance decade (M642, Meatest, Czech Republic) and the output voltage measured using a potentiostat (VMP3, Bio-Logic, France) in open circuit voltage mode with an input impedance of 10¹⁴ Ω .

4.4 Results and discussion

4.4.1 Inks, printing and optical properties

For extrusion printing, PVDF-TrFE inks were prepared by dissolving PVDF-TrFE (30 wt%) in a solvent mixture containing acetone (60 vol%) and DMF (40 vol%). For the SWCNT/PVDF-TrFE inks, the acetone:DMF (60:40 vol%) solvent mixture contained suspended SWCNTs at concentrations ranging from 0.005 wt% to 0.500 wt% relative to the PVDF-TrFE (Supplementary Figure 4.S1).

The rheological properties of the PVDF-TrFE (0.000 wt%) and SWCNT/PVDF-TrFE (0.005 wt% to 0.200 wt%) inks were studied in order to determine their printability, shown in Supplementary Figure 4.S2. For the SWCNT/PVDF-TrFE inks, the viscosity values showed low deviation from that of the PVDF-TrFE ink, while the viscosity profile retained non-Newtonian, shear thinning properties, which are optimal for extrusion printing.⁴⁷ The results showed a zero shear viscosity (η_0) between 260 Pa s and 638 Pa s, while the viscosity approaching printing shear rates was between 2.9 Pa s and 4.8 Pa s, corresponding to the values for the inks at rest before and after printing, and during the extrusion step, respectively.

Figure 4.1a shows a composite photograph of the printed single layer films with increasing SWCNT concentration from left (0.000 wt%) to right (0.200 wt%), placed on top of a graphic to demonstrate their optical properties. The films containing SWCNT concentrations below 0.050 wt% were indistinguishable from the PVDF-TrFE control film, while those at 0.050 wt% and above exhibited an increasing dark colouration. The films appeared homogeneous and did not show visible aggregation at SWCNT concentrations up to 0.200 wt%, suggesting that the SWCNTs were stable during the printing and drying processes. The visible wavelength transmittance and haze of the films, measured between 380 nm and 780 nm, are shown as a function of SWCNT concentration in Figure 4.1b. At low SWCNT concentrations (<0.050 wt%), the composite films absorbed minimal light and were transparent over the entire measured spectrum (Supplementary Figure 4.S3). The haze values, shown in Figure 4.1b, were found to be constant at 3.5% below 0.050 wt% SWCNTs, further showing the stability of dispersed SWCNTs in the PVDF-TrFE with minimal deviation from the spectrum of the pure polymer. However, at

SWCNT concentrations >0.050 wt%, increased haze was observed, attributed to SWCNT bundling (see Supplementary Figure 4.S4).

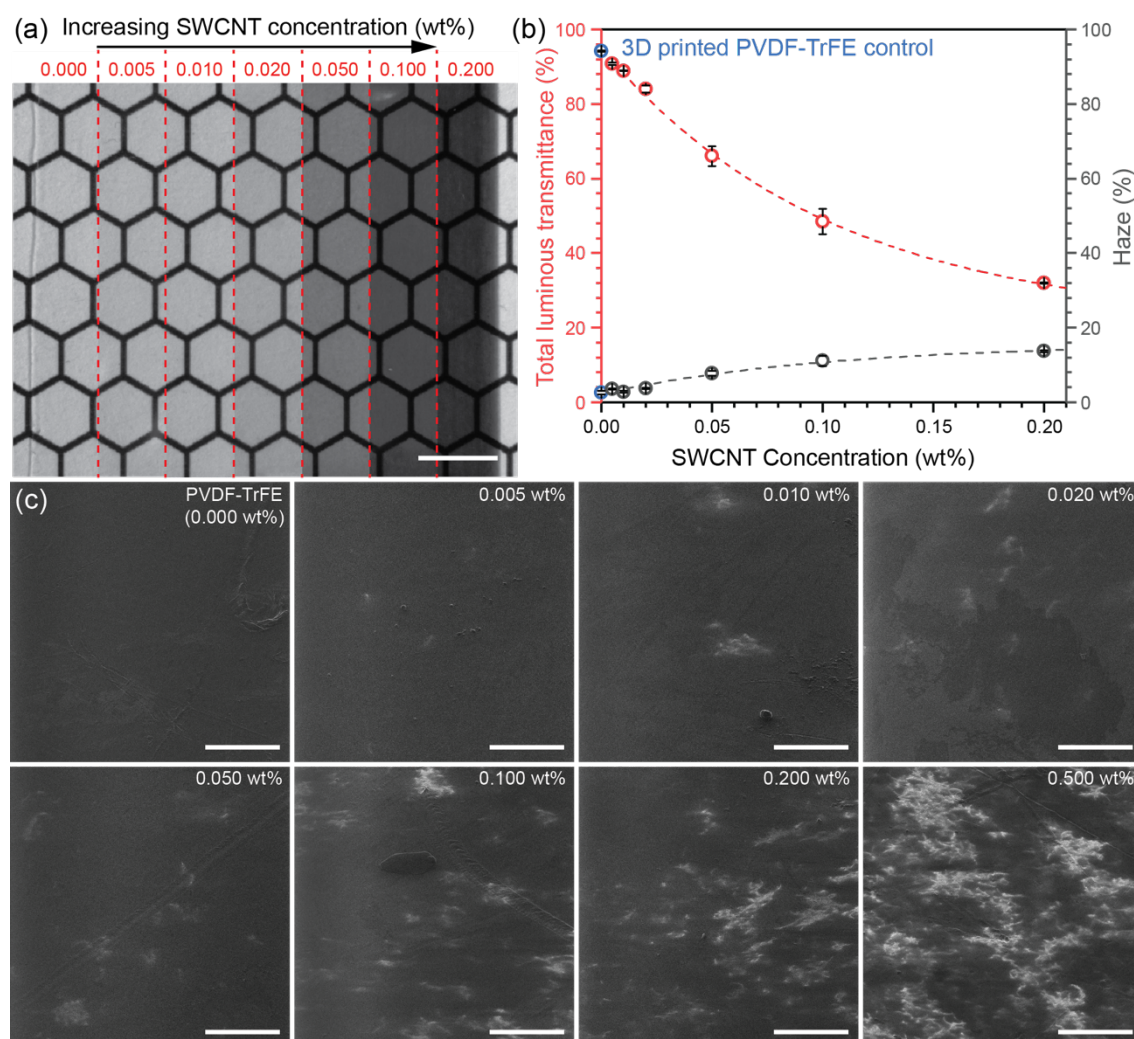


Figure 4.1: (a) Optical images demonstrating the transparency of extrusion printed PVDF-TrFE films with increasing SWCNT concentration (0.000 wt% to 0.200 wt%) from left to right. Scale bar represents 5 mm. (b) Visible wavelength transmittance and haze as a function of SWCNT concentration (blue datapoints denote the PVDF-TrFE control). (c) HIM images showing the surface of the films for PVDF-TrFE (0.000 wt%) and SWCNT/PVDF-TrFE (0.005 wt% to 0.500 wt%). Scale bar represents 10 μ m.

Figure 4.1c shows the HIM images of the surface of the extrusion printed PVDF-TrFE films as a function of SWCNT concentration. The overall surface morphology was found to be free of visible porosity, confirming the formation of solid, non-porous thin films

upon printing. The HIM technique allows for strong contrast between the dielectric, non-conductive PVDF-TrFE surface, shown as dark regions in the micrographs, and the conducting SWCNTs shown in the light regions. This contrast decreased for SWCNTs embedded further below the surface. Minimal bundling and aggregation of the SWCNTs was observed on the surface of the samples with concentrations below 0.050 wt%; however, larger bundles of nanotubes were visible at higher concentrations with the 0.500 wt% film exhibiting continuous networks of SWCNTs over its entire surface.

4.4.2 Phase determination and materials properties

The PVDF-TrFE and SWCNT/PVDF-TrFE films were characterised to investigate the polymer phase behaviour with SWCNT loading relative to PVDF-TrFE. Figure 4.2a shows the XRD spectra for the printed films. The broad peak at $18.1^\circ 2\theta$ corresponds to the (110/200) paraelectric (PE) phase reflection and the peak at $20.2^\circ 2\theta$ corresponds to the (110/200) ferroelectric (FE) phase reflection commonly attributed to the β phase of PVDF-TrFE.¹⁹ The two lower intensity peaks at $35.0^\circ 2\theta$ and $40.8^\circ 2\theta$ were attributed to the (001) FE reflection and (111/201), (400/220) FE reflections, respectively, further indicating the presence of the β phase within the polymer matrix.^{49,50}

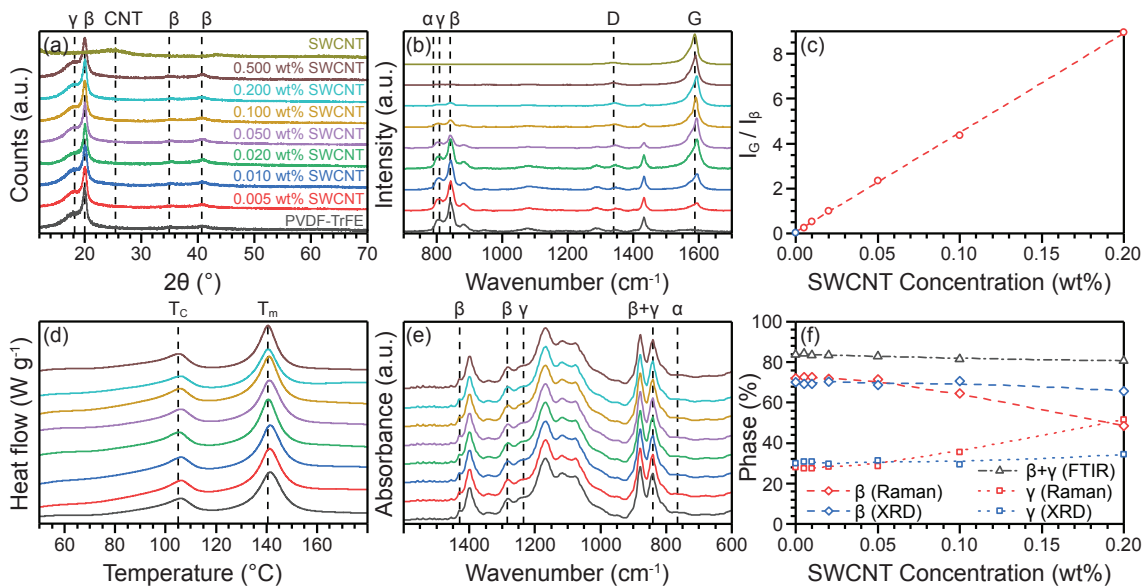


Figure 4.2: Analysis of extrusion printed PVDF-TrFE films with SWCNT concentrations between 0.000 wt% and 0.500 wt%, showing (a) XRD spectra. (b) Raman spectra. (c) Ratio of the intensities of the G-band peak relative to the β phase peak from Raman spectra. (d) DSC heating traces. (e) ATR-FTIR spectra. (f) The relative

phase ratios calculated from ATR-FTIR spectra (grey), Raman spectra (red) and XRD spectra (blue) for the electroactive ($\beta + \gamma$) phase (triangle), β phase (diamond) and γ phase (square).

The Raman spectra for the SWCNTs, PVDF-TrFE films and SWCNT/PVDF-TrFE (0.005 wt% to 0.500 wt%) films are shown in Figure 4.2b. All polymer samples showed peaks characteristic of fluoropolymers at 1432 cm^{-1} and 880 cm^{-1} , as well as the characteristic β phase peak at 842 cm^{-1} and γ phase peak at 810 cm^{-1} .^{7,51,52} There was a notable absence of the non-polar α phase peak typically observed at 794 cm^{-1} .⁵³ The Raman spectra of the SWCNT/PVDF-TrFE films all showed a strong contribution from the characteristic SWCNT graphitic G-band (1587 cm^{-1}), along with a slight contribution from the disordered defect D-band (1340 cm^{-1}).⁵⁴ The ratio of the intensity of the G-band (I_G) to the intensity of the β phase peak (I_β) was plotted as a function of SWCNT concentration and is shown in Figure 4.2c. The linear trend up to a 0.200 wt% SWCNT concentration suggested a homogeneous dispersion.

Figure 4.2d shows the DSC traces for the SWCNT/PVDF-TrFE (0.000 wt% to 0.500 wt%) films during a heating cycle. The position of the T_m was at approximately $140.5\text{ }^\circ\text{C}$, within the typical range for PVDF-TrFE (75 mol% VDF:25 mol% TrFE, 420 kDa, Solvay). The FE to PE transition, representing the T_C , was found to be $105\text{ }^\circ\text{C}$ suggesting piezoelectric stability for temperatures up to approximately $100\text{ }^\circ\text{C}$.

The crystallinity (χ_c) of the SWCNT/PVDF-TrFE (0.000 wt% to 0.500 wt%) films was calculated from the DSC traces using Equation (4.1) with values shown in Table 4.1.

$$\chi_c(\%) = \frac{\Delta H_m}{\Delta H_0} \times 100 \quad (4.1)$$

Here, the enthalpy of melting (ΔH_m) was calculated from the mass-normalised area of the T_m peak and the literature value for the enthalpy of purely crystalline PVDF-TrFE (ΔH_0) was taken as 45 J g^{-1} .^{55,56} For SWCNT/PVDF-TrFE (0.000 wt% to 0.100 wt%) films, the χ_c was found to remain relatively unchanged, between 37% and 41%. At SWCNT concentrations in the films of 0.200 wt% and above, the χ_c was observed to decrease to between 31% and 34%.

Table 4.1: Degree of crystallinity (χ_c) and the relative fractions of the electroactive phase (F_{EA}), β -phase (F_β) and γ -phase (F_γ) obtained *via* DSC, ATR-FTIR spectroscopy, Raman spectroscopy and XRD.

	χ_c^a (%)	F_{EA}^b (%)	F_β^c (%)	F_β^d (%)	F_γ^c (%)	F_γ^d (%)
PVDF-TrFE	37.2	83.8	72.0	70.0	28.0	30.0
0.005 wt% SWCNT	39.7	84.3	72.5	69.2	27.5	30.8
0.010 wt% SWCNT	40.5	83.4	72.7	69.3	27.3	30.7
0.020 wt% SWCNT	41.1	83.5	71.7	70.3	28.3	29.7
0.050 wt% SWCNT	39.0	82.9	71.6	68.7	28.4	31.3
0.100 wt% SWCNT	41.3	81.4	64.5	70.7	35.5	29.3
0.200 wt% SWCNT	30.6	80.7	48.4	65.7	51.6	34.3
0.500 wt% SWCNT	33.9	72.5	— ^e	69.3	— ^e	30.7

^aObtained *via* DSC; ^bObtained *via* ATR-FTIR spectroscopy; ^cObtained *via* Raman spectroscopy; ^dObtained *via* XRD; ^eNo polymer peaks were detected due to high SWCNT Raman signal

ATR-FTIR spectroscopy was used to further confirm the phase composition of the extrusion printed SWCNT/PVDF-TrFE (0.000 wt% to 0.500 wt%) films, shown in Figure 4.2e. The presence of both the β phase and γ phase of PVDF-TrFE was shown as the combined β + γ phase peak at 840 cm^{-1} , with separate peaks for the β phase at 1285 cm^{-1} and γ phase at 1235 cm^{-1} .⁵⁷ An additional shoulder at 1430 cm^{-1} was attributed to the β phase. The region commonly ascribed to the α phase at 766 cm^{-1} showed no peaks, further showing the films consisted of purely piezoelectric polymorphs.⁵⁸

Figure 4.2f shows a summary of the percentage phase fractions calculated from the ATR-FTIR spectra (grey), Raman spectra (red) and XRD spectra (blue), with the values presented in Table 4.1. Using the ATR-FTIR data, the electroactive phase fraction F_{EA} , consisting of the β + γ phases, was calculated from the FTIR spectra using Equation (4.2).^{7,57}

$$F_{EA}(\%) = \frac{I_{EA}}{(K_{EA}/K_{\alpha})I_{\alpha} + I_{EA}} \times 100 \quad (4.2)$$

In Equation (4.2), I_{EA} is the intensity of the FTIR peak at 840 cm^{-1} ($\beta+\gamma$ phase), I_{α} is the intensity of the FTIR peak at 766 cm^{-1} (α phase), and K_{EA} and K_{α} are the absorption coefficients for the respective peaks at 840 cm^{-1} and 766 cm^{-1} , with the values given as $7.7 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ and $6.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$, respectively.^{57,59} The values for the $\beta+\gamma$ phase fraction were found to be constant for all measured samples, with a small decrease to 72.5% at a SWCNT concentration of 0.500 wt%. No contribution was observed from the α phase of the polymer, showing the extrusion printed films contained primarily both piezoelectric β and γ phases.

The Raman data was used to calculate the relative fractions of β and γ phases in the polymer. Commonly, phase analysis in literature consists of the intensity ratio of the α and β phase peaks, resulting in a value of zero for pure β phase or infinity for pure α phase.^{53,60} To quantify the relative phase content of the β and γ phases in the SWCNT/PVDF-TrFE (0.000 wt% to 0.500 wt%) films, a series of equations were used in this study and are shown in Equation (4.3) and Equation (4.4), respectively.

$$F_{\beta}(\%) = \frac{I_{842}}{I_{842} + I_{811}} \times 100 \quad (4.3)$$

$$F_{\gamma}(\%) = \frac{I_{811}}{I_{842} + I_{811}} \times 100 \quad (4.4)$$

In this form, I_{842} corresponds to the intensity of the β phase Raman peak at 842 cm^{-1} and similarly, I_{811} corresponds to the intensity of the γ phase Raman peak at 811 cm^{-1} .^{51,52} These fractions are presented in red in Figure 4.2f. Films with low concentrations of SWCNTs showed similar relative β phase fractions compared to pristine PVDF-TrFE films. Conversely, at higher SWCNT concentrations, the β phase fraction dropped significantly from the maximum of 72.7% at 0.010 wt% SWCNT to a minimum of 48.4% at 0.200 wt% SWCNT and the γ phase increased from 27.3% at 0.010 wt% SWCNT to 51.6% at 0.200 wt% SWCNT. Nonetheless, it should be noted that at the higher concentrations, the SWCNT G-band signal was significantly larger than that of the PVDF-TrFE peaks and variations between phases became increasingly difficult to quantify.

The final set of data presented in blue in Figure 4.2f was the quantification of phases from the XRD spectra. The peaks at $18.1^\circ 2\theta$ and $20.2^\circ 2\theta$ were deconvoluted, and their relative intensity fractions are shown in Figure 4.2f and Table 4.1. The PE peak at $18.2^\circ 2\theta$ showed values in line with F_γ from the Raman analysis and therefore was attributed to the presence of the γ phase, although it has been commonly misattributed to the non-polar α phase in previous studies.^{11,61}

From the data presented in Figure 4.2, it was concluded that minimal changes in phase composition were observed with incorporation of low concentrations of SWCNTs into PVDF-TrFE.

4.4.3 Nanoscale piezoelectric phenomena

PFM was carried out on the samples to further investigate their nanoscale piezoelectric properties. A cantilever with diameter of below 25 nm was rastered across a $5\ \mu\text{m} \times 5\ \mu\text{m}$ sample area with voltages applied in a sweeping manner using a pre-defined pattern, shown in Figure 4.3. For each line of scanning, the cantilever swept through the entire range of voltages between -20 V and +20 V to minimise artefacts arising from the instrument (Figure 4.3a).

Figure 4.3b shows the corresponding PFM amplitude output after exposing the samples to the range of desired voltages at SWCNT concentrations from 0.000 wt% to 0.200 wt% relative to PVDF-TrFE. The amplitude response, corresponding to the piezoelectric output, was found to increase with increasing SWCNT concentration up to 0.020 wt%, showing a 20-fold increase in amplitude at 0.020 wt% relative to the PVDF-TrFE sample, exhibiting a sharp decrease at SWCNT concentrations higher than 0.020 wt%. It was evident that while the phase fractions were not significantly altered by the incorporation of SWCNTs (see, Figure 4.2 and Table 4.1), the piezoelectric response showed significantly enhanced properties. Further, the phase switching behaviour, shown in Figure 4.3c, was significantly altered by the inclusion of SWCNTs. The switching voltage in this case is proportional to the coercive field (E_C), which is the electric field required to pole the fluoropolymers. At higher SWCNT concentrations (between 0.100 wt% and 0.200 wt%), the switching voltage between -14 V and -10 V was comparable to the pristine PVDF-

TrFE film; however, at lower SWCNT concentrations (between 0.010 wt% and 0.020 wt%) the switching voltage dropped to between -2 V and 0 V. A switching voltage below 2 V corresponds to an electric field below 50 kV m^{-1} , which is orders of magnitude lower than any previous reported values for electrical poling of fluoropolymers (typically 4 MV m^{-1} to 500 MV m^{-1}).^{7,9,19}

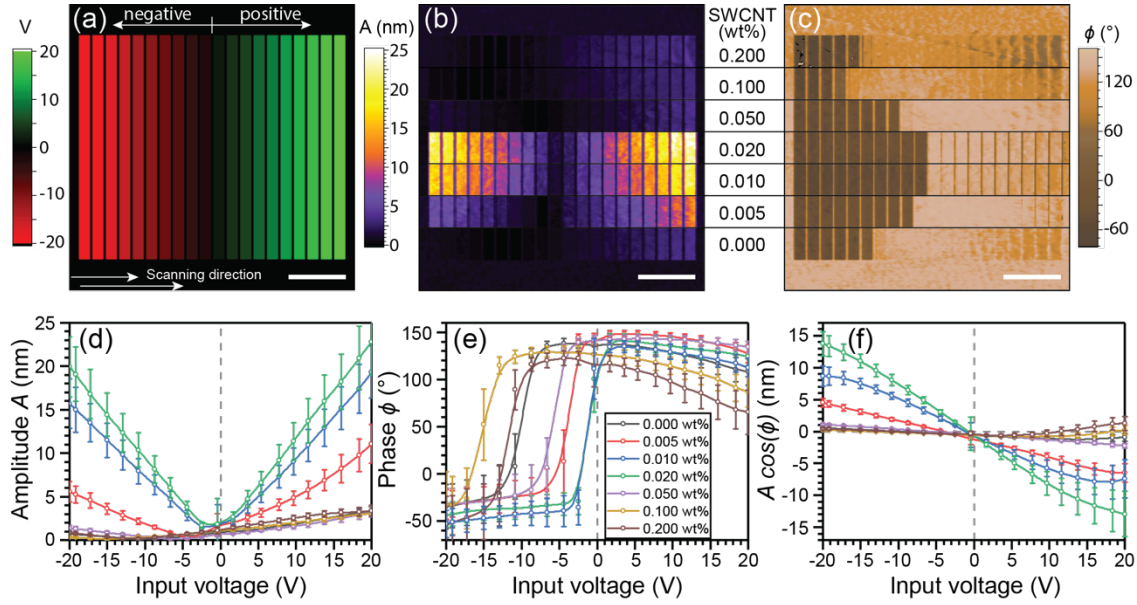


Figure 4.3: PFM characterisation of extrusion printed SWCNT/PVDF-TrFE (0.000 wt% to 0.200 wt%) films, (a) the pattern of the applied voltage to the cantilever during raster. (b) The piezoelectric amplitude response of the printed samples upon the application of voltage between the cantilever and the substrate and (c) the corresponding PFM phase response, showing representative slices for each sample. The scale bar represents 1 μm . (d) The raw amplitude (A). (e) The raw phase (ϕ). (f) The resultant processed PFM amplitude ($A \cos(\phi)$) as a function of the applied voltage for the investigated SWCNT concentrations.

The amplitude and phase were then extracted from the PFM data as a function of the input voltage and are presented in Figure 4.3d and Figure 4.3e, respectively. The amplitude was shown to scale linearly with the input voltage over the range of -20 V and +20 V. The amplitude minima were attributed to the dipole orientation switching of the PVDF-TrFE. The phase was found to be maximised in the direction of the positive voltage, even when no voltage was applied, for all samples excluding those containing SWCNT concentrations of 0.010 wt% and 0.020 wt%. Further increase in phase were found for 0.010 wt%

and 0.020 wt% SWCNT/PVDF-TrFE films upon the application of +2 V. Additionally, the phase angle of the 0.200 wt% SWCNT/PVDF-TrFE film was found to degrade at positive applied voltages, with a maximum at -2 V.

The effective d_{33} coefficient can be obtained from the PFM data using Equation (4.5).⁶²

$$d_{33} = \frac{A \cos(\phi)}{Q V} \quad (4.5)$$

Here, A represents the PFM amplitude in units of pm, ϕ represents the PFM phase angle, Q represents the unitless quality factor of the cantilever resonance peak obtained during the PFM experiments, which in this case was consistent between 70 and 92 with slight variations between samples, and V represents the applied voltage. For the analysis of the data, individual pixels at each position and corresponding to their respective voltages were used for the calculation and an average was taken for the entire set of pixels corresponding to the respective applied voltage.

Figure 4.3f shows the $A \cos(\phi)$ plotted as a function of the applied voltage for the extrusion printed SWCNT/PVDF-TrFE (0.000 wt% to 0.200 wt%) films investigated during this experiment. Typically in literature, a linear trend is observed at low applied voltages, with a decreasing slope as the films approach the maximum induced strain. All of the investigated films showed trends following literature for fluoropolymers. Degradation was observed at high magnitudes of applied voltage in the positive direction for 0.000 wt%, 0.100 wt% and 0.200 wt% SWCNT/PVDF-TrFE films, as the E_C values for these samples were below -10 V. Therefore, a moderate voltage of +10 V was chosen for the characterisation of the d_{33} coefficient, corresponding to approximately 0.25 MV m⁻¹ and well below the typical values for E_C for fluoropolymers, while additionally probing in the direction the films were polarised during deposition.

The extrusion printed PVDF-TrFE (0.000 wt% SWCNT) film showed a low response under voltage (+10 V), suggesting low relative polarisation with a d_{33} coefficient of -1.9 pm V⁻¹ at +10 V (Supplementary Figure 4.S5). A moderate increase in SWCNT concentration to 0.005 wt% resulted in a sharp increase of the amplitude and therefore the d_{33} coefficient to -5.9 pm V⁻¹, corresponding to a 210% enhancement. The maximum d_{33} was

found at 0.020 wt% SWCNT, at -12 pm V^{-1} , a 500% improvement over that of the pristine PVDF-TrFE films. This d_{33} value is comparable to work by Bodkhe *et al.*⁴⁵ (d_{31} at 18 pm V^{-1}) for BTO/PVDF composite structures and commercially available piezoelectric PVDF (d_{33} at -33 pm V^{-1} , PFM results shown in Supplementary Figure 4.S6) for mechanically drawn and poled films.²⁰ Further increases in SWCNT concentration resulted in a reduction back to a lower d_{33} coefficient of -1.7 pm V^{-1} (0.050 wt% SWCNTs), similar to that of the pristine PVDF-TrFE (0.000 wt% SWCNTs) films. A further decrease in the d_{33} coefficient at 0.100 wt% and 0.200 wt% SWCNTs was also observed.

In literature, increases in energy harvesting efficiencies of nanocomposite fluoropolymer PEGs have been largely attributed to enhancements in crystallinity and relative β phase fractions within the polymer. Here, no crystallinity or relative β phase fraction were observed with increased SWCNT content in the PVDF-TrFE (see Figure 4.2 and Table 4.1); however, a marked increase in the polarisation were found (Figure 4.3). This result demonstrates that maximising the net polarisation vector is a key consideration for optimising piezoelectric energy harvesting and can be achieved by either aligning the local dipoles or enhancing the relative β phase fraction. The incorporation of SWCNTs into fluoropolymers at low concentrations, as shown *via* PFM (Figure 4.3) and polymer phase composition analysis (Figure 4.2), does not result in an increase in β phase, and thus the improvement in net polarisation must arise from dipole alignment.

4.4.4 Macroscale piezoelectric phenomena

To further explore the piezoelectric energy harvesting properties of the extrusion printed SWCNT/PVDF-TrFE films, PEGs were fabricated by coating the films with Cr/Au electrodes, attaching external wires *via* conductive Cu foil adhesive and packaging with insulating polyimide tape. Energy harvesting experiments were undertaken through cyclic compression of the PEGs to investigate the correlation between the phase properties, nanoscale piezoelectric phenomena and bulk energy conversion capabilities.

Figure 4.4a shows the generated voltage traces under 5 Hz cyclic compression of the PEGs for the extrusion printed SWCNT/PVDF-TrFE (0.000 wt% to 0.500 wt%) PEGs, reported using an oscilloscope with a $10 \text{ M}\Omega$ input impedance. Here, similar trends were

observed to the PFM data (see Supplementary Figure 4.S7). The data for the pristine PVDF-TrFE (0.000 wt% SWCNTs) PEG showed the presence of electrical output arising from shear-induced alignment during extrusion printing, however the magnitude was found to be low. When the shear alignment from extrusion printing was coupled with the incorporation of SWCNTs, the generated peak-to-peak voltage (V_{pp}) trend was in close agreement with the d_{33} values obtained from PFM. The V_{pp} was found to increase with increases in SWCNT concentration of the PEGs up to a maximum at 0.020 wt% SWCNT. At SWCNT concentrations above 0.020 wt%, decreases in V_{pp} were observed, with values similar to the pristine PVDF-TrFE (0.000 wt% SWCNTs) PEGs. The sample containing 0.500 wt% SWCNT did not exhibit any voltage output from cyclic compression, which was attributed to conductive SWCNT networks forming between the electrodes in the film. This was supported by HIM imaging (Figure 4.1c) and confirmed using cyclic voltammetry, shown in Supplementary Figure 4.S8, whereby the 0.500 wt% SWCNT/PVDF-TrFE PEG exhibited conductive behaviour.

Given the maximum V_{pp} , the energy harvesting characteristics of extrusion printed SWCNT/PVDF-TrFE (0.020 wt%) PEG were investigated further. The output voltage was measured under cyclic compression at 5 Hz with the load resistor placed in parallel with the PEG, for resistances between 1 k Ω and 130 M Ω , with the V_{pp} values shown in Figure 4.4b in grey. The voltage signal was shown to increase up to 1 M Ω , and at 10 M Ω began to decrease due to the load resistance reaching the input impedance of the measuring system and therefore presenting voltage values lower than expected. Furthermore, it was noted that the voltage at 1 M Ω was lower relative to the measurement with no load resistance (shown in Figure 4.4a), suggesting the maximum P_D could occur at load resistances between 1 M Ω and 10 M Ω . The current output was calculated using $I=V/R$ and showed close agreement in the trend to previous reports, with a maximum generated current of 0.9 μ A, corresponding to the short-circuit current (I_{sc}) at the plateau for load resistance below 10⁵ Ω . The I_{sc} for the SWCNT/PVDF-TrFE (0.020 wt%) PEG corresponds closely to previous work on other self-poled fluoropolymer-based energy harvesters.^{37,63–}

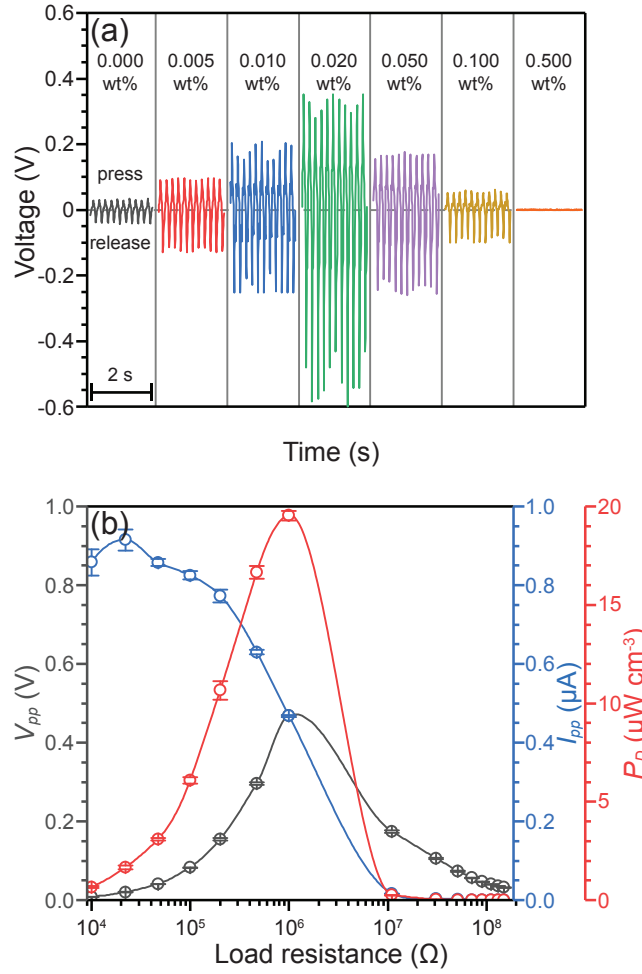


Figure 4.4: Energy generation characteristics of the extrusion printed SWCNT/PVDF-TrFE (0.000 wt% to 0.500 wt%) PEGs, showing (a) the output voltage as a function of time arising from imparted cyclic compression of the samples at 5 Hz for the SWCNT concentrations between 0.000 wt% and 0.500 wt% using an Instron testing machine at a controlled strain rate. (b) The V_{pp} (grey), peak to peak current (I_{pp}) (red) and power density (P_D) (blue) for the 3D printed SWCNT/PVDF-TrFE (0.020 wt%) PEG as a function of the load resistance. The input impedance of measurement for the tests was 10 M Ω .

The volumetric power density P_D was then calculated for the extrusion printed SWCNT/PVDF-TrFE (0.020 wt%) PEG using Equation (4.6) and shown in Figure 4.4b as a function of load resistance.

$$P_D = \frac{V_{pp}^2}{R(t \times A_e)} \quad (4.6)$$

In Equation (4.6), R represents the load resistance, t represents the sample thickness (shown in Supplementary Figure 4.S9 and Supplementary Figure 4.S10) and A_e represents the active electrode area overlapping on both surfaces of the film, taken as 2.1 cm^2 . The maximum P_D for the SWCNT/PVDF-TrFE (0.020 wt%) PEG was found to be $19.8 \mu\text{W cm}^{-3}$ at $1 \text{ M}\Omega$ load resistance (shown in Figure 4.4b in blue, and in Figure 4.5 as a solid red diamond). The comparison to literature values for the P_D of PEGs incorporating CNTs is shown in Figure 4.5 as a function of CNT concentration. PEGs poled *via* electric fields are shown as circles and unpoled PEGs are shown as diamonds. The data is further expanded upon in Supplementary Table 4.S1.

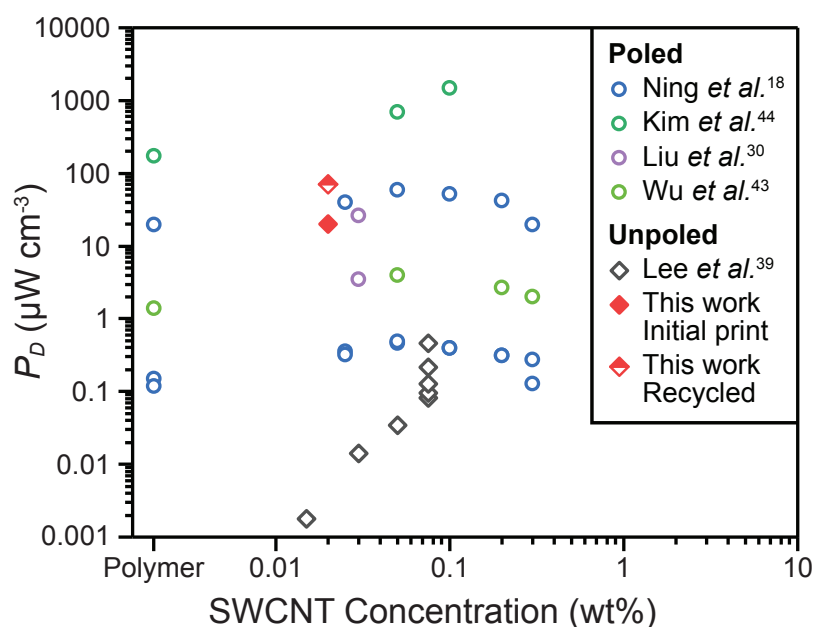


Figure 4.5: Volumetric power density P_D for PEGs containing CNTs as a function of CNT concentration for this study and previous publications reporting energy harvesting capabilities. Circles represent electrically poled PEGs and diamonds represent unpoled PEGs. Fluoropolymer PEGs without CNTs are presented where found in the literature for comparison.

Comparatively, Lee *et al.*³⁹ have reported on unpoled MWCNT/PVDF composites at MWCNT concentrations up to 0.075 wt%. They observed enhancements in energy harvesting (maximum 1.2 V and 3.8 nA for 0.075 wt% MWCNT) without using electrical poling (Figure 4.5, grey diamonds). Few details were given on the device characteristics and measurement conditions, therefore the device thickness was assumed to be $100 \mu\text{m}$

to obtain P_D values, which were calculated as $0.46 \mu\text{W cm}^{-3}$. In comparison, the value for maximum resistance-matched P_D in this study of $19.8 \mu\text{W cm}^{-3}$ is greater than one order of magnitude higher than that of Lee *et al.*³⁹.

The P_D values from this work fall well within the range of PEGs consisting of CNTs and fluoropolymers, obtained through mechanical drawing at elevated temperatures and electrical poling, namely that of Ning *et al.*¹⁸ (poling electric field at 60 MV m^{-1}) and Liu *et al.*³⁰ (7 MV m^{-1}) (Figure 4.5).

4.4.5 Computational analysis of behaviour at the interface between SWCNT and PVDF-TrFE

To further investigate the atomic-scale interfacial phenomena between SWCNTs and PVDF-TrFE, and confirm the enhancements in polarisation arising from SWCNT incorporation, all-atom MD simulations were employed. Two SWCNT chiralities were analysed, namely the armchair (12,0) and the zig-zag (8,8), corresponding to semiconducting and conducting SWCNTs, respectively.

Figure 4.6a shows the probability distribution of the angle φ , $P(\varphi)$, formed between the SWCNT axis of symmetry vector and the SWCNT/PVDF-TrFE dipole moment vector for the (8,8) (black line) and the (12,0) (red line) SWCNT configurations. The representative simulation configurations are shown in the inset in Figure 4.6a. The results were averaged over the simulation time for three independent simulation iterations in order to obtain statistical significance. The shaded regions in Figure 4.6a-c represent the error bar obtained from three different MD simulations. For $\varphi = 0^\circ$ and 180° , the dipole moment vector of the SWCNT/PVDF-TrFE system was found to be either parallel or antiparallel to the SWCNT axis of symmetry. For both SWCNT configurations, the probability of forming angles of $\varphi = 90^\circ$ (dipole moment vector perpendicular to the SWCNT) was small. Initially ($t = 0 \text{ ns}$), the two PVDF-TrFE chains were placed randomly away from each other and close to the SWCNT (Figure 4.6d, top snapshots) with initial φ angle almost perpendicular to the SWCNT axis of symmetry. The interactions between the SWCNT and the PVDF-TrFE caused the latter to fold around the SWCNT (first frames of Supplementary Video 4.S1), aligning their dipole moment vector immediately with the

SWCNT backbone. The PVDF-TrFE chains have flexible backbones, coiling around each other and exhibiting little or no wrapping around the SWCNT. In fact, the dipole moment vector of the SWCNT/PVDF-TrFE was found to be more likely to form small angles (0° to 45° or 135° to 180°) with the SWCNT axis of symmetry, especially when arranged in the (12,0) SWCNT. The copolymer chains had higher interaction energy with the (12,0) SWCNT than with the (8,8) SWCNT, indicating that the SWCNT chirality affects the alignment of the dipole moment vector with the SWCNT backbone, as both SWCNT types investigated here had comparable radii. Furthermore, MD simulations with one PVDF-TrFE co-polymer chain exhibited slightly larger φ angles than those of the system with two co-polymer chains for the (8,8) SWCNT, revealing that steric effects between the chains affect the direction of the dipole moment vector. Videos showing the temporal evolution of the dipole moment vector of the SWCNT/PVDF-TrFE system, as well as the dipole moment vectors of each of the two PVDF-TrFE chains, are presented in Supplementary Video 4.S1.

The probability distribution of the minimum distance, d , of fluoride (blue) and hydrogen atoms (red) of the TrFE units within the PVDF-TrFE chains from the SWCNT with (8,8) and (12,0) chiralities is shown in Figure 4.6b and Figure 4.6c. The minimum distance is calculated only for the H – C – F branch of the TrFE units (highlighted unit in the inset of Figure 4.6b) of the PVDF-TrFE chains as the branches of the VDF units are symmetric with either two H atoms (H – C – H) or two F atoms (F – C – F). The results were averaged over all the TrFE units within the two co-polymer chains for the entire simulation time. The C and F atoms of the TrFE H – C – F branch were found to be most probable in two distinct regions: at approximately $3.5 \text{ \AA}$ and $5.5 \text{ \AA}$ away from the SWCNT surface. However, the F atoms were more likely to be arranged closer to the SWCNT surface than the H atoms, as indicated by their higher probability distribution at $3.5 \text{ \AA}$. This preference of fluoride to remain closer to the SWCNT surface was even more pronounced when the PVDF-TrFE chains interact with the zig-zag (12,0) SWCNTs, revealing larger differences in their probability distributions compared to the H atoms. The H and F arrangement with respect to the SWCNT surface hardly changes during the simulations indicated by the narrow error bars in their probability distributions. Furthermore, the H – C and the C – F bonds of the TrFE H – C – F branch arrange perpendicularly to the CNT surface as shown by the probability distribution of their angle with the CNT axis of symmetry with a peak at 90° (Supplementary Figure 4.S11).

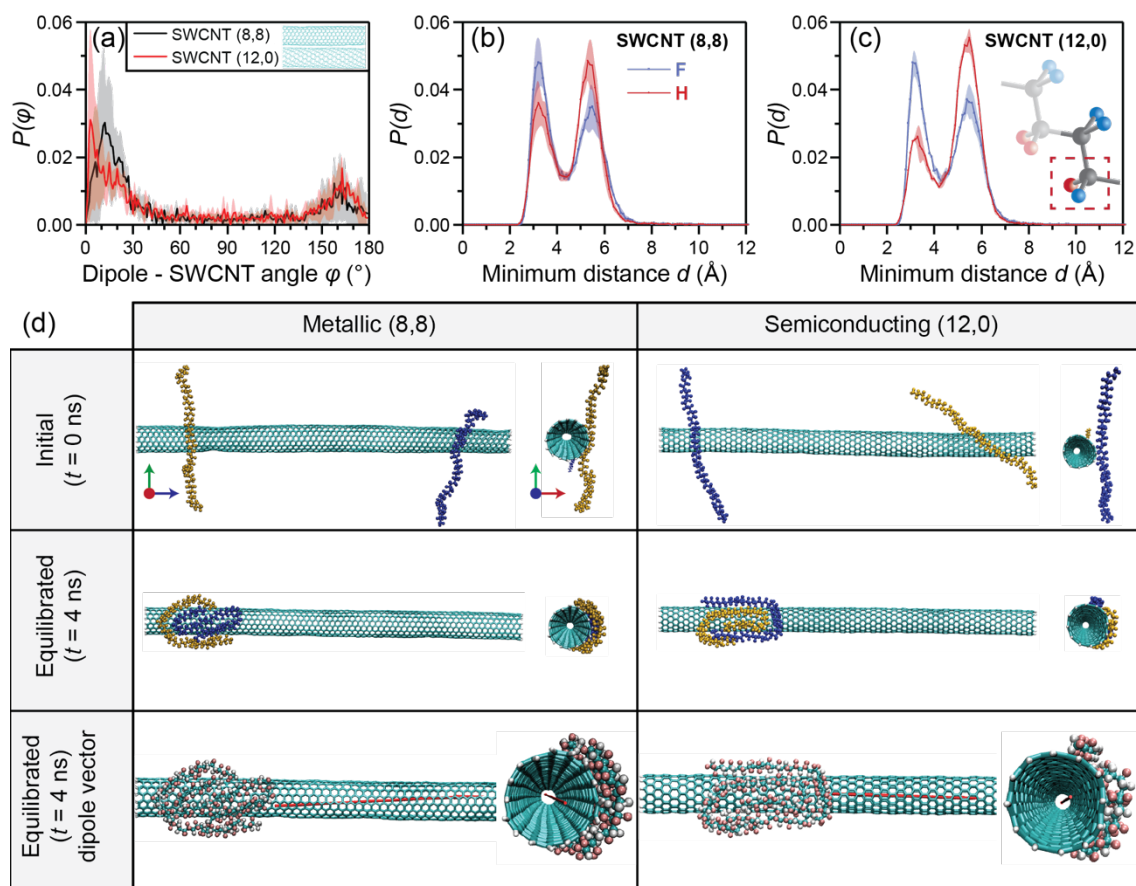


Figure 4.6: (a) The probability distribution of the angle, ϕ , between the vectors of the SWCNT axis of symmetry and the SWCNT/PVDF-TrFE dipole moment for the (8,8) (black line) and the (12,0) (red line) SWCNT configurations (insets). The probability distribution of the minimum distance, d , between fluoride (blue lines) or hydrogen atoms (red lines) of the TrFE units (inset of a faded VDF and a highlighted TrFE monomer) and the CNT with (b) (8,8) and (c) (12,0) chirality. The shaded regions represent the error bar obtained from three independent MD simulations. (d) Representative initial spatial arrangement at 0 ns (top) of two PVDF-TrFE chains (gold and blue) relative to SWCNTs (cyan) with (8,8) (left) and (12,0) (right) chiralities, the spatial arrangement after equilibration at 4 ns (middle) and the representative PVDF-TrFE dipole moment vector direction after equilibration at 4 ns (bottom).

The PVDF-TrFE chain was initially placed tangential to the SWCNT surface, perpendicular to the SWCNT length axis (Figure 4.6c). Rapidly, the PVDF-TrFE was found to adsorb to the SWCNT surface, indicating the attractive interaction between the polymer and the SWCNT. The orientation of the dipoles within PVDF-TrFE, as shown in Figure

4.6a, showed preferential alignment toward low angles relative to the SWCNT length axis, with values between 0° and 30° , as well as 135° and 180° , confirming the presence of preferential alignment of the dipole to the SWCNT within the extrusion printed polymer. Additionally, the fluorine-hydrogen dipole vector within the H – C – F group was found to preferentially orient away from the SWCNT when simulating a single PVDF-TrFE chain on the SWCNT (Figure 4.6b and Figure 4.6c).

The MD simulations were in close agreement with the nanoscale PFM data presented in Figure 4.3, which showed a five-fold increase in polarisation upon the incorporation of low (0.020 wt%) concentrations of SWCNTs. At concentrations above 0.020 wt%, however, the SWCNTs reached a concentration stability threshold with an increased tendency to aggregate and therefore exhibited a decrease in the polarisation. Similar results were found in the macroscale energy harvesting experiments (Figure 4.4). The maximum energy conversion was found to occur in the SWCNT/PVDF-TrFE (0.020 wt%) PEGs, subsequently showing a decreased templating effect at higher SWCNT concentrations. For SWCNT/PVDF-TrFE (0.100 wt%) PEGs, the output voltage under cyclic compression was found to be comparable to the SWCNT/PVDF-TrFE (0.000 wt%) PEGs. Furthermore, at a SWCNT concentration of 0.500 wt%, the SWCNTs formed a conductive pathway (Supplementary Figure 4.S5), crossing the percolation threshold and therefore showing no energy harvesting characteristics (Figure 4.4a).

These MD calculations have shown conclusively that the SWCNTs can template the PDVF-TrFE molecules inducing dipole alignment around a $\pm 45^\circ$ arc relative to the SWCNT backbone. This alignment, however, is only expected to occur when there are non-bundled SWCNTs and thus, at higher mass loadings where aggregated SWCNTs dominate the material properties, a sharp reduction in energy harvesting outputs was observed. In contrast to previous literature of CNT/PVDF-TrFE composites, the use of SWCNTs in this work enabled a consistent dipole alignment as the electrons are localised around a single CNT layer. In the literature, which focuses on MWCNTs, this alignment effect for inducing preferential polarisation is expected to be significantly lower. The concentric structure of the MWCNTs reduces the ability for PVDF-TrFE to influence the total electron density and therefore not produce the dipole alignment effect observed in SWCNTs. It is inferred that this effect was similarly observed in poled fluoropolymers,

by Kim *et al.*⁴⁴, showing a significantly higher P_D when incorporating SWCNTs than any reported MWCNT/fluoropolymer systems such as Ning *et al.*¹⁸. Based on this fundamental understanding, the combination of the dipole alignment *via* SWCNT templating with partial dipole alignment of the polymers and SWCNTs through extrusion printing, enables this work to achieve power densities and peak to peak voltages comparable to electrically poled PVDF.

4.4.6 Recyclability of extrusion printed films

The recent review presented by Stadlober *et al.*⁷¹ discussed the need for finding recyclable materials for energy harvesting. Tamang *et al.*⁷² proposed a route to biodegradable PEGs through the introduction of DNA into PVDF, however the publication lacked data to support the claim of biodegradation characteristics. Fluoropolymers, owing to their inherent chemically inert nature, as well as thermal stability, have seen few reports on degradation and recycling in the past. A key aspect towards the commercial applicability of recyclable PEGs is the utilisation of green solvents and quick timeframe of the recycling procedure.

Figure 4.7 shows the capability of the extrusion printed SWCNT/PVDF-TrFE (0.020 wt%) films (Figure 4.7a), with the highest polarisation templating effect, to be recycled and reprinted for further use. The initial extrusion printed films (acetone and DMF, 60:40 vol%) exhibited complete dissolution in pure acetone, classified as a green solvent, in less than 20 s (Figure 4.7a-c and Supplementary Video 4.S2).^{73,74} Figure 4.7b and Figure 4.7c show the sample dissolution at 2 s after initial immersion and 9 s after initial immersion, respectively (0.200 wt% SWCNT/PVDF-TrFE shown for visual clarity). For reprinting, four initial extrusion printed SWCNT/PVDF-TrFE (0.020 wt%) films weighing 214 mg were dissolved in 904 μ L acetone, corresponding to a polymer concentration of 23 wt%.

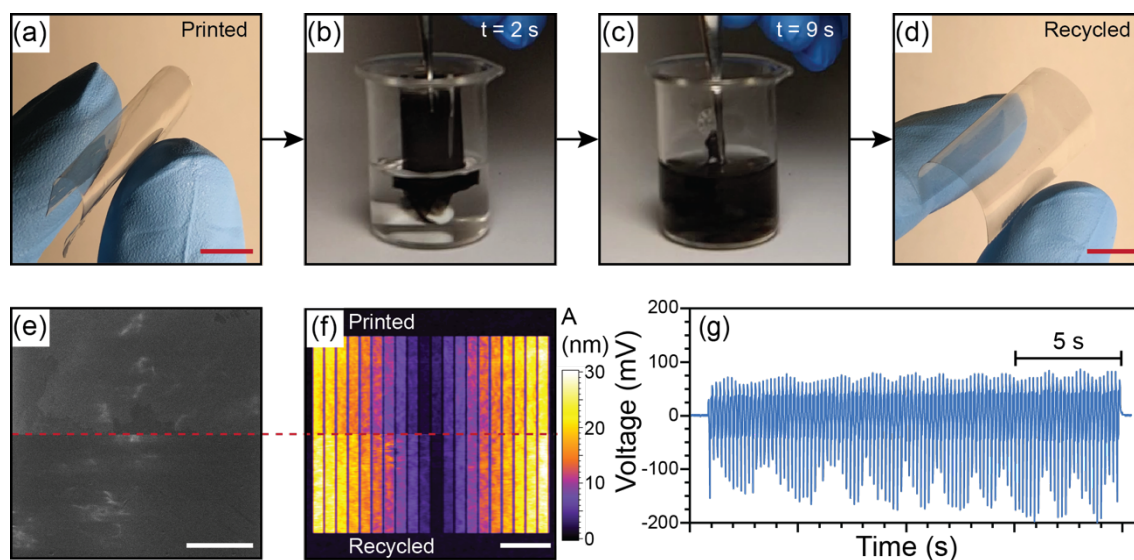


Figure 4.7: Recyclability of SWCNT/PVDF-TrFE films (extrusion printed from acetone and DMF, 60:40 vol%) in pure acetone, with (a) optical image demonstrating the transparency and mechanical flexibility of the initial extrusion printed SWCNT/PVDF-TrFE (0.020 wt%) film. (b) After 2 s of immersion in pure acetone. (c) After 9 s immersion in pure acetone. (d) SWCNT/PVDF-TrFE (0.020 wt%) film after recycling and reprinting from pure acetone. The 0.200 wt% sample is shown in (b) and (c) for visual clarity. (e) Top, HIM micrograph of SWCNT/PVDF-TrFE (0.020 wt%) film printed from acetone/DMF. Bottom, recycled and reprinted film from pure acetone. (f) Top, PFM amplitude trace after application of voltage to the SWCNT/PVDF-TrFE (0.020 wt%) film printed from acetone/DMF. Bottom, recycled and reprinted film. (g) Voltage output under cyclic compression for a recycled and reprinted SWCNT/PVDF-TrFE (0.020 wt%) PEG, obtained with an input impedance at 10 M Ω . Scale bars in (a) and (d) correspond to 10 mm, scale bar in (e) corresponds to 10 μ m and scale bar in (f) corresponds to 1 μ m.

After the dissolution of the SWCNT/PVDF-TrFE (0.020 wt%) films (extrusion printed from acetone and DMF, 60:40 vol%) in pure acetone, they were reprinted directly from acetone without any additional pre-processing. The printing was undertaken at extremely low extrusion pressures relative to the initial print, decreasing by 82.3% to 0.3 Bar. Furthermore, the lower solvent boiling point noticeably decreased the solvent evaporation time within the printed film. Figure 4.7d shows an optical image of the film reprinted directly from acetone. The recycled films exhibited transparency and flexibility similar to the films prior to recycling with no visible aggregation of SWCNTs. The comparative

HIM micrographs are shown in Figure 4.7e for the SWCNT/PVDF-TrFE (0.020 wt%) film printed from acetone and DMF mixture (Figure 4.7e, top) and the film recycled from acetone (Figure 4.7e, bottom). The recycled SWCNT/PVDF-TrFE (0.020 wt%) film showed minimal SWCNT aggregation, with only slightly higher affinity to bundle, which was attributed to the lack of sonication.

Interestingly, the γ and β phase ratios appeared to remain relatively unchanged after recycling and reprinting. The Raman analysis showed that the recycled films had comparable phase ratios after reprinting with respect to the γ and β phase peak ratios at 811 cm^{-1} and 842 cm^{-1} , respectively (Supplementary Figure 4.S12). Furthermore, the XRD analysis (Supplementary Figure 4.S13) showed similar β and γ phase peaks to the initial extrusion printed SWCNT/PVDF-TrFE (0.020 wt%) films.

The nanoscale piezoelectricity was probed with the piezoelectric amplitude shown as a comparison to the initial extrusion printed SWCNT/PVDF-TrFE (0.020 wt%) film in Figure 4.7f. The amplitude showed good agreement between the film prior to recycling and post-recycling, confirming the recycled film retained its piezoelectric activity. The d_{33} coefficient value for the recycled and reprinted film was found to be -10 pm V^{-1} (Supplementary Figure 4.S5), which was slightly lower than that of the films printed from acetone and DMF (-12 pm V^{-1}).

The recycled SWCNT/PVDF-TrFE (0.020 wt%) films were then used to fabricate PEGs. The final devices were tested under cyclic compression to demonstrate the retention of energy harvesting after recycling. The voltage is shown as a function of time for 5 Hz compression in Figure 4.7g. The PEG, recycled from a printed SWCNT/PVDF-TrFE (0.020 wt%) film using pure acetone without any highly energetic processing techniques, was found to produce an average V_{pp} of 209 mV under controlled strain rate at $10\text{ M}\Omega$ input impedance, corresponding to a P_D of $0.5\text{ }\mu\text{W cm}^{-3}$.

The recycled SWCNT/PVDF-TrFE (0.020 wt%) PEG was then tested using a technique most commonly found in literature, namely cyclic compression under low force using finger pinching.^{75,76} In this case, a V_{pp} of 1.6 V was obtained at an input impedance of 10

M Ω (Figure 4.8a). The maximum V_{pp} for the recycled 0.020 wt% SWCNT/PVDF-TrFE PEG was 2.0 V, obtained at an input impedance of 20 M Ω representing open-circuit voltage conditions (Figure 4.8b). The maximum V_{pp} was in close agreement with that of a PEG fabricated using commercial poled PVDF film obtained from Measurement Specialties (Supplementary Figure 4.S14).

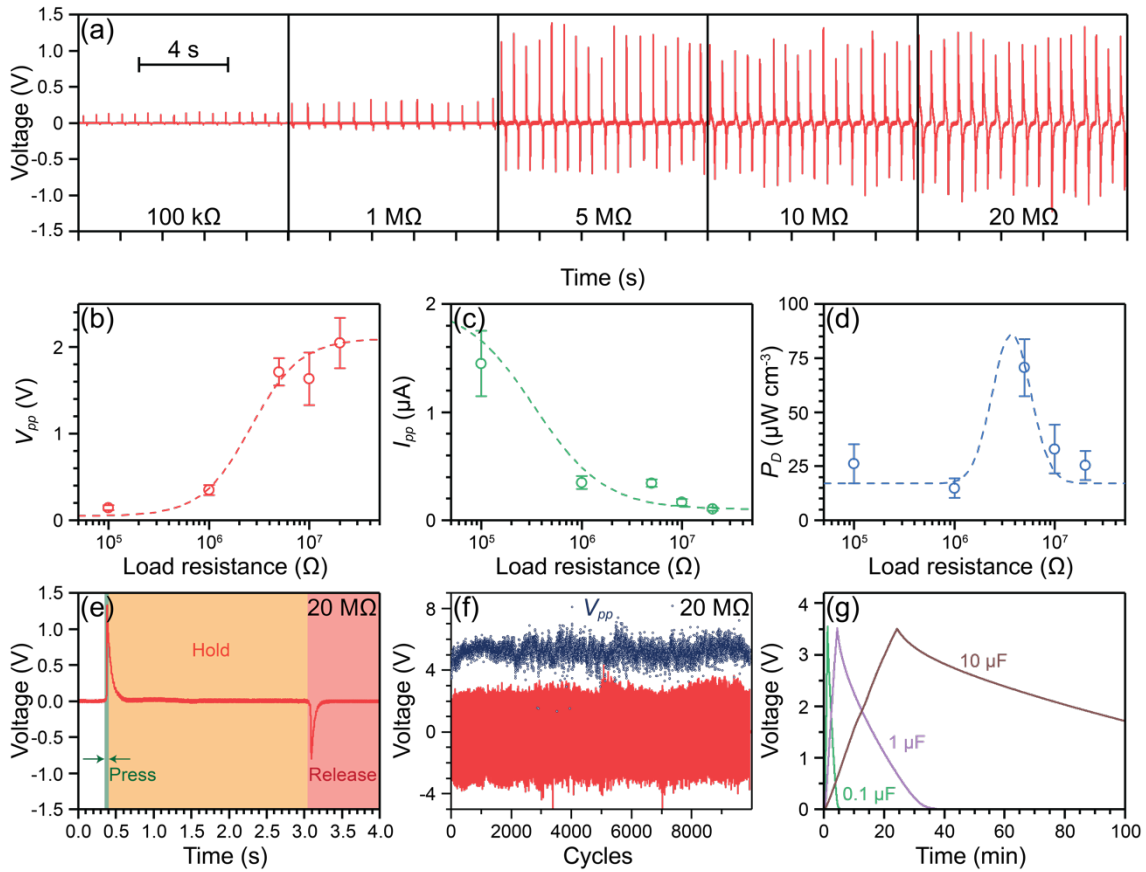


Figure 4.8: Energy harvesting characteristics of a PEG fabricated from a recycled extrusion printed SWCNT/PVDF-TrFE (0.020 wt%) film under low-force cyclic compression using finger pinching, showing (a) the generated voltage as a function of time with a load resistance between 100 k Ω and 20 M Ω . (b) The V_{pp} as a function of load resistance. (c) The I_{pp} as a function of load resistance. (d) The P_o as a function of load resistance. (e) The generated voltage at 20 M Ω as a function of time, where the PEG was compressed and held for approximately 1.7 s prior to release. (f) The generated voltage stability (red) and the V_{pp} (blue) as a function of the number of compression cycles under a load resistance of 20 M Ω . (g) The charging and discharging profiles of capacitors under 3.5 Hz cyclic compression *via* a bridge rectifier.

The maximum I_{pp} of the recycled 0.020 wt% SWCNT/PVDF-TrFE PEG was calculated to be 1.2 μA at 100 k Ω , corresponding to the short-circuit current (Figure 4.8c). The maximum P_D for the recycled PEG, obtained under the low-force compression through load resistance matching experiments (Figure 4.8d), was 70.6 $\mu\text{W cm}^{-3}$ at 5 M Ω , significantly higher than that of the controlled strain rate experiments. A maximum P_D of 70.6 $\mu\text{W cm}^{-3}$ places these recycled and reprinted SWCNT/PVDF-TrFE (0.020 wt%) PEGs in line with that of poled CNT-fluoropolymer composite PEGs. In fact, they are far higher than the approximately 10 $\mu\text{W cm}^{-3}$ obtained by Ning *et al.*¹⁸ and thus show an incredible promise for future applications in this area. When the PEG was compressed and held prior to release, only a positive peak was observed, with the negative peak following the release, as shown in Figure 4.8e, confirming the energy harvesting signal was occurring due to piezoelectricity.

The recycled 0.020 wt% SWCNT/PVDF-TrFE PEG was further subjected to extensive cycling study, shown in Figure 4.8f. The data exhibited no notable decrease in energy harvesting capability after approximately 10000 cycles, confirming long-term cycling stability of the extrusion printed SWCNT/PVDF-TrFE PEGs. Additionally, to demonstrate the potential to capture and store this energy for future use, charging 0.1 μF , 1 μF and 10 μF capacitors through the simple application of a finger press on the PEG (Figure 4.8e). These capacitors were charged through a bridge rectifier to 3.5 V over 1.2 minutes, 4.5 minutes, and 24.3 minutes, respectively, with a linear charging profile for the 0.1 μF and 1 μF capacitor. The self-poled, recycled, 0.020 wt% SWCNT/PVDF-TrFE PEG charged these capacitors faster than state-of-the-art piezoelectric polymer PEGs in the literature, demonstrating the feasibility of using these devices to capture human motion to power remote and portable electronics.^{77,78}

4.5 Conclusion

Lowering the energy input required to manufacture polymer-based piezoelectric generators is crucial for their low-cost implementation into flexible and wearable electronics. This work has demonstrated the low energy production of a transparent and flexible piezoelectric generator and is the first report of non-poled fluoropolymer-based piezoelectric generators printed with a power density greater than 10 $\mu\text{W cm}^{-3}$. By combining one-dimensional additives, in the form of SWCNTs, with polymer chain orientation *via*

extrusion printing, figures of merit comparable to electrically poled PVDF-TrFE are obtained. Further, this result is observed to arise from an increased dipole alignment of the crystalline phase relative to the SWCNT backbone, supported *via* molecular dynamics simulations. The ability to recycle the SWCNT/PVDF-TrFE films using just a green solvent (acetone) is demonstrated, giving a low energy tool to reshape the form factor of the piezoelectric generator. This form factor reshaping would allow piezoelectric generators to be made to size for wearable electronics, or for custom contours within the body to power devices such as pacemakers. The highly touted chemical stability of both SWCNTs and PVDF-TrFE means that this recycling process does not affect the fundamental chemistry, and hence the piezoelectric performance of the materials.

4.6 References

1. Y. Wurmser, *Wearables 2019: Advanced Wearables Pick Up Pace as Fitness Trackers Slow*, eMarketer (2019).
2. Y. Huang, L. Zhao, L. Li, M. Xie, F. Wu and R. Chen, Electrolytes and Electrolyte/Electrode Interfaces in Sodium-Ion Batteries: From Scientific Research to Practical Application, *Advanced Materials*, **31**, 1808393 (2019).
3. Y. Yang and W. Gao, Wearable and flexible electronics for continuous molecular monitoring, *Chemical Society Reviews*, **48**, 1465–1491 (2019).
4. H. Wang, A. Guerrero, A. Bou, A. M. Al-Mayouf and J. Bisquert, Kinetic and material properties of interfaces governing slow response and long timescale phenomena in perovskite solar cells, *Energy & Environmental Science*, **12**, 2054–2079 (2019).
5. Y. Wang, L. Yang, X. L. Shi, X. Shi, L. Chen, M. S. Dargusch, J. Zou and Z. G. Chen, Flexible Thermoelectric Materials and Generators: Challenges and Innovations, *Advanced Materials*, **31**, 1807916 (2019).
6. C. R. Bowen, J. Taylor, E. LeBoulbar, D. Zabek, A. Chauhan and R. Vaish, Pyroelectric materials and devices for energy harvesting applications, *Energy & Environmental Science*, **7**, 3836–3856 (2014).
7. N. A. Shepelin, A. M. Glushenkov, V. C. Lussini, P. J. Fox, G. W. Dicinoski, J. G. Shapter and A. V. Ellis, New developments in composites, copolymer technologies and processing techniques for flexible fluoropolymer piezoelectric generators for efficient energy harvesting, *Energy & Environmental Science*, **12**, 1143–1176 (2019).
8. C. Kolm and P. H. Fowler, Piezoelectric power system, *US Patent*, US3239678A (1966).
9. K. S. Ramadan, D. Sameoto and S. Evoy, A review of piezoelectric polymers as functional materials for electromechanical transducers, *Smart Materials and Structures*, **23**, 033001 (2014).
10. F. R. Fan, W. Tang and Z. L. Wang, Flexible Nanogenerators for Energy Harvesting and Self-Powered Electronics, *Advanced Materials*, **28**, 4283–4305 (2016).
11. N. Weber, Y. S. Lee, S. Shanmugasundaram, M. Jaffe and T. L. Arinzeh, Characterization and *in vitro* cytocompatibility of piezoelectric electrospun scaffolds, *Acta Biomaterialia*, **6**, 3550–3556 (2010).

12. J. Li, L. Kang, Y. Yu, Y. Long, J. J. Jeffery, W. Cai and X. Wang, Study of long-term biocompatibility and bio-safety of implantable nanogenerators, *Nano Energy*, **51**, 728–735 (2018).
13. V. Sencadas, S. Lanceros-Méndez and J. F. Mano, Characterization of poled and non-poled β -PVDF films using thermal analysis techniques, *Thermochimica Acta*, **424**, 201–207 (2004).
14. D. B. Deutz, J. A. Pascoe, B. Schelen, S. Van Der Zwaag, D. M. De Leeuw and P. Groen, Analysis and experimental validation of the figure of merit for piezo-electric energy harvesters, *Materials Horizons*, **5**, 444–453 (2018).
15. P. Martins, A. C. Lopes and S. Lanceros-Mendez, Electroactive phases of poly(vinylidene fluoride): Determination, processing and applications, *Progress in Polymer Science*, **39**, 683–706 (2014).
16. J. C. Dias, A. C. Lopes, B. Magalhães, G. Botelho, M. M. Silva, J. M. S. S. Esperança and S. Lanceros-Mendez, High performance electromechanical actuators based on ionic liquid/poly(vinylidene fluoride), *Polymer Testing*, **48**, 199–205 (2015).
17. J. Y. Lim, S. Kim and Y. Seo, Enhancement of β -phase in PVDF by electrospinning, *AIP Conference Proceedings*, **1664**, 070006 (2015).
18. H. M. Ning, N. Hu, T. Kamata, J. H. Qiu, X. Han, L. M. Zhou, C. Chang, Y. Liu, L. K. Wu, J. H. Qiu, H. L. Ji, W. X. Wang, Y. Zemba, S. Atobe, Y. Li, Alamusi and H. Fukunaga, Improved piezoelectric properties of poly(vinylidene fluoride) nanocomposites containing multi-walled carbon nanotubes, *Smart Materials and Structures*, **22**, 065011 (2013).
19. R. Su, J. K. Tseng, M. S. Lu, M. Lin, Q. Fu and L. Zhu, Ferroelectric behavior in the high temperature paraelectric phase in a poly(vinylidene fluoride-co-trifluoroethylene) random copolymer, *Polymer*, **53**, 728–739 (2012).
20. Measurement Specialties Inc., *Piezo Film Sensors Technical Manual*, Norristown, PA (1999).
21. M. S. Sebastian, A. Larrea, R. Gonçalves, T. Alejo, J. L. Vilas, V. Sebastian, P. Martins and S. Lanceros-Mendez, Understanding nucleation of the electroactive β -phase of poly(vinylidene fluoride) by nanostructures, *RSC Advances*, **6**, 113007–113015 (2016).
22. N. Jia, Q. Xing, X. Liu, J. Sun, G. Xia, W. Huang and R. Song, Enhanced electroactive properties of poly(vinylidene fluoride) by controlling crystallization

- and interfacial interactions with low loading polydopamine coated BaTiO₃, *Journal of Colloid and Interface Science*, **453**, 169–176 (2015).
23. C. B. Osman, S. Nowak, A. Garcia-Sanchez, Y. Charles, S. Ammar, S. Merccone and F. Mammeri, *In situ* monitored stretching induced α to β allotropic transformation of flexible poly(vinylidene fluoride)-CoFe₂O₄ hybrid films: The role of nanoparticles inclusion, *European Polymer Journal*, **84**, 602–611 (2016).
 24. M. M. Alam, A. Sultana and D. Mandal, Biomechanical and Acoustic Energy Harvesting from TiO₂ Nanoparticle Modulated PVDF Nanofiber Made High Performance Nanogenerator, *ACS Applied Energy Materials*, **1**, 3103–3112 (2018).
 25. X. Hu, X. Yan, L. Gong, F. Wang, Y. Xu, L. Feng, D. Zhang and Y. Jiang, Improved Piezoelectric Sensing Performance of P(VDF-TrFE) Nanofibers by Utilizing BTO Nanoparticles and Penetrated Electrodes, *ACS Applied Materials & Interfaces*, **11**, 7379–7386 (2019).
 26. S. Manna and A. K. Nandi, Piezoelectric β Polymorph in Poly(vinylidene fluoride)-Functionalized Multiwalled Carbon Nanotube Nanocomposite Films, *Journal of Physical Chemistry C*, **111**, 14670–14680 (2007).
 27. G. Mago, F. T. Fisher and D. M. Kalyon, Deformation-Induced Crystallization and Associated Morphology Development of Carbon Nanotube-PVDF Nanocomposites, *Journal of Nanoscience and Nanotechnology*, **9**, 3330–3340 (2009).
 28. S. Chen, X. Tao, W. Zeng, B. Yang and S. Shang, Quantifying Energy Harvested from Contact-Mode Hybrid Nanogenerators with Cascaded Piezoelectric and Triboelectric Units, *Advanced Energy Materials*, **7**, 1601569 (2017).
 29. L. He, J. Sun, X. Wang, L. Yao, J. Li, R. Song, Y. Hao, Y. He and W. Huang, Enhancement of β -crystalline phase of poly(vinylidene fluoride) in the presence of hyperbranched copolymer wrapped multiwalled carbon nanotubes, *Journal of Colloid and Interface Science*, **363**, 122–128 (2011).
 30. Z. H. Liu, C. T. Pan, L. W. Lin and H. W. Lai, Piezoelectric properties of PVDF/MWCNT nanofiber using near-field electrospinning, *Sensors and Actuators A: Physical*, **193**, 13–24 (2013).
 31. A. Mandal and A. K. Nandi, Ionic Liquid Integrated Multiwalled Carbon Nanotubes in a Poly(vinylidene fluoride) Matrix: Formation of a Piezoelectric β -Polymorph with Significant Reinforcement and Conductivity Improvement, *ACS Applied Materials & Interfaces*, **5**, 747–760 (2013).

32. L. He, G. Xia, J. Sun, Q. Zhao, R. Song and Z. Ma, Unzipped multiwalled carbon nanotubes-incorporated poly(vinylidene fluoride) nanocomposites with enhanced interface and piezoelectric β phase, *Journal of Colloid and Interface Science*, **393**, 97–103 (2013).
33. X. Guan, Y. Zhang, H. Li and J. Ou, PZT/PVDF composites doped with carbon nanotubes, *Sensors and Actuators A: Physical*, **194**, 228–231 (2013).
34. W. Huang, Z. Li, X. Chen, P. Tian, J. Lu, Z. Zhou, R. Huang, D. Hui, L. He, C. Zhang and X. Wang, Pressure-controlled growth of piezoelectric low-dimensional structures in ternary fullerene C60/carbon nanotube/poly(vinylidene fluoride) based hybrid composites, *Composites Part B: Engineering*, **62**, 126–136 (2014).
35. A. Sarvi, V. Chimello, A. B. Silva, R. E. S. Bretas and U. Sundararaj, Coaxial electrospun nanofibers of poly(vinylidene fluoride)/polyaniline filled with multi-walled carbon nanotubes, *Polymer Composites*, **35**, 1198–1203 (2014).
36. F. Bai, G. Chen, M. Nie and Q. Wang, Assistant effect of poly(methyl methacrylate)-grafted carbon nanotubes on the beta polymorph of poly(vinylidene fluoride) during microinjection, *RSC Advances*, **5**, 54171–54174 (2015).
37. R. M. Habibur, U. Yaqoob, S. Muhammad, A. S. M. I. Uddin and H. C. Kim, The effect of RGO on dielectric and energy harvesting properties of P(VDF-TrFE) matrix by optimizing electroactive β phase without traditional polling process, *Materials Chemistry and Physics*, **215**, 46–55 (2018).
38. R. Tian, Q. Xu, C. Lu, X. Duan and R. G. Xiong, Spontaneous polarization switching and piezoelectric enhancement of PVDF through strong hydrogen bonds induced by layered double hydroxides, *Chemical Communications*, **53**, 7933–7936 (2017).
39. S. Lee and Y. Lim, Generating Power Enhancement of Flexible PVDF Generator by Incorporation of CNTs and Surface Treatment of PEDOT:PSS Electrodes, *Macromolecular Materials and Engineering*, **303**, 1700588 (2018).
40. P. C. Sherrell, A. Cieřlar-Pobuda, M. S. Ejneby, L. Sammalisto, A. Gelmi, E. de Muinck, J. Brask, M. J. Łos and M. Rafat, Rational Design of a conductive Collagen Heart Patch, *Macromolecular Biosciences*, **17**, 1600446 (2017).
41. V. Flexer, J. Chen, B. C. Donose, P. Sherrell, G. G. Wallace and J. Keller, The nanostructure of three-dimensional scaffolds enhances the current density of microbial bioelectrochemical systems, *Energy & Environmental Science*, **6**, 1291–1298 (2013).

42. P. M. Ajayan, L. S. Schadler, C. Giannaris and A. Rubio, Single-Walled Carbon Nanotube-Polymer Composites: Strength and Weakness, *Advanced Materials*, **12**, 750–753 (2000).
43. L. Wu, W. Yuan, T. Nakamura, S. Atobe, N. Hu, H. Fukunaga, C. Chang, Y. Zemba, Y. Li, T. Watanabe, Y. Liu, Alamusi, H. Ning, J. Li, H. Cui and Y. Zhang, Enhancement of PVDF's piezoelectricity by VGCF and MWNT, *Advanced Composite Materials*, **22**, 49–63 (2013).
44. J. Kim, K. J. Loh and J. P. Lynch, Piezoelectric polymeric thin films tuned by carbon nanotube fillers, *SPIE Smart Structures and Materials + Nondestructive Evaluation and Health Monitoring*, San Diego, USA (2008).
45. S. Bodkhe, G. Turcot, F. P. Gosselin and D. Therriault, One-Step Solvent Evaporation-Assisted 3D Printing of Piezoelectric PVDF Nanocomposite Structures, *ACS Applied Materials & Interfaces*, **9**, 20833–20842 (2017).
46. S. Bodkhe, P. S. M. Rajesh, F. P. Gosselin and D. Therriault, Simultaneous 3D Printing and Poling of PVDF and Its Nanocomposites, *ACS Applied Energy Materials*, **1**, 2474–2482 (2018).
47. N. A. Shepelin, V. C. Lussini, P. J. Fox, G. W. Dicinoski, A. M. Glushenkov, J. G. Shapter and A. V. Ellis, 3D printing of Poly(vinylidene fluoride-trifluoroethylene): a poling-free technique to manufacture flexible and transparent piezoelectric generators, *MRS Communications*, **9**, 159–164 (2019).
48. Z. Zhu, S. Z. Guo, T. Hirdler, C. Eide, X. Fan, J. Tolar and M. C. McAlpine, 3D Printed Functional and Biological Materials on Moving Freeform Surfaces, *Advanced Materials*, **30**, 1707495 (2018).
49. M. C. García-Gutiérrez, A. Linares, I. Martín-Fabiani, J. J. Hernández, M. Socio, D. R. Rueda, T. A. Ezquerro and M. Reynolds, Understanding crystallization features of P(VDF-TrFE) copolymers under confinement to optimize ferroelectricity in nanostructures, *Nanoscale*, **5**, 6006–6012 (2013).
50. E. Bellet-Amalric and J. F. Legrand, Crystalline structures and phase transition of the ferroelectric P(VDF-TrFE) copolymers, a neutron diffraction study, *European Physical Journal B*, **3**, 225–236 (1998).
51. C. J. L. Constantino, A. E. Job, R. D. Simões, J. A. Giacometti, V. Zucolotto, O. N. Oliveira Jr., G. Gozzi and D. L. Chinaglia, Phase Transition in Poly(Vinylidene Fluoride) Investigated with Micro-Raman Spectroscopy, *Applied Spectroscopy*, **59**, 275–279 (2005).

52. S. Zhang, H. Wang, D. Xu, W. Yang, P. Tang and Y. Bin, Study of crystallization behavior of neat poly(vinylidene fluoride) and transcrystallization in carbon fiber/poly(vinylidene fluoride) composite under a temperature gradient, *Journal of Applied Polymer Science*, **133**, 43605 (2016).
53. M. T. Riosbaas, K. J. Loh, G. O'Bryan and B. R. Loyola, *SPIE Smart Structures and Materials + Nondestructive Evaluation and Health Monitoring*, San Diego, USA (2014).
54. A. C. Ferrari and J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon, *Physical Review B*, **61**, 14095–14107 (2000).
55. X. Chen, J. Shao, N. An, X. Li, H. Tian, C. Xu and Y. Ding, Self-powered flexible pressure sensors with vertically well-aligned piezoelectric nanowire arrays for monitoring vital signs, *Journal of Materials Chemistry C*, **3**, 11806–11814 (2015).
56. P. Cebe and J. Runt, P(VDF-TrFE)-layered silicate nanocomposites. Part 1. X-ray scattering and thermal analysis, *Polymer*, **45**, 1923–1932 (2004).
57. X. Cai, T. Lei, D. Sun and L. Lin, A critical analysis of the α , β and γ phases in poly(vinylidene fluoride) using FTIR, *RSC Advances*, **7**, 15382–15389 (2017).
58. S. K. Ghosh and D. Mandal, Synergistically enhanced piezoelectric output in highly aligned 1D polymer nanofibers integrated all-fiber nanogenerator for wearable nano-tactile sensor, *Nano Energy*, **53**, 245–257 (2018).
59. R. Gregorio Jr. and M. Cestari, Effect of crystallization temperature on the crystalline phase content and morphology of poly(vinylidene fluoride), *Journal of Polymer Science Part B: Polymer Physics*, **32**, 859–870 (1994).
60. F. Xu, K. Zhang, Y. Zhou, Z. Qu, H. Wang, Y. Zhang, H. Zhou and C. Yan, Facile preparation of highly oriented poly(vinylidene fluoride) uniform films and their ferro- and piezoelectric properties, *RSC Advances*, **7**, 17038–17043 (2017).
61. X. Li, Y. F. Lim, K. Yao, F. E. H. Tay and K. H. Seah, P(VDF-TrFE) ferroelectric nanotube array for high energy density capacitor applications, *Physical Chemistry Chemical Physics*, **15**, 515–520 (2013).
62. S. Florczak, T. Lorson, T. Zheng, M. Mrlik, D. W. Hutmacher, M. J. Higgins, R. Luxenhofer and P. D. Dalton, Melt electrowriting of electroactive poly(vinylidene difluoride) fibers, *Polymer International*, **68**, 735–745 (2019).
63. U. Yaqoob, R. M. Habibur, M. Sheeraz and H. C. Kim, Realization of self-poled, high performance, flexible piezoelectric energy harvester by employing PVDF-

- rGO as sandwich layer between P(VDF-TrFE)-PMN-PT composite sheets, *Composites Part B: Engineering*, **159**, 259–268 (2019).
64. M. Pusty, L. Sinha and P. M. Shirage, A flexible self-poled piezoelectric nanogenerator based on a rGO-Ag/PVDF nanocomposite, *New Journal of Chemistry*, **43**, 284–294 (2019).
 65. P. Thakur, A. Kool, N. A. Hoque, B. Bagchi, F. Khatun, P. Biswas, D. Brahma, S. Roy, S. Banerjee and S. Das, Superior performances of *in situ* synthesized ZnO/PVDF thin film based self-poled piezoelectric nanogenerator and self-charged photo-power bank with high durability, *Nano Energy*, **44**, 456–467 (2018).
 66. A. Biswas, S. Garain and D. Mandal, In situ synthesis of bismuth oxide nanorods and fabrication of self-poled PVDF nanogenerator for mechanical energy harvesting application, *AIP Conference Proceedings*, **1832**, 040024 (2017).
 67. M. Pusty, A. Sharma, L. Sinha, A. Chaudhary and P. Shirage, Comparative Study with a Unique Arrangement to Tap Piezoelectric Output to Realize a Self Poled PVDF Based Nanocomposite for Energy Harvesting, *ChemistrySelect*, **2**, 2774–2782 (2017).
 68. P. Adhikary, S. Garain, S. Ram and D. Mandal, Flexible eu^{3+} doped P(VDF-HFP) nanocomposite film possess hypersensitive electronic transitions and piezoelectric throughput, *Journal of Polymer Science Part B: Polymer Physics*, **54**, 2335–2345 (2016).
 69. S. K. Karan, R. Bera, S. Paria, A. K. Das, S. Maiti, A. Maitra and B. B. Khatua, An Approach to Design Highly Durable Piezoelectric Nanogenerator Based on Self-Poled PVDF/AlO-rGO Flexible Nanocomposite with High Power Density and Energy Conversion Efficiency, *Advanced Energy Materials*, **6**, 1601016 (2016).
 70. R. A. Whiter, V. Narayan and S. Kar-Narayan, A Scalable Nanogenerator Based on Self-Poled Piezoelectric Polymer Nanowires with High Energy Conversion Efficiency, *Advanced Energy Materials*, **4**, 1400519 (2014).
 71. B. Stadlober, M. Zirkel and M. Irimia-Vladu, Route towards sustainable smart sensors: ferroelectric polyvinylidene fluoride-based materials and their integration in flexible electronics, *Chemical Society Reviews*, **48**, 1787–1825 (2019).
 72. A. Tamang, S. K. Ghosh, S. Garain, M. M. Alam, J. Haeberle, K. Henkel, D. Schmeisser and D. Mandal, DNA-Assisted β -phase Nucleation and Alignment of Molecular Dipoles in PVDF Film: A Realization of Self-Poled Bioinspired

- Flexible Polymer Nanogenerator for Portable Electronic Devices, *ACS Applied Materials & Interfaces*, **7**, 16143–16147 (2015).
73. P. G. Jessop, D. A. Jessop, D. Fu and L. Phan, Solvatochromic parameters for solvents of interest in green chemistry, *Green Chemistry*, **14**, 1245–1259 (2012).
 74. K. Alfonsi, J. Colberg, P. J. Dunn, T. Fevig, S. Jennings, T. A. Johnson, H. P. Kleine, C. Knight, M. A. Nagy, D. A. Perry and M. Stefaniak, Green chemistry tools to influence a medicinal chemistry and research chemistry based organisation, *Green Chemistry*, **10**, 31–36 (2008).
 75. L. Zhang, J. Gui, Z. Wu, R. Li, Y. Wang, Z. Gong, X. Zhao, C. Sun and S. Guo, Enhanced performance of piezoelectric nanogenerator based on aligned nanofiber and three-dimensional interdigital electrodes, *Nano Energy*, **65**, 103924 (2019).
 76. K. I. Park, J. H. Son, G. T. Hwang, C. K. Jeong, J. Ryu, M. Koo, I. Choi, S. H. Lee, M. Byun, Z. L. Wang and K. J. Lee, Highly Efficient, Flexible Piezoelectric PZT Thin Film Nanogenerator on Plastic Substrates, *Advanced Materials*, **26**, 2514–2520 (2014).
 77. Y. Zhang, M. Wu, Q. Zhu, F. Wang, H. Su, G. Li, C. Diao, H. Zheng, Y. Wu and Z.L. Wang, Performance Enhancement of Flexible Piezoelectric Nanogenerator via Doping and Rational Design For Self-Powered Mechanosensational System, *Advanced Functional Materials*, **29**, 1904259 (2019).
 78. V. Sencadas, C. Garvey, S. Mudie, J. J. K. Kirkensgaard, G. Gouadec and S. Hauser, Electroactive properties of electrospun silk fibroin for energy harvesting applications, *Nano Energy*, **66**, 104106 (2019).
 79. W. C. Swope, H. C. Andersen, P. H. Berens and K. R. Wilson, A computer simulation method for the calculation of equilibrium constants for the formation of physical clusters of molecules: Application to small water clusters, *Journal of Chemical Physics*, **76**, 637–649 (1982).
 80. S. Plimpton, Fast Parallel Algorithms for Short-Range Molecular Dynamics, *Journal of Computational Physics*, **117**, 1–19 (1995).

4.7 Supplementary information

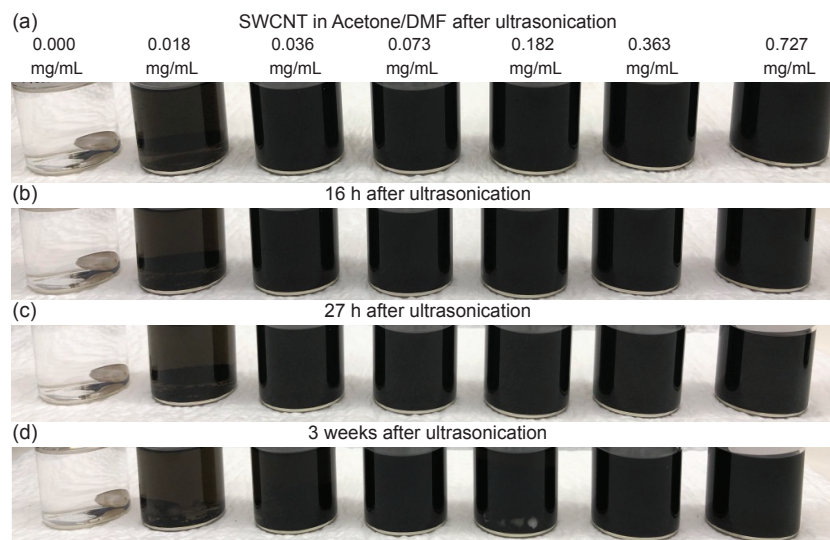


Figure 4.S1: Images showing the SWCNTs dispersed in acetone (60 vol%) and DMF (40 vol%) after 30 min bath ultrasonication, showing concentrations between 0.000 mg mL⁻¹ and 0.727 mg mL⁻¹, corresponding to SWCNT concentrations of between 0.000 wt% and 0.200 wt% relative to PVDF-TrFE. (a) Directly after ultrasonication in a bath sonicator. (b) 16 h after ultrasonication. (c) 27 h after ultrasonication. (d) 3 weeks after ultrasonication.

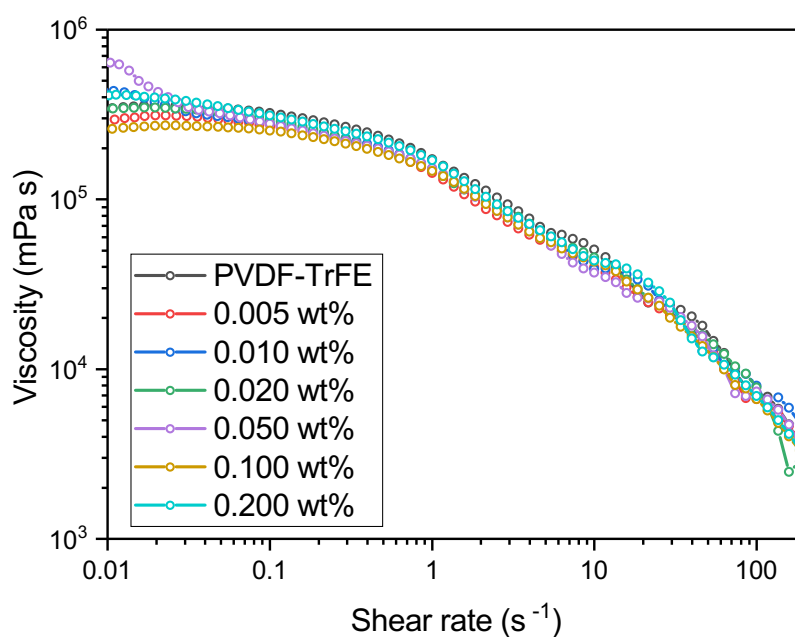


Figure 4.S2: The viscosity of SWCNT/PVDF-TrFE (0.000 wt% to 0.200 wt%) inks as a function of shear rate.

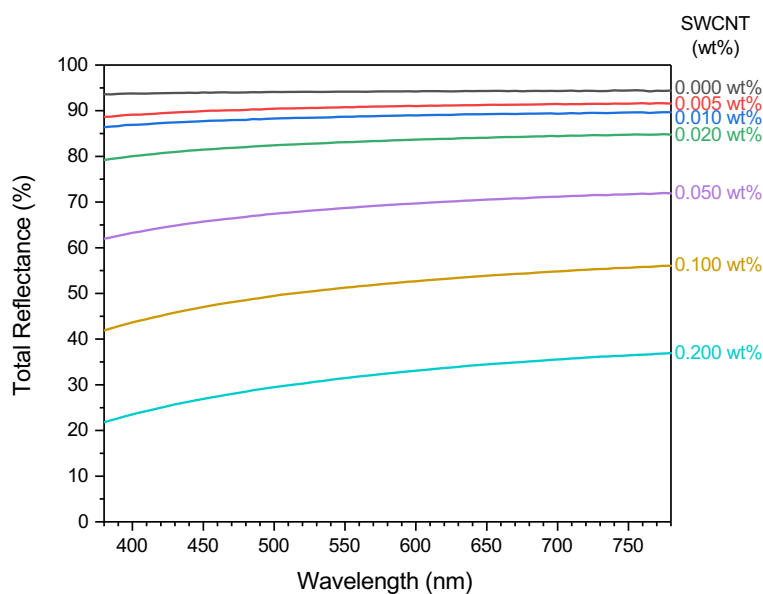


Figure 4.S3: The visible wavelength ($380 \text{ nm} < \lambda < 780 \text{ nm}$) transmittance of the SWCNT/PVDF-TrFE (between 0.000 wt% and 0.200 wt%) films, shown as the total reflectance within the integrating sphere.

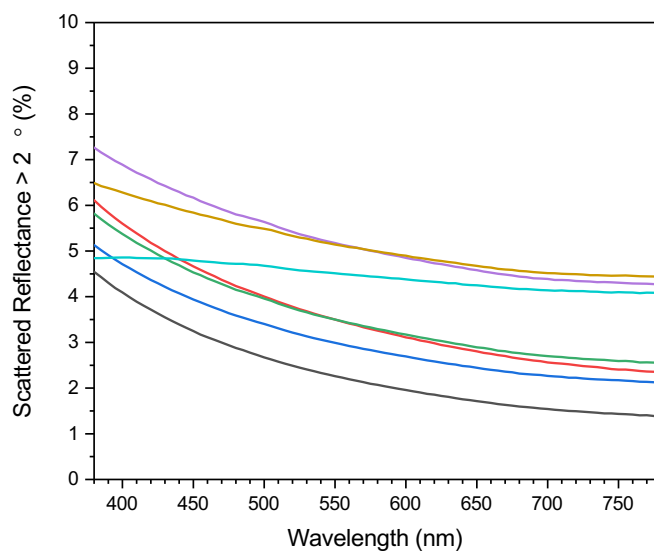


Figure 4.S4: The visible wavelength ($380 \text{ nm} < \lambda < 780 \text{ nm}$) transmittance at angles $> 2^\circ$ of the SWCNT/PVDF-TrFE (between 0.000 wt% and 0.200 wt%) films, shown as the scattered reflectance within the integrating sphere.

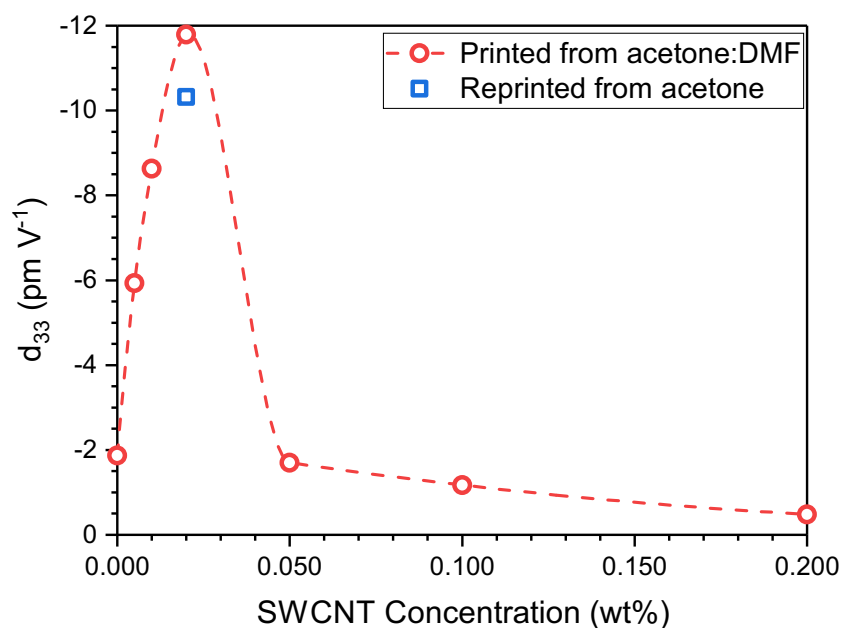


Figure 4.S5: The d_{33} values calculated using PFM at +10 V for the initial 3D printed SWCNT/PVDF-TrFE (0.000 wt% to 0.200 wt%) films (shown in red) and the SWCNT/PVDF-TrFE (0.020 wt%) film recycled and reprinted from acetone (shown in blue).

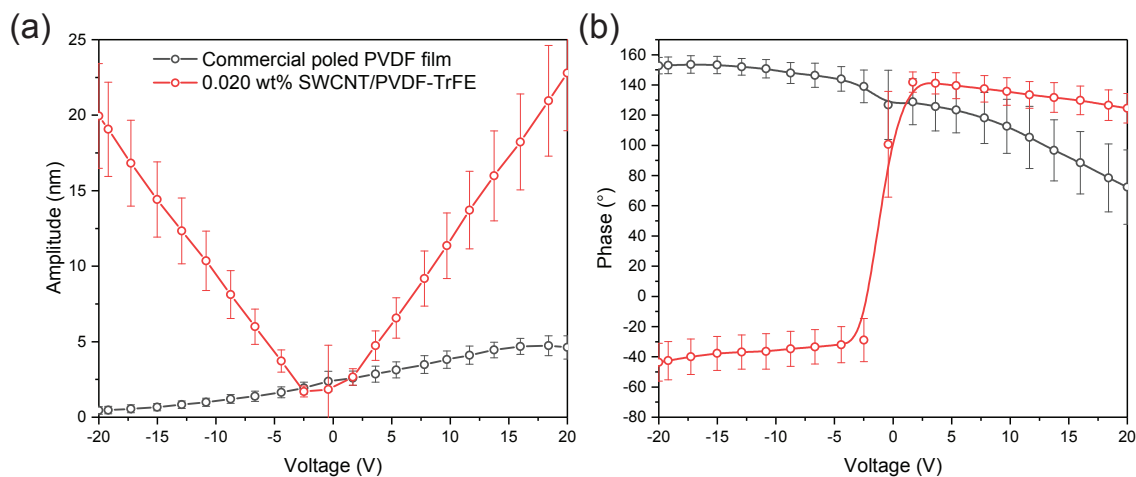


Figure 4.S6: PFM lithography (a) A and (b) ϕ plots showing the data obtained for the extrusion printed 0.020 wt% SWCNT/PVDF-TrFE film (red) and the commercially available poled PVDF film (grey) (Measurement Specialties).

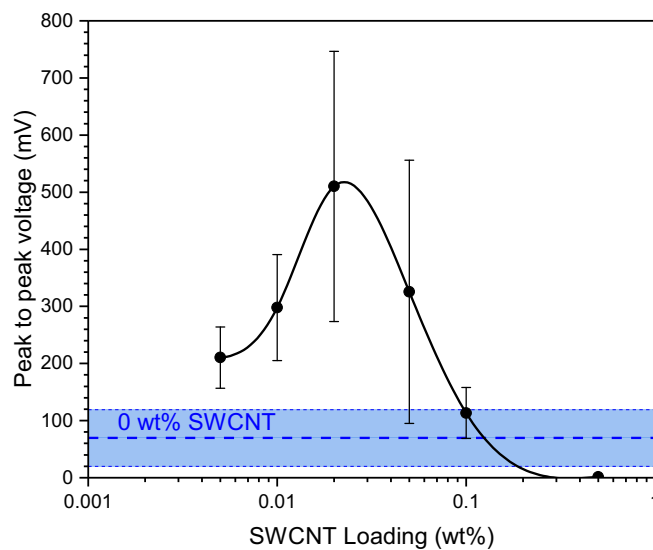


Figure 4.S7: The V_{pp} of SWCNT/PVDF-TrFE (0.000 wt% to 0.500 wt%) PEGs, with error presented for three separate samples at each data point.

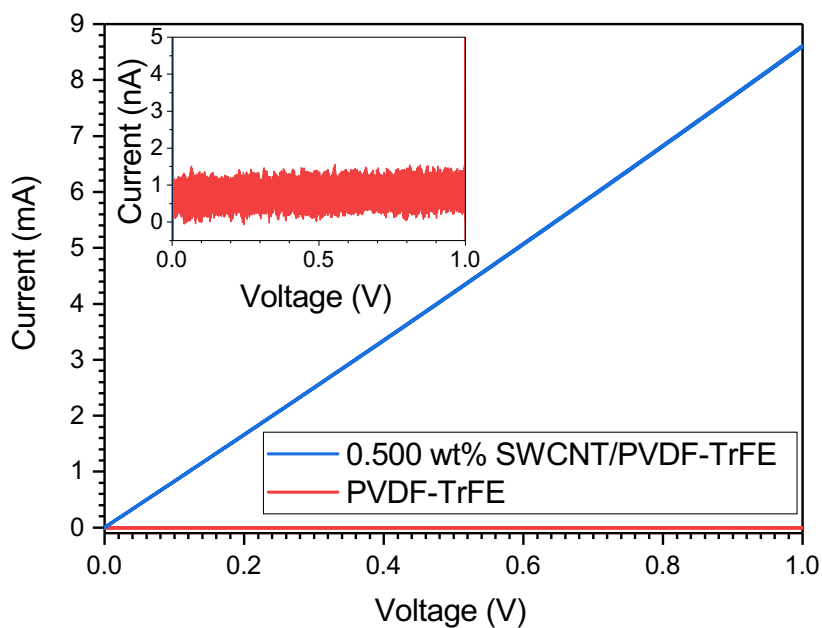


Figure 4.S8: Cyclic voltammetry (CV) for 3D printed SWCNT/PVDF-TrFE (0.000 wt% and 0.500 wt%) films. Inset shows the y-axis expanded to a maximum of 5×10^{-6} mA.

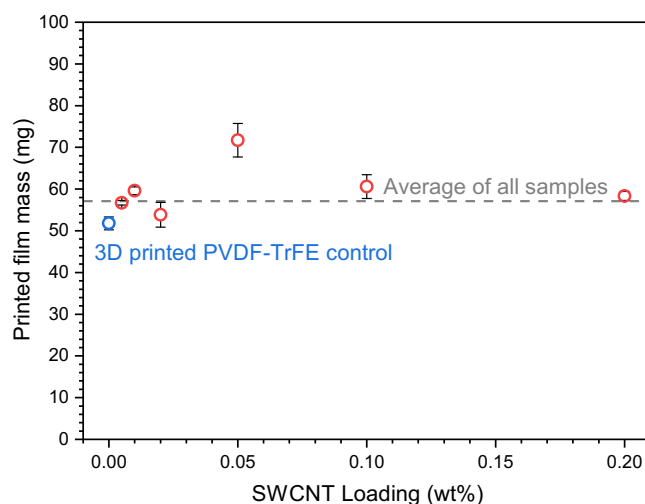


Figure 4.S9: The measured mass for SWCNT/PVDF-TrFE (between 0.000 wt% and 0.200 wt%) films.

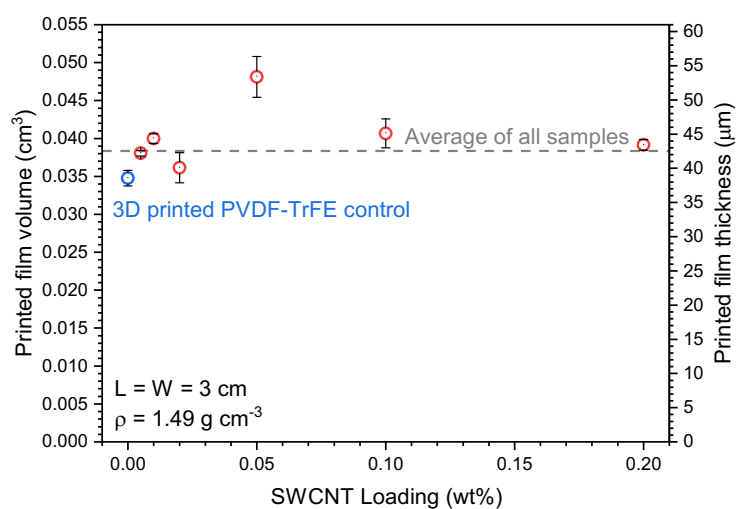


Figure 4.S10: The volume and thickness calculated from Supplementary Figure 4.S9 for SWCNT/PVDF-TrFE (between 0.000 wt% and 0.200 wt%) films. The length and width of the films was 3 cm and density was 1.49 g cm^{-3} (75 mol% VDF and 25 mol% TrFE, 420 kDa, Solvay).

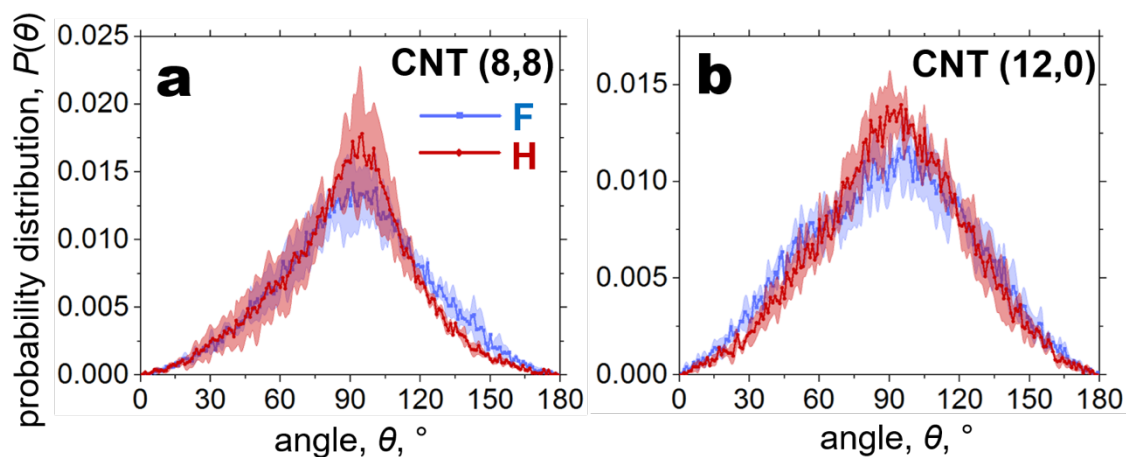


Figure 4.S11: The probability distribution of the angle, θ , between the F – C (blue lines) or the C – H (red lines) of the TrFE units and the CNT axis of symmetry having (a) armchair (8,8) and (b) zig-zag (12,0) chirality. The F – C and the C – H branches are mostly perpendicular to the CNT surface. The shaded regions represent the error bar obtained from three different MD simulations.

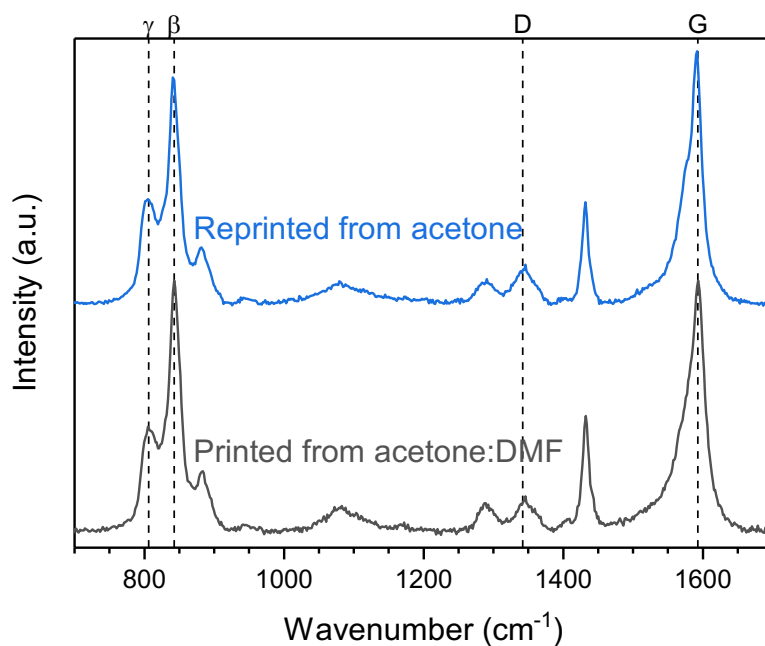


Figure 4.S12: The Raman spectra for the initial 3D printed SWCNT/PVDF-TrFE (0.020 wt%) film (grey line) and SWCNT/PVDF-TrFE (0.020 wt%) recycled and reprinted from acetone (blue line).

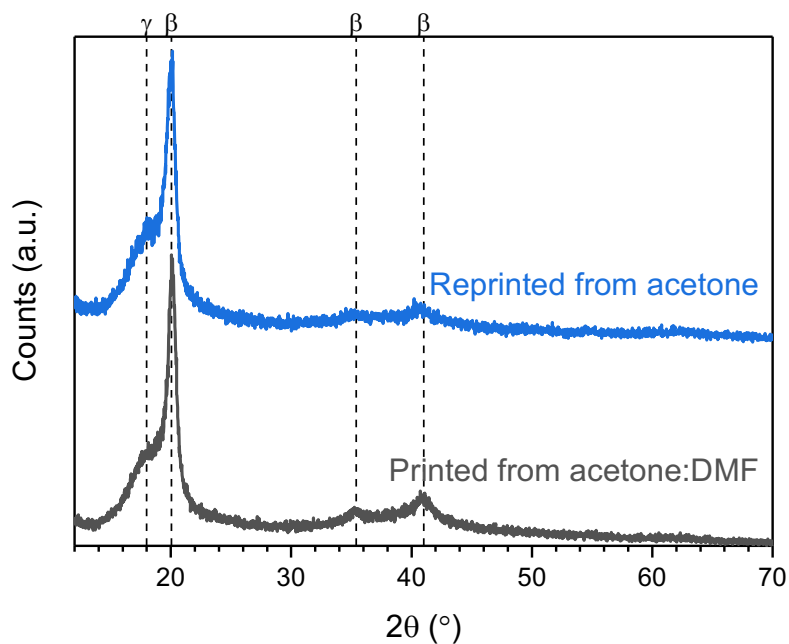


Figure 4.S13: The XRD spectra for the initial 3D printed SWCNT/PVDF-TrFE (0.020 wt%) film (grey line) and SWCNT/PVDF-TrFE (0.020 wt%) recycled and reprinted from acetone (blue line).

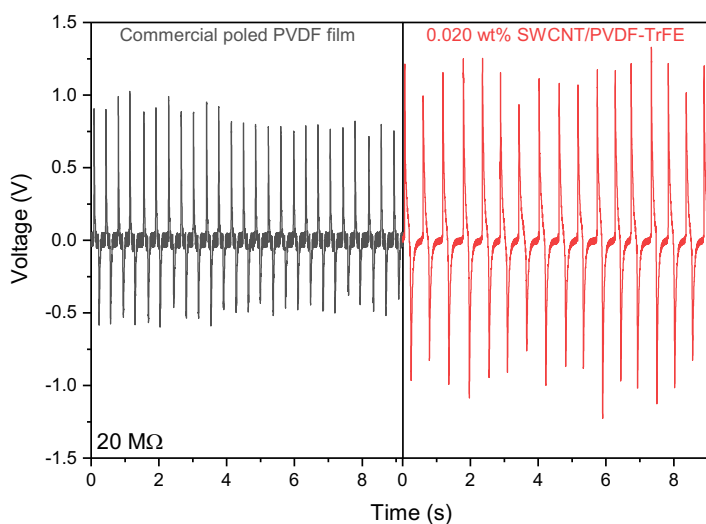


Figure 4.S14: The voltage as a function of time for a PEG made from commercially available poled PVDF film (grey) and a PEG made using the extrusion printed 0.020 wt% SWCNT/PVDF-TrFE film (red). Low force cyclic compression using a finger pinch was used, with a load resistance of 20 MΩ.

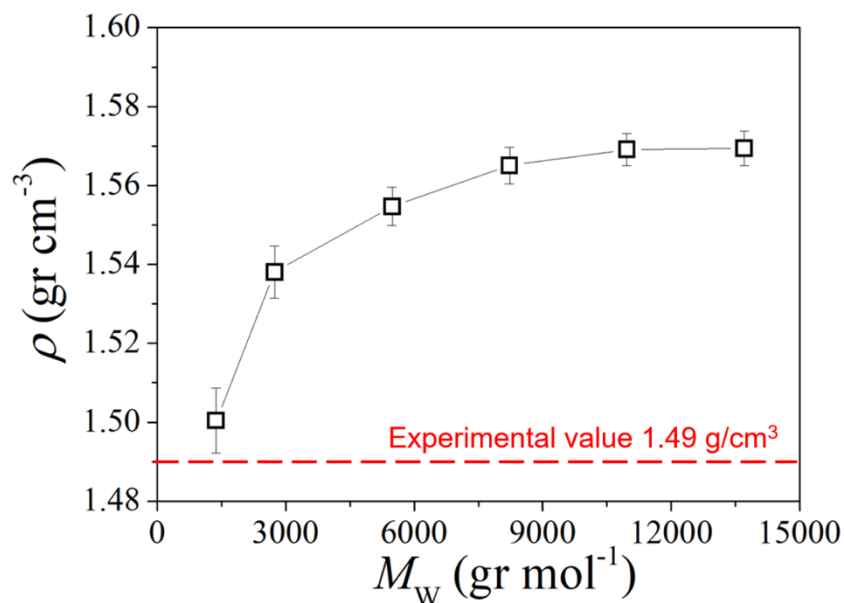


Figure 4.S15: The density of the PVDF-TrFE melt at 230 °C as function of the co-polymer molecular weight obtained by MD simulations (symbols). Increasing the molecular weight leads to a slight increase in the co-polymer density which attains asymptotically a value of about 1.57 g cm⁻³ for molecular weights bigger than about 10,000 g mol⁻¹. The MD-obtained density is in excellent agreement with the experimental value provided by the PVDF-TrFE manufacturer (Solvay, horizontal broken line).

Table 4.S1: The CNT/fluoropolymer energy harvesting figures of merit found in recent literature and the materials and processes used to fabricate the PEGs.

CNT type	Polymer type	[CNT] (wt%)	Power density (μW/cm ³)	Deposition technique	Poling technique	Ref
MWCNT	PVDF	0.075	0.45	Spray coating	Unpoled	¹
MWCNT	PVDF	0.050	59.4	Solvent casting	Drawing (60 °C) up to 400-500% and electrode poling up	²

					to 60 MV/m in silicone oil
SWCNT	PVDF- TrFE	0.100	1481.5	Solvent casting	Electrode pol- ³ ing 58 MV/m at 43 °C in sili- cone oil
MWCNT	PVDF	0.030	26.2	Electrospin- ning (1.5 MV/m)	Electrode pol- ⁴ ing 7 MV/m at 80 °C
MWCNT	PVDF- HFP	0.050	4.0	Solvent casting	Drawing (60 ⁵ °C) up to 400- 500% and elec- trode poling up to 60 MV/m in silicone oil
SWCNT (This work)	PVDF- TrFE	0.020	20.0	3D printing	Unpoled
SWCNT (This work)	PVDF- TrFE (recycled from acetone)	0.020	70.6	3D printing in green sol- vent	Unpoled

4.7.1 Supplementary videos

Video 4.S1: Time evolution of the dipole moment vector for the adsorption of two PVDF-TrFE chains on SWCNTs with (8,8) chirality on top and (12,0) chirality on the bottom. Found at: <https://doi.org/10.1039/c9ee03059j>

Video 4.S2: The dissolution of PVDF and PVDF-TrFE in 5 mL acetone at 1/8 speed. 3D printed PVDF-TrFE film, 3D printed SWCNT/PVDF-TrFE (0.020 wt%) film, 3D printed SWCNT/PVDF-TrFE (0.200 wt%) film, melt-extruded and poled PVDF film, solvent-cast PVDF-TrFE film and PVDF-TrFE powder are shown. Found at: <https://doi.org/10.1039/c9ee03059j>

4.7.2 References

1. S. Lee and Y. Lim, Generating Power Enhancement of Flexible PVDF Generator by Incorporation of CNTs and Surface Treatment of PEDOT:PSS Electrodes, *Macromolecular Materials and Engineering*, **303**, 1700588 (2018).
2. H. M. Ning, N. Hu, T. Kamata, J. H. Qiu, X. Han, L. M. Zhou, C. Chang, Y. Liu, L. K. Wu, J. H. Qiu, H. L. Ji, W. X. Wang, Y. Zemba, S. Atobe, Y. Li, Alamusi and H. Fukunaga, Improved piezoelectric properties of poly(vinylidene fluoride) nanocomposites containing multi-walled carbon nanotubes, *Smart Materials and Structures*, **22**, 065011 (2013).
3. J. Kim, K. J. Loh and J. P. Lynch, Piezoelectric polymeric thin films tuned by carbon nanotube fillers, *SPIE Smart Structures and Materials + Nondestructive Evaluation and Health Monitoring*, San Diego, USA (2008).
4. Z. H. Liu, C. T. Pan, L. W. Lin and H. W. Lai, Piezoelectric properties of PVDF/MWCNT nanofiber using near-field electrospinning, *Sensors and Actuators A: Physical*, **193**, 13–24 (2013).
5. L. Wu, W. Yuan, T. Nakamura, S. Atobe, N. Hu, H. Fukunaga, C. Chang, Y. Zemba, Y. Li, T. Watanabe, Y. Liu, Alamusi, H. Ning, J. Li, H. Cui and Y. Zhang, Enhancement of PVDF's piezoelectricity by VGCF and MWNT, *Advanced Composite Materials*, **22**, 49–63 (2013).

5 POLARISATION LOCKING IN FLUOROPOLYMERS AT THE INTERFACE WITH MXENES

The information presented in this chapter has been submitted as:

Nick A. Shepelin, Peter C. Sherrell, Emmanuel N. Skountzos, Eirini Goudeli, Jizhen Zhang, Vanessa C. Lussini, Beenish Imtiaz, Ken Aldren S. Usman, Greg W. Dicinoski, Joseph G. Shapter, Joselito M. Razal and Amanda V. Ellis, Interfacial Piezoelectric Polarization Locking in Printable $\text{Ti}_3\text{C}_2\text{T}_x$ MXene-Fluoropolymer Composites, *submitted for publication to Nature Communications*.

5.1 Abstract

Piezoelectric fluoropolymers convert mechanical energy to electricity and are ideal for sustainably providing power to electronic devices. To convert mechanical energy, a net polarisation must be induced in the fluoropolymer, which is currently achieved *via* an energy intensive electrical poling process. Eliminating this process will enable the low-energy production of efficient energy harvesters. Here, by combining molecular dynamics simulations, piezoresponse force microscopy, and electrodynamic measurements, a hitherto unseen polarisation locking phenomena of PVDF-TrFE is revealed perpendicular to the basal plane of two-dimensional (2D) $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets. This polarisation locking, driven by strong electrostatic interactions enabled exceptional energy harvesting performance, with a measured piezoelectric charge coefficient, d_{33} , of -52.0 pC N^{-1} , significantly higher than electrically poled PVDF-TrFE (approximately -38 pC N^{-1}). This study provides a new fundamental and low energy input mechanism of poling fluoropolymers, which enables new levels of performance in electromechanical technologies.

5.2 Introduction

For dielectric materials exhibiting piezoelectricity, inducing polarisation through the alignment of the dipoles is paramount to couple mechanical and electrical energy.¹ To achieve dipole alignment, electrical poling is considered a necessary task in the post-processing of piezoelectric materials.² Electrical poling is energy intensive, with electric fields on the order of tens to hundreds of megavolts per meter commonly used.^{3–5} In fluoropolymers such as PVDF, a class of semicrystalline linear-chain polymers exhibiting a dipole moment between the hydrogen and fluorine moieties perpendicular to the carbon backbone, the poling process additionally requires high temperature conditions, above the T_C .^{3,4,6} The highly valorised commercial applications for piezoelectric materials, including precision motorised stages and inkjet printheads, utilise the converse piezoelectric effect,⁷ converting an applied electric field to discrete mechanical outputs.⁶ In contrast, emerging applications which utilise the direct piezoelectric effect⁷ to convert mechanical to electrical energy, the electrical poling process is a roadblock to commercialisation, requiring a higher energy input than can be harvested in the device lifespan. These emergent applications, including energy harvesting,^{3,8} robotic interfaces,⁹

piezocatalysis¹⁰ and piezophotonics,¹¹ require revisiting of the electrical poling process and examination of the pathways for inducing polarisation without high input energies.^{1,12}

Recent efforts have investigated alternative pathways to polarise fluoropolymers by tuning solvent composition¹³ or using nanofillers.^{8,14–18} The templating of polarisation has been realised by nanomaterial-fluoropolymer interactions from piezoelectric BTO NPs,^{14,15} reduced GO (rGO) nanosheets,^{16,17} hexagonal boron nitride (hBN) nanoflakes,¹⁸ and SWCNTs.⁸ However, the mechanism of dipole alignment arising from templating piezoelectric polymers with nanofillers remains poorly understood. Notably, the aforementioned nanomaterials provide limited scope to probe dipole moment alignment, as they possess piezoelectric properties such as BTO,¹⁴ or they alter the number of dipoles through changes in polymer conformation (e.g., by rGO or hBN).^{16,17} The single-walled carbon nanotube template has shown promise on a nanoscale,⁸ although the mechanism of polarisation templating was not elucidated.

To investigate the mechanism of polarisation templating, a nanofiller must have out-of-plane polarisability without out-of-plane piezoelectric properties.¹⁹ Further, it should be mechanically rigid with well-defined surface properties and functionality. To this end, the rapidly evolving class of MXenes is an excellent candidate to probe polarisation templating, with $\text{Ti}_3\text{C}_2\text{T}_x$ being the most well characterised MXene.^{20–27} Importantly, it has out-of-plane polarisability²¹ with symmetry perpendicular to the basal plane^{23,28} and is therefore hypothesised to not possess out-of-plane piezoelectric properties.

In this work, a deep mechanistic understanding is presented of how polarisation templating can be achieved in fluoropolymers from $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet templates. MD simulations are employed to probe the evolution of the polarisation of PVDF-TrFE in relation to the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet, revealing that the electrostatic interactions between the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet and the fluoropolymer are crucial to achieve effective induced local polarisation locking. This induced local polarisation locking is subsequently extended to a macroscale net polarisation using SEA 3D printing to impart enhanced shear alignment.^{8,29} The resultant composites show a d_{33} of -52.0 pC N^{-1} , higher than electrically poled PVDF-TrFE co-polymer (approximately -38 pC N^{-1}),^{3,30} which demonstrates the composites are fully polarised within the electroactive crystalline phase. The advancements herein enable

rapid, cost-effective, energy-efficient, and scalable production of fluoropolymers for emerging applications utilising the direct piezoelectric effect, including as a power supply for broad scale wearable electronics.

5.3 Experimental

5.3.1 Synthesis of $\text{Ti}_3\text{C}_2\text{T}_x$ dispersion

$\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets were synthesised by selectively etching aluminium atoms out of a Ti_3AlC_2 (MAX phase) parent ternary carbide precursor.⁴⁷ Briefly, 1 g of Ti_3AlC_2 powder (<40 μm , Carbon-Ukraine Ltd., Ukraine) was slowly added into hydrochloric acid (HCl, 20 mL, 9 M) containing lithium fluoride (LiF, 1.6 g, 99.5%). The dispersion was then stirred at room temperature for 24 h to etch out the aluminium from the Ti_3AlC_2 MAX phase. Afterwards, the dispersion was repeatedly centrifuged at 3500 r min^{-1} (10 min each time) and washed using ultra-pure water to raise the pH of the dispersion. When the pH approached 6, the $\text{Ti}_3\text{C}_2\text{T}_x$ suspension was probe sonicated for 10 min (2 s on and 2 s off) in an ice-bath under an argon gas flow. The dispersion was then centrifuged at $1,500\text{ r min}^{-1}$ for 30 min to remove any multi-layer $\text{Ti}_3\text{C}_2\text{T}_x$ and unetched Ti_3AlC_2 . The supernatant containing single-layer $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets was concentrated by further centrifuging at $8,000\text{ r min}^{-1}$ for 30 min and the sediment was dispersed into DMF. This process was repeated three times to prepare dispersions of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets in DMF (at 4.4 mg mL^{-1}).

5.3.2 Molecular dynamics simulations

All-atom MD simulations were used to elucidate the interactions between PVDF-TrFE co-polymer films and the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate. Each PVDF-TrFE chain contained 21 VDF and 9 TrFE monomers, corresponding to molar concentrations of 70 mol% VDF and 30 mol% TrFE, similar to the work outlined in Chapter 4.⁸ The co-polymer chains were introduced at 2 nm from the substrate having an initial film density of 1.3 g cm^{-3} using the materials and processes simulations (MAPS) 4.3 platform (Scienomics). The $\text{Ti}_3\text{C}_2\text{T}_x$ monolayer nanosheet-PVDF-TrFE co-polymer film interactions were simulated in the NVT (constant number of atoms, volume, and temperature) ensemble at 298.15 K in a simulation box with periodic boundary conditions. All subsequent simulations were

performed on the University of Melbourne's High-Performance Computing system using the large-scale atomic/molecular massively parallel simulator (LAMMPS).⁴⁸ The equations of motion were integrated using the velocity-Verlet algorithm⁴⁹ with a time step of 1 fs using the transferable, extensible, accurate and modular force field (TEAM-FF) for both the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet and the PVDF-TrFE co-polymer. Partial charges were assigned to each atom of the PVDF-TrFE using the bond increments method, while the charges for the atoms of the $\text{Ti}_3\text{C}_2\text{T}_x$ surface were adopted from first-principle calculations.⁵⁰ The interatomic potential was validated with the density (ρ) of bulk PVDF-TrFE melts of various molecular weights at 230 °C, converging to a plateau at approximately 1.42 g cm^{-3} (Supplementary Figure 5.S4). The obtained density agreed well (deviation <5%) with the experimental value ($\rho_{\text{bulk}} = 1.49 \text{ g cm}^{-3}$) of the bulk PVDF-TrFE co-polymer, validating the TEAM-FF interatomic potential used in the present MD simulations. It should be mentioned that in these simulations the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate was kept frozen, interacting with the atoms of the PVDF-TrFE co-polymer chains only *via* van der Waals and electrostatic interactions.

To quantify the strength of the interaction between the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate and a single PVDF-TrFE chain, individual NVT MD simulations were carried out by applying a constant force normal and opposite to the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet surface to each atom of the PVDF-TrFE chain and gradually increasing it from 0.00 pN to 6.95 pN with a step of 0.695 pN. At each one of these simulations, the position of the co-polymer chain is monitored and recorded at which applied force the chain was fully desorbed from the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet surface.

5.3.3 Extrusion printing ink preparation

PVDF-TrFE co-polymer powder (75 mol% VDF and 25 mol% TrFE, M_w at 420 kDa, density at 1.49 g cm^{-3} , Solvay, Belgium) and acetone (AR grade, Chem-Supply Pty Ltd, Australia) were used without further purification. The stock $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet dispersion ($\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets in DMF at 4.4 mg mL^{-1}) was diluted in acetone to provide solutions with $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet concentrations of 0.00 mg mL^{-1} , 0.10 mg mL^{-1} , 0.52 mg mL^{-1} , 1.05 mg mL^{-1} and 2.61 mg mL^{-1} . PVDF-TrFE co-polymer powder was added to the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet/acetone solutions at 40 wt% relative to acetone and stirred at 23 °C until homogeneous inks formed containing $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet concentrations relative to

PVDF-TrFE at 0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt% and 0.50 wt%, respectively. The PVDF-TrFE co-polymer concentration optimisation in acetone is presented in the Supplementary Information.

5.3.4 Extrusion printing and PEG device fabrication

The $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE composite inks (0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt% and 0.50 wt%) were transferred into 3D printing dispensing barrels (30 mL, Optimum, Nordson EFD, United States), then sealed and stored at $-5\text{ }^\circ\text{C}$ prior to printing. A 3D printer (Bioplotter 3D, Envisiontec, Germany) was preset to print a single-layer square film (3 cm x 3 cm) onto a clean glass plate substrate using a raster pattern with a line spacing of $350\text{ }\mu\text{m}$. During printing, the cartridge containing the ink was kept at $5\text{ }^\circ\text{C}$ and the glass plate substrate at $23\text{ }^\circ\text{C}$, the xy speed was 30 mm s^{-1} and extrusion pressure was 1.7 bar through a tapered nozzle with an internal diameter of $200\text{ }\mu\text{m}$ (SmoothFlow, Nordson EFD, United States). After printing the films were placed in a vacuum oven set at $23\text{ }^\circ\text{C}$ for 20 min to ensure the complete extraction of the solvent.

To fabricate the PEGs, the SEA extrusion printed films were removed from the glass plate, and coated with a seeding layer of chromium (Cr) and an electrode layer of gold (Au) (total thickness of 60 nm) *via* sputter deposition (Nanochrome I, Intlvac Thin Film Corporation, USA) through a shadow mask on both sides of the film with a total overlapping electrode area of 2.4 cm^2 . Wires (FLEXI-E 0.15, Stäubli Electrical Connectors AG, Switzerland) were soldered to copper (Cu) foil with conductive adhesive (1181, 3M, United States) and adhered to each side of the printed film without overlap, ensuring strong contact between the Cu tape and Cr/Au coating. The printed films were finally encapsulated in insulating Kapton (polyimide) adhesive on both surfaces to complete the PEGs. The extended fabrication details are presented in the Supplementary Information.

5.3.5 Materials characterisation

5.3.5.1 Rheology

The rheological characterisation of the pristine PVDF-TrFE co-polymer and the $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE (0.20 wt%) inks in acetone was undertaken using a strain-controlled

rheometer (MCR 702, Anton Paar, Austria) with cone-plate geometry at 5 °C. The gap was set at 102 μm , with a cone diameter of 25 mm and an angle of 2°. Frequency and shear strain measurements were undertaken in oscillatory mode with an upwards logarithmic ramp of the frequency under fixed shear strain at 1% and shear strain under fixed frequency at 1 Hz, respectively. The printing simulation measurement was performed in oscillatory mode with the frequency fixed at 1 Hz and controlled shear stress. Initially, 1 Pa shear stress was applied to the inks for 50 s to demonstrate the properties of the inks at rest. Subsequently, 5 kPa shear stress was applied to the sample for 70 s, followed by 1 Pa for 70 s to demonstrate recovery of the ink, repeated for an additional high shear stress cycle.

5.3.5.2 Helium ion microscopy

The surface of the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) film was imaged using HIM (Orion NanoFab, Zeiss, Germany) in order to determine the orientation and distribution of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets in the PVDF-TrFE co-polymer. The micrographs were obtained with a 100 μm field of view using a dwell time of 0.5 μs and accelerating voltage of 30 kV.

5.3.5.3 Tensile testing

Tensile tests were performed on a mechanical tester (Electroforce 5500, Bose, United States). The $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ SEA extrusion printed films (0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt% and 0.50 wt%) were cut into strips (27 mm x 5 mm) and mounted in the grips, with an exposed length at 5 mm. The samples, with average thickness at 45 μm , were extended at 0.01 mm s^{-1} up to a maximum of 11.4 mm.

5.3.5.4 Crystallinity

The crystallinity of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ SEA extrusion printed films (0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt% and 0.50 wt%) was obtained using DSC (STA 8000, Perkin Elmer, United States). The samples were placed in a ceramic crucible at 25 °C and heated at 10 °C min^{-1} to 200 °C under a nitrogen gas flow (20 mL min^{-1}). The crystallinity calculation methods are presented in the Supplementary Information.

5.3.5.5 Vibrational spectroscopy

The distribution of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets in the PVDF-TrFE co-polymer, along with the $\beta:\gamma$ intensity ratio was confirmed using Raman confocal microscopy (inVia, Renishaw, United Kingdom), equipped with a 532 nm laser, an 1,800 line mm^{-1} grating and a 50x objective. Typical maps were obtained for a surface area of 20 μm length and width, at a pixel density of 1 px μm^{-1} . Each pixel of the map consisted of a spectrum, centred at 1,300 cm^{-1} and obtained with an exposure time of 0.15 s accumulated over 1,000 scans.

5.3.5.6 Piezoresponse force microscopy

Nanoscale polarisation of the $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE SEA extrusion printed films (0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt% and 0.50 wt%) was measured using an Asylum Research Cypher ES atomic force microscope. The data was obtained at 23 °C in air using conductive platinum cantilevers (12PT400B, Rocky Mountain Nanotechnology, United States) with spring constant at 0.3 N m^{-1} and tip radius below 20 nm. The scans were undertaken on an area of 5 μm x 5 μm at 256 pixels per line, corresponding to approximately 20 nm per pixel. The PFM was carried out in contact lithography, whereby a potential was applied by the tip to the sample following a pre-defined pattern, observing the amplitude and phase changes relative to the unbiased areas. The applied potential ranged between -20 V and +20 V in increments of 2 V on each scan line at a scan rate of 0.2 Hz, with each voltage step applied to a total area of 0.195 μm in the x direction and 3.906 μm in the y direction. The resultant piezoelectric amplitude and phase values, collected during the application of voltage, were then correlated to the corresponding voltage for each pixel of the scan. The on-voltage measurements were collected at voltages below the electrical poling voltage for the films in order to measure the effective d_{33} from the resultant strain. Extended details of the PFM technique are presented in the Supplementary Information.

5.3.5.7 Macroscale electromechanical quantification

Macroscale polarisation of the $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE PEGs (0.00 wt% and 0.50 wt%) was measured *via* the input of cyclic compressive force and measurement of the resulting surface charges. The force was applied by a mechanical tester (Electroforce 5500, Bose, United States) to the active area of the PEG using a sinusoidal waveform with frequency at 2 Hz, the minimum force set at 5 N and maximum force set at 15 N, corresponding to

ΔF at 10 N and stress at 25 kPa. The surface charge was measured with a charge amplifier (Nexus 2692, Brüel & Kjær, Denmark) and recorded through a data acquisition system (9223, National Instruments, United States). The cycling stability testing was undertaken at 10 Hz. The extended data and discussion are presented in the Supplementary Information.

5.4 Results and discussion

5.4.1 Preparation of $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE composite SEA 3D printing inks

$\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets are a 2D material with the point group of P63/mmc, which is symmetric (and therefore non-piezoelectric) in the z-direction (i.e., no out-of-plane polarisation).^{23,28} The $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets were exfoliated from a Ti_3AlC_2 MAX phase (Supplementary Figure 5.S1a) using the minimally intensive layer delamination (MILD) exfoliation method with LiF and HCl, exhibiting an average lateral size of 310 nm (Supplementary Figure 5.S1b, c) and a thickness of ~ 1 nm (Supplementary Figure 5.S1d).^{24,27} This soft exfoliation technique resulted in a dominant OH surface termination (T_x), with trace amounts of F and O functionality (Supplementary Figure 5.S1e-g).^{25,26}

Composites of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and PVDF-TrFE were prepared as inks by a simple mixing process, whereby a small volume of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets in DMF were added to a PVDF-TrFE (40 wt%) solution in acetone and homogenised *via* stirring at room temperature. Concentrations between 0.00 wt% and 0.50 wt% $\text{Ti}_3\text{C}_2\text{T}_x$, relative to the mass of PVDF-TrFE, were produced as viscous inks (Supplementary Figure 5.S2). Interestingly, all inks showed sustained stability, with retention of their initial colour and flow properties for up to 5 months post-mixing (Supplementary Figure 5.S3). This stability is primarily due to the retardation of either/or the surface oxidation and agglomeration of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, that can typically occur.²⁶

5.4.2 MD simulations of the $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE interface

To understand the interface between the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and the PVDF-TrFE co-polymer, MD calculations were performed using the periodic lattice of $\text{Ti}_3\text{C}_2\text{T}_x$ (where $\text{T}_x = \text{OH}$) and 70 ‘mer’ chains of PVDF-TrFE (Figure 5.1a, left). This was then compared to a

periodic lattice of graphene (Figure 5.1b, left) with an equivalent polymer film. These simulations revealed an extremely strong electrostatic interaction between the PVDF-TrFE chains and the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet, requiring ~ 4.17 pN of force to desorb one PVDF-TrFE chain from the $\text{Ti}_3\text{C}_2\text{T}_x$. This strong interaction limits the motion of the polymer (Supplementary Video 5.S1), with chains adjacent to the surface elongated and unable to move, forming a tightly packed structure (Figure 5.1a) with density of approximately 2 g cm^{-3} (Supplementary Figure 5.S5). Over 4 ns, more chains preferentially fill the free space on the $\text{Ti}_3\text{C}_2\text{T}_x$ lattice, leading to the decrease in the density of the second layer. Interestingly, there is no statistical difference between the H and F positions on the PVDF-TrFE chains relative to the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet (Supplementary Figure 5.S6, shown for a film of 14 chains). There is a clear difference in the proportion of *trans* (63%) and *gauche* (37%) conformations within the PVDF-TrFE chains at the interface of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet (Supplementary Figure 5.S7, shown for a film of 14 chains). A similar trend in the *trans* (65%) and *gauche* (35%) conformation distributions is observed in a film containing 70 PVDF-TrFE co-polymer chains (Supplementary Figure 5.S8). This ratio of bond conformations suggests the inhibition of local electroactive phase within the fluoropolymer.

The orientation of the net dipole moment vector of the PVDF-TrFE co-polymer film was compared to that of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet, quantified through the angle θ (Figure 5.1a, right). The spatial and temporal evolution of θ against the separation (s) reveals the fluoropolymer layers adjacent to the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet (within $5 \text{ \AA}$ from the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet surface, directly experiencing the strong electrostatic attraction) have a preferential orientation parallel to the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet (Figure 5.1c). However, with increasing separation from the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet, this PVDF-TrFE co-polymer net dipole moment becomes increasingly perpendicular to the basal plane of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate. Interestingly, thicker co-polymer films (within $39 \text{ \AA}$ from the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet surface) exhibit an extremely tight distribution of the polarisation orientation (Figure 5.1c), which remains perpendicular to the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet for the entire simulation (Supplementary Figure 5.S9 and Supplementary Video 5.S1). These results show that on a local scale, a net polarisation of the PVDF-TrFE co-polymer is formed perpendicular to the basal plane of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet. Given that the electrostatic screening length in 2D materials is between $10 \text{ \AA}$ and $100 \text{ \AA}$, and considering the strength of the electrostatic interaction observed between the PVDF-TrFE co-polymer and the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet, it is highly probable that this polarisation locking occurs as a consequence of electrostatic forces.^{19,31}

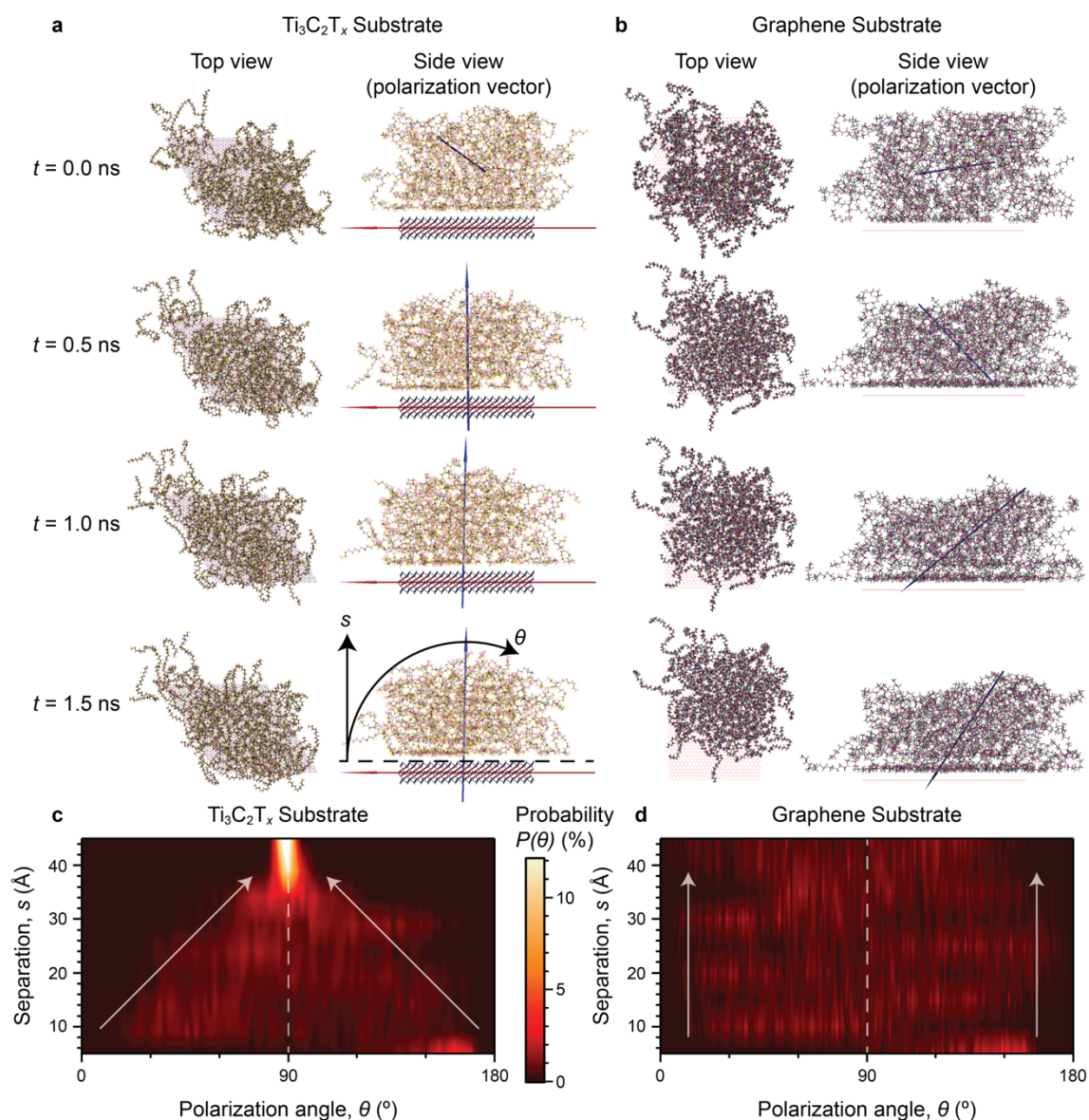


Figure 5.1: Comparative MD simulations of the PVDF-TrFE co-polymer film polarisation on $\text{Ti}_3\text{C}_2\text{T}_x$ and graphene substrates. (a, b) The top view (left column) and side view (right column) snapshots at $t = 0$ ns, 0.5 ns, 1 ns and 1.5 ns, with the resultant dipole moment vectors (right column) of the PVDF-TrFE co-polymer film (blue arrow) and the (a) $\text{Ti}_3\text{C}_2\text{T}_x$ substrate or (b) graphene substrate. The annotated s and θ in a represent the separation of the fluoropolymer from the substrate and the PVDF-TrFE co-polymer dipole angle relative to the substrate, respectively. (c, d) Probability distributions of the angle (θ) between the dipole moment vector of the PVDF-TrFE co-polymer film layers and the (c) $\text{Ti}_3\text{C}_2\text{T}_x$ or (d) graphene substrates as a function of separation (s), as calculated from the equilibrated region of the obtained MD simulation.

For comparison, the net dipole moment vector of the same PVDF-TrFE co-polymer film on a graphene sheet was investigated under identical simulation conditions (Figure 5.1b, right). In contrast to the fluoropolymer film on $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet, the fluoropolymer film on graphene is able to migrate on the periodic lattice easily and requires a significantly lower force (~ 2.78 pN) to detach a single fluoropolymer chain from the lattice, indicating a weaker interaction between the components (Supplementary Video 5.S1). Further, the net dipole moment vector of the fluoropolymer film always exhibits random orientations with respect to the graphene surface, regardless of the layer thickness (Figure 5.1b, right, Figure 5.1d).

The MD simulations show a clear and strong binding interaction between the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet and the PVDF-TrFE co-polymer chains, driven by electrostatic interactions. This binding results in the subsequent self-assembly of the fluoropolymer film, oriented in such a way as to tightly lock the polarisation of the PVDF-TrFE perpendicular to the $\text{Ti}_3\text{C}_2\text{T}_x$ basal plane, providing guidance towards an experimental tool for self-assembly driven polarisation in bulk fluoropolymer materials.

5.4.3 Towards printing and net polarisation

For the translation of this fundamental understanding of the induced local net polarisation, developed using MD simulations into PEGs, a careful selection of the $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE composite processing route is required. SEA 3D printing can enable shear alignment of both nanofillers^{27,29} and polymer chains,^{8,32} parallel to the direction of printing. Given the formation of induced local polarisation, perpendicular to the basal plane of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, this parallel alignment is hypothesised to give out-of-plane piezoelectricity without the need for electric poling.

To understand the interaction between the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and the PVDF-TrFE co-polymer in solution, as well as assess the suitability for relevant solution processing routes including extrusion printing, the shear strain (γ_s) response of the $\text{Ti}_3\text{C}_2\text{T}_x$ loaded PVDF-TrFE (40 wt%) inks was studied (Figure 5.2a). The extended rheological characterisation of the pristine PVDF-TrFE ink is presented in the Supplementary Information (Supplementary Figure 5.S10, Supplementary Figure 5.S11 and Supplementary Figure 5.S12).

Both the pristine PVDF-TrFE co-polymer and the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ inks demonstrated exceptional flow properties for printing. This was clearly demonstrated by the storage modulus (G') being greater than the loss modulus (G'') at low γ_s , indicating the ability of the ink to retain a physical shape. With increasing γ_s , analogous to the strain applied during extrusion printing, both inks exhibited yielding and liquid-like behaviour, indicated by the cross-over of G' and G'' , and the subsequent region with $G' < G''$. Similarly, the angular frequency (ω) response (Figure 5.2b) confirmed the formation of a strong physical gel in both the pristine PVDF-TrFE co-polymer and the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ inks, highly desirable for extrusion printing.³³ A weakening of the PVDF-TrFE/acetone interaction was apparent through the presence of a larger shoulder at $\omega \approx 0.15 \text{ rad s}^{-1}$ in the G'' of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ ink. The weakening of the physical gel was attributed to a strong interaction between the PVDF-TrFE co-polymer and the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. However, the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ ink, nonetheless, exhibited solid-like behaviour ($G' > G''$) at ω as low as 0.10 rad s^{-1} . The PVDF-TrFE co-polymer ink was subjected to consecutive small amplitude oscillatory shear (SAOS, 1 Pa) and large amplitude oscillatory shear (LAOS, 5 kPa) cycling at 1 Hz to replicate the shear stress of extrusion printing, shown in Figure 5.2c.³⁴ It was found to consistently flow under 5 kPa shear stress (σ_s), with immediate G'' recovery and $>60\%$ G' recovery after 70 s at $\sigma_s = 1 \text{ Pa}$, retaining similar characteristics with $>85\%$ G' recovery on the second σ_s cycle. This testing method showed the ability of the PVDF-TrFE co-polymer and $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ inks to print continuous and complex structures without void formation or defects in the resultant structures.

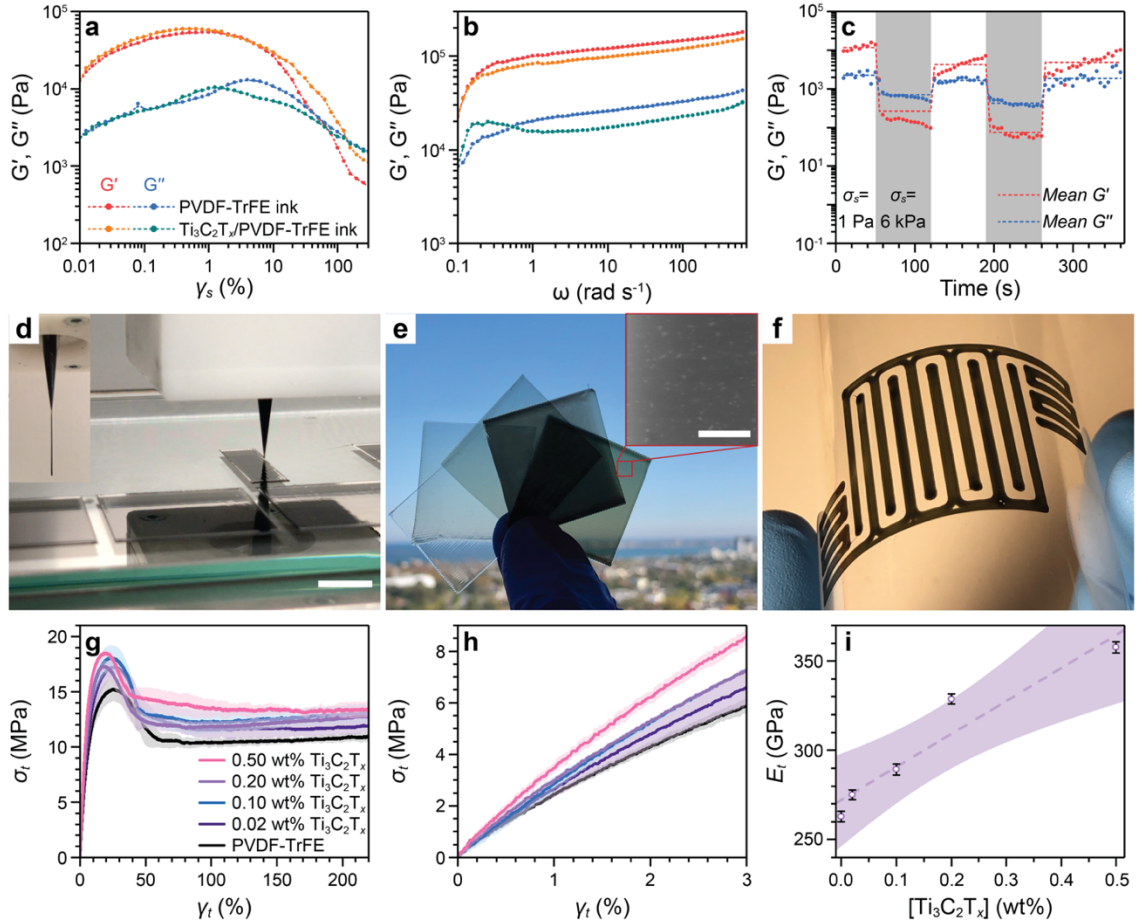


Figure 5.2: SEA extrusion printing of strengthened $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ films. (a) Oscillatory γ_s sweep ($\omega = 1$ Hz) and (b) oscillatory ω sweep ($\gamma_s = 1\%$) of the 40 wt% PVDF-TrFE ink with and without 0.20 wt% $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. (c) The temporal evolution of the G' and G'' during σ_s cycling between 1 Pa (white regions, representing the stationary state) and 5 kPa (grey regions, representing printing stress). (d) Photograph showing the SEA extrusion printing process for the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) ink, scale bar 10 mm. Inset shows a self-supporting single filament. (e) Photograph of the free-standing $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ films at various $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet loadings (from left to right: 0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt%, 0.50 wt%). Inset shows HIM image of $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) film surface, demonstrating the distribution of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets near the surface of the film. Scale bar represents 40 μm . (f) Photograph demonstrating an interdigitated structure of 0.50 wt% $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ composite printed onto a flexible poly(ethylene terephthalate) (PET) substrate. (g) Tensile strain (γ_t)-stress (σ_t) profiles of the printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ films (shaded region shows the error from replicates). (h) The elastic region of (g). (i) The Young's modulus (E_t) obtained from (h) (overlay represents a 95% confidence interval).

5.4.4 SEA extrusion printed and mechanically robust $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ composite films

With a clear understanding of the rheological performance of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ inks, as well as evidence of weakening of the PVDF-TrFE/acetone interaction due to the strong $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ interface, thin films were prepared for studies of the macroscale polarisation and energy harvesting properties.

$\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ inks at various $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet loadings (0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt% 0.50 wt%) were SEA extrusion printed as single-layer thin films (Figure 5.2d) through a nozzle (internal diameter (ID) = 200 μm) onto a clean glass plate and then subsequently removed to form free-standing films (Figure 5.2e). The distribution of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets was homogeneous in the resultant films with the basal plane appearing aligned parallel to the printing direction (Figure 5.2e, inset), as expected from an extrusion process. This SEA extrusion printing process could be further extended to print complex shapes on flexible substrates, such as poly(ethylene terephthalate) (PET), as shown in Figure 5.2f. The versatility of the SEA extrusion printing technique enables the deposition of multi-layer systems,³² on conformal³⁵ and moving substrates,³⁶ allowing the resultant PEGs to be deployed in broad and highly specialised applications such as in the point-of-care printing of *in-vivo* energy harvesters.^{37,38}

The mechanical properties of the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt% 0.50 wt%) composite films were studied *via* tensile extension (Figure 5.2g). All films were shown to yield at $\gamma_t < 50\%$ and did not break at $\gamma_t = 220\%$ (displacement limit of the instrument), confirming the high ductility of all tested materials. Subsequent elongation at uncontrolled force by hand showed a maximum $\gamma_t > 1,000\%$ prior to failure (Supplementary Figure 5.S13). The Young's modulus (E_t), obtained from the low- γ_t region (Figure 5.2h), increased linearly with an increase in $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet loadings in the PVDF-TrFE co-polymer up to 358 MPa at a $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet loading of 0.5 wt% (Figure 5.2i). This linear increase showed that there is a homogenous dispersion of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets through the fluoropolymer at all concentrations, as aggregation would lead to poor load transfer between the components. The E_t of the

pristine PVDF-TrFE co-polymer film (263 MPa) was comparable to literature values for 3D printed PVDF (419 MPa), although lower than other processing routes.³⁹

5.4.5 PVDF-TrFE phase dependence in $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE composites

The semi-crystalline PVDF-TrFE co-polymer exists in three favourable conformations, the symmetric and therefore non-electroactive α phase, the semi-polar and moderately electroactive γ phase, and the polar and highly electroactive β phase.³ These phases arise from the presence and order of *trans* (T) and *gauche* (G) bond conformations, whereby the α phase consists of alternating conformations (TGTG'), the γ phase is an intermediate (TTTG) and the β phase is all-*trans* (TTTT).⁴ Inherently, changes in the crystallinity and phase composition affect the maximum polarisation of fluoropolymers. Understanding how these parameters change is crucial to elucidating a mechanism for enhanced piezoelectric response. Ultimately, entropy within the polymer during deposition results in negligible polarisation of the polymer films, thus requiring electrical poling to align the dipole moment vectors.⁸ To achieve this understanding of crystallinity and phase composition, thorough phase characterisation (DSC and Raman confocal microscopy) was performed (Figure 5.3). These tools enable the determination of both the total crystallinity of the fluoropolymer, and the relative proportion of β and γ phases, enabling the exhaustive understanding of the material for the assessment of energy harvesting capabilities.

Raman spectroscopy showed a clear increase in the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet spectrum vibrational modes ($150\text{ cm}^{-1} - 740\text{ cm}^{-1}$) with increasing concentration (Figure 5.3a). An initial decrease was observed in the intensity ratio I_β/I_γ (β phase at 840 cm^{-1} and γ phase at 811 cm^{-1}) from 2.4 for the pristine PVDF-TrFE co-polymer to 2.2 for the 0.02 wt% $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE composite, before an increase to 2.5 for the 0.5 wt% $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE composite (Figure 5.3b).³

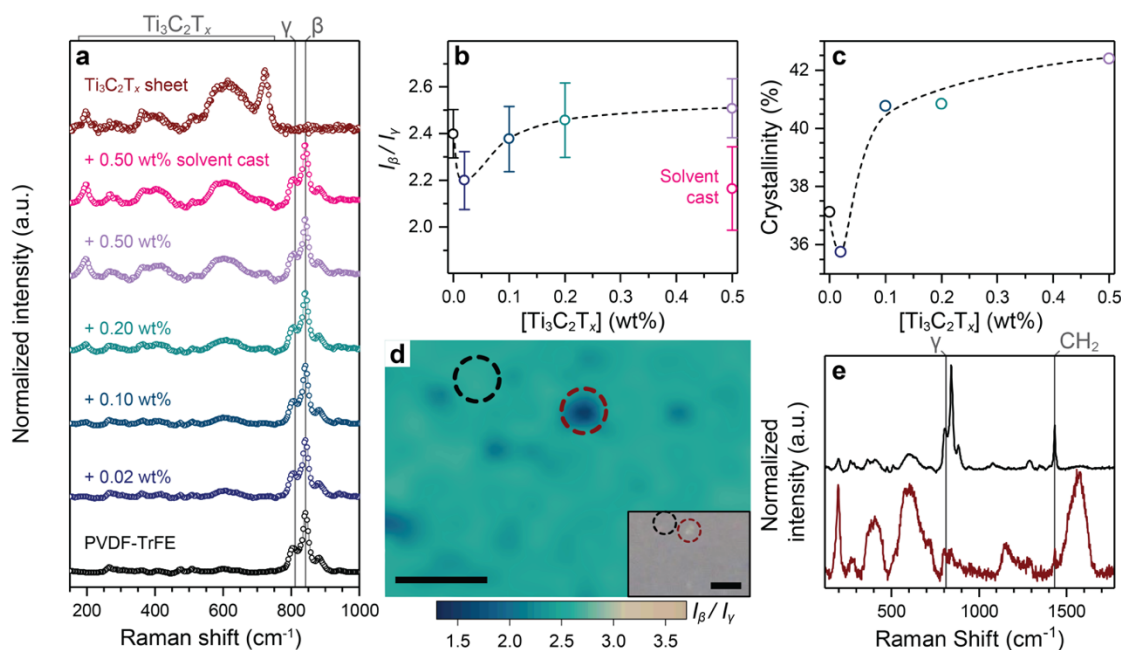


Figure 5.3: Material characteristics of $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ films. (a) Raman spectra of $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ composites (at various $\text{Ti}_3\text{C}_2\text{T}_x$ loadings) and $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. (b) The β/γ phase ratio, I_β/I_γ , calculated from the intensities of the β phase (840 cm^{-1}) and γ phase (811 cm^{-1}) from Raman confocal mapping (Supplementary Figure 5.S15). The dashed line represents a visual guide. (c) The effect of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet loading on the PVDF-TrFE co-polymer crystallinity, as measured by DSC. The dashed line is a visual guide (d) The Raman I_β/I_γ map of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) film, where the dark point corresponds to a large $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet at the film surface (red circle). The inset shows a confocal microscope image of the area analysed using Raman confocal mapping. Both scale bars represent $5\text{ }\mu\text{m}$. (e) The representative Raman spectra for the area designated by the black circle and the red circle in d, showing the clear inhibition of β phase locally at the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet surface.

DSC revealed that small $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet loadings (0.02 wt%) resulted in a notable decrease in the overall crystallinity of the PVDF-TrFE co-polymer matrix (Figure 5.3c).

Confocal Raman mapping was also performed (Figure 5.3d, e) to probe the decrease in both the I_β/I_γ and the crystallinity, as shown by the average Raman spectra (Figure 5.3b) and DSC (Figure 5.3c), respectively. Notably, the analysis of these maps found a clear difference in the I_β/I_γ between the bulk PVDF-TrFE co-polymer (Figure 5.3d, black

circle) and the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ interface (Figure 5.3d, red circle), decreasing from 2.65 to 1.45, respectively. The individual spectra for these regions (Figure 5.3e) showed a disproportionate suppression of the β phase peak intensity at the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet surface, while the intensity ratio between γ and the CH_2 stretch (1432 cm^{-1}) maintains the same ratio.⁴⁰ Importantly, these findings suggest a local inhibition of the electroactive β phase crystallisation at the interface between the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet and the PVDF-TrFE co-polymer (Supplementary Figure 5.S7), as well as the local densification of the fluoropolymer film (Supplementary Figure 5.S5).

Thus, the decrease in the crystallinity at 0.02 wt% $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (Figure 5.3c) was attributed to a lower fraction of the electroactive β phase in the PVDF-TrFE co-polymer forming directly on the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet surface.

Given the understanding developed through MD simulations (Figure 5.1), the fluoropolymer densification was hypothesised to occur in solution prior to printing, rather than during printing. There are two factors to consider here: (1) the effect of shear alignment on the fluoropolymer itself,^{32,41} and (2) the effect of shear on orienting the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets.^{27,29} At 0.02 wt% $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, it is proposed that the decrease in the β phase at the PVDF-TrFE/ $\text{Ti}_3\text{C}_2\text{T}_x$ interface, coupled to minimal shear orientation of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet, has a stronger negative effect compared to shear aligning of the fluoropolymer molecules. For higher $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet loadings, extruded through the nozzle, a greater shear alignment phenomenon is observed within the material, resulting in a very slight net increase in β phase and overall crystallinity. This hypothesis is supported by the Raman spectra of the solvent cast 0.50 wt% $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ composite film (Figure 5.3b, Supplementary Figure 5.S15f), which does not undergo shear induced crystallisation and has a I_β/I_γ comparable to the printed 0.02 wt% $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ composite film.

5.4.6 Energy harvesting of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ composite films

Prior to printing, the strong electrostatic binding interactions between the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and the PVDF-TrFE co-polymer chains, as described by the MD simulations, enables the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet to remain sterically stabilised in the inks, without

aggregation (Supplementary Figure 5.S3). This lack of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet aggregation enables the enhancement in the E_t (Figure 5.2i). To understand how this induced local polarisation locking translates to bulk and macroscopic energy harvesting, both PFM and bulk electromechanical testing were performed.

PFM was carried out by applying a bias between -20 V and +20 V to a conductive platinum (Pt) cantilever in contact with the $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE films (at various $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet loadings) and the subsequent local changes in thickness (arising from the expansion or contraction of the unit cell in the polarised electroactive phases of the PVDF-TrFE co-polymer) were measured.⁶ At voltages below the poling electric field ($<50 \text{ MV m}^{-1}$), piezoelectric materials exhibit a strong correlation between the induced strain (γ_3) and the piezoelectric charge coefficient (d_{33}).^{3,4} In PFM, the correlation is qualitative⁴² and the $d_{33} = A \cos(\varphi) / Q_f V$, where A is the amplitude, φ is the phase, Q_f is the Q-factor of the cantilever and V is the applied bias.⁸ The extended discussion surrounding the PFM is presented in the Supplementary Information (Supplementary Figure 5.S20, Supplementary Figure 5.S22 and Supplementary Figure 5.S23).

To confirm the lack of piezoelectric contribution arising in the z-direction of the P63/mmc point group of the $\text{Ti}_3\text{C}_2\text{T}_x$, a $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet on a gold-coated silicon (Au@Si) substrate was probed using DART-PFM, whereby a constant bias (1 V) was applied to the cantilever (Supplementary Figure 5.S20). The $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet, approximately 300 nm in the lateral dimension, was visible topographically, however no discernible changes were observed in the A and φ traces between the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet and the underlying substrate (Figure 5.4a). Therefore, the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet exhibited no observable out-of-plane piezoelectric effect (perpendicular to the nanosheet basal plane).

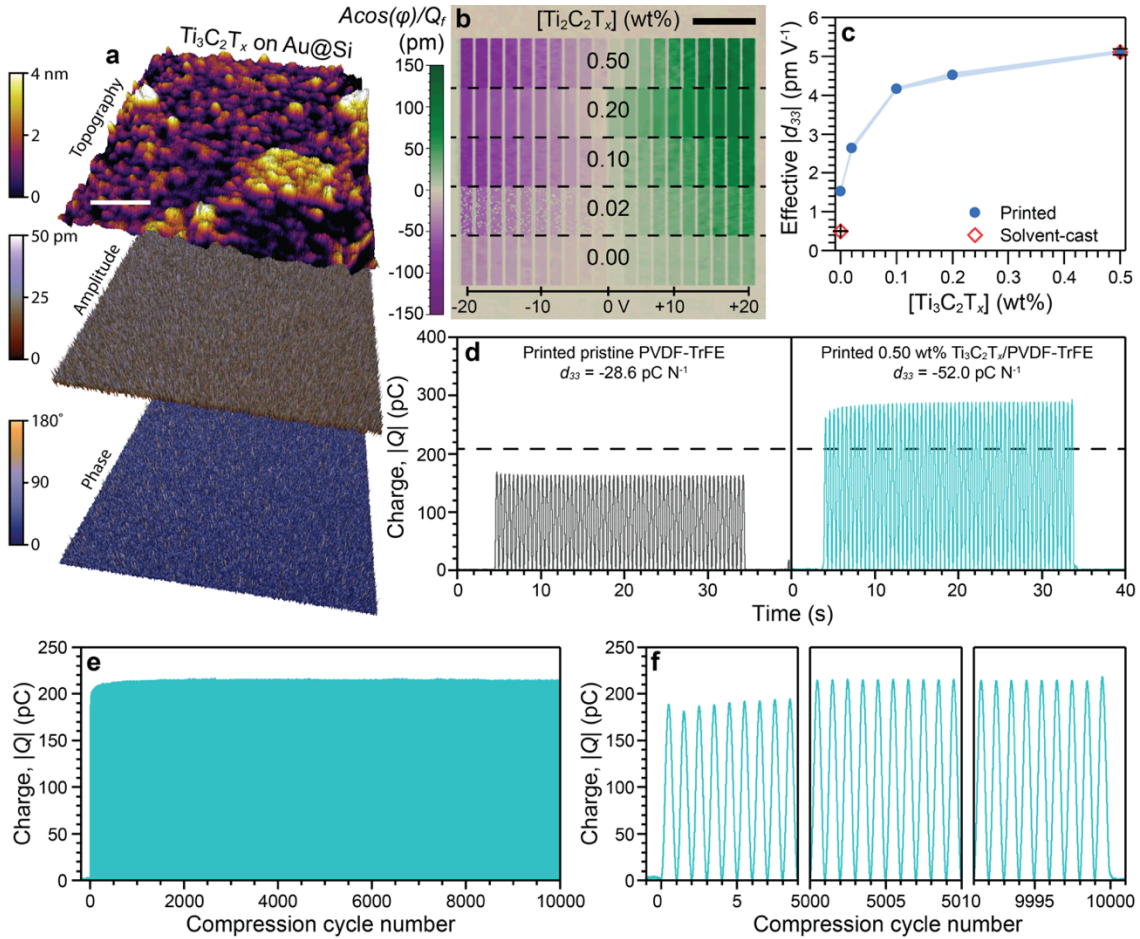


Figure 5.4: Polarisation and energy harvesting of $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ composites. (a) DART-PFM of a $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet on a gold-coated silicon (Au@Si) substrate, showing the topography (top), piezoelectric amplitude (middle) and piezoelectric phase (bottom) traces. Scale bar represents 200 nm. (b) PFM of $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt% and 0.50 wt%) SEA extrusion printed films, showing the piezoresponse ($A\cos(\varphi)/Q_f$) under an applied voltage between -20 V and +20 V. Scale bar represents 1 μm . (c) The effective piezoelectric charge coefficient (d_{33}) calculated from the PFM data, including for solvent-cast PVDF-TrFE and $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) films as controls. (d-f) The macroscale energy harvesting characterisation of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.00 wt% and 0.50 wt%) SEA extrusion printed PEGs with input force (ΔF) at 10 N following a sinusoidal input signal. (d) The generated surface charge as a function of time for 60 compression cycles at 2 Hz. The horizontal dashed line represents the charge generated from completely polarised ($d_{33} = -38 \text{ pC N}^{-1}$) PVDF-TrFE co-polymer for a PEG with similar dimensions. (e) The stability of the generated charge as a function of cycle count over 10,000 cycles for the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) PEG

at 10 Hz and (f) the expanded initial, middle and end regions of the charge stability data in (e) showing 1 s of data (10 cycles) in each panel.

To measure the d_{33} of the composite $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ films, a variable bias was applied, with the spatial map of the applied bias shown in Supplementary Figure 5.S21. The representative PFM response for the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt% and 0.50 wt%) films is shown in Figure 5.4b (extended data presented in Supplementary Figure 5.S22, and Supplementary Figure 5.S23). The amplitude, corrected for the directionality of strain and the Q-factor of the cantilever ($A\cos(\phi)/Q_f$), exhibited a maximum at -41.6 pm for the pristine PVDF-TrFE co-polymer film at -20 V (Supplementary Figure 5.S24), confirming a spatial alignment effect arising from shear stresses during the extrusion printing process, as previously reported.^{8,32} The $A\cos(\phi)/Q_f$ value was shown to increase sharply with an increase in $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet loading within the PVDF-TrFE co-polymer (Supplementary Figure 5.S24). A substantial increase was observed in the maximum $A\cos(\phi)/Q_f$ at -20 V for the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) SEA extrusion printed film (-182.3 pm), compared to the pristine PVDF-TrFE co-polymer film (-41.6 pm), indicating an intensified piezoelectric response upon the addition of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets.

The measured d_{33} as a function of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet concentration in the printed films is shown in Figure 5.4c. The effective d_{33} for the pristine PVDF-TrFE co-polymer SEA extrusion printed film was -1.53 pm V^{-1} , 207% higher than that of the solvent-cast PVDF-TrFE co-polymer ($d_{33} = -0.50 \text{ pm V}^{-1}$). These results are consistent with reports on solvent-cast fluoropolymer films and shear stress-induced partial polarisation.^{8,32,41,43,44} The d_{33} of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) SEA extrusion printed film increased up to a maximum at -5.11 pm V^{-1} , an ultimate improvement of 234% over the printed pristine PVDF-TrFE co-polymer film and 926% over the solvent-cast PVDF-TrFE co-polymer film.

Unexpectedly, considering the lower I_β/I_γ ratio (Figure 5.3b) and net crystallinity (Figure 5.3c) of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.02 wt%) film, an increase in the d_{33} of 72% relative to the pristine PVDF-TrFE co-polymer film was observed (Figure 5.4c). This would suggest that even at low $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet loadings there is a sufficient increase in induced

polarisation locking of the PVDF-TrFE co-polymer to offset the net decrease in the electroactive phase within the composite.

Surprisingly, the effective d_{33} for the solvent-cast $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) film matched that of the extrusion printed film with the same $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet loading (-5.11 pm V^{-1}), suggesting the effect of induced polarisation locking from the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet surface is favoured over the shear-induced polarisation with high $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet loading. It is hypothesised that this arises due to surface area minimisation of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets during solvent casting, where the sheets settle perpendicular to gravity in order to maximise the area upon which the force is acting.²⁷ This result, while unintuitive, confirms that the driving force for the polarisation enhancement is the fundamental interaction and local dipole locking occurring in solution between the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet and the PVDF-TrFE co-polymer, rather than fluoropolymer chain alignment induced through SEA 3D printing.

5.4.7 Macro energy harvesting using $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ composite PEGs

Macroscale electromechanical testing confirmed the trends in the d_{33} observed by PFM and quantified the energy output from the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ PEGs. For the measurements, the PEGs were compressed following a sinusoidal force pattern as a function of time with amplitude (ΔF) at 10 N (Supplementary Figure 5.S26a, b), pre-loaded to 5 N to minimise artefacts from contact electrification (i.e., contact-separation and lateral-sliding triboelectric modes).^{44,45} The harvested energy was measured by a charge amplifier, negating any inherent effects of capacitance from the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ composite films and the electrical cables, commonly unaccounted for during voltage measurements.

Macroscale d_{33} measurements were performed on the SEA extrusion printed pristine PVDF-TrFE and $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.5 wt%) PEGs (Figure 5.4d). The d_{33} of the pristine SEA printed pristine PVDF-TrFE PEG (-28.6 pC N^{-1}) was lower than literature reports for poled PVDF-TrFE (approximately -38 pC N^{-1}), however, this is not unexpected.^{3,30} More importantly, the d_{33} of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) was significantly larger than any prior reports on unpoled fluoropolymers at -52.0 pC N^{-1} .⁴ Notably, the ratio observed between the d_{33} of pristine PVDF-TrFE to the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$

(0.50 wt%) *via* the direct piezoelectric effect (macroscale measurements, $D_3 = d_{33}\sigma_3$) of $\sim 1:2$ correlated well to the trend observed *via* the converse piezoelectric effect (PFM, $\gamma_3 = d_{33}E_3$) of $\sim 1:3$. The improvement in measured charge arises from the piezoelectric effect, connecting the induced local polarisation locking described by MD to the macroscale polarisation and subsequent energy harvesting.

To demonstrate the stability of the PEGs, a compressive cycling stability study on the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) PEG was performed for 10,000 cycles with a $\Delta F = 10$ N and frequency of 10 Hz (Figure 5.4e). Figure 5.4f shows selected regions at the beginning, middle and end of the measurement. Aside from the initial period of cycling, which exhibited a rising generated charge from compressive stress to approximately -185 pC, the measured charge remained stable for the entire cycling period at -215 pC. The stability of the generated charge infers these completely solid-state PEGs can be used for long-term energy harvesting from human motion.

5.5 Conclusion

In summary, a mechanistic understanding was developed of how nanofillers with no out-of-plane piezoelectricity can influence the local and macroscale polarisation of fluoropolymers using 2D $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets as templates. $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets were conclusively shown to have a strong electrostatic interaction with the PVDF-TrFE co-polymer, resulting in the evolution of a locked polarisation in the fluoropolymer, perpendicular to the basal plane of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet. This effect is not observed using graphene nanosheets. The unique 2D geometry of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets means that by either SEA extrusion printing or solvent casting, this induced local net polarisation can elegantly and simply translate into macroscale polarisation, demonstrating an exceptional d_{33} of -52.0 pC N⁻¹, without the need for arduous and energy intensive electrical poling. The strong electrostatic interactions between the nanofiller and fluoropolymer resulted in a mechanically robust and flexible PEG device, capable of harvesting energy over 10,000 cycles without any degradation in performance.

Tuning surface terminations on MXenes and other 2D materials could afford enhanced electrostatic interactions leading to further improvements in piezoelectric outputs in

fluoropolymers. Leveraging this new understanding of nanoscale phenomena at the interface of a fluoropolymer and a 2D sheet now opens up a plethora of research opportunities to design piezoelectric composites with broad applicability, including in wearable energy harvesting,⁸ piezo-catalysis,¹⁰ piezo-photonics,¹¹ and anisotropic sensors.⁴⁶ Coupled to the elegant and versatile fabrication methods, this sustainable system can enable bespoke device design in emerging fields for robotic interfaces,⁹ biomedical implants,⁹ and direct-on-organ printed electronics.³⁷

5.6 References

1. Y. Tian, L. Wei, Q. Zhang, H. Huang, Y. Zhang, H. Zhou, F. Ma, L. Gu, S. Meng, L. Q. Chen, C. W. Nan and J. Zhang, Water printing of ferroelectric polarization, *Nature Communications*, **9**, 3809 (2018).
2. S. Horiuchi, Y. Tokunaga, G. Giovannetti, S. Picozzi, H. Itoh, R. Shimano, R. Kumai and Y. Tokura, Above-room-temperature ferroelectricity in a single-component molecular crystal, *Nature*, **463**, 789–792 (2010).
3. N. A. Shepelin, A. M. Glushenkov, V. C. Lussini, P. J. Fox, G. W. Dicinoski, J. G. Shapter and A. V. Ellis, New developments in composites, copolymer technologies and processing techniques for flexible fluoropolymer piezoelectric generators for efficient energy harvesting, *Energy & Environmental Science*, **12**, 1143–1176 (2019).
4. A. J. Lovinger, Ferroelectric polymers, *Science*, **220**, 1115–1121 (1983).
5. K. S. S. Ramadan, D. Sameoto and S. Evoy, A review of piezoelectric polymers as functional materials for electromechanical transducers, *Smart Materials and Structures*, **23**, 033001 (2014).
6. I. Katsouras, K. Asadi, M. Li, T. B. Van Driel, K. S. Kjær, D. Zhao, T. Lenz, Y. Gu, P. W. M. Blom, D. Damjanovic, M. M. Nielsen and D. M. De Leeuw, The negative piezoelectric effect of the ferroelectric polymer poly(vinylidene fluoride), *Nature Materials*, **15**, 78–84 (2016).
7. Publication and Proposed Revision of ANSI/IEEE Standard 176-1987 “ANSI/IEEE Standard on Piezoelectricity”, *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*, **43**, 717 (1996).
8. N. A. Shepelin, P. C. Sherrell, E. Goudeli, E. N. Skountzos, V. C. Lussini, G. W. Dicinoski, J. G. Shapter and A. V. Ellis, Printed recyclable and self-poled polymer piezoelectric generators through single-walled carbon nanotube templating, *Energy & Environmental Science*, **13**, 868–883 (2020).
9. M. Han, H. Wang, Y. Yang, C. Liang, W. Bai, Z. Yan, H. Li, Y. Xue, X. Wang, B. Akar, H. Zhao, H. Luan, J. Lim, I. Kandela, G. A. Ameer, Y. Zhang, Y. Huang and J. A. Rogers, Three-dimensional piezoelectric polymer microsystems for vibrational energy harvesting, robotic interfaces and biomedical implants, *Nature Electronics*, **2**, 26–35 (2019).

10. Y. Wang, X. Wen, Y. Jia, M. Huang, F. Wang, X. Zhang, Y. Bai, G. Yuan and Y. Wang, Piezo-catalysis for nondestructive tooth whitening, *Nature Communications*, **11**, 1328 (2020).
11. J. Hao and C. N. Xu, Piezophotonics: From fundamentals and materials to applications, *MRS Bulletin*, **43**, 965–969 (2018).
12. A. S. Tayi, A. Kaeser, M. Matsumoto, T. Aida and S. I. Stupp, Supramolecular ferroelectrics, *Nature Chemistry*, **7**, 281–294 (2015).
13. J. Kim, J. H. Lee, H. Ryu, J. H. Lee, U. Khan, H. Kim, S. S. Kwak and S. W. Kim, High-Performance Piezoelectric, Pyroelectric, and Triboelectric Nanogenerators Based on P(VDF-TrFE) with Controlled Crystallinity and Dipole Alignment, *Advanced Functional Materials*, **27**, 1700702 (2017).
14. F. E. Bouharras, M. Raihane and B. Ameduri, Recent progress on core-shell structured BaTiO₃@polymer/fluorinated polymers nanocomposites for high energy storage: Synthesis, dielectric properties and applications, *Progress in Materials Science*, **113**, 100670 (2020).
15. S. Bodkhe, G. Turcot, F. P. Gosselin and D. Therriault, One-Step Solvent Evaporation-Assisted 3D Printing of Piezoelectric PVDF Nanocomposite Structures, *ACS Applied Materials & Interfaces*, **9**, 20833–20842 (2017).
16. M. Pusty, L. Sinha and P. M. Shirage, A flexible self-poled piezoelectric nanogenerator based on a rGO-Ag/PVDF nanocomposite, *New Journal of Chemistry*, **43**, 284–294 (2019).
17. S. K. Karan, R. Bera, S. Paria, A. K. Das, S. Maiti, A. Maitra and B. B. Khatua, An Approach to Design Highly Durable Piezoelectric Nanogenerator Based on Self-Poled PVDF/AlO-rGO Flexible Nanocomposite with High Power Density and Energy Conversion Efficiency, *Advanced Energy Materials*, **6**, 1601016 (2016).
18. P. Yadav, T. D. Raju and S. Badhulika, Self-Poled hBN-PVDF Nanofiber Mat-Based Low-Cost, Ultrahigh-Performance Piezoelectric Nanogenerator for Biomechanical Energy Harvesting, *ACS Applied Electronic Materials*, **2**, 1970–1980 (2020).
19. T. Tian, D. Scullion, D. Hughes, L. H. Li, C. J. Shih, J. Coleman, M. Chhowalla and E. J. G. Santos, Electronic Polarizability as the Fundamental Variable in the Dielectric Properties of Two-Dimensional Materials, *Nano Letters*, **20**, 841–851 (2020).

20. G. Deysher, C. E. Shuck, K. Hantanasirisakul, N. C. Frey, A. C. Foucher, K. Maleski, A. Sarycheva, V. B. Shenoy, E. A. Stach, B. Anasori, B. Anasori and Y. Gogotsi, Synthesis of Mo_4VAlC_4 MAX Phase and Two-Dimensional Mo_4VC_4 MXene with Five Atomic Layers of Transition Metals, *ACS Nano*, **14**, 204–217 (2020).
21. J. K. El-Demellawi, S. Lopatin, J. Yin, O. F. Mohammed and H. N. Alshareef, Tunable Multipolar Surface Plasmons in 2D $\text{Ti}_3\text{C}_2\text{T}_x$ MXene Flakes, *ACS Nano*, **12**, 8485–8493 (2018).
22. A. Lipatov, H. Lu, M. Alhabeb, B. Anasori, A. Gruverman, Y. Gogotsi and A. Sinitskii, Elastic properties of 2D $\text{Ti}_3\text{C}_2\text{T}_x$ MXene monolayers and bilayers, *Science Advances*, **4**, eaat0491 (2018).
23. H. W. Wang, M. Naguib, K. Page, D. J. Wesolowski and Y. Gogotsi, Resolving the Structure of $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes through Multilevel Structural Modeling of the Atomic Pair Distribution Function, *Chemistry of Materials*, **28**, 349–359 (2016).
24. M. Ghidui, M. R. Lukatskaya, M. Q. Zhao, Y. Gogotsi and M. W. Barsoum, Conductive two-dimensional titanium carbide “clay” with high volumetric capacitance, *Nature*, **516**, 78–81 (2015).
25. D. Xiong, X. Li, Z. Bai, and S. Lu, Recent Advances in Layered $\text{Ti}_3\text{C}_2\text{T}_x$ MXene for Electrochemical Energy Storage, *Small*, **14**, 1703419 (2018).
26. A. Lipatov, M. Alhabeb, M. R. Lukatskaya, A. Boson, Y. Gogotsi and A. Sinitskii, Effect of Synthesis on Quality, Electronic Properties and Environmental Stability of Individual Monolayer Ti_3C_2 MXene Flakes, *Advanced Electronic Materials*, **2**, 1600255 (2016).
27. J. Zhang, N. Kong, S. Uzun, A. Levitt, S. Seyedin, P. A. Lynch, S. Qin, M. Han, W. Yang, J. Liu, X. Wang, Y. Gogotsi and J. M. Razal, Scalable Manufacturing of Free-Standing, Strong $\text{Ti}_3\text{C}_2\text{T}_x$ MXene Films with Outstanding Conductivity, *Advanced Materials*, **32**, 2001093 (2020).
28. W. N. Zou, C. X. Tang and E. Pan, Symmetry types of the piezoelectric tensor and their identification, *Proceedings of the Royal Society A*, **469**, 20120755 (2013).
29. C. Zhao, P. Zhang, J. Zhou, S. Qi, Y. Yamauchi, R. Shi, R. Fang, Y. Ishida, S. Wang, A. P. Tomsia, L. Jiang and M. Liu, Layered nanocomposites by shear-flow-induced alignment of nanosheets, *Nature*, **580**, 210–215 (2020).

30. C. R. Bowen, H. A. Kim, P. M. Weaver and S. Dunn, Piezoelectric and ferroelectric materials and structures for energy harvesting applications, *Energy & Environmental Science*, **7**, 25–44 (2014).
31. M. E. Beck and M. C. Hersam, Emerging Opportunities for Electrostatic Control in Atomically Thin Devices, *ACS Nano*, **14**, 6498–6518 (2020).
32. N. A. Shepelin, V. C. Lussini, P. J. Fox, G. W. Dicinoski, A. M. Glushenkov, J. G. Shapter and A. V. Ellis, 3D printing of poly(vinylidene fluoride-trifluoroethylene): a poling-free technique to manufacture flexible and transparent piezoelectric generators, *MRS Communications*, **9**, 159–164 (2019).
33. G. M. Kavanagh and S. B. Ross-Murphy, Rheological characterisation of polymer gels, *Progress in Polymer Science*, **23**, 533–562 (1998).
34. A. Corker, H. C. H. Ng, R. J. Poole and E. García-Tuñón, 3D printing with 2D colloids: Designing rheology protocols to predict “printability” of soft-materials, *Soft Matter*, **15**, 1444–1456 (2019).
35. J. J. Adams, E. B. Duoss, T. F. Malkowski, M. J. Motala, B. Y. Ahn, R. G. Nuzzo, J. T. Bernhard and J. A. Lewis, Conformal printing of electrically small antennas on three-dimensional surfaces, *Advanced Materials*, **23**, 1335–1340 (2011).
36. Z. Zhu, S. Z. Guo, T. Hirdler, C. Eide, X. Fan, J. Tolar and M. C. McAlpine, 3D Printed Functional and Biological Materials on Moving Freeform Surfaces, *Advanced Materials*, **30**, 1707495 (2018).
37. Z. Zhu, H. S. Park and M. C. McAlpine, 3D printed deformable sensors, *Science Advances*, **6**, eaba5575 (2020).
38. J. Li, L. Kang, Y. Yu, Y. Long, J. J. J. Jeffery, W. Cai and X. Wang, Study of long-term biocompatibility and bio-safety of implantable nanogenerators, *Nano Energy*, **51**, 728–735 (2018).
39. D. A. Porter, T. V. T. Hoang and T. A. Berfield, Effects of in-situ poling and process parameters on fused filament fabrication printed PVDF sheet mechanical and electrical properties, *Additive Manufacturing*, **13**, 81–92 (2017).
40. C. J. L. Constantino, A. E. Job, R. D. Simões, J. A. Giacometti, V. Zucolotto, O. N. Oliveira Jr., G. Gozzi and D. L. Chinaglia, Phase transition in poly(vinylidene fluoride) investigated with micro-Raman spectroscopy, *Applied Spectroscopy*, **59**, 275–279 (2005).

41. J. H. Yang, T. Ryu, Y. Lansac, Y. H. Jang and B. H. Lee, Shear stress-induced enhancement of the piezoelectric properties of PVDF-TrFE thin films, *Organic Electronics*, **28**, 67–72 (2016).
42. A. Gruverman, M. Alexe and D. Meier, Piezoresponse force microscopy and nanoferroic phenomena, *Nature Communications*, **10**, 1661 (2019).
43. P. H. Ducrot, I. Dufour and C. Ayela, Optimization of PVDF-TrFE Processing Conditions for the Fabrication of Organic MEMS Resonators, *Scientific Reports*, **6**, 19426 (2016).
44. F. Xu, F. Chu and S. Trolier-McKinstry, Longitudinal piezoelectric coefficient measurement for bulk ceramics and thin films using pneumatic pressure rig, *Journal of Applied Physics*, **86**, 588–594 (1999).
45. A. Šutka, P. C. Sherrell, N. A. Shepelin, L. Lapčinskis, K. Mālnieks and A. V. Ellis, Measuring Piezoelectric Output—Fact or Friction?, *Advanced Materials*, **32**, 2002979 (2020).
46. H. Cui, R. Hensleigh, D. Yao, D. Maurya, P. Kumar, M. G. Kang, S. Priya and X. Zheng, Three-dimensional printing of piezoelectric materials with designed anisotropy and directional response, *Nature Materials*, **18**, 234–241 (2019).
47. J. Zhang, S. Seyedin, S. Qin, Z. Wang, S. Moradi, F. Yang, P. A. Lynch, W. Yang, J. Liu, X. Wang, X. Wang and J. M. Razal, Highly Conductive $\text{Ti}_3\text{C}_2\text{T}_x$ MXene Hybrid Fibers for Flexible and Elastic Fiber-Shaped Supercapacitors, *Small*, **15**, 1804732 (2019).
48. S. Plimpton, Fast parallel algorithms for short-range molecular dynamics, *Journal of Computational Physics*, **117**, 1–19 (1995).
49. W. C. Swope, H. C. Andersen, P. H. Berens and K. R. Wilson, A computer simulation method for the calculation of equilibrium constants for the formation of physical clusters of molecules: Application to small water clusters, *Journal of Chemical Physics*, **76**, 637–649 (1982).
50. G. R. Berdiyrov, M. E. Madjet and K. A. Mahmoud, Ionic sieving through $\text{Ti}_3\text{C}_2(\text{OH})_2$ MXene: First-principles calculations, *Applied Physics Letters*, **108**, 113110 (2016).

5.7 Supplementary information

5.7.1 $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets and properties

The XRD patterns of the Ti_3AlC_2 MAX phase and the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets were obtained using a powder diffractometer (X'Pert Powder, PANalytical, United Kingdom) equipped with a Cu $K\alpha$ radiation (40 kV, 30 mA) with an X-ray wavelength (λ) of 1.54 Å at a 2θ scan step of 0.013° . Transmission electron microscopy (TEM) (JEM-2100, JEOL Ltd., Japan) characterisation was employed to study the exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. Topographical atomic force microscopy (AFM) images were obtained using Bruker's proprietary ScanAsyst scan mode (MultiMode 8-HR, Bruker, United States) to measure the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet thickness. AFM samples were prepared by drop casting the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet in DMF solutions onto clean silicon wafers. Dynamic light scattering (DLS) was performed using a Zetasizer (Nano ZS, Malvern Instruments, United Kingdom) to measure the size distribution of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. The X-ray photoelectron spectroscopy (XPS) data on the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets were acquired using an AXIS Nova (Kratos Analytical Ltd., United Kingdom) equipped with a monochromated Al $K\alpha$ source ($h\nu = 1486.6$ eV) operating at 150 W at a step of 0.1 eV.

The $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets were synthesised from the Ti_3AlC_2 parent ternary carbide precursor (MAX phase) by selective etching of the aluminium layer (A-group element) using a mixture of lithium fluoride (LiF) and hydrochloric acid (HCl) at room temperature for 24 h.¹⁻³ The subsequent intercalation of water (H_2O) molecules and Li^+ ions within the negatively charged surface resulted in a volume increase during washing with ultra-pure water, indicating the self-delamination of multi-layered $\text{Ti}_3\text{C}_2\text{T}_x$ to few/single layers.⁴ The delamination and the removal of the aluminium was confirmed by the down-shifting of the (002) peak and a disappearance of the aluminium peak at 2θ of 39° in the XRD spectra (Supplementary Figure 5.S1a).⁵ The TEM image (Supplementary Figure 5.S1b) and DLS data (Supplementary Figure 5.S1c) showed that the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets exhibited an average lateral size of approximately 310 nm. The AFM image showed that the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets exhibited a clean surface at the edge (Supplementary Figure 5.S1d). The thickness profile of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets (Supplementary Figure 5.S1d, inset) showed an average height of 1.6 nm, corresponding to single-layer $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets.¹

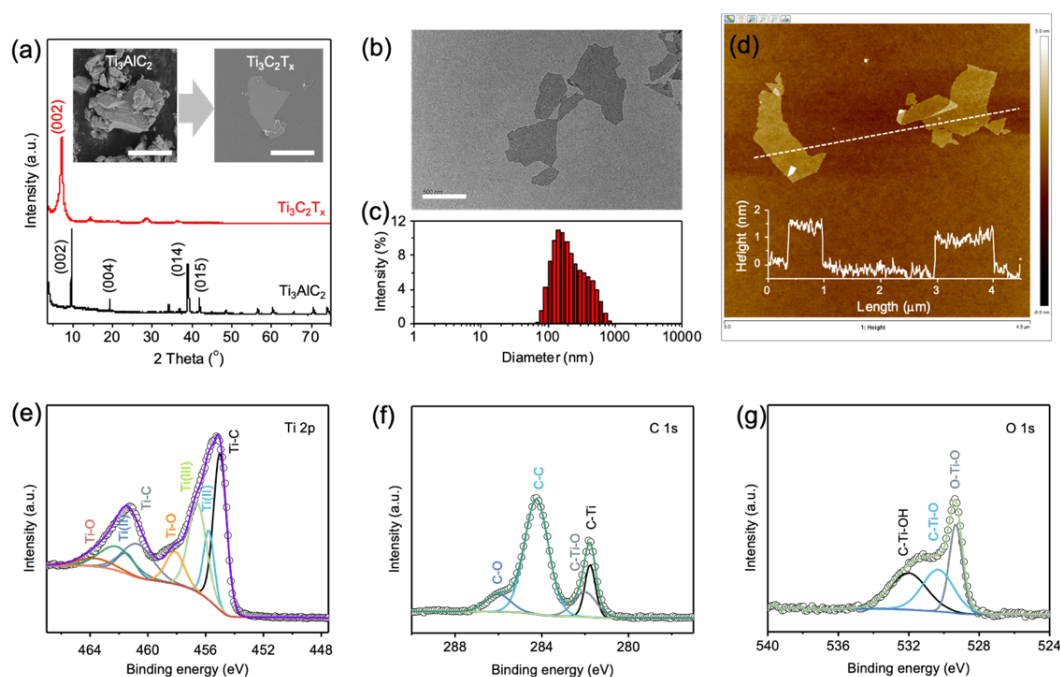


Figure 5.S1: $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheet characterisation. (a) XRD pattern and SEM images (insets) of Ti_3AlC_2 MAX phase and $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets after etching. Scale bar for SEM of Ti_3AlC_2 represents $5\ \mu\text{m}$ and that of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets represents $1\ \mu\text{m}$. (b) TEM image of single-layer 2D $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. Scale bar represents $500\ \text{nm}$. (c) The DLS result showing the hydrodynamic size of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets in water. (d) AFM image of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets deposited on a silicon wafer. Inset, represents the thickness profile along the line indicated. Deconvolution of high-resolution XPS spectra for the (e) Ti 2p, (f) C 1s and (g) O 1s orbitals, showing the surface termination and state of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets.

XPS of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets (Supplementary Figure 5.S1e-g) revealed surface termination dominated by Ti-O and O-Ti-O bonding. The Ti 2p region (Supplementary Figure 5.S1e) showed doublets corresponding to Ti-C, Ti (III), Ti (II) and Ti-O bonding. The dominant Ti-C peak arises from the bridging C atoms between Ti atoms, whereas the Ti-O peaks corresponds to surface termination functional groups of hydroxides (Ti-OH) or epoxide (Ti-O-Ti) structures.⁶ The C 1s spectral region (Supplementary Figure 5.S1f), shows four singlet peaks, C-Ti, C-Ti-O, C-C, and C-O. The C-Ti peak corresponds to internal bridging C atoms. The C-Ti-O peak, occurring at slightly higher binding energies, arises from the long-range influence of oxygen-based surface termination on the electronic state of the internal C atoms. The C-C signal, while anomalous given the crystal structure of $\text{Ti}_3\text{C}_2\text{T}_x$, is always observed in literature⁷ and is understood to arise from residual hydrocarbons⁸ in the XPS chamber. The C-O peak occurs as Ti is an extremely

mobile metal, known to leave vacancies and thus slightly altered stoichiometry.⁹ These vacancies result in C-O bonding in the top or bottom Ti metal layer. The O 1s region (Supplementary Figure 5.S1g) confirms the predominant binding of O moieties to Ti atoms in the form of O-Ti-O, which can correspond to either hydroxide (favourable) or epoxide (unfavourable) surface terminations. Higher binding energy peaks for C-Ti-O and C-Ti-OH suggest hydroxy termination is dominant of the surface of the flakes.

5.7.1.1 Preparation of PVDF-TrFE and $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE inks

Recently, the dissolution and recycling of SEA extrusion printed PVDF-TrFE co-polymer films have been described using acetone as the only solvent.¹⁰ Here, DMF was completely eliminated as a solvent for extrusion printing entirely and replaced by acetone. Acetone has inherent advantages, with faster evaporation rates that enable rapid crystallisation and drying of SEA extrusion printed polymer films.¹¹

Initially, pristine PVDF-TrFE inks were prepared in acetone, which were used to optimise the SEA extrusion printing parameters. These inks were prepared by a simple mixing method, whereby PVDF-TrFE powder was slowly added to acetone under mechanical stirring. The pristine PVDF-TrFE co-polymer inks were prepared at PVDF-TrFE co-polymer concentrations of 35 wt%, 40 wt% and 45 wt%, based on the concentrations of inks prepared in the previously reported DMF:acetone solvent mixture.¹² The prepared inks were viscous (Supplementary Figure 5.S2), moving slower when tilted to a 45° angle as the concentration increased. The rheological optimisation of the inks for printing is shown further in this document.

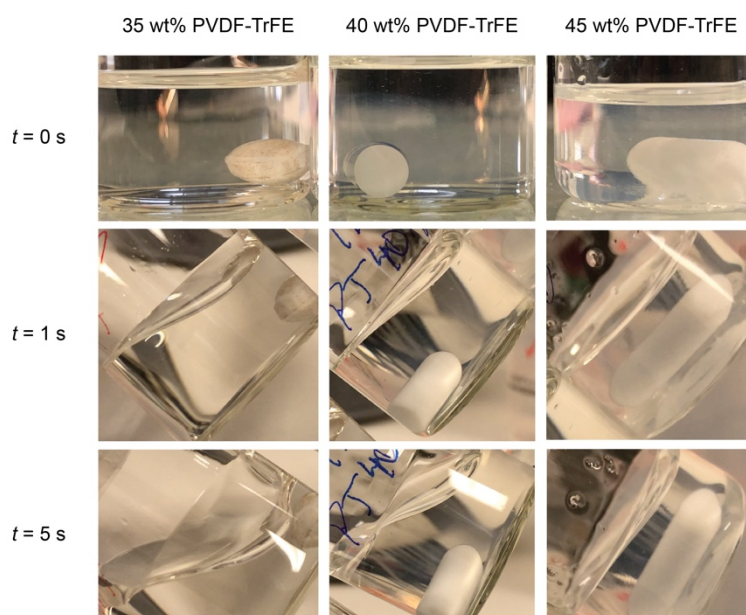


Figure 5.S2: Photographs of the 35 wt% (left column), 40 wt% (middle column) and 45 wt% (right column) PVDF-TrFE/acetone inks, demonstrating the viscosity of the inks before rotating the vial to 45° (top row, $t = 0$ s), 1 s after rotating the vial (middle row) and 5 s after rotating the vial (bottom row).

Similarly, $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ inks were prepared at $\text{Ti}_3\text{C}_2\text{T}_x$ concentrations at 0.02 wt%, 0.10 wt%, 0.20 wt% and 0.50 wt%. Here, a small aliquot of the $\text{Ti}_3\text{C}_2\text{T}_x$ stock dispersion in DMF (4.4 mg mL^{-1}) was added to acetone to form dispersions at 0.00 mg mL^{-1} , 0.10 mg mL^{-1} , 0.52 mg mL^{-1} , 1.05 mg mL^{-1} and 2.61 mg mL^{-1} in acetone. Subsequently, the PVDF-TrFE powder was added slowly to the $\text{Ti}_3\text{C}_2\text{T}_x$ dispersions in acetone at 23°C while stirring, at 40 wt% relative to the mass of the dispersion, to form the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ inks. The inks were stirred until homogeneous, then sealed with parafilm and stored at -5°C to minimise solvent evaporation.

Throughout the experimental procedure, the stability of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet dispersion was monitored in the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ ink, for up to five months (Supplementary Figure 5.S3, middle). The $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ ink was compared to a SWCNT/PVDF-TrFE ink, which has been recently reported (Supplementary Figure 5.S3, right).¹⁰ Notably, after five months of storage, all three inks exhibited similar flow properties to recently prepared inks. The SWCNTs were found to aggregate in the SWCNT/PVDF-TrFE ink, causing occasional blocking of the nozzle during printing. Conversely, the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets showed minimal aggregation in the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ ink due to exceptional electrostatic interactions between the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and the PVDF-TrFE co-

polymer (Supplementary Figure 5.S5, Supplementary Video 5.S1). The $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ ink could be printed following long-term storage with no required changes in the extrusion printing parameters.



Figure 5.S3: Comparison of the stability of the PVDF-TrFE ink (left), $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ ink (middle) and SWCNT/PVDF-TrFE ink (right), five months after preparation of the ink.

5.7.2 MD modelling of the interface between the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and the PVDF-TrFE co-polymer

The density of the PVDF-TrFE co-polymer melt was investigated as a function of the monomer units (alternatively the molecular weight) to validate the interatomic potential used for the simulations (Supplementary Figure 5.S4). The density was found to increase with increasing number of monomer units, reaching an asymptotic plateau corresponding to 1.42 g cm^{-3} . The value obtained using MD simulations was in excellent agreement with the value of 1.49 g cm^{-3} provided by the manufacturer of the PVDF-TrFE co-polymer (Solvay), validating the interatomic potential used in the MD simulations.

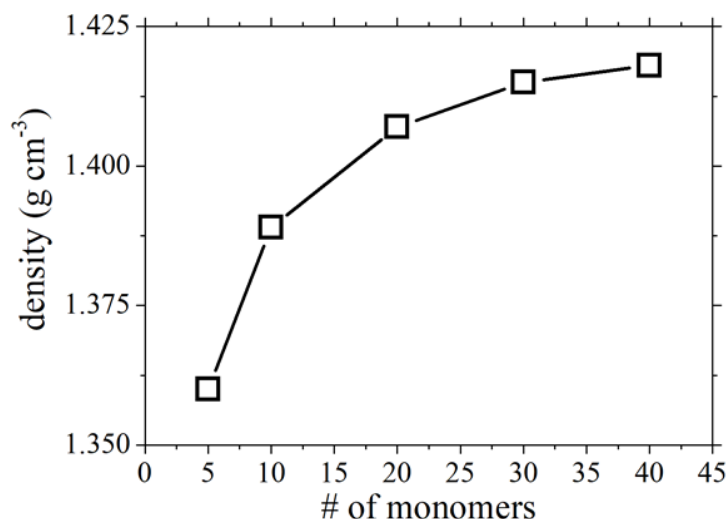


Figure 5.S4: Evolution of the density of the PVDF-TrFE co-polymer melt as a function of the number of monomers.

The distribution of the local density of the PVDF-TrFE co-polymer film (14 chains) was investigated as a function of distance from the substrate, for a graphene substrate (Supplementary Figure 5.S5, black line) and a $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate (Supplementary Figure 5.S5, red line). The density distribution was calculated from the mass within each separation distance interval, normalised to the volume within said interval and averaged over the duration of the simulation (1.8 ns timespan). The shaded regions correspond to the minimum and maximum values of the local density at each separation distance interval relative to the graphene or $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate. The layer adjacent to the substrate were found to adsorb to both the graphene and the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrates, exhibiting a local density of approximately 2 g cm^{-3} . Notably, the PVDF-TrFE co-polymer film adsorbs closer to the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet relative to graphene, as the first local density peak appears at a lower separation. This decreased separation indicates a stronger attractive interaction between the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet and the PVDF-TrFE co-polymer in comparison to the graphene substrate.

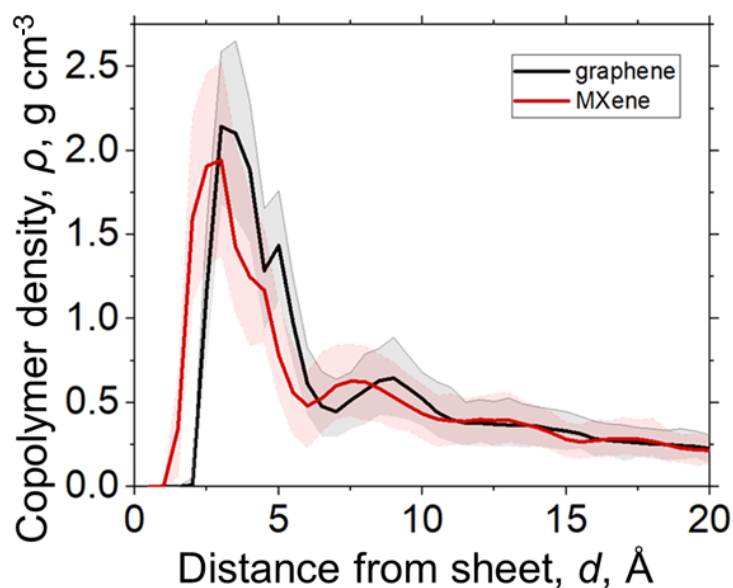


Figure 5.S5: Distribution of the local density (ρ) of the PVDF-TrFE co-polymer film (14 chains) as a function of the distance from the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet (red line) and the graphene sheet (black line) substrates.

This enhanced adhesion phenomenon was investigated by adhesion strength studies. Here, a PVDF-TrFE co-polymer chain was placed in close proximity to either the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet or graphene sheet substrate. A force was applied to the PVDF-TrFE co-polymer perpendicular to the basal plane of the substrate to measure the desorption force. The force was increased from 0.00 pN to 6.95 pN with a step size of 0.695 pN, monitoring the position of the PVDF-TrFE co-polymer chain for the desorption from the substrate. It was found that the PVDF-TrFE co-polymer chain desorbed from the graphene substrate at approximately 2.78 pN, whereas the required desorption force increased on the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet to approximately 4.17 pN, indicating a greater adhesion strength at the interface between the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet and the PVDF-TrFE co-polymer.

The distribution of the H and F atoms in the PVDF-TrFE co-polymer film was further investigated as a function of the distance from the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate to investigate whether preferential orientation of these dipolar atoms in the PVDF-TrFE co-polymer were giving rise to the polarisation locking mechanism (Supplementary Figure 5.S6). The datapoints represent average values for 14 PVDF-TrFE co-polymer chains and the shaded areas represent the minimum and maximum number of H and F atoms over

the entire simulation. The H and F probability distributions were observed to be approximately equal at all distances from the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate, indicating the PVDF-TrFE did not preferentially orient on the substrate. Small deviations at a low distance (up to 2 Å) were observed, whereby the H atoms were found closer to the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate relative to the F atoms. This was attributed to the shortest non-covalent hydrogen bonds between the H atoms of the PVDF-TrFE co-polymer and the hydroxyl terminations (T_x) of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate.

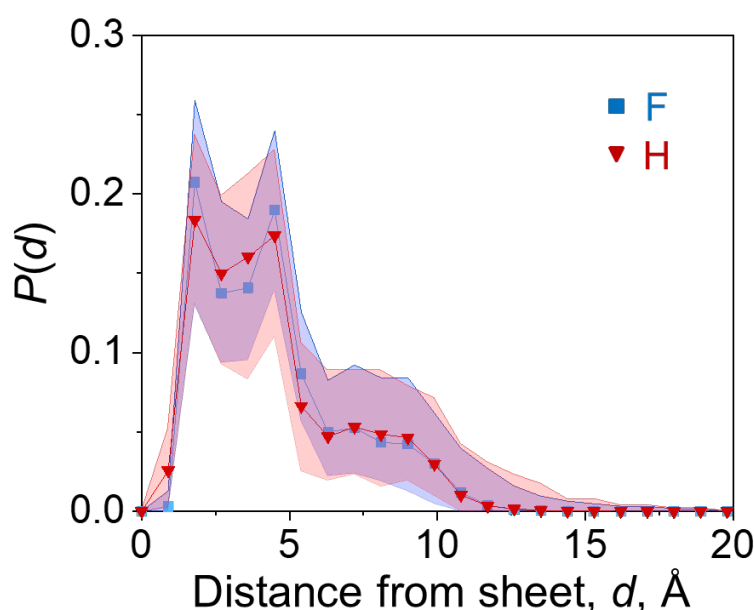


Figure 5.S6: Probability distribution ($P(d)$) of the number of F (squares) and H atoms (triangles) within the PVDF-TrFE co-polymer film (14 chains) as a function of the distance from the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate (d). The shaded areas represent the minimum and maximum number of F and H atoms over the entire simulation.

To understand the phase distributions of the PVDF-TrFE co-polymer film adjacent to the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate, the probability distributions of the dihedral angles were monitored for a 14-chain PVDF-TrFE co-polymer film (Supplementary Figure 5.S7). The PVDF-TrFE co-polymer consists of three commonly found phases, namely the α phase (non-polar), γ phase (semi-polar) and the β phase (highly polar).¹³ These phases correspond to spatial conformation of the bonds, either *trans* (T) or *gauche* (G). The α phase is thermodynamically favoured in fluoropolymers, due to its *trans-gauche* (TGTG'TGTG') conformation, which consists of 50% *trans* bonds and 50% *gauche* bonds.¹⁴ Conversely, the β phase is an all-*trans* (TTTTTTTT) conformation, which

spatially separates the H moieties on one C atom from the F atoms on the adjacent C atom, giving rise to a strong H-F dipole moment.¹⁵ The γ phase is a stable intermediate state between the α phase and the β phase, as evidenced by the 75% *trans* and 25% *gauche* fraction (TTTGTTTG'), giving rise to dipole moments which result in a lower maximum polarisation relative to the β phase.¹⁴ Hence, the distribution of the dihedral angles and subsequently the phase fractions can provide insight on the changes in local electroactivity of the PVDF-TrFE co-polymer film adjacent to the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate.

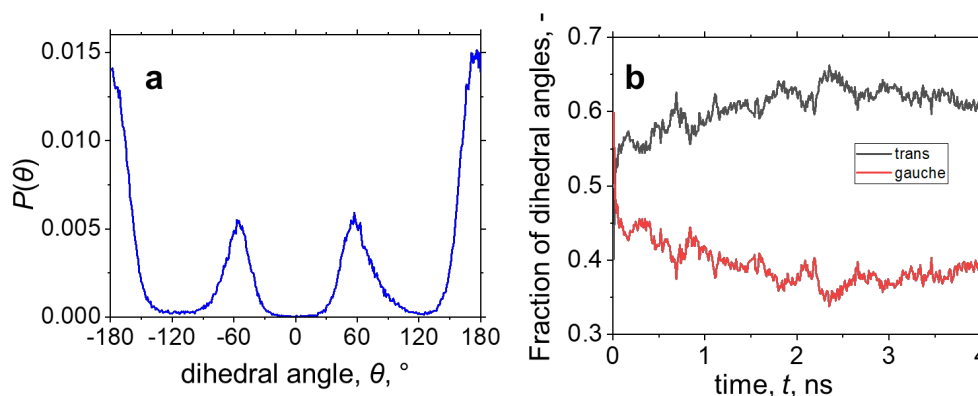


Figure 5.S7: Bond angle distributions of the PVDF-TrFE co-polymer on the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate. (a) Probability distribution ($P(\theta)$) of the dihedral angles (θ) averaged over 4 ns for a film of 14 PVDF-TrFE chains interacting with an immobile $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet. (b) Time evolution of the fraction of the *trans* (black line) and *gauche* angles (red line).

The distribution of the dihedral angles (Supplementary Figure 5.S7a) was taken as the average of all angles in a 14-chain PVDF-TrFE co-polymer film interacting with an immobile $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate over the span of the simulation (4 ns). The PVDF-TrFE co-polymer chains exhibited configurations at four main dihedral angles, $\pm 180^\circ$ (*trans*) and $\pm 60^\circ$ (*gauche*).¹⁵ As a function of simulation time, the fraction of *trans* conformation (Supplementary Figure 5.S7b, black line) was found to increase and attain a final value of approximately 63%, whereas approximately 37% of the bonds were observed in the *gauche* conformation (Supplementary Figure 5.S7, red line). These values correspond to either a majority of α phase (74%) with low prevalence of the β phase (26%), or a near-even distribution of the α phase (48%) and γ phase (52%), or a combination of the two. Importantly, while the PVDF-TrFE generally crystallises into the β

phase due to the third F atom in the TrFE monomer, these values suggest a large presence of the α phase.¹⁰ Indeed, at the local level, the experimental data observed the presence of the α and γ phases adjacent to the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet (Figure 5.3d, e); however, the FTIR (Supplementary Figure 5.S16) and XRD (Supplementary Figure 5.S17, Supplementary Figure 5.S18) data, presented below, suggest the β phase as the primary conformation in the bulk of the $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE composites.

Similarly, the temporal evolution of the dihedral angles was repeated for a 70-chain PVDF-TrFE co-polymer film on the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet or graphene substrate (Supplementary Figure 5.S8). Similar to the 14-chain PVDF-TrFE co-polymer films (Supplementary Figure 5.S7b), the larger films on a $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate exhibited a larger *trans* fraction (approximately 65%) relative to the *gauche* fraction (approximately 35%). Interestingly, when simulated adjacent to a graphene substrate, the same 70-chain PVDF-TrFE copolymer film exhibited a lower fraction of *trans* bonds (approximately 57%) and subsequently a higher fraction of *gauche* bonds (approximately 43%).

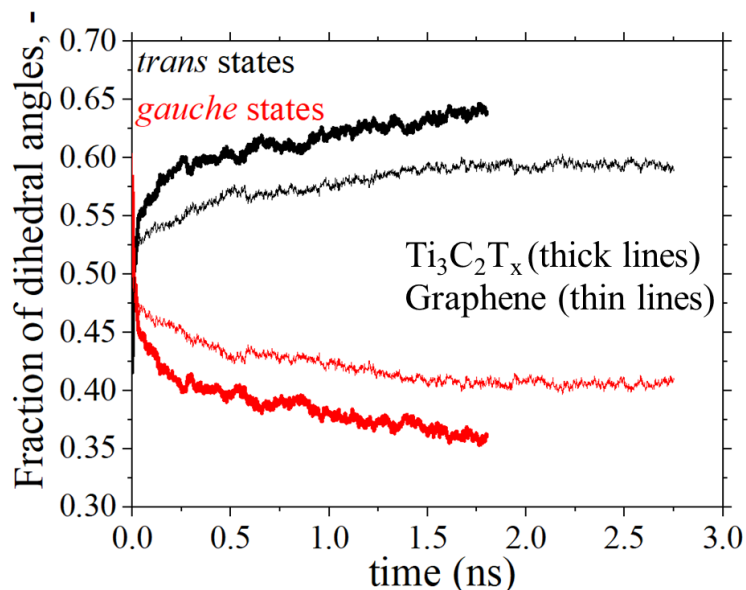


Figure 5.S8: The temporal evolution of the fraction of *trans* bond angles (black lines) and *gauche* bond angles (red lines) in the 70-chain PVDF-TrFE co-polymer film on a $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate (thick lines) and graphene substrate (thin lines).

The evolution of the polarisation angle (θ) in the PVDF-TrFE co-polymer film relative to the basal plane of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate was investigated as a function of the simulation time and the distance from the substrate (Supplementary Figure 5.S9). The θ was obtained as a function of time for PVDF-TrFE co-polymer chains within 24 Å (Supplementary Figure 5.S9, green line), 29 Å (Supplementary Figure 5.S9, red line), 34 Å (Supplementary Figure 5.S9, blue line) and 39 Å (Supplementary Figure 5.S9, grey line) from the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate. The PVDF-TrFE co-polymer chains closer to the substrate (<24 Å) exhibited a broad range of θ values, found to sporadically change orientation throughout the simulation. Conversely, as the separation from the $\text{Ti}_3\text{C}_2\text{T}_x$ increased to 39 Å, the θ was found to orient perpendicular to the basal plane of the $\text{Ti}_3\text{C}_2\text{T}_x$. Additionally, the orientation of the polarisation vector at 39 Å was not found to significantly deviate from the perpendicular orientation throughout the equilibrated region ($t > 0.5$ ns) of the simulation, indicating that the polarisation locking spontaneously occurs near the interface of the two materials directly upon contact (in solution) and maintains the perpendicular orientation in the solid state (after deposition).

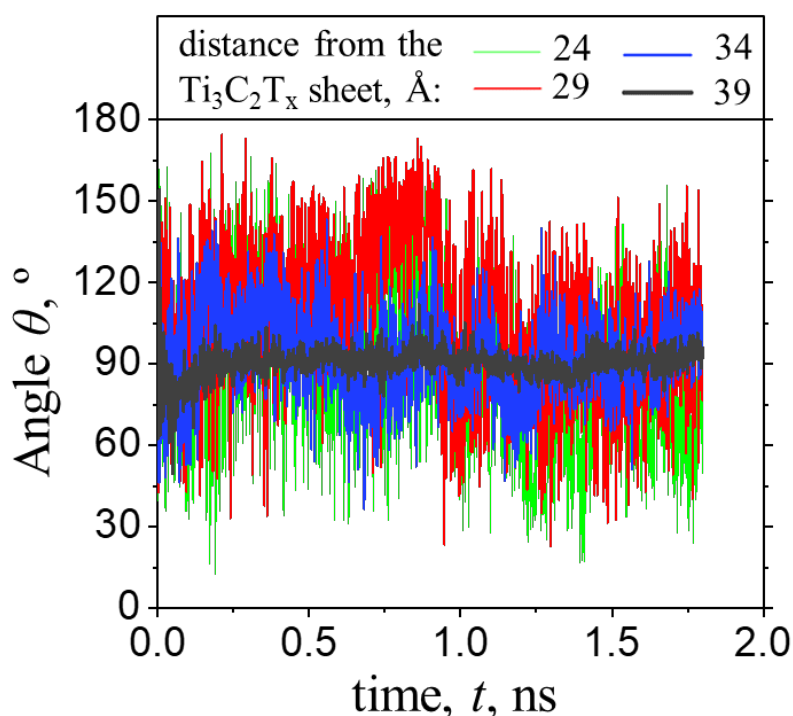


Figure 5.S9: Time evolution of the angle (θ) between the total dipole vector (polarisation) in the PVDF-TrFE co-polymer film and the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet basal plane, for PVDF-TrFE co-polymer chains that are within 24 Å (green line), 29 Å (blue line), 34 Å (blue line) and 39 Å (grey line) from the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate.

5.7.3 Rheological printing optimisation of pristine PVDF-TrFE in acetone

To optimise the ink system (PVDF-TrFE in acetone) for SEA 3D printing, the rheological properties of the inks were first studied for PVDF-TrFE (35 wt%, 40 wt% and 45 wt%) loadings. PVDF-TrFE powder (75 mol% VDF, 25 mol% TrFE, $M_w = 420$ kDa) was slowly added into acetone and stirred at 23 °C until the powder completely dissolved, forming viscous inks (Supplementary Figure 5.S2). The rheology of these inks was assessed using a rheometer (MCR702, Anton Paar, Austria) in a cone-plate geometry, with a cone diameter of 25 mm, a cone angle of 2° and a gap at 102 μm (CP25-2, Anton Paar, Austria). The temperature in all measurements was held at 5°C.

5.7.3.1 Steady state rheology

Initial steady-state logarithmic shear rate ramps were used to compare the η of the PVDF-TrFE ink in acetone to that of the commonly reported solvent mixture of DMF and acetone (40:60 vol%), with polymer concentration at 35 wt% (Supplementary Figure 5.S10a).^{10,12} Both inks showed non-Newtonian (shear thinning) behaviour, which is required for extrusion printing.¹⁶ At a shear rate of 0.01 s^{-1} , which corresponded to the rest-ing state (prior to and post printing), the η of the ink in the DMF:acetone solvent system was measured at 670 Pa s, drastically lower than that of the ink in acetone as the solvent, measured at 430,000 Pa s. The extreme increase in the viscosity at low shear represents a three order of magnitude increase in shape retention capability of the ink directly upon printing, further aided by the faster evaporation rate of acetone relative to DMF. Interestingly, the viscosity of the ink with acetone as the only solvent exhibited a lower η (7 Pa s) at high shear rate (1,000 s^{-1} , corresponding to conditions during printing) relative to the ink with DMF:acetone as the solvent system (12 Pa s). This signifies a lower pressure is required to extrude the same volume of ink, following the Hagen-Poiseuille equation.¹⁷ This initial testing confirmed the significant improvement in the rheological properties of the PVDF-TrFE/acetone ink relative to the PVDF-TrFE/(DMF:acetone) ink and further suggested the formation of a gel, consistent with prior reports of acetone as a swelling agent for fluoropolymers.¹⁸

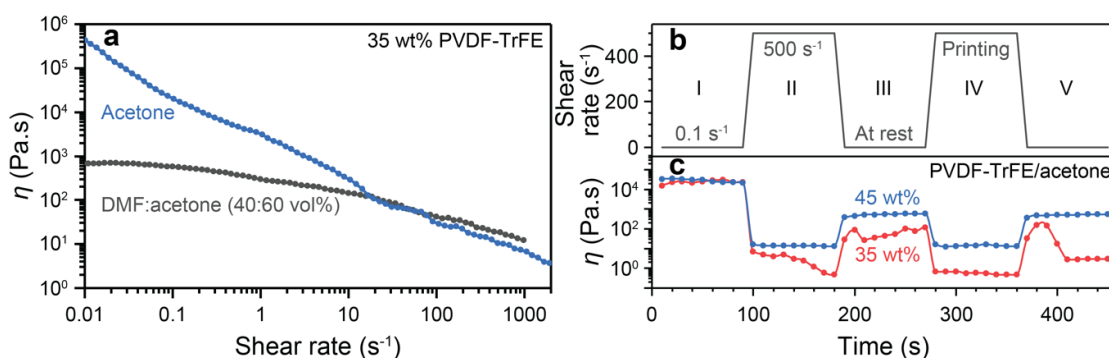


Figure 5.S10: Steady-state rheology. (a) The shear rate sweeps for inks of PVDF-TrFE/(DMF:acetone, 40:60 vol%) and PVDF-TrFE/acetone, containing PVDF-TrFE (35 wt%). (b) The applied shear rate profile as a function of time and (c) the resultant viscosity (η) for PVDF-TrFE/acetone inks with PVDF-TrFE concentration at 35 wt% and 45 wt%.

Additional steady state testing was undertaken on the PVDF-TrFE/acetone ink at two concentrations, 35 wt% and 45 wt%, to simulate the flow and recovery parameters found during extrusion printing (Supplementary Figure 5.S10b, c). Here, the shear rate was kept constant for 90 s, cycling between 1 s⁻¹ and 500 s⁻¹ (Supplementary Figure 5.S10b), and measuring the η (Supplementary Figure 5.S10c). Both inks exhibited similar η values in region I (between 21,000 Pa s and 23,000 Pa s at 90 s), decreasing under increased shear in region II to 16 Pa s in the 45 wt% ink and 7 Pa s in the 35 wt% ink. Notably, the η of the 35 wt% ink exhibited further decreases at the constant shear rate to 0.5 Pa s, which is likely to arise from elongation and disentanglement of the polymer chains. Region III showed partial recovery in both inks to 588 Pa s (2.7%) and 113 Pa s (0.5%) in the 45 wt% and 35 wt% inks, respectively. This suggests the higher concentration of PVDF-TrFE assists in stabilising the entanglement in the polymer chains; however, the application of shear nonetheless reduces the entanglement between the polymer chains, correlating to a pseudo-1D material.¹⁹ In region IV, the 35 wt% ink was found to drop in η to the lower value of that in region II, suggesting that the disentanglement is irreversible, whereas the η of the 45 wt% ink was found to be consistent throughout the region, with the same values as region II. Surprisingly, upon decrease in shear rate in region V, the η of the 35 wt% ink decreased to similar values as the high shear rate region II, unable to reliably recover to the values of region III, confirming the disentanglement effects and therefore proving unsuitable for a printing system where the printed ink must retain its shape.

5.7.3.2 Oscillatory rheology

Oscillatory rheology was employed at 5 °C to further probe the hypothesis of gel formation and determine the flow parameters in the PVDF-TrFE/acetone inks with PVDF-TrFE concentration at 35 wt%, 40 wt% and 45 wt% (Supplementary Figure 5.S11).¹⁶ Oscillatory ω sweeps were performed (Supplementary Figure 5.S11a-c), which can give insight into the time-dependent flow properties of the inks.²⁰ The tests were performed with fixed γ_s at 1%. All measured samples exhibited a similar trend in the G' and G'' as a function of the ω , confirming the increased η (Supplementary Figure 5.S10a) relative to PVDF-TrFE/(DMF:acetone) inks was due to enhanced swelling of the fluoropolymer, which has lower dependence on the fluoropolymer concentration.²¹ Furthermore, minimal deviation in the slope of G' and G'' over the entire measured ω range strongly suggested the formation of a strongly bound gel, which was solid-like ($G' > G''$) for all measured frequencies.²⁰

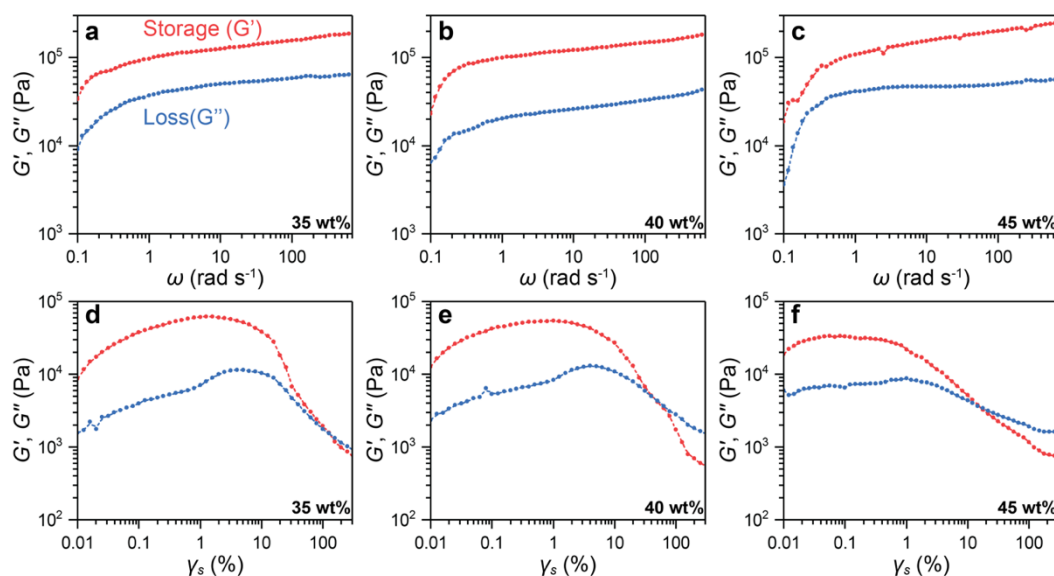


Figure 5.S11: Oscillatory rheology measurements on PVDF-TrFE/acetone inks. (a-c) The oscillatory ω sweeps for (a) 35 wt%, (b) 40 wt% and (c) 45 wt% PVDF-TrFE/acetone inks, obtained at fixed shear strain ($\gamma_s = 1\%$). (d-f) The oscillatory γ_s sweeps for (d) 35 wt%, (e) 40 wt% and (f) 45 wt% PVDF-TrFE/acetone inks, obtained at fixed frequency ($\omega = 1 \text{ Hz} \approx 6.28 \text{ rad s}^{-1}$).

Similarly, the oscillatory γ_s sweeps (Supplementary Figure 5.S11d-f) at low ω (1 Hz) exhibited similar characteristics between all three PVDF-TrFE concentrations in acetone. All three tested samples showed solid-like behaviour ($G' > G''$) at low γ_s , followed by a liquid-like region ($G' < G''$) at high γ_s ($>100\%$).¹⁶ Interestingly, the flow point (γ_s at cross-over of G' and G'') was found to decrease with increasing concentration, which, while counterintuitive, suggests the strong binding between the PVDF-TrFE and acetone.²² As the concentration increases, the number of polymer-solvent contact points decreases (increasing polymer-polymer binding points), therefore the gel becomes weakened and is able to flow with a lower γ_s . In translating this theory to extrusion printing, all of the three tested inks were suitable for printing; however, a lower flow point would decrease the required pressure input to extrude the sample, meaning the inks with higher PVDF-TrFE concentration are preferred for the printing.¹⁷

Finally, oscillatory σ_s cycling was undertaken to probe the recovery parameters of G' and G'' within the inks and determine the optimal PVDF-TrFE concentration (35 wt%, 40 wt% or 45 wt%) in acetone for extrusion printing (Supplementary Figure 5.S12).¹⁶ Here, the σ_s was cycled at constant ω (1 Hz) between 1 Pa and 5 kPa, representing the induced σ_s at rest and during printing, respectively, held constant for at least 70 s (Supplementary Figure 5.S12a). At PVDF-TrFE (35 wt%), the ink was unable to maintain σ_s at 5 kPa, whereas the inks containing 40 wt% and 45 wt% PVDF-TrFE exhibited consistent response to the input σ_s . The value for the $\tan(\delta)$, or the ratio of G'' and G' was <1 (marked by grey horizontal line) for all samples at 1 Pa σ_s and increased to >1 upon the application of 5 kPa σ_s for 70 s (Supplementary Figure 5.S12b). For the inks containing 40 wt% and 45 wt% PVDF-TrFE, the $\tan(\delta)$ remained constant throughout the 5 kPa σ_s region and completely recovered for all concentrations after 70 s at 1 Pa σ_s . During the second cycle, the 35 wt% ink was found to flow with the lowest resistance, represented by a $\tan(\delta)$ value of 20,000 (instrument limit), whereas the 40 wt% and 45 wt% inks retained similar values to the first cycle. Supplementary Figure 5.S12c shows the complex viscosity (η^*) of the PVDF-TrFE inks. As expected, the starting η^* was found to increase with increasing PVDF-TrFE concentration. During the first high σ_s cycle, the η^* was found to decrease significantly for the 35 wt% ink as a function of time and unable to recover to initial values in the subsequent low stress cycle. Conversely, the 40 wt% and 45 wt% PVDF-TrFE inks exhibited full recovery after two high stress cycles.

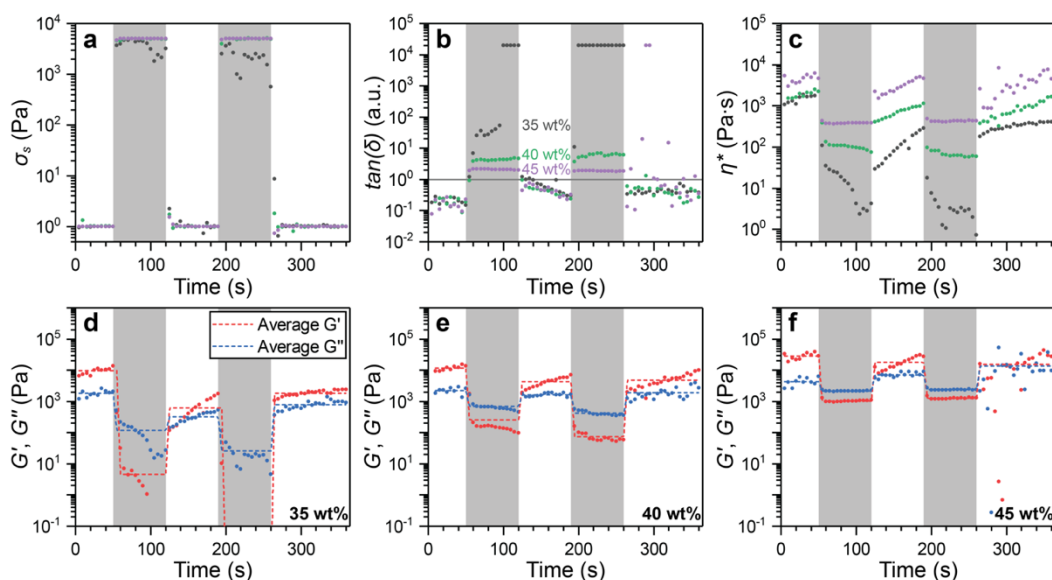


Figure 5.S12: Time-dependent oscillatory σ_s cycling for the PVDF-TrFE/acetone (35 wt%, 40 wt% and 45 wt%) inks. (a) The applied σ_s with the high stress regions shaded grey. (b) The $\tan(\delta)$ response to the shear stress with the liquid-solid transition point ($\tan(\delta) = 1$) represented by a solid grey line. (c) The η^* response to the shear stress. (d-f) The G' and G'' response to the shear stress for (d) 35 wt% PVDF-TrFE/acetone ink, (e) 40 wt% PVDF-TrFE/acetone ink and (f) 45 wt% PVDF-TrFE ink, performed with ω at 1 Hz.

The temporal evolution of the G' and G'' during the σ_s cycling is shown in Supplementary Figure 5.S12d-f for the three concentrations of PVDF-TrFE in acetone. For the 35 wt% ink (Supplementary Figure 5.S12d), the G' was observed to decrease rapidly as a function of time at $\sigma_s = 5$ kPa, with an average decrease over the timespan of greater than 1,000-fold. In the subsequent low- σ_s period, the slope of G' was higher than that of G'' ; however, the G' was unable to recover to the initial value of 9,600 Pa, reaching a maximum of 1,736 Pa. Throughout the second $\sigma_s = 5$ kPa cycle, the G' for the 35 wt% ink decreased significantly to below 1 mPa and subsequently exhibited a significantly lower slope during recovery. Conversely, the 40 wt% (Supplementary Figure 5.S12e) and 45 wt% (Supplementary Figure 5.S12f) PVDF-TrFE inks were stable under high- σ_s for at least one cycle and showed considerably higher G' recovery relative to the PVDF-TrFE (35 wt%) ink, from initial values of 11,800 Pa and 28,300 Pa, to final maxima of 7,000 Pa and 27,500 Pa, respectively. While the PVDF-TrFE (40 wt%) ink exhibited similar characteristics throughout the second $\sigma_s = 5$ kPa cycle (Supplementary Figure 5.S12e), the PVDF-TrFE (45 wt%) ink was unable to consistently recover to initial values (Supplementary Figure

5.S12f). Therefore, PVDF-TrFE (40 wt%) ink was selected for further experiments involving the incorporation of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets.

5.7.4 Properties of the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE films

5.7.4.1 Mechanical properties

The tensile mechanical properties of the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE films were measured by a dynamic mechanical tester (ElectroForce 5500, Bose, United States). Samples, with a length of 27 mm and a width of 5 mm (Supplementary Figure 5.S13a), were secured in grips by friction adhesive, with the distance between grips set at 5 mm (Supplementary Figure 5.S13b). The width (w) and thickness (t) of each sample is given in Supplementary Table 5.S1. The films were extended parallel to the printing axis at a rate of 0.01 mm s^{-1} . Notably, the instrument displacement limit was approximately 11 mm, significantly below the breaking strain of the sample.

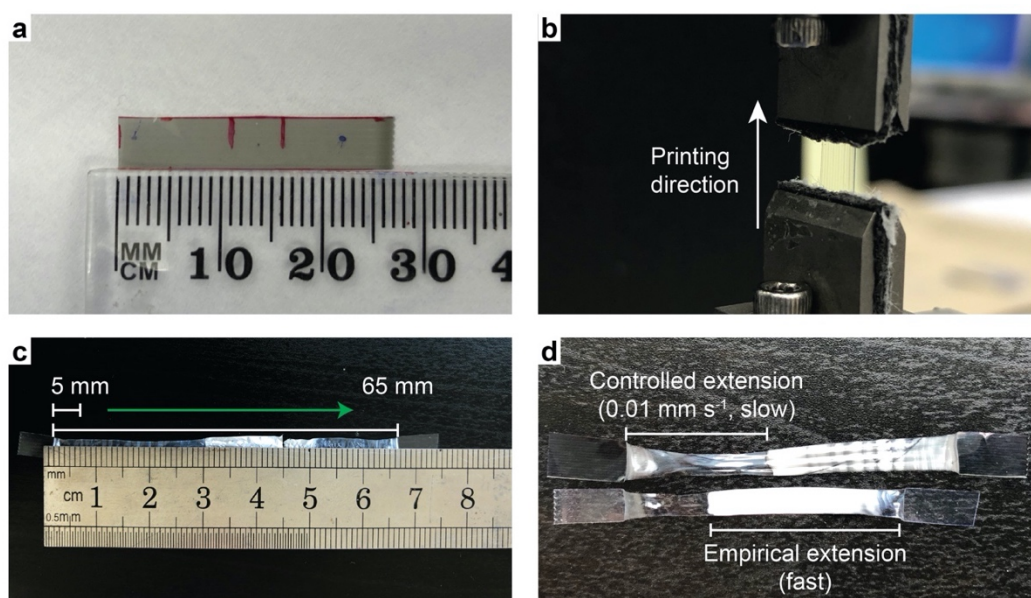


Figure 5.S13: The experimental layout of the mechanical testing. (a) Photograph of the geometry of the tested samples, with markings representing the position of the grips. (b) Photograph showing the sample inserted into the grips prior to extension. (c) Photograph showing the extent of extension required to break the SEA extrusion printed pristine PVDF-TrFE co-polymer film. (d) Photograph showing the dependence of transparency on the extension rate, shown for the SEA extrusion printed

Ti₃C₂T_x/PVDF-TrFE (0.10 wt%) film (top) and SEA extrusion printed pristine PVDF-TrFE co-polymer film (bottom).

Table 5.S1: Experimentally determined width (w) and thickness (t) for each sample measured during the tensile mechanical testing. The S values designate the sample number.

	Width (w , mm)			Thickness (t , μm)		
	S1	S2	S3	S1	S2	S3
Ti ₃ C ₂ T _x /PVDF-TrFE (0.00 wt%)	4.3	5.0	4.9	53	53	59
Ti ₃ C ₂ T _x /PVDF-TrFE (0.02 wt%)	5.2	5.0	5.2	54	49	51
Ti ₃ C ₂ T _x /PVDF-TrFE (0.10 wt%)	5.1	5.1	5.2	45	46	47
Ti ₃ C ₂ T _x /PVDF-TrFE (0.20 wt%)	4.8	5.1	5.0	36	37	37
Ti ₃ C ₂ T _x /PVDF-TrFE (0.50 wt%)	5.0	5.0	5.0	35	35	35

The tensile strain (γ_t) was calculated from the data obtained during tests following Supplementary Equation (5.S1), where L is the displacement and L_0 is the distance between grips at the beginning of the test (5 mm):

$$\gamma_t = L/L_0 \quad (5.S1)$$

The tensile stress (σ_t) was calculated from the data obtained during tests, using the cross-sectional area of the sample (A_{cs}), following Supplementary Equation (5.S2):

$$\sigma_t = \frac{F}{A_{cs}} = \frac{F}{t \times w} \quad (5.S2)$$

Here, F is the measured force, t is the thickness of the sample, and w is the width of the sample (cut to approximately 5 mm).

Due to the low displacement limit of the instrument, the strain at break was approximated *via* empirical measurements (Supplementary Figure 5.S13c), namely extending by hand. While these tests were merely representative, the samples were found to stretch to at least

65 mm prior to breaking, corresponding to 1,300% of the L_0 (5 mm). Additionally, the final transparency in the extended regions was observed to be higher when the extension rate was slower (Supplementary Figure 5.S13d).

5.7.4.2 Optical properties

The optical properties of the extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ films were characterised by ultraviolet, visible and near-infrared (UV-vis-NIR) spectrophotometry (Lambda 950, Perkin Elmer, United States). Spectra were obtained in the visible wavelength range (between 380 nm and 780 nm) with a step size of 5 nm. The incident light (T_i) was captured with no sample in place. The samples were then placed into a custom-made holder and secured to the entry port of a 150 mm diameter integrating sphere to capture all non-absorbed light (T_2). The total transmittance (T_t) of the sample was then taken as the fraction between T_2 and T_i (Supplementary Figure 5.S14a). The scattered light intensity in the instrument (T_3) was measured without the sample, using a light trap directly in the path of the beam (with diameter corresponding to 2° of the integrating sphere). Finally, the sample scatter (T_4) was measured with the light trap in place and the sample covering the entry port of the integrating sphere. The diffuse transmittance (T_d) was calculated following Supplementary Equation (5.S3) (Supplementary Figure 5.S14b) and the haze was calculated in accordance with the ASTM D1003 standard,²³ using Supplementary Equation (5.S4) (Supplementary Figure 5.S14c).

$$T_d = (T_4 - T_3 T_t) / T_i \quad (5.S3)$$

$$\text{Haze (\%)} = T_d / T_t \times 100 \quad (5.S4)$$

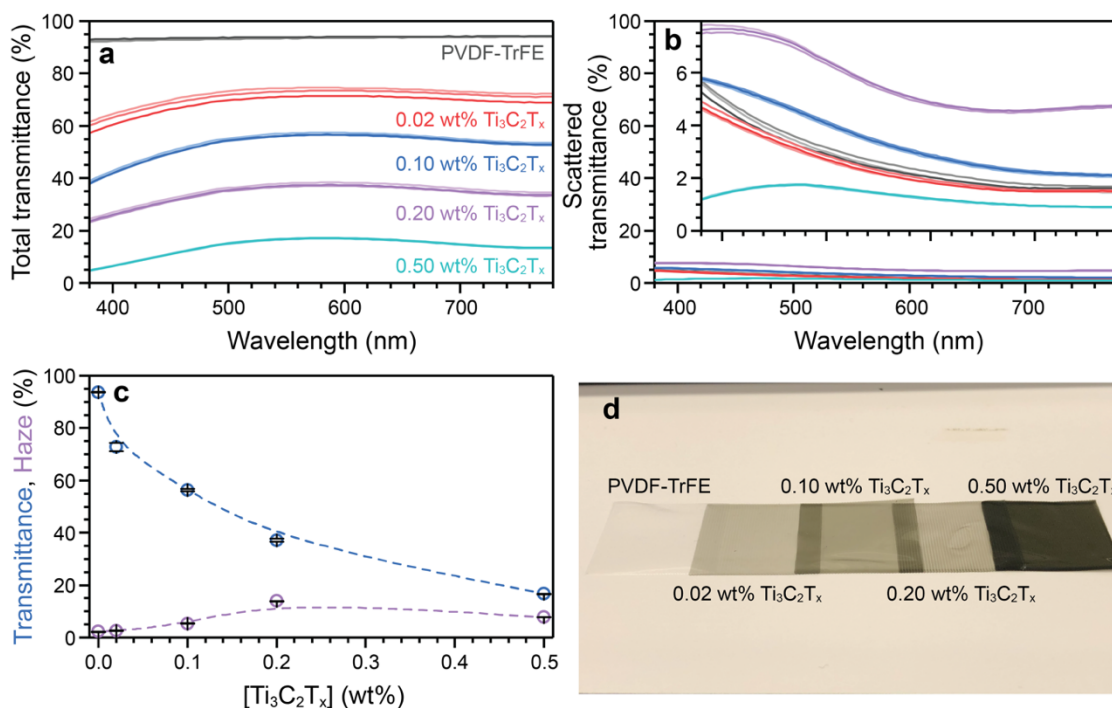


Figure 5.S14: Optical properties of SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt% and 0.50 wt%) films. (a) The total light transmittance (T_t). (b) The scattered light transmittance (T_d), inset shows the scattered transmittance below 7%. (c) The transmittance and haze as a function of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet concentration. (d) Side by side photograph showing the colour and transmittance of the films.

As expected, the transmittance was found to decrease as the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet concentration increased, from 94% for pristine PVDF-TrFE co-polymer to 20% for the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) film (Supplementary Figure 5.S14a, c, d). Surprisingly, the addition of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets did not significantly increase the scattered light intensity and haze (Supplementary Figure 5.S14b, c, Figure 5.2e), with the maximum obtained haze found in the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.20 wt%) film to be 13.9%, compared to the pristine PVDF-TrFE co-polymer film (2.2%). In fact, the scattered light transmittance (Supplementary Figure 5.S14b) was found to be lower at all wavelengths in the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.02 wt% and 0.50 wt%) films, compared to the pristine PVDF-TrFE film, suggesting the increase in haze with the incorporation of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets was largely governed by the decrease in the transmittance, as opposed to the scattering from aggregated $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets.

5.7.4.3 Raman analysis

The evolution of the Raman spectra when the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets are added to the PVDF-TrFE co-polymer reveals a clear suppression of out-of-plane vibrational modes occurring in $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE films. These modes occurring at $700 - 720 \text{ cm}^{-1}$ and 200 cm^{-1} correspond to the out-of-plane A_{1g} vibrational modes for oxygen functional groups bound to the $\text{Ti}_3\text{C}_2\text{T}_x$ lattice, whereas the peaks between 250 cm^{-1} and 700 cm^{-1} all correspond to in-plane E_g vibrational modes.²⁴ Notably, the A_{1g} modes at $700 - 720 \text{ cm}^{-1}$ disappear almost completely, even in the $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE (0.50 wt%) films, with no difference between solvent-cast and extrusion printed films (Figure 5.3a). In contrast, the intensity of the higher energy A_{1g} mode at 200 cm^{-1} appears unchanged or even have an increased intensity relative to the main E_{2g} modes (Figure 5.3a). While this contrast in intensity change appears anomalous, it supports the data for well exfoliated flakes in literature.²⁴ Here, it should be noted that the Raman spectrum of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets was attained by drop-casting $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets in DMF on a silicon wafer, likely resulting in restacking and stronger A_{1g} modes. The absence, or weak intensity, of these A_{1g} modes in the $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE films therefore implies two key points, (1) that the PVDF-TrFE co-polymer is an excellent stabilising agent for the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets as there is no evidence of restacking; and (2) there is a strong binding between the PVDF-TrFE co-polymer and $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets (and subsequent polymer densification) such that the A_{1g} modes are even further weakened and shifted.²⁵ These results confirm the strong electrostatic binding as predicted by MD simulations (Figure 5.1a).

Raman mapping of the surface of the $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE films showed a significantly variable response in the I_β/I_γ ratio (Supplementary Figure 5.S15). This variation was most noticeable for the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE (0.02 wt%) film and decreased with an increased $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet loading up to 0.50 wt%, where the sample presented a homogenous ratio. This improvement in sample homogeneity at higher $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet loadings is hypothesised to be due to the discrepancy in the state of the PVDF-TrFE co-polymer when it is bound to the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet basal plane. At higher $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet loadings, a high proportion of the PVDF-TrFE co-polymer is within the electrostatic sphere of influence (between 1 nm and 10 nm) of the $\text{Ti}_3\text{C}_2\text{T}_x$, thus presenting a homogenous I_β/I_γ .²⁶ The data from these maps was averaged and used for describing the average sample spectra and I_β/I_γ (Figure 5.3a,b). The solvent cast $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE film shows a higher variation in I_β/I_γ (Supplementary Figure 5.S15f)

which is attributed to the lack of homogenisation of 2D materials by the extrusion printing process.

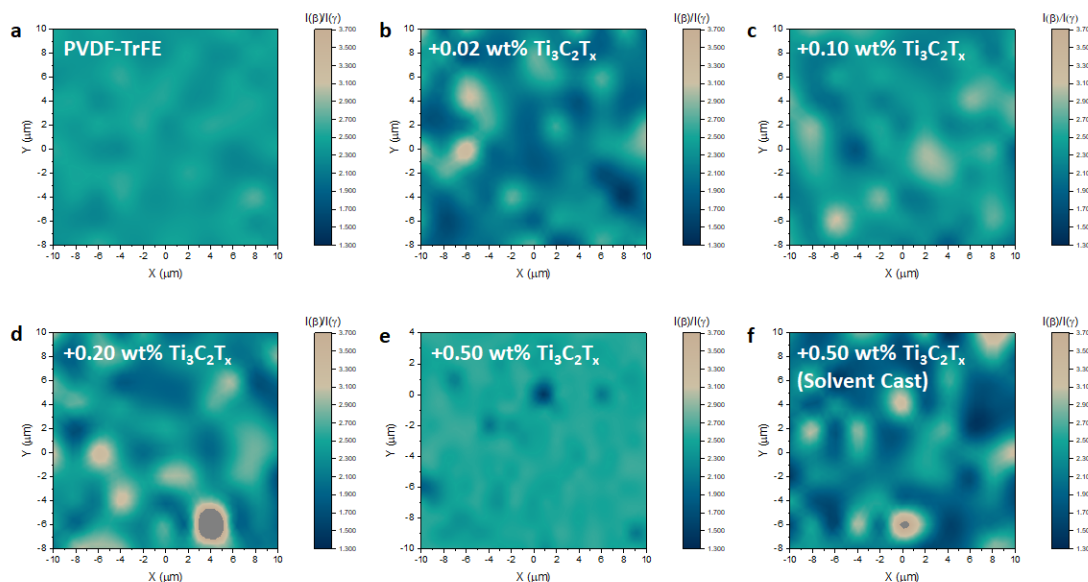


Figure 5.S15: The confocal Raman microscopy maps of the surface of the films, showing the intensity ratio (I_{β}/I_{γ}) between the β phase peak (842 cm^{-1}) and γ phase peak (811 cm^{-1}). (a) The SEA extrusion printed pristine PVDF-TrFE co-polymer film. (b) The SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.02 wt%) film. (c) The SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.10 wt%) film. (d) The SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.20 wt%) film. (e) The SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) film. (f) The solvent cast $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) film.

5.7.4.4 ATR-FTIR spectroscopy

ATR-FTIR spectroscopy was performed on the samples using an ALPHA II spectrometer (Bruker, United States). Absorbance spectra were collected by taking an average of 128 individual scans at a resolution of 1 cm^{-1} , between 600 cm^{-1} and 4000 cm^{-1} .

ATR-FTIR spectroscopy was used to estimate the fraction of phases in the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ films, for $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet concentrations at 0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt% and 0.50 wt% (Supplementary Figure 5.S16a). The peak commonly attributed to the α phase (766 cm^{-1}) was not distinctly visible in all the

measured spectra, suggesting the low fraction of the α phase in the bulk of the samples.¹⁴ Notably, as was determined by Raman microscopy (Figure 5.3d,e), the α phase was present in close proximity to the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet surface; however, the ATR-FTIR spectra suggested a low fraction of the α phase in the bulk of the $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE films. The peak at 840 cm^{-1} , indicative of the total electroactive phase (consisting of β and γ phases, denoted as $\beta+\gamma$), was present in all measured samples.¹³ The separate peaks γ phase (1235 cm^{-1}) and β phase (1290 cm^{-1}) were both observed, confirming the presence of both electroactive phases ($\beta+\gamma$); however, the separate peaks could not be deconvoluted as the γ phase peak was present as a shoulder.

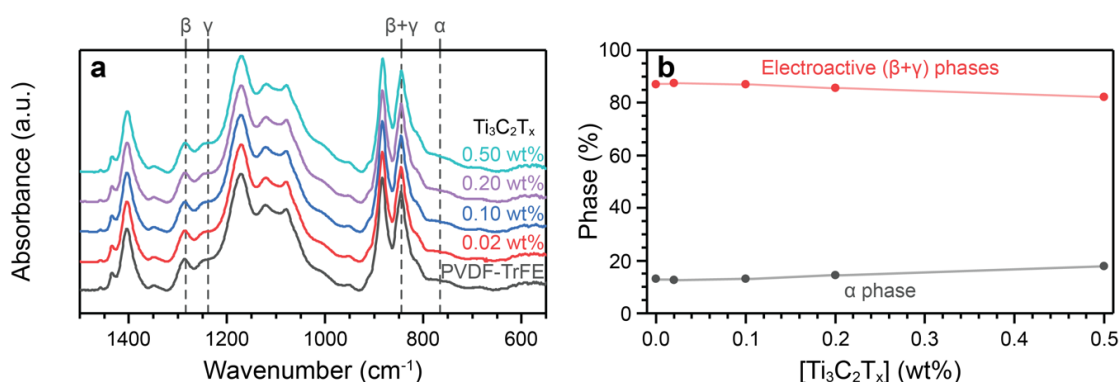


Figure 5.S16: ATR-FTIR spectroscopy characterisation of SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE (0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt% and 0.50 wt%) films. (a) The FTIR spectra, offset for clarity. (b) The relative fractions of the electroactive ($\beta+\gamma$) phases and the α phase as a function of $\text{Ti}_3\text{C}_2\text{T}_x$ concentration.

The total electroactive phase fraction (F_{ea}) was calculated using ATR-FTIR data by Supplementary Equation (5.S5):

$$F_{ea}(\%) = \frac{I_{ea}}{\left(\frac{K_{ea}}{K_{\alpha}}\right)I_{\alpha} + I_{ea}} \quad (5.S5)$$

Here, I_{ea} is the intensity of $\beta+\gamma$ peak, I_{α} is the intensity of α peak, K_{α} and K_{ea} are the absorption coefficients for the peaks at 766 cm^{-1} and 840 cm^{-1} , with values of $6.1 \times 10^4\text{ cm}^2\text{ mol}^{-1}$ and $7.7 \times 10^4\text{ cm}^2\text{ mol}^{-1}$, respectively.¹³ The F_{ea} of the pristine PVDF-TrFE copolymer film was 87.0% (Supplementary Figure 5.S16b), significantly higher relative to the pristine PVDF-TrFE films SEA extrusion printed from a solvent mixture of DMF and

acetone (40:60 vol%).¹⁰ The highest F_{ea} value was observed at 87.5% for the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.02 wt%) film, although this value exhibited little deviation from that of the pristine PVDF-TrFE film. Notably, at $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%), the F_{ea} was found to decrease to 82.0%, consistent with the local α phase formation in the PVDF-TrFE on the surface of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets (Figure 5.3e).

5.7.4.5 XRD analysis

XRD spectra were obtained for the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ films (0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt%, 0.50 wt%) using Bragg–Brentano geometry (D8 Advance, Bruker, United States) using Cu-K α radiation ($\lambda = 1.54060 \text{ \AA}$). The Bragg angle, 2θ , was varied between 5° and 70° with a step size of 0.02° and 1 s per step, with the sample rotated at 15 rpm. The films were placed on silicon low background holders for the measurements.

The phase distribution in the SEA extrusion printed films was analysed with XRD (Supplementary Figure 5.S17). Two main peaks were visible in the spectra. The broad peak at 18.1° was attributed to the (110/200) paraelectric γ phase reflection. The sharp peak at 20.2° corresponds to the (110/200) ferroelectric β phase reflection in PVDF-TrFE.²⁷ Due to the low concentration of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, no peaks were observed for the additive (Supplementary Figure 5.S1a) in the spectra. Additional peaks were found at 35.0° and 40.8° , attributed to the (001) ferroelectric phase reflection and (111/201), (400/220) ferroelectric phase reflections, respectively, confirming the primary presence of the β phase.^{28,29}

The primary fingerprint region (Supplementary Figure 5.S17b) region was further deconvoluted to investigate the distribution of phase fractions (Supplementary Figure 5.S18). The region required four peaks to ensure the correct fit. The strongest peak was assigned to the β phase (blue), the broad second peak was assigned to the γ phase (purple), the third peak was attributed to the α phase (yellow) and the final peak corresponded to the amorphous regions of the polymer (grey).

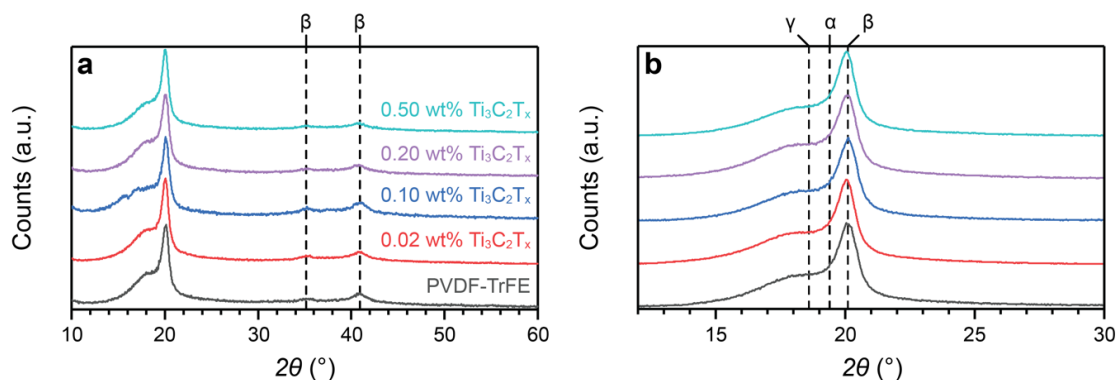


Figure 5.S17: XRD spectra of the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE films. (a) Survey scan. (b) Phase fingerprint region. Spectra offset for clarity.

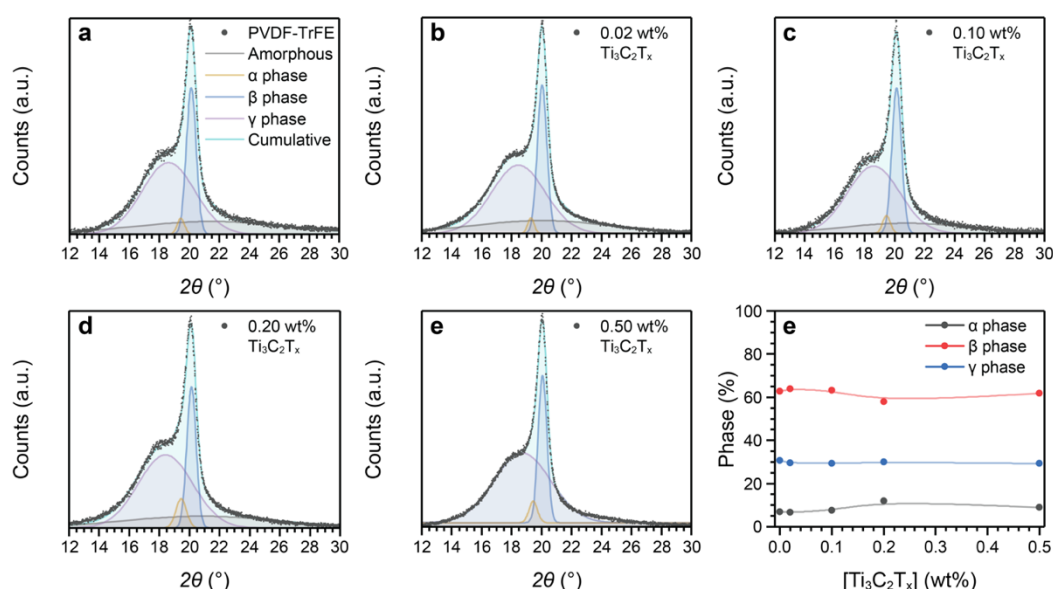


Figure 5.S18: XRD deconvolution for the phases in SEA extrusion printed films. (a) Pristine PVDF-TrFE copolymer. (b) $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE (0.02 wt%). (c) $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE (0.10 wt%). (d) $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE (0.20 wt%). (e) $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE (0.50 wt%). (f) Phase fractions determined from XRD as a function of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet concentration.

The deconvoluted XRD spectra (Supplementary Figure 5.S18a-e) were used to calculate the phase fractions (Supplementary Figure 5.S18f) within the PVDF-TrFE co-polymer in the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE (0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt%, 0.50 wt%) films from the intensities for the respective peaks following Supplementary Equation (5.S6a-c):

$$F_{\alpha} = \frac{I_{\alpha}}{I_{\alpha} + I_{\beta} + I_{\gamma}} \quad (5.S6a)$$

$$F_{\beta} = \frac{I_{\beta}}{I_{\alpha} + I_{\beta} + I_{\gamma}} \quad (5.S6b)$$

$$F_{\gamma} = \frac{I_{\gamma}}{I_{\alpha} + I_{\beta} + I_{\gamma}} \quad (5.S6c)$$

Here, I_{α} , I_{β} and I_{γ} correspond to the intensities for the peaks found at 19.4°, 20.2° and 18.1°, respectively. The phase distributions were found to correlate well with the data obtained from Raman spectroscopy (Figure 5.3b) and FTIR spectroscopy (Supplementary Figure 5.S16b). In particular, the F_{ea} calculated from the FTIR spectra for the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ films at $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet concentrations below 0.50 wt% (87%) matched closely with the sum of F_{β} and F_{γ} calculated from the deconvoluted XRD (between 85% and 90%). Furthermore, the Raman spectroscopy has suggested the primary phases in the bulk are the β and γ phases (Figure 5.3a), with the β phase as the primary component, which is in close agreement with the XRD data.

5.7.4.6 Differential scanning calorimetry

The crystallinity of the PVDF-TrFE co-polymer in the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt%, 0.50 wt%) films was measured by DSC (STA 5000, Perkin Elmer, United States). The samples were heated from 25 °C in a ceramic sample pan (N5200040, Perkin Elmer, United States) to 200 °C at a rate of 10 °C min⁻¹ under a nitrogen flow at 20 mL min⁻¹ (99.999% purity, BOC, United Kingdom).

The DSC thermograms (Supplementary Figure 5.S19) showed two endothermic peaks for all analysed samples, centred at approximately 105 °C and 142 °C.¹⁰ The peak at 105 °C corresponded to the ferroelectric to paraelectric transition (T_C), whereby the samples exhibit piezoelectric properties below the T_C and lose polarisation above the T_C .³⁰ The primary peak at 142 °C corresponds to the T_m , with the ΔH_m correlating to the crystallinity (χ_c) following Supplementary Equation (5.S7), where the enthalpy of melting for

completely crystalline PVDF-TrFE (ΔH_0) is given as 45 J g^{-1} , shown in Figure 5.3c of the main text.^{31,32}

$$\chi_c = \frac{\Delta H_m}{\Delta H_0} \quad (5.S7)$$

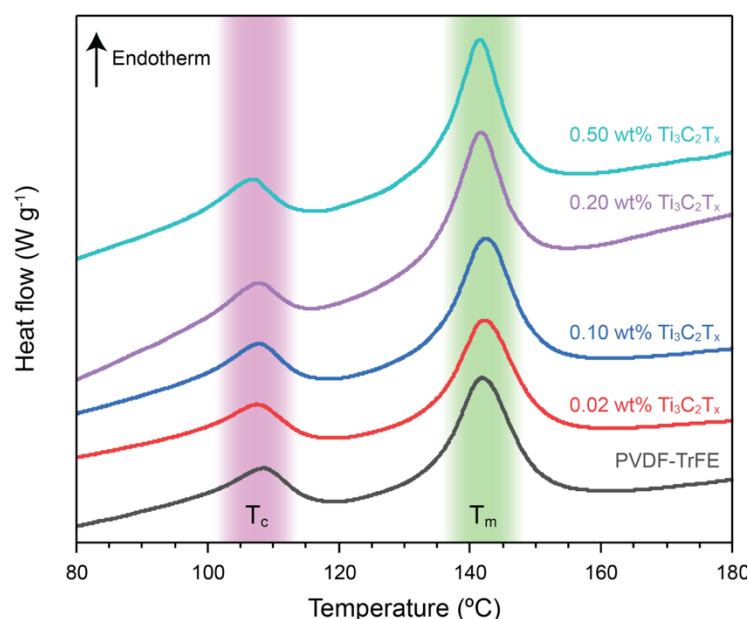


Figure 5.S19: DSC thermograms of the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE films, offset for clarity.

5.7.5 PFM of $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE films

PFM was carried out on the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE (0.00 wt%, 0.02 wt%, 0.10 wt%, 0.20 wt% and 0.50 wt%) films and solvent cast $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE (0.00 wt% and 0.50 wt%) films in order to probe the trends in the out-of-plane polarisation at the nanoscale. An atomic force microscope (Cypher ES, Oxford Instruments, United Kingdom) with a high voltage accessory, equipped with a solid platinum cantilever (12Pt400A, Rocky Mountain Nanotechnology, United States) was used for this testing.

The PFM of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets was carried out in DART mode at a bias of 1 V to confirm the absence of out-of-plane piezoelectricity. The scans were taken with 512

pixels per line and frequency at 0.5 Hz. To prepare the samples, the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets were cast from solvent (DMF) onto gold (Au) coated silicon (Si) wafers and dried under vacuum. The DART-PFM scans were taken at three scales, 5 μm (Supplementary Figure 5.S20a, d, g), 2 μm (Supplementary Figure 5.S20b, e, h), and 1 μm (Supplementary Figure 5.S20c, f, i and Figure 5.4a). No discernible difference between the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets (visible in the topography trace, Supplementary Figure 5.S20a-c) and the Si substrate was found in the phase (Supplementary Figure 5.S20d-f) or amplitude (Supplementary Figure 5.S20g-i) traces. Therefore, the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets were not observed to exhibit out-of-plane polarisation and assumed as a non-piezoelectric additive in these experiments.

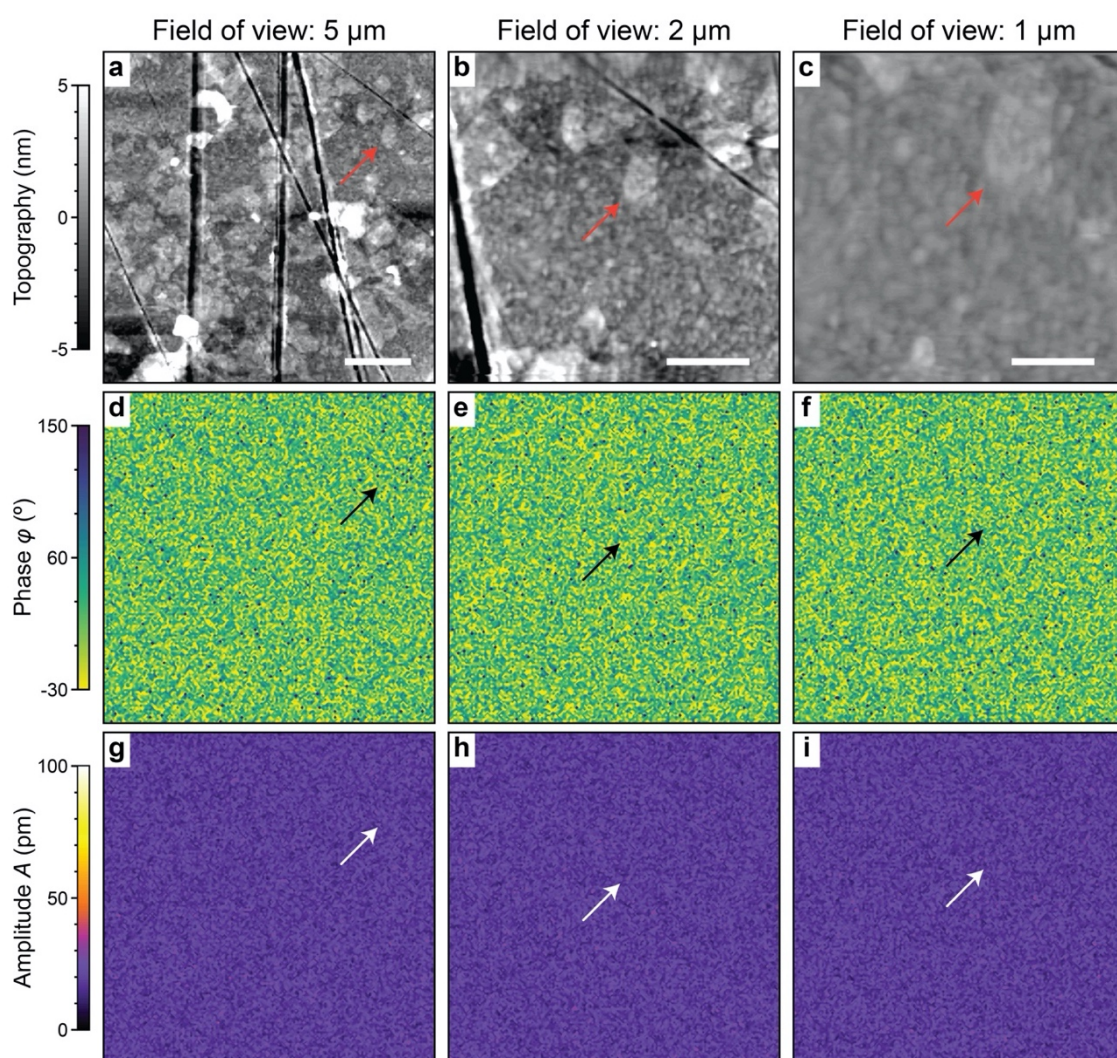


Figure 5.S20: DART-PFM maps of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets adsorbed on an Au-coated Si wafer. (a-c) The topography traces. (d-f) The piezoelectric phase (ϕ) traces. (g-i) The piezoelectric amplitude (A) traces. (a, d, g) Field of view corresponding to 5 μm . Scale bar represents 1 μm . (b, e, h) Field of view corresponding to 2 μm . Scale bar

represents 500 nm. (c, f, i) Field of view corresponding to 1 μm . Scale bar represents 250 nm. The arrow in each panel points to the location of the same $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet.

The PFM of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ films was carried out in lithography mode,¹⁰ whereby a bias was applied to individual regions, monitoring the piezoelectric response through the converse piezoelectric effect ($\gamma_3 = d_{33}E_3$, whereby γ_3 is the out-of-plane strain, d_{33} is the piezoelectric coefficient and E_3 is the out of plane electric field).^{13,33,34} The lithography mode was chosen to obtain data below the poling field, where typical ferroelectric hysteresis loops cannot be formed, such that the poling state of the material would be minimally altered.¹⁰ The applied voltage was between -20 V and +20 V, in increments of 2 V (Supplementary Figure 5.S21), imaged over an area with lateral dimensions at 5 μm and 256 lines per scan, corresponding to a resolution of approximately 19 nm per pixel, with a scan rate of 0.2 Hz.

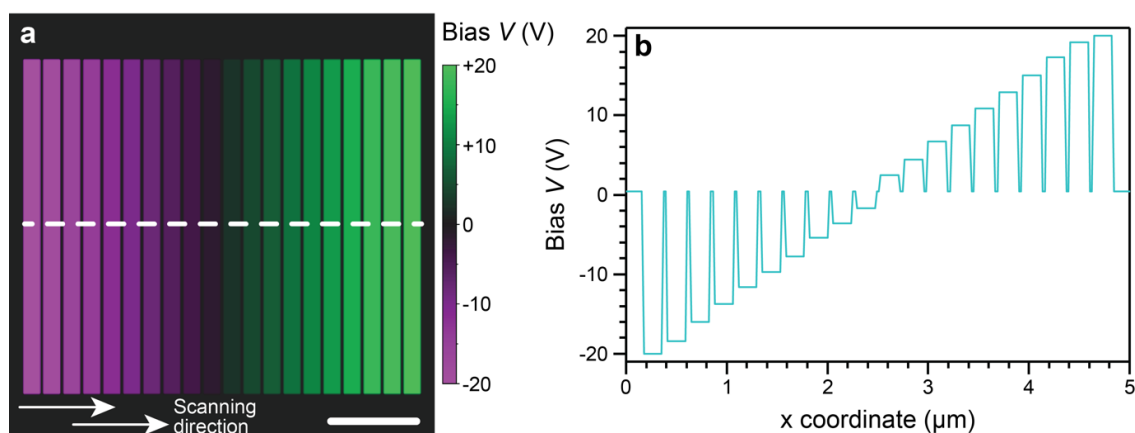


Figure 5.S21: Applied bias characteristics during the PFM measurements on the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ films. (a) Map of applied bias. Scale bar represents 1 μm . (b) Bias as a function of the x coordinate for a single line in the scan direction, which is signified by the dashed line in a.

Each voltage was applied to the sample in a rectangular pattern, with the length at 200 pixels and width at 10 pixels, such that each scanned line contains the PFM data for all applied voltages (Supplementary Figure 5.S21b). The measured data contained the topography, piezoelectric amplitude (A) and piezoelectric phase (φ). The data was obtained

both for SEA extrusion printed (Supplementary Figure 5.S22) and solvent-cast (Supplementary Figure 5.S23) $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ films.

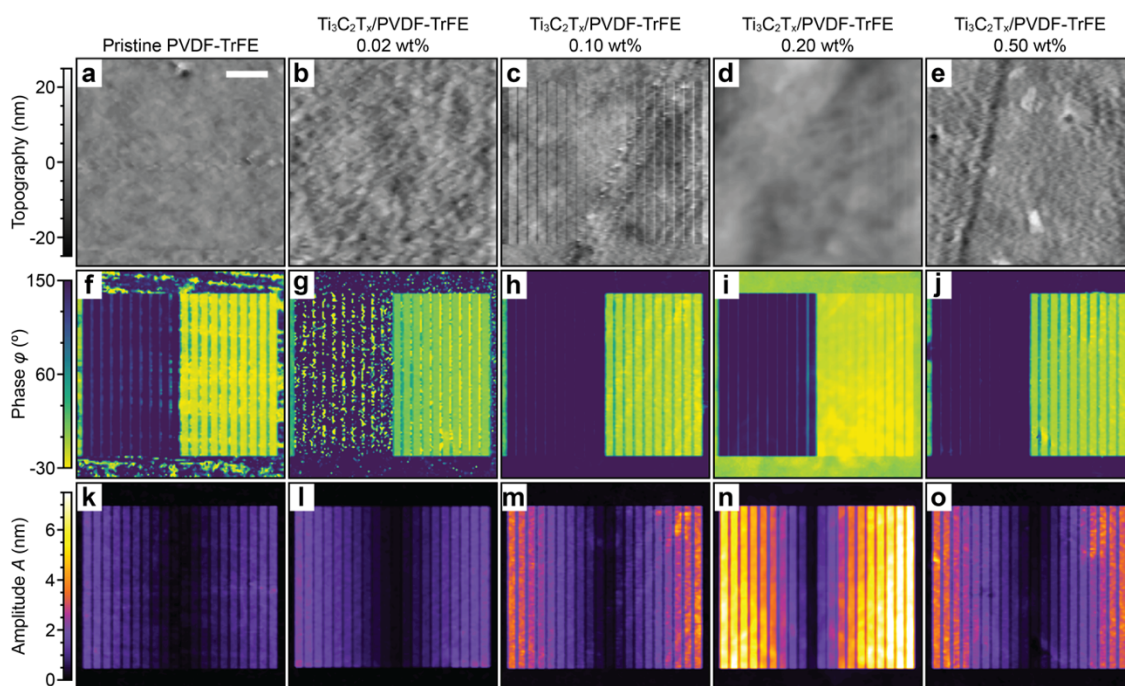


Figure 5.S22: Raw PFM data obtained for the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ films. (a-e) The topography. (f-j) The piezoelectric phase (φ). (k-o) The piezoelectric amplitude (A). The data was obtained for (a, f, k) pristine PVDF-TrFE (0.00 wt% $\text{Ti}_3\text{C}_2\text{T}_x$), (b, g, l) $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.02 wt%), (c, h, m) $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.10 wt%), (d, i, n) $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.20 wt%), (e, j, o) $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%). The scale bar represents 1 μm .

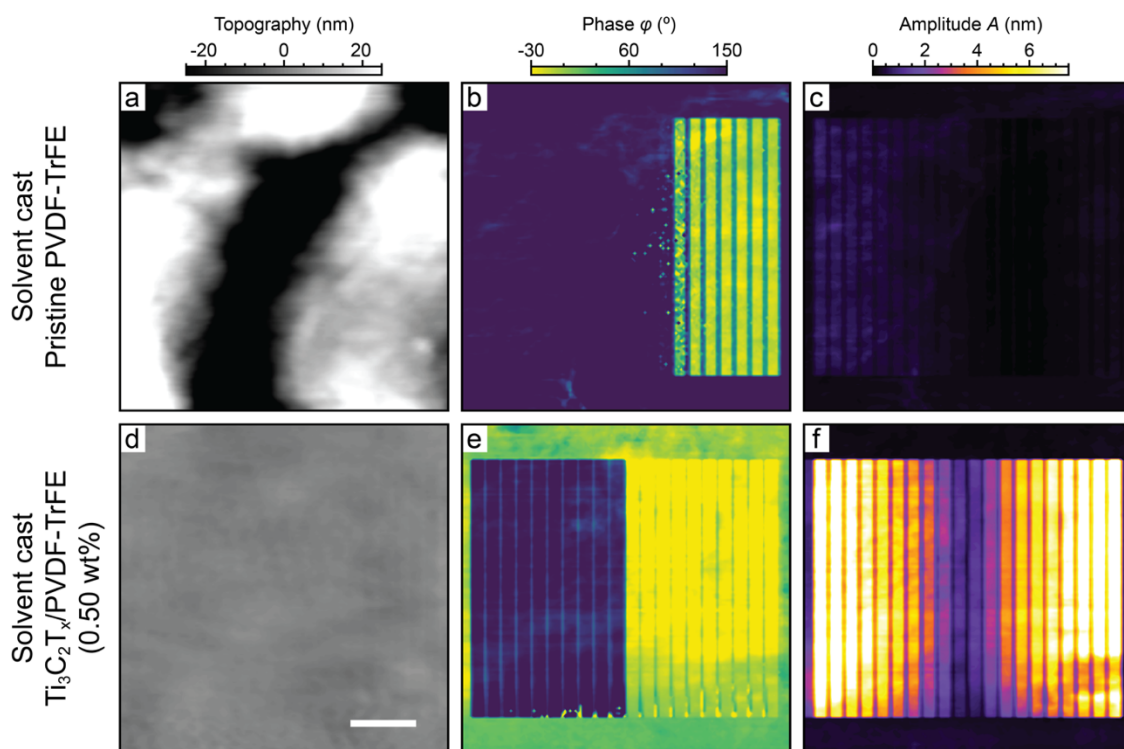
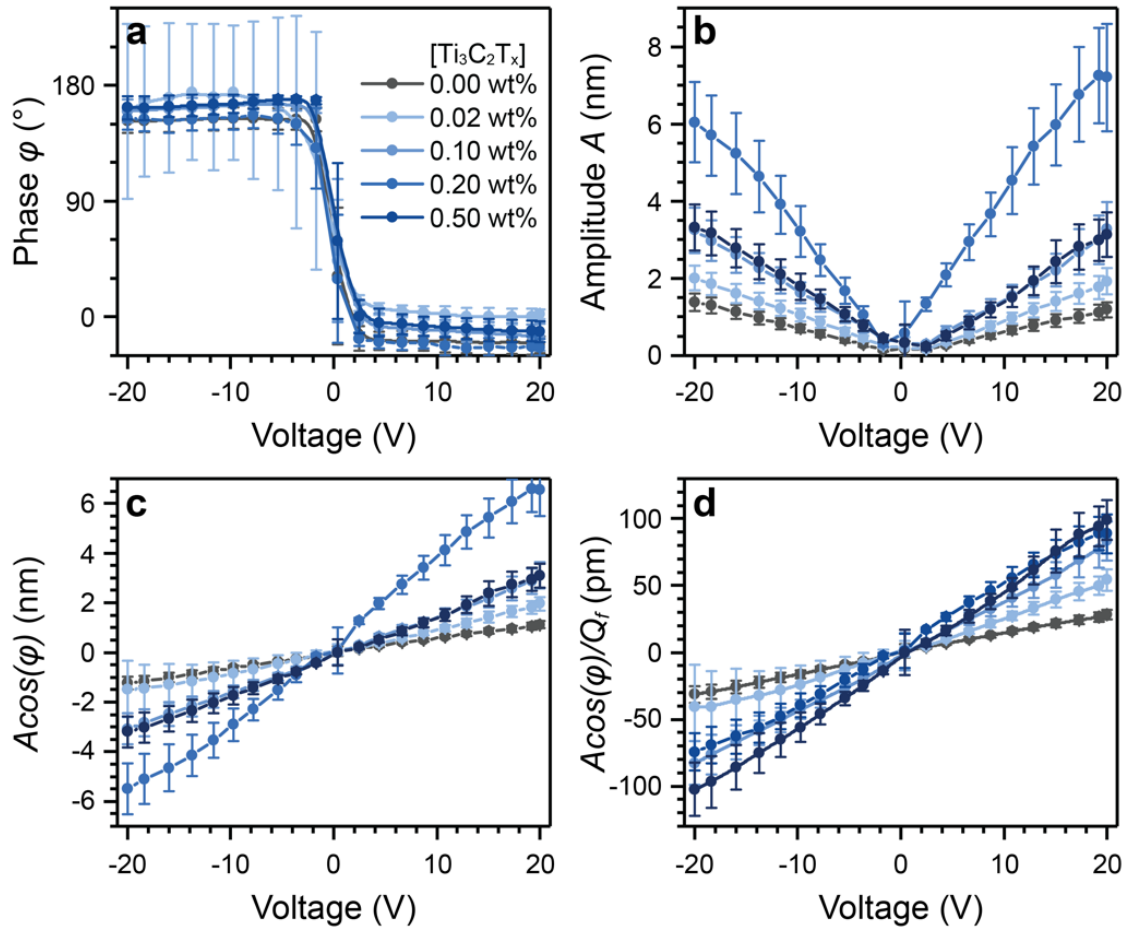


Figure 5.S23: Raw PFM data obtained for the solvent cast (a-c) pristine PVDF-TrFE and (d-f) $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) films. (a, d) The topography. (b, e) The piezoelectric phase (ϕ). (c, f) The piezoelectric amplitude (A).

The A and ϕ data (Supplementary Figure 5.S22f-o, Supplementary Figure 5.S23b, c, e, f) was processed using purpose-built Matlab code, which undertook pixel-by-pixel operations (Supplementary Figure 5.S24) to form the data obtained in Figure 5.4b by multiplying the A signal (Supplementary Figure 5.S24b) by the cosine of the ϕ signal (Supplementary Figure 5.S24a,c) and dividing by the Q factor of the cantilever (Q_f) for each applied bias (Supplementary Figure 5.S24d). The Q_f was measured in the tuning stage directly prior to the measurement (Supplementary Table 5.S2). To calculate the effective d_{33} , the $A\cos(\phi)/Q_f$ data was separated by the applied bias and averaged, obtaining a plot for $A\cos(\phi)/Q_f$ as a function of the applied bias for the samples (Supplementary Figure 5.S24d).

Table 5.S2: Experimentally determined Q_f for each PFM scan.

	Q_f (a.u.)	
	SEA extrusion printed	Solvent-cast
Pristine PVDF-TrFE (0.00 wt% $\text{Ti}_3\text{C}_2\text{T}_x$)	39.389	41.244
$\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.02 wt%)	36.083	-
$\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.10 wt%)	37.185	-
$\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.20 wt%)	73.754	-
$\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%)	31.188	75.479

**Figure 5.S24: Processed PFM results as a function of the input bias (V) for the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ films. (a) The phase (ϕ). (b) The amplitude (A). (c) The $\text{Acos}(\phi)$. (d) The $\text{Acos}(\phi)/Q_f$.**

In the converse piezoelectric effect, the d_{33} is given as shown in Supplementary Equation (5.S8a):³⁴

$$d_{33} = \left(\frac{\partial \gamma_3}{\partial E_3} \right)^\sigma \quad (5.S8a)$$

Here, the superscript σ denotes constant stress. In order to minimise the stress on the sample, the cantilever is required to possess a sufficiently low spring constant, in this case approximately 0.3 N m^{-1} . It should be noted, however, that the cantilever will nonetheless apply stress to the sample, therefore restricting the expansion in the measured material and providing an underestimate to the calculated d_{33} . The out-of-plane strain is given as $\gamma_3 = L/L_0$, whereby L is the magnitude of the expansion or contraction, and L_0 is the material thickness. In PFM, L corresponds to the normalised amplitude, shown in Supplementary Equation (5.S8b):

$$L = \frac{A \cos(\varphi)}{Q_f} \quad (5.S8b)$$

Therefore, the out-of-plane strain then takes on the form shown in Supplementary Equation (5.S8c):

$$\gamma_3 = \frac{A \cos(\varphi)}{Q_f L_0} \quad (5.S8c)$$

Moreover, the E_3 is given as the V applied per unit distance. In the case of PFM, as the material expands upon applied V , the expansion should include the distance of expansion, shown in Supplementary Equation (5.S8d):

$$E_3 = \frac{V}{L + L_0} \quad (5.S8d)$$

Hence, substituting Supplementary Equation (5.S8b) for L , the expression becomes as shown in Supplementary Equation (5.S8e):

$$E_3 = \frac{V}{(A \cos(\varphi)/Q_f) + L_0} \quad (5.S8e)$$

Finally, substituting Supplementary Equation (5.S8c) and Supplementary Equation (5.S8e) into Supplementary Equation (5.S8a), it takes on the form as shown in Supplementary Equation (5.S8f):

$$d_{33} = \frac{A \cos(\varphi)}{Q_f V} + \frac{(A \cos(\varphi))^2}{Q_f^2 L_0 V} \quad (5.S8f)$$

Notably, this expression still does not account for the stress applied to the sample by the cantilever, however it becomes a more accurate equation to obtain the d_{33} . Nonetheless, when a 10 nm A (1.00×10^{-8} m) is observed at $180^\circ \varphi$ (corresponding to $\cos(\varphi) = 1$) in a sample with 40 μm (4.00×10^{-5} m) L_0 under 20 V applied bias and Q_f at 30, the additional term corresponds to an increase in the effective d_{33} of 1.39×10^{-4} pm V $^{-1}$, a minute increase relative to an effective d_{33} at 16.67 pm V $^{-1}$. Therefore, for these experiments, the effective d_{33} was taken as $A \cos(\varphi)/Q_f V$.

As the applied V was below the poling voltage (maximum V at 20 V, minimum thickness at 37 μm , corresponding to a maximum $E_3 = 0.54$ MV m $^{-1}$, minimum poling E_3 at 50 MV m $^{-1}$),¹⁵ the slope of the plot for $A \cos(\varphi)/Q_f$ as a function of V was expected to be linear for all samples. Indeed, the data shown in Supplementary Figure 5.S24d was found to be linear over the measured range, taking into account the deviation over the measured scan area. The data was fit with a linear trendline for each sample, whereby the slope of the trendline, accounting for the error in each sample, was the effective d_{33} value.

The accuracy of the nanoscale polarisation measurements *via* PFM has been widely debated in recent literature, demonstrating the values can underrepresent or overrepresent the macroscale d_{33} both due to an empirical calculation methodology and the localised measurement approach.^{33,35} Nonetheless, these PFM experiments are able to show trends of the d_{33} in samples with similar composition, as has been demonstrated here. Notably, the most accurate methodology is to utilise a single cantilever, as has been undertaken in these experiments. The utilisation of multiple cantilevers has the potential to vary in the spring constant and therefore dampen the amplitude signal, subsequently changing the observed trends.

5.7.6 PEG fabrication and macroscale energy harvesting

PEGs were produced by sputter coating a metal electrode layer on both sides of the SEA extrusion printed Ti₃C₂T_x/PVDF-TrFE (0.00 wt% and 0.50 wt%) films, attaching wires

onto each electrode, and subsequently encapsulating the entire device in insulating adhesive. The sputter coated (Nanochrome I, Intlvac Thin Film Corporation, USA) electrodes consisted of a seeding chromium (Cr) layer and a gold (Au) layer, with a total thickness of 60 nm, deposited onto both sides through a shadow mask. The two electrode layers were deposited sequentially, without outgassing the chamber. The chamber pressure was maintained at 2 mTorr, with an argon (Ar) gas flow of $20 \text{ cm}^3 \text{ min}^{-1}$. The Cr layer deposition utilised an AC dual magnetron source at 500 W power, with a 10 s deposition time, corresponding to a Cr layer with thickness between 2 nm and 3 nm. The Au layer deposition utilised a DC magnetron source at 100 W power, with a 210 s deposition time, corresponding to an Au layer with thickness at 70 nm. The thickness of both layers was measured by AFM at 60 nm. The shadow mask was laser-cut from a 1 mm thick polymer sheet, pre-set for an opening with 1.5 cm length and 1.6 cm width, corresponding to an active area of 2.4 cm^2 . Additional tabs were laser-cut adjacent to the width axis, with 0.5 cm length and 0.8 cm width, which were used for the attachment of wires and did not overlap between the two electrodes, therefore did not provide additional active area. The shadow mask design is shown in Supplementary Figure 5.S25a and the sputter coated SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) films are shown in Supplementary Figure 5.S25b.

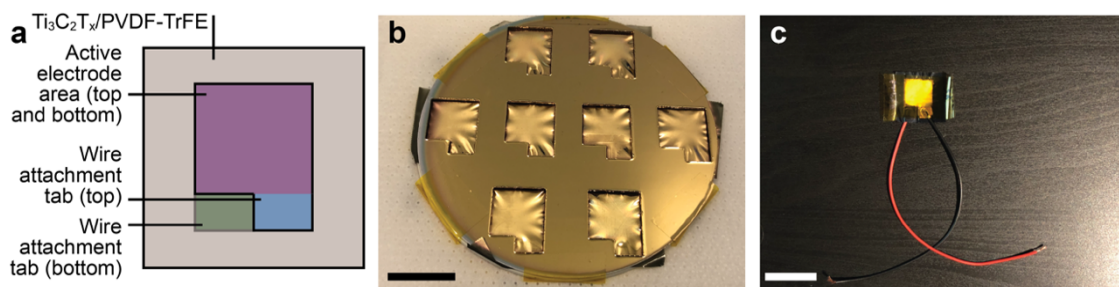


Figure 5.S25: Piezoelectric generator layout. (a) Schematic showing the layout of the electrodes and the wire attachment tabs on both surfaces of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ films. **(b)** Photograph of the layout of the laser-cut shadow mask, with sputter-coated SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) films as the active layer of the PEGs. Scale bar represents 2 cm. **(c)** Photograph showing the final SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) PEG. Scale bar represents 3 cm.

The wires (FLEXI-E 0.15, Stäubli Electrical Connectors AG, Switzerland) were cut to a length of 15 cm, with 0.6 cm stripped and exposed at each end. One end of each wire was soldered to the non-adhesive side of copper (Cu) foil adhesive (1181, 3M, United States), after cleaning the surface with propan-2-ol. Subsequently, the adhesive side of the Cu foil adhesive was attached to the designated tabs (Supplementary Figure 5.S25a) on each side of the sputter coated SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.00 wt% and 0.50 wt%) films. The final step in the PEG fabrication was the encapsulation in insulating polyimide (Kapton) adhesive, which was adhered to both sides of the film to ensure no external electrical influences affect the macroscale energy harvesting experiments. A photograph of the completed PEG is shown in Supplementary Figure 5.S25c.

The macroscale energy harvesting experiments were undertaken by the application of cyclic compression force and monitoring of the generated surface charge, configured to replicate the quasi-static Berlincourt method.³⁶ The cyclic compression was applied by a dynamic mechanical tester (ElectroForce 5500, Bose, United States) following a sinusoidal force pattern (Supplementary Figure 5.S26a, b). The surface charge was measured and converted to a voltage signal by a charge amplifier (Nexus 2692, Brüel & Kjær, Denmark). The resultant voltage signal was logged directly to file by a data acquisition instrument (9223, National Instruments, United States). The PVDF-TrFE PEGs possess a large source impedance,¹⁰ between 1 M Ω and 10 M Ω , therefore the majority of voltage measurement techniques will introduce error arising from the capacitance of the connection cables and the input impedance of the measurement device. For these experiments, the charge amplifier was chosen as it eliminates these errors.^{37,38}

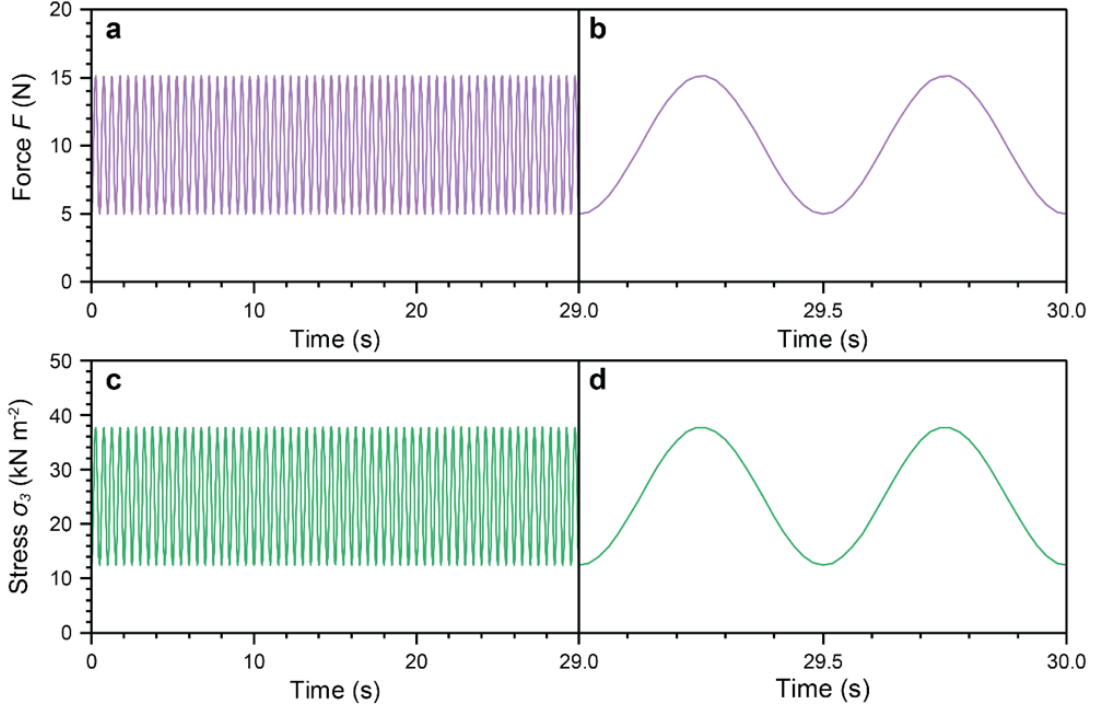


Figure 5.S26: Representative mechanical excitation input. (a) The input force (F) over 30 s with frequency at 2 Hz and (b) the enlarged view of the final 1 s. (c) The input stress (σ_3), calculated from a, with (d) the enlarged view of the final 1 s.

The generated surface charge as a result of input force follows the constitutive equation for the direct piezoelectric effect,^{13,34} given in Supplementary Equation (5.S9):

$$D_3 = d_{33}\sigma_3 + \varepsilon_{33}^\sigma E_3 \quad (5.S9)$$

Here, D_3 is the electric displacement field, d_{33} is the piezoelectric charge coefficient, σ_3 is the applied stress, ε_{33}^σ is the dielectric permittivity at constant stress, E_3 is the electric field and the subscripts correspond to the directionality, in this instance all parallel to the thickness axis. Notably, in short circuit conditions where the input impedance of the load (in this instance the charge amplifier) is significantly lower than the output impedance of the PEG, the charge is transferred with no resistance.³⁸ In this instance, minimal voltage is generated and therefore $E_3 \approx 0 \text{ V m}^{-1}$. Hence, the ε_{33}^σ can be ignored and the expression takes on the form shown in Supplementary Equation (5.S10):

$$D_3 = d_{33}\sigma_3 \quad (5.S10)$$

The d_{33} can then be directly calculated from the input stress and the resultant electric displacement field, as shown in Supplementary Equation (5.S11):

$$d_{33} = \left(\frac{\partial D_3}{\partial \sigma_3} \right)^E \quad (5.S11)$$

Here, the superscript E denotes a constant electric field ($\partial E_3 = 0$). The stress is calculated from Supplementary Equation (5.S2) and is shown as a function of time in Supplementary Figure 5.S26c, d. The load cell of the mechanical tester, used to apply the stress, was cylindrical with a radius (r) of 12.5 mm. The compressive area (A_σ) (Supplementary Figure 5.S27, blue line, Supplementary Figure 5.S28, blue dashed line) was calculated individually for the samples, as the placement of the sputter coated electrodes was variable relative to the dimensions of the SEA extrusion printed films. The height (h) from the top of the Cu adhesive foil to the top of the sample (Supplementary Figure 5.S27) was measured (Supplementary Table 5.S3) and the A_σ was calculated following Supplementary Equation (5.S12) for a circular segment:³⁹

$$A_\sigma = \pi r^2 - \left(r \cos^{-1} \left(\frac{r-h}{r} \right) - (r-h) \sqrt{2rh - h^2} \right) \quad (5.S12)$$

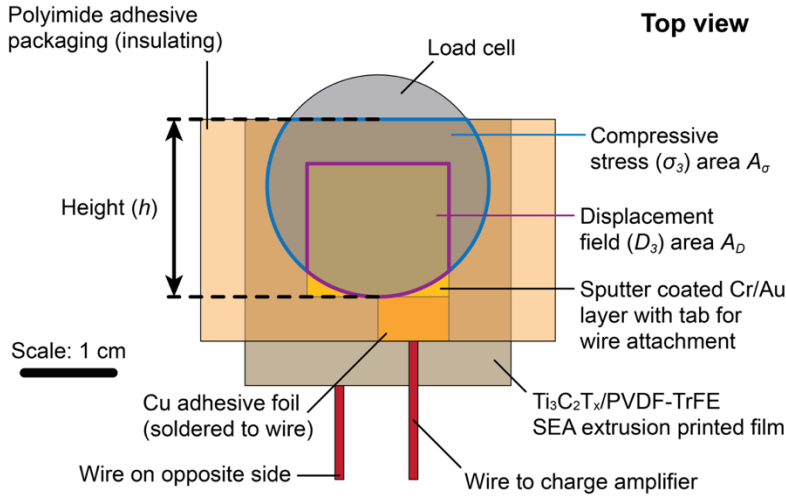


Figure 5.S27: Schematic showing the layout of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ PEG for energy harvesting tests.

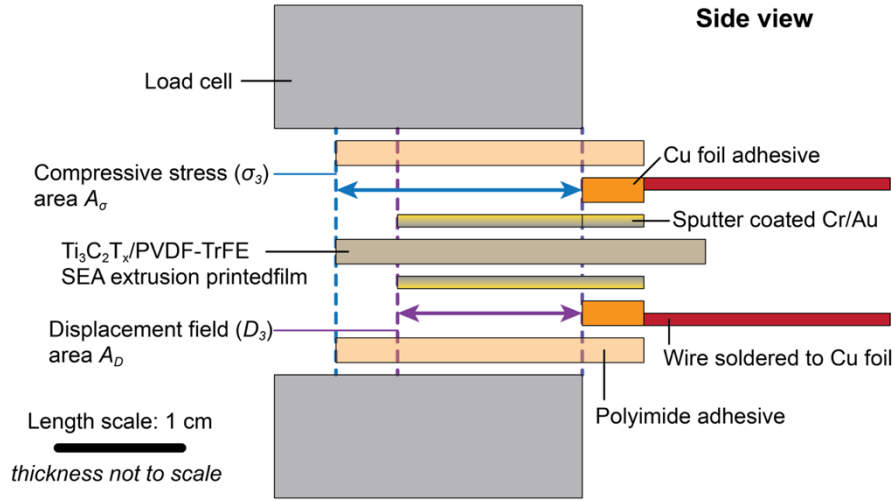


Figure 5.S28: Schematic showing the side view of the components of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ PEG during energy harvesting characterisation.

Table 5.S3: Values for the height (h) and the area under stress (A_σ) for energy harvesting experiments.

$\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet concentration in PVDF-TrFE	h (mm)	A_σ (10^{-4} m^2)
0.00 wt%	6.0	4.00
0.50 wt%	5.3	4.15

Similarly, the electric displacement field is a value normalised to the active area (A_D), shown in Supplementary Equation (5.S13):

$$D_3 = \frac{Q}{A_D} \quad (5.S13)$$

In this instance, the A_D corresponded to the area with sputter coated electrodes on both sides, which is under impact (Supplementary Figure 5.S27, purple line, Supplementary Figure 5.S28, dashed purple line). The load cell was placed on the PEG such that the load cell did not make contact with the Cu foil adhesive (Supplementary Figure 5.S27, Supplementary Figure 5.S28). The A_D was measured as 2.25 cm^2 ($2.25 \times 10^{-4} \text{ m}^2$), based on the active electrode dimensions at 15 mm length and 16 mm width, whereby the major part of the electrode was compressed (Supplementary Figure 5.S27).

In order to ensure the generated charge arose only from the piezoelectric effect, the dependence of D_3 on σ_3 was investigated. In piezoelectric materials, as demonstrated in Supplementary Equation (5.S11), the slope must be linear, corresponding to the d_{33} . In the instances where the slope is not linear, either the constant E requirement is not satisfied, or contributions from contact electrification and/or flexoelectricity are present.^{40–43} A representative SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) PEG was tested for this dependence. The minimum force was set at 5 N, to minimise the effects from contact electrification. The resultant data is shown in Supplementary Figure 5.S29. The slope was found to be linear, confirming the sole contribution of the direct piezoelectric effect to the measured surface charge.

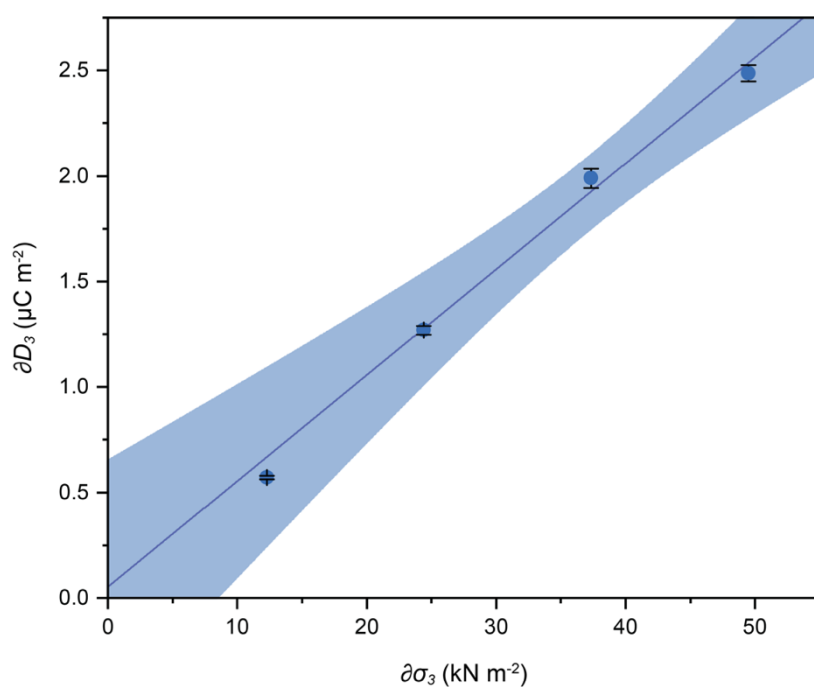


Figure 5.S29: The generated electric displacement field (∂D_3) as a function of the input stress ($\partial\sigma_3$) for the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) PEG. The solid line represents a linear fit to the data and the band represents a 95% confidence interval.

Upon the analysis of the generated surface charge (Q) in the SEA extrusion printed pristine PVDF-TrFE co-polymer PEG and the SEA extrusion printed $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ (0.50 wt%) PEG (Figure 5.4d), it was evident that a significant enhancement in the energy harvesting was observed upon the incorporation of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets into the

PVDF-TrFE co-polymer. In this instance, the D_3 is related to the polarisation (P_3) following Supplementary Equation (5.S14):³⁴

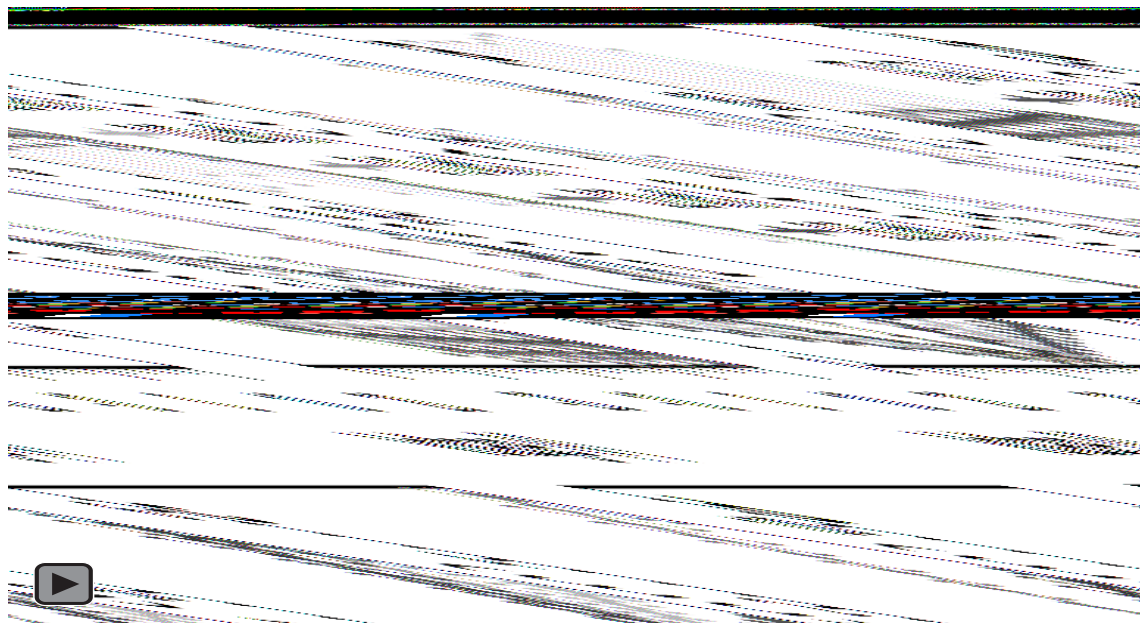
$$D_3 = \varepsilon_{33}^{\sigma} E_3 + P_3 \quad (5.S14)$$

Here, the previously reported enhancements in the ε of $\text{Ti}_3\text{C}_2\text{T}_x$ /fluoropolymer composites⁴⁴ are neglected due to the absence of external electric fields ($E \approx 0 \text{ V m}^{-1}$), therefore the enhancements in Q (and subsequently the D_3) were attributed directly to enhancements in the P_3 . The polarisation is given as the sum of the individual dipole moment vectors (μ_3) within a given volume (V), as shown in Supplementary Equation (5.S15), supporting the enhanced dipole moment alignment within the materials, as the dipole moment magnitude and the volume were constant.

$$P_3 = \frac{\sum \mu_3}{V} \quad (5.S15)$$

The d_{33} of the $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE (0.50 wt%) PEG (at -52.0 pC N^{-1}) was found to be higher than that of completely poled PVDF-TrFE in literature (at approximately -38 pC N^{-1}),^{13,45} suggesting that the electrical poling technique commonly utilised in literature does not completely polarise the pristine PVDF-TrFE co-polymer.^{15,46} The presence of dielectric breakdown at a high poling electric field strength is hypothesised as the limiting factor in achieving completely polarised PVDF-TrFE for their utilisation as PEGs.⁴⁷ Overcoming the limitation posed by the dielectric breakdown has profound opportunities in a multitude of fields where piezoelectric materials are used. The dipole locking mechanism from a nanomaterial template, as described in this study, has tremendous potential to unlock new applications for flexible piezoelectric materials, where the cost and energy input during manufacture is currently limiting commercial adoption.

5.7.7 Supplementary videos



Video 5.S1: Temporal evolution of the PVDF-TrFE co-polymer polarisation vector direction adsorbed on a $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet substrate (left) and graphene substrate (right) over a 1.6 ns timespan. The PVDF-TrFE film consists of 70 co-polymer chains.

5.7.8 Supplementary references

1. J. Zhang, S. Seyedin, S. Qin, Z. Wang, S. Moradi, F. Yang, P. A. Lynch, W. Yang, J. Liu, X. Wang, X. Wang and J. M. Razal, Highly Conductive $\text{Ti}_3\text{C}_2\text{T}_x$ MXene Hybrid Fibers for Flexible and Elastic Fiber-Shaped Supercapacitors, *Small*, **15**, 1804732 (2019).
2. M. R. Lukatskaya, S. Kota, Z. Lin, M. Q. Zhao, N. Shpigel, M. D. Levi, J. Halim, P. L. Taberna, M. W. Barsoum, P. Simon and Y. Gogotsi, Ultra-high-rate pseudocapacitive energy storage in two-dimensional transition metal carbides, *Nature Energy*, **2**, 17105 (2017).
3. Y. Xia, T. S. Mathis, M. Q. Zhao, B. Anasori, A. Dang, Z. Zhou, H. Cho, Y. Gogotsi and S. Yang, Thickness-independent capacitance of vertically aligned liquid-crystalline MXenes, *Nature*, **557**, 409–412 (2018).

4. M. R. Lukatskaya, O. Mashtalir, C. E. Ren, Y. Dall'Agnese, P. Rozier, P. L. Taberna, M. Naguib, P. Simon, M. W. Barsoum and Y. Gogotsi, Cation intercalation and high volumetric capacitance of two-dimensional titanium carbide, *Science*, **341**, 1502–1505 (2013).
5. J. Zhang, N. Kong, S. Uzun, A. Levitt, S. Seyedin, P. A. Lynch, S. Qin, M. Han, W. Yang, J. Liu, X. Wang, Y. Gogotsi and J. M. Razal, Scalable Manufacturing of Free-Standing, Strong $\text{Ti}_3\text{C}_2\text{T}_x$ MXene Films with Outstanding Conductivity, *Advanced Materials*, **32**, 2001093 (2020).
6. C. J. Zhang, S. Pinilla, N. McEvoy, C. P. Cullen, B. Anasori, E. Long, S. H. Park, A. Seral-Ascaso, A. Shmeliov, D. Krishnan, C. Morant, X. Liu, G. S. Duesberg, Y. Gogotsi and V. Nicolosi, Oxidation Stability of Colloidal Two-Dimensional Titanium Carbides (MXenes), *Chemistry of Materials*, **29**, 4848–4856 (2017).
7. A. Rosenkranz, P. G. Grützmacher, R. Espinoza, V. M. Fuenzalida, E. Blanco, N. Escalona, F. J. Gracia, R. Villarroel, L. Guo, R. Kang, F. Mücklich, S. Suarez and Z. Zhang, Multi-layer $\text{Ti}_3\text{C}_2\text{T}_x$ -nanoparticles (MXenes) as solid lubricants – Role of surface terminations and intercalated water, *Applied Surface Science*, **494**, 13–21 (2019).
8. J. Halim, K. M. Cook, M. Naguib, P. Eklund, Y. Gogotsi, J. Rosen and M. W. Barsoum, X-ray photoelectron spectroscopy of select multi-layered transition metal carbides (MXenes), *Applied Surface Science*, **362**, 406–417 (2016).
9. P. C. Sherrell, K. Sharda, C. Grotta, J. Ranalli, M. S. Sokolikova, F. M. Pesci, P. Palczynski, V. L. Bemmer and C. Mattevi, Thickness-Dependent Characterization of Chemically Exfoliated TiS_2 Nanosheets, *ACS Omega*, **3**, 8655–8662 (2018).
10. N. A. Shepelin, P. C. Sherrell, E. Goudeli, E. N. Skountzos, V. C. Lussini, G. W. Dicinoski, J. G. Shapter and A. V. Ellis, Printed recyclable and self-poled polymer piezoelectric generators through single-walled carbon nanotube templating, *Energy & Environmental Science*, **13**, 868–883 (2020).
11. N. Yamada, A. Shiratori and G. Murasawa, A poly(vinylidene fluoride) film printing system using solution droplet casting, *Smart Materials and Structures*, **28**, 044003 (2019).
12. N. A. Shepelin, V. C. Lussini, P. J. Fox, G. W. Dicinoski, A. M. Glushenkov, J. G. Shapter and A. V. Ellis, 3D printing of poly(vinylidene fluoride-

- trifluoroethylene): a poling-free technique to manufacture flexible and transparent piezoelectric generators, *MRS Communications*, **9**, 159–164 (2019).
13. N. A. Shepelin, A. M. Glushenkov, V. C. Lussini, P. J. Fox, G. W. Dicinoski, J. G. Shapter and A. V. Ellis, New developments in composites, copolymer technologies and processing techniques for flexible fluoropolymer piezoelectric generators for efficient energy harvesting, *Energy & Environmental Science*, **12**, 1143–1176 (2019).
 14. P. Martins, A. C. C. Lopes and S. Lanceros-Mendez, Electroactive phases of poly(vinylidene fluoride): Determination, processing and applications, *Progress in Polymer Science*, **39**, 683–706 (2014).
 15. A. J. Lovinger, Ferroelectric polymers. *Science*, **220**, 1115–1121 (1983).
 16. L. Li, Q. Lin, M. Tang, A. J. E. Duncan and C. Ke, Advanced Polymer Designs for Direct-Ink-Write 3D Printing, *Chemistry: A European Journal*, **25**, 10768–10781 (2019).
 17. G. M. Gratson and J. A. Lewis, Phase behavior and rheological properties of polyelectrolyte inks for direct-write assembly, *Langmuir*, **21**, 457–464 (2005).
 18. A. Bottino, G. Capannelli, S. Munari and A. Turturro, Solubility parameters of poly(vinylidene fluoride), *Journal of Polymer Science Part B: Polymer Physics*, **26**, 785–794 (1988).
 19. M. H. Wagner and J. Meissner, Network disentanglement and time-dependent flow behaviour of polymer melts, *Die Makromolekulare Chemie*, **181**, 1533–1550 (1980).
 20. G. M. Kavanagh and S. B. Ross-Murphy, Rheological characterisation of polymer gels, *Progress in Polymer Science*, **23**, 533–562 (1998).
 21. P. Gao and M. R. Mackley, General model for the diffusion and swelling of polymers and its application to ultra-high molecular mass polyethylene, *Proceedings of the Royal Society A*, **444**, 267–285 (1994).
 22. A. L. Kjøniksen, B. Nyström and B. Lindman, Dynamic viscoelasticity of gelling and nongelling aqueous mixtures of ethyl(hydroxyethyl)cellulose and an ionic surfactant, *Macromolecules*, **31**, 1852–1858 (1998).
 23. American Society for Testing and Materials. *ASTM D1003-13, Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics* (2013).
 24. A. Sarycheva and Y. Gogotsi, Raman Spectroscopy Analysis of the Structure and Surface Chemistry of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, *Chemistry of Materials*, **32**, 3480–3488 (2020).

25. A. Weerasinghe, C. T. Lu, D. Maroudas and A. Ramasubramaniam, Multiscale Shear-Lag Analysis of Stiffness Enhancement in Polymer-Graphene Nanocomposites, *ACS Applied Materials & Interfaces*, **9**, 23092–23098 (2017).
26. M. E. Beck and M. C. Hersam, Emerging Opportunities for Electrostatic Control in Atomically Thin Devices, *ACS Nano*, **14**, 6498–6518 (2020).
27. R. Su, J. K. Tseng, M. S. Lu, M. Lin, Q. Fu and L. Zhu, Ferroelectric behavior in the high temperature paraelectric phase in a poly(vinylidene fluoride-co-trifluoroethylene) random copolymer, *Polymer*, **53**, 728–739 (2012).
28. M. C. García-Gutiérrez, A. Linares, I. Martín-Fabiani, J. J. Hernández, M. Soccio, D. R. Rueda, T. A. Ezquerra and M. Reynolds, Understanding crystallization features of P(VDF-TrFE) copolymers under confinement to optimize ferroelectricity in nanostructures, *Nanoscale*, **5**, 6006–6012 (2013).
29. E. Bellet-Amalric and J. F. Legrand, Crystalline structures and phase transition of the ferroelectric P(VDF-TrFE) copolymers, a neutron diffraction study, *European Physical Journal B*, **3**, 225–236 (1998).
30. M. Piedrahita-Bello, B. Martin, L. Salmon, G. Molnár, P. Demont and A. Bousseksou, Mechano-electric coupling in P(VDF-TrFE)/spin crossover composites, *Journal of Materials Chemistry C*, **8**, 6042–6051 (2020).
31. P. Cebe and J. Runt, P(VDF-TrFE)-layered silicate nanocomposites. Part 1. X-ray scattering and thermal analysis studies, *Polymer*, **45**, 1923–1932 (2004).
32. X. Chen, J. Shao, N. An, X. Li, H. Tian, C. Xu and Y. Ding, Self-powered flexible pressure sensors with vertically well-aligned piezoelectric nanowire arrays for monitoring vital signs, *Journal of Materials Chemistry C*, **3**, 11806–11814 (2015).
33. A. L. Kholkin, S. V. Kalinin, A. Roelofs and A. Gruverman, Review of Ferroelectric Domain Imaging by Piezoresponse Force Microscopy, in *Scanning Probe Microscopy*, ed. S. V. Kalinin and A. Gruverman, Springer, New York (2007).
34. Publication and Proposed Revision of ANSI/IEEE Standard 176-1987 “ANSI/IEEE Standard on Piezoelectricity”, *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*, **43**, 717 (1996).
35. A. Gruverman, M. Alexe and D. Meier, Piezoresponse force microscopy and nanoferroic phenomena, *Nature Communications*, **10**, 1661 (2019).

36. D. B. Deutz, J. A. Pascoe, B. Schelen, S. Van Der Zwaag, D. M. De Leeuw, and P. Groen, Analysis and experimental validation of the figure of merit for piezoelectric energy harvesters, *Materials Horizons*, **5**, 444–453 (2018).
37. A. J. Fleming and S. O. R. Moheimani, Precision current and charge amplifiers for driving highly capacitive piezoelectric loads, *Electronics Letters*, **39**, 282–284 (2003).
38. B. Y. Lee, J. Zhang, C. Zueger, W. J. Chung, S. Y. Yoo, E. Wang, J. Meyer, R. Ramesh and S. W. Lee, Virus-based piezoelectric energy generation, *Nature Nanotechnology*, **7**, 351–356 (2012).
39. J. W. Harris and H. Stöcker, *Handbook of Mathematics and Computational Science*, Springer, New York (1998).
40. A. Šutka, P. C. Sherrell, N. A. Shepelin, L. Lapčinskis, K. Mālnieks and A. V. Ellis, Measuring Piezoelectric Output—Fact or Friction?, *Advanced Materials*, **32**, 2002979 (2020).
41. L. Zhou, D. Liu, J. Wang and Z. L. Wang, Triboelectric nanogenerators: Fundamental physics and potential applications, *Friction*, **8**, 481–506 (2020).
42. A. Ahmed, I. Hassan, M. F. El-Kady, A. Radhi, C. K. Jeong, P. R. Selvaganapathy, J. Zu, S. Ren, Q. Wang and R. B. Kaner, Integrated Triboelectric Nanogenerators in the Era of the Internet of Things, *Advanced Science*, **6**, 1802230 (2019).
43. T. D. Nguyen, S. Mao, Y. W. Yeh, P. K. Purohit and M. C. McAlpine, Nanoscale flexoelectricity, *Advanced Materials*, **25**, 946–974 (2013).
44. S. Tu, Q. Jiang, J. Zhang, X. He, M. N. Hedhili, X. Zhang and H. N. Alshareef, Enhancement of Dielectric Permittivity of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene/Polymer Composites by Controlling Flake Size and Surface Termination, *ACS Applied Materials & Interfaces*, **11**, 27358–27362 (2019).
45. C. R. Bowen, H. A. Kim, P. M. Weaver and S. Dunn, Piezoelectric and ferroelectric materials and structures for energy harvesting applications, *Energy & Environmental Science*, **7**, 25–44 (2014).
46. Y. Liu, H. Aziguli, B. Zhang, W. Xu, W. Lu, J. Bernholc and Q. Wang, Ferroelectric polymers exhibiting behaviour reminiscent of a morphotropic phase boundary, *Nature*, **562**, 96–100 (2018).
47. J. Claude, Y. Lu, K. Li and Q. Wang, Electrical storage in poly(vinylidene fluoride) based ferroelectric polymers: Correlating polymer structure to electrical breakdown strength, *Chemistry of Materials*, **20**, 2078–2080 (2008).

6 CONCLUDING REMARKS

The translation of piezoelectric technologies to commercial devices is a multi-faceted problem. Due to the coupling between mechanical and electrical phenomena, and hence the breadth of scope between mechanical, materials and electrical engineering disciplines, these aspects must be addressed. The understanding of parameters relating the material properties to the electromechanical energy conversion efficiency enables the elegant tailoring of these parameters through a toolbox of techniques commonly found in the fields of physics and chemistry of materials.

The overarching aim of this thesis was the intelligent enhancement of the net polarisation vector in PVDF-TrFE, as a model piezoelectric polymer, in order to eliminate electrical poling from the production pathway for flexible piezoelectric energy conversion devices. To achieve this, tools and techniques readily available in materials science and engineering were used, altering the processes of polymer deposition and poling. The polymerisation of fluoropolymers was not experimentally investigated in this thesis; however, the literature concerning this production step was critically reviewed in Chapter 2. This thesis demonstrated the utility of SEA 3D printing for the deposition of PVDF-TrFE at low temperatures, inducing partial dipole alignment through shear stress. The addition of non-piezoelectric SWCNTs to the SEA 3D printing of PVDF-TrFE revealed a dipole templating mechanism at the interface between the polymer and the additive, complementing the partial alignment of the dipoles in PVDF-TrFE. The PVDF-TrFE and its composites were observed to form a physical gel in acetone, which allowed the recycling and reshaping of the SEA 3D printed energy conversion devices. Finally, the addition of non-piezoelectric 2D $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes to the SEA 3D printing of PVDF-TrFE from acetone enabled the elucidation of the dipole templating and polarisation locking mechanism at the polymer-nanomaterial interface, forming *via* electrostatic interactions. The resultant polarisation-locked $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF-TrFE}$ composites exhibited a bulk piezoelectric charge coefficient of 52.0 pC N^{-1} without poling, significantly higher than that of literature reports for electrically poled PVDF-TrFE at approximately 38 pC N^{-1} .

The literature review in Chapter 2 investigated the relevant and recent literature in order to understand the fundamental phenomenon of piezoelectricity, how it occurs in fluoropolymers, and the critical parameters influencing the energy conversion capabilities of fluoropolymers. In particular, the correlation between materials properties and the

piezoelectric figures of merit was addressed. The crystallinity, polymorph distribution and net dipole moment vector direction all play a pivotal role, thus requiring all parameters to be carefully monitored during the research and development stages. The crystallinity and polymorph distributions were reported to change in response to the introduction of co-monomers and controlling the defects during polymerisation, as well as the introduction of multiple nanoscale additives. The dipole moment vector direction was reported to be tailored by the deposition and processing techniques, primarily through the utilisation of electric fields during either step. New methods to enhance these parameters were presented throughout this chapter and form the basis for the subsequent research chapters.

The optimisation of SEA 3D printing in Chapter 3 utilised a deposition technique with imparted shear stress and investigated the influence of the shear stress on the piezoelectric energy conversion, as a function of the layer number. The PVDF-TrFE, dissolved in a binary solvent mixture of DMF and acetone was optimised for multiple 3D printing parameters, such as solvent ratios and polymer concentration, relating to viscosity, extrusion pressure, temperature, nozzle internal diameter, substrate and speed of printing, in order to obtain well-resolved structures. The printed PVDF-TrFE was optically transparent and flexible, with the electroactive phase fraction observed at above 75% and exhibiting minimal variation as a function of layer number. This printed PVDF-TrFE was found to possess energy conversion characteristics, with a printed thin film generating a peak-to-peak voltage of 69.6 mV under mechanical compression, which is not observed in solvent cast thin films. The addition of a structured layer on top of the printed thin film enhanced the generated voltage by 316% to 289.3 mV. The capability to convert energy in the SEA 3D printed PVDF-TrFE was hypothesised to arise from the induced shear stress acting to partially align the dipole moments in the polymer.

Building on the technique developed in Chapter 3, the role of SWCNTs as a 1D additive was investigated in SWCNT/PVDF-TrFE nanocomposite 3D printed thin films, with SWCNT concentrations between 0.00 wt% and 0.50 wt% relative to the polymer. The SWCNTs, as 1D additives, are able to align parallel to the nozzle wall and are non-piezoelectric, therefore any changes in the energy conversion characteristics were expected to arise due to the crystallinity, polymorph distribution or polarisation vector changes. The crystallinity and polymorph distributions of the SEA 3D printed composite films

were found to be stable with increasing SWCNT concentration, contrary to prior literature on CNT/fluoropolymer composites. Importantly, the PFM and cyclic compression analysis revealed an enhancement in energy conversion efficiency at an optimised SWCNT concentration of 0.02 wt%, which confirmed a polarisation enhancement effect from a non-piezoelectric additive. This phenomenon was investigated further by MD simulations, observing a templating of the net dipole moment of the PVDF-TrFE parallel to the SWCNT length axis. Furthermore, a recycling method was proposed and validated using acetone in order to reprint the 0.02 wt% SWCNT/PVDF-TrFE films. The recycled films exhibited minimal changes in the materials properties, however, were found to generate a higher electrical power density at $70.6 \mu\text{W cm}^{-3}$ from a single finger tap. This power density places the unpoled composite energy conversion device well within the range reported for electrically poled fluoropolymers and is capable of powering implanted medical devices such as pacemakers. The recycled 0.02 wt% SWCNT/PVDF-TrFE energy conversion devices can be used for at least 10,000 compression cycles, exhibiting a peak-to-peak voltage at approximately 6 V throughout testing, and are able to charge a 100 nF dielectric capacitor to 3.5 V in 1.2 min *via* a bridge rectifier.

The dipole templating effect due to the incorporation of SWCNTs was the first report of such a phenomenon, however the mechanism of this effect was not deduced. In Chapter 5, a 2D $\text{Ti}_3\text{C}_2\text{T}_x$ MXene was used as an additive in order to understand the dipole templating effect. The interface between the OH terminated MXene and a PVDF-TrFE film was modelled *via* MD simulations, uncovering the dipole templating and polarisation locking in the PVDF-TrFE chains. Furthermore, a similar experiment set on a graphene substrate did not exhibit these effects, confirming the polarisation locking mechanism occurred due to electrostatic interactions between the MXene nanosheet and the PVDF-TrFE. The incorporation of the $\text{Ti}_3\text{C}_2\text{T}_x$, prepared by the MILD technique, into the PVDF-TrFE at 0.02 wt% $\text{Ti}_3\text{C}_2\text{T}_x$ resulted in a small decrease in the crystallinity and the electroactive β phase fraction, localised to the interface between the additive and the polymer, correlating to MD simulations. Importantly, the effective piezoelectric charge coefficient, d_{33} , was found to increase in this composite relative to the pristine PVDF-TrFE *via* PFM, experimentally confirming the polarisation locking in the $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE composites. Moreover, the effective d_{33} grew logarithmically with the $\text{Ti}_3\text{C}_2\text{T}_x$ concentration, nearing a saturation point at a concentration of 0.50 wt%. A three-fold enhancement of the effective d_{33} was observed in the SEA 3D printed pristine PVDF-TrFE films relative

to the solvent cast films due to the shear-induced polarisation. Conversely, no difference in the effective d_{33} was observed between the solvent cast and SEA 3D printed composite films at 0.50 wt% $\text{Ti}_3\text{C}_2\text{T}_x$, suggesting the polarisation locking occurs during mixing of the polymer and the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, rather than during printing. The bulk energy conversion characterisation uncovered a significantly higher d_{33} in the SEA 3D printed 0.50 wt% $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF-TrFE composite film relative to the literature values for electrically poled PVDF-TrFE and showed no degradation after 10,000 compression cycles. This finding suggests the dielectric breakdown at high electric fields limits the maximum polarisation in fluoropolymers. More importantly, this chapter highlighted the potential to control the magnitude and direction of the polarisation vector of fluoropolymers through electrostatic forces at the nanoscale.

Nonetheless, in answering the research questions of this thesis, additional questions have been raised throughout the duration of this research, which should be addressed in order to further develop the flexible piezoelectric energy conversion technology. These questions encompass both the fundamental research on the polarisation control and the integration of the flexible energy conversion devices into emerging applications.

Currently, the relationship between the physical parameters of fluoropolymers and the resultant energy conversion efficiency is poorly understood.¹ Therefore, it is of increasing importance to understand this structure-property interaction. Within the polymerisation step, a variety of input parameters could be investigated in relation to the electromechanical performance, such as the molecular weight, polydispersity, polymerisation pressure, polymerisation temperature, defect type, defect frequency or the type of initiator (subsequently the terminal groups).

The influence of the electrode material used to harvest the converted energy is another variable, which is sparsely addressed from a materials engineering perspective. The presence of energy loss in piezoelectric energy conversion devices is known, reported recently by Roscow *et al.*²; however, a lack of understanding on the influence of matching the electronic and physical properties of the electrodes to the fluoropolymer further limits enhancement of the electromechanical conversion efficiency. The phenomena of work function matching and band engineering are well documented³ in solid-state physics and

can be extended to piezoelectric materials, relating the difference in work function to the measured energy conversion performance. Furthermore, the measured electromechanical properties could be correlated to other relevant properties such as the interfacial adhesion,⁴ electrode material conductivity⁵ or electrode thickness,⁶ in order to obtain a more complete understanding of the influence of these effects.

The work in this thesis has developed the SEA 3D printing parameters and fine-tuned these parameters by eliminating DMF from the solvent mixture. Decreasing the internal diameter of the 3D printing nozzle will enable the printing of finer structures (reducing the filament width) and decrease the thickness. To date, nozzles with internal diameters as low as 5 μm have been employed for SEA 3D printing applications,⁷ which is promising for energy conversion applications due to higher shear stress at the nozzle wall, which results in higher alignment of the fluoropolymer chains.⁸ The increased pressure required for extrusion, which follows the Hagen-Poiseuille equation,⁹ requires the careful tailoring of the rheology of the inks. This advancement has great potential to substitute current micro-electro-mechanical systems with polymeric materials.¹⁰

The dipole templating enables the systematic net polarisation vector control in fluoropolymers by electrostatic interactions. By modulating the fraction of aligned dipole moments in a certain direction, the polarisation can either be maximised in the desired direction, or fixed at a desired FOM with respect to the required application. The MXene class is appealing as the surface termination can be controlled.¹¹ For example, an amine-functionalised MXene, which possesses a positive surface charge¹² in contrast to the hydroxyl terminated MXene in Chapter 5, could be used to investigate the direction reversal of the PVDF-TrFE polarisation vector. Alternatively, the magnitude of surface charge could be modulated through the fraction of electron-withdrawing surface terminations. In addition, alternative structured materials could be probed for their effects on the polarisation of fluoropolymers, such as metal-organic frameworks or transition metal dichalcogenides.¹³

The ability to pattern the polarisation enables the substitution of brittle ceramic materials, some of which are lead based (e.g., PZT) and therefore toxic, for fluoropolymers in order to target both piezoelectric and ferroelectric applications. As an example, polarisation-patterned fluoropolymers give rise to flexible non-volatile memories, allowing for large

storage densities with decreasing feature dimensions.^{14, 15} Furthermore, multi-layer polarisation-patterned fluoropolymers films enable complex states, further increasing information density by patterning along the thickness axis. This technology can be extended to a larger scale for the manufacture of soft and flexible human-machine interfaces, with multiple dimensions of interaction based on location and polarisation state.

The widely accepted *P-E* hysteresis technique, which has been outlined in Chapter 2, applies an electric field to the material in order to measure the polarisation, altering the polarisation state in the process.¹⁶ Conversely, for the development of highly polarised piezoelectric materials without utilising electric fields, alternative characterisation techniques must be employed. The direction dependent piezoelectric polarisation-induced signals have been reported in nuclear magnetic resonance (NMR) spectroscopy by Hughes and Pandey.¹⁷ Such a technique could thus be utilised for the measurement of polarisation in piezoelectric materials. By extension, an imaging technique such as magnetic resonance imaging (MRI) has the potential to image the distribution of polarisation vectors within the material and enable further development of alternative polarisation locking mechanisms.

The key limitation of PFM as a tool to probe polarisation at the nanoscale is the qualitative nature of the measurements. The PFM technique can compare the polarisation between two similar materials; however, it is not currently capable of quantitatively determining the piezoelectric coefficients of these materials.¹⁸ This deviation is hypothesised to arise from the stress imparted onto the measured sample by the cantilever during measurements, following Equation (2.6). Overcoming this limitation is an important aspect to the field of piezoelectric and ferroelectric materials, which could subsequently enable the determination of the piezoelectric FOMs at the nanoscale.

A possible extension of this research is the further development of the SEA 3D printing technique for fluoropolymer energy conversion materials. Prior reports on 3D printing have demonstrated the capability to SEA 3D print in three dimensions⁷ (in comparison to the layer-by-layer approach demonstrated in this thesis), print onto moving substrates,¹⁹ and print directly onto a living organ.²⁰ These advancements unlock tremendous opportunity in the SEA 3D printing of fluoropolymers for the direct application as wearable

and/or implantable devices.^{21, 22} The opportunity to SEA 3D print directly onto the skin results in single-step, disposable and conformal energy harvesters for powering portable electronics.¹⁹ Meanwhile, the opportunity to print directly onto an exposed organ allows for the powering of cardiac pacemakers, where the surgical removal is currently required ten years post-implantation to replace the battery.²³ A piezoelectric energy harvester could therefore be SEA 3D printed directly onto the heart, conformal to the curvature of the heart, and provide long-term supplemental power to the pacemaker.

In order to effectively manufacture energy conversion devices utilising the piezoelectric materials and processes developed in this thesis, the electrode coating step must be integrated into the device fabrication process. The electrode material, which coats the surface of the fluoropolymer on both sides, could be SEA 3D printed before (in the case of the bottom electrode) and after the fluoropolymer layer (the top electrode). The printing technique allows for the patterning of the electrode layer, enabling advanced geometries. Silver-based inks are promising candidates and have been reported as advanced 3D printed geometries,⁷ as well as possible printing onto skin.¹⁹ The integration of the fluoropolymer deposition with electrode deposition would act to minimise the number of processing steps, in turn reducing the cost of manufacture. Furthermore, this method could be utilised for a multitude of applications by varying the electrode patterns using computer-aided design, ranging from the on-skin and implantable energy harvesters to flexible human-machine interfaces and soft robotics.

6.1 References

1. T. Soulestin, V. Ladmiral, F. D. D. Santos and B. Améduri, Vinylidene fluoride- and trifluoroethylene-containing fluorinated electroactive copolymers. How does chemistry impact properties?, *Progress in Polymer Science*, **72**, 16-60 (2017).
2. J. I. Roscow, H. Pearce, H. Khanbarez, S. Kar-Narayan and C. R. Bowen, Modified energy harvesting figures of merit for stress- and strain-driven piezoelectric systems, *European Physics Journal Special Topics*, **228**, 1537-1554 (2019).
3. J. L. Freeouf and J. M. Woodall, Schottky barriers: An effective work function model, *Applied Physics Letters*, **39**, 727-729 (1981).
4. K. L. Mittal, Adhesion aspects of metallization of organic polymer surfaces, *Journal of Vacuum Science and Technology*, **13**, 19-25 (1976).
5. S. Kasap, C. Koughia and H. E. Ruda, Electrical Conduction in Metals and Semiconductors, in *Springer Handbook of Electronic and Photonic Materials*, ed. S. Kasap and P. Capper, Springer, Cham (2017).
6. F. Lacy, Developing a theoretical relationship between electrical resistivity, temperature, and film thickness for conductors, *Nanoscale Research Letters*, **6**, 636 (2011).
7. N. Zhou, C. Liu, J. A. Lewis and D. Ham, Gigahertz Electromagnetic Structures via Direct Ink Writing for Radio-Frequency Oscillator and Transmitter Applications, *Advanced Materials*, **29**, 1605198 (2017).
8. M. K. Hausmann, P. A. Rühs, G. Siqueira, J. Läger, R. Libanori, T. Zimmermann and A. R. Studart, Dynamics of Cellulose Nanocrystal Alignment during 3D Printing, *ACS Nano*, **12**, 6926-6937 (2018).
9. G. M. Gratson and J. A. Lewis, Phase behavior and rheological properties of polyelectrolyte inks for direct-write assembly, *Langmuir*, **21**, 457-464 (2005).
10. S. Trolier-McKinstry and P. Muralt, Thin Film Piezoelectrics for MEMS, *Journal of Electroceramics*, **12**, 7-17 (2004).
11. D. Xiong, X. Li, Z. Bai and S. Lu, Recent Advances in Layered $\text{Ti}_3\text{C}_2\text{T}_x$ MXene for Electrochemical Energy Storage, *Small*, **14**, 1703419 (2018).
12. H. Riazi, M. Anayee, K. Hantanasirisakul, A. A. Shamsabadi, B. Anasori, Y. Gogotsi and M. Soroush, Surface Modification of a MXene by an Aminosilane Coupling Agent, *Advanced Materials Interfaces*, **7**, 1902008 (2020).

13. T. Tian, D. Scullion, D. Hughes, L. H. Li, C. J. Shih, J. Coleman, M. Chhowalla and E. J. G. Santos, Electronic Polarizability as the Fundamental Variable in the Dielectric Properties of Two-Dimensional Materials, *Nano Letters*, **20**, 841-851 (2020).
14. L. W. Martin and A. M. Rappe, Thin-film ferroelectric materials and their applications, *Nature Reviews Materials*, **2**, 16087 (2017).
15. A. Chanthbouala, A. Crassous, V. Garcia, K. Bouzehouane, S. Fusil, X. Moya, J. Allibe, B. Dlubak, J. Grollier, S. Xavier, C. Deranlot, A. Moshar, R. Proksch, N. D. Mathur, M. Bibes and A. Barthélémy, Solid-state memory based on ferroelectric tunnel junctions, *Nature Nanotechnology*, **7**, 101-104 (2012).
16. A. J. Lovinger, Ferroelectric Polymers, *Science*, **220**, 1115-1121 (1983).
17. D. G. Hughes and L. Pandey, Spurious signals caused by the piezoelectric ringing of NaNO_2 in pulsed NMR, *Journal of Magnetic Resonance (1969)*, **56**, 428-442 (1984).
18. A. Gruverman, M. Alexe and D. Meier, Piezoresponse force microscopy and nanoferroic phenomena, *Nature Communications*, **10**, 1661 (2019).
19. Z. Zhu, S. Z. Guo, T. Hirdler, C. Eide, X. Fan, J. Tolar and M. McAlpine, 3D Printed Functional and Biological Materials on Moving Freeform Surfaces, *Advanced Materials*, **30**, 1707495 (2018).
20. Z. Zhu, H. S. Park and M. McAlpine, 3D printed deformable sensors, *Science Advances*, **6**, eaba5575 (2020).
21. J. Li, Y. Long, F. Yang and X. Wang, Degradable piezoelectric biomaterials for wearable and implantable electronics, *Current Opinion in Solid State and Materials Science*, **24**, 100806 (2020).
22. J. Li, Y. Long, F. Yang, H. Wei, Z. Zhang, Y. Wang, J. Wang, C. Li, C. Carlos, Y. Dong, Y. Wu, W. Cai and X. Wang, Multifunctional Artificial Artery from Direct 3D Printing with Built-In Ferroelectricity and Tissue-Matching Modulus for Real-Time Sensing and Occlusion Monitoring, *Advanced Functional Materials*, 2002868 (2020). DOI: 10.1002/adfm.202002868
23. J. Dean and N. Sulke, Pacemaker battery scandal, *BMJ*, **352**, i228 (2016).

SCIENTIFIC CONTRIBUTIONS

Peer-reviewed publications

M. J. H Worthington, R. L. Kucera, I. S. Albuquerque, C. T. Gibson, A. Sibley, A. D. Slattery, J. A. Campbell, S. F. K. Alboaiji, K. A. Muller, J. Young, N. A. Shepelin, J. R. Gascooke, D. Jampaiah, Y. M. Sabri, S. K. Bhargava, S. J. Ippolito, D. A. Lewis, J. S. Quinton, A. V. Ellis, A. Johs, G. J. L. Bernardes and J. M. Chalker, Laying Waste to Mercury: Inexpensive Sorbents Made from Sulfur and Recycled Cooking Oils, *Chemistry: A European Journal*, **23**, 16219-16230 (2017).

N. A. Lundquist, M. J. H. Worthington, N. A. Shepelin, C. T. Gibson, M. R. Johnston, A. V. Ellis and J. M. Chalker, Polysulfides Made from Re-purposed Waste are Sustainable Materials for Removing Iron from Water, *RSC Advances*, **8**, 1232-1236 (2018).

N. A. Shepelin, A. M. Glushenkov, V. C. Lussini, P. J. Fox, G. W. Dicinoski, J. G. Shapter and A. V. Ellis, New Developments in Composites, Copolymer Technologies and Processing Techniques for Flexible Fluoropolymer Piezoelectric Generators for Efficient Energy Harvesting, *Energy & Environmental Science*, **12**, 1143-1176 (2019).

N. A. Shepelin, V. C. Lussini, P. J. Fox, G. W. Dicinoski, A. M. Glushenkov, J. G. Shapter and A. V. Ellis, 3D Printing of Poly(vinylidene fluoride-trifluoroethylene): a Poling-free Technique to Manufacture Flexible and Transparent Piezoelectric Generators, *MRS Communications*, **9**, 159-164 (2019).

N. A. Shepelin, P. C. Sherrell, E. Goudeli, E. N. Skountzos, V. C. Lussini, G. W. Dicinoski, J. G. Shapter and A. V. Ellis, Printed Recyclable and Self-poled Polymer Piezoelectric Generators Through Single-walled Carbon Nanotube Templating, *Energy & Environmental Science*, **13**, 868-883 (2020).

A. Šutka, P. C. Sherrell, N. A. Shepelin, L. Lapčinskis, K. Mālnieks and A. V. Ellis, Measuring Piezoelectric Output—Fact or Friction?, *Advanced Materials*, **32**, 2002979 (2020).

N. A. Shepelin, P. C. Sherrell, E. N. Skountzos, E. Goudeli, J. Zhang, V. C. Lussini, B. Imtiaz, K. A. S. Usman, G. W. Dicinoski, J. G. Shapter, J. M. Razal and A. V. Ellis, Interfacial Piezoelectric Polarization Locking in Printable $\text{Ti}_3\text{C}_2\text{T}_x$ MXene-fluoropolymer Composites, *submitted to Nature Communications*.

Non-peer-reviewed publications

N. A. Shepelin, P. C. Sherrell, E. Goudeli and A. V. Ellis, Wearable Devices that Use Human Energy, Pursuit (2020).

Oral Presentations

N. A. Shepelin, Fabrication of 3D Printed Polymer Piezoelectric Nanogenerators: Towards Thin Film Self-Powered Supercapacitors, Royal Australian Chemical Institute (RACI) PolymerVIC Workshop, Melbourne, Australia (27th to 28th September 2017).

N. A. Shepelin, Fabrication of 3D Printed Polymer Piezoelectric Nanogenerators: Towards Thin Film Self-Powered Supercapacitors, International Conference on Nanoscience and Nanotechnology (ICONN), Wollongong, Australia (29th January to 2nd February 2018).

N. A. Shepelin, 3D Printed Flexible and Transparent Polymer Piezoelectric Generators for Powering Electronic Devices, Materials Research Society (MRS) Fall Meeting, Boston, USA (25th to 30th November 2018).

N. A. Shepelin, 3D Printed Flexible Piezoelectric Generators for Passive Energy Harvesting, ChemComm Symposium 2019: Chemistry for Global Challenges, Melbourne, Australia (10th April 2019).

N. A. Shepelin, Printing of Recyclable, Flexible and Transparent Piezoelectric Generators Through SWCNT Templating, International Conference on Nanoscience and Nanotechnology (ICONN), Brisbane, Australia (9th to 13th February 2020).

N. A. Shepelin, Piezoresponse Force Microscopy: Nanoscale Electromechanical Phenomena, Materials Characterisation and Fabrication Platform (MCFP) Atomic Force Microscopy Workshop, Melbourne Australia (27th February 2020).

N. A. Shepelin, 3D printing of Flexible and Efficient Polymeric Piezoelectric Energy Conversion Materials, PhD Completion Seminar, Melbourne, Australia (4th August 2020).

Poster presentations

N. A. Shepelin, Fabrication of 3D Printed Polymer Piezoelectric Nanogenerators: Towards Thin Film Self-Powered Supercapacitors, International Conference on Nanoscience and Nanotechnology (ICONN), Wollongong, Australia (29th January to 2nd February 2018).

N. A. Shepelin, 3D Printed Flexible Piezoelectric Generators for Passive Energy Harvesting, ChemComm Symposium 2019: Chemistry for Global Challenges, Melbourne, Australia (10th April 2019).