Improving the extraction performance of polymer inclusion membranes by cross-linking their polymeric backbone

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Abstract

This study aims at comprehensively investigating the possibility of fabricating cross-linked polymer inclusion membranes (PIMs) using the most common base polymers (i.e., poly(vinyl chloride), cellulose triacetate and poly(vinylidene fluoride-co-hexafluoropropylene)), cross-linking polymers or monomers (i.e., poly(ethylene glycol) dimethylacrylate, poly(ethylene glycol) divinylether and N-ethylmaleimide) and photo-initiators (i.e., 2,2-dimethoxy-2-phenyl acetophenone, triarylsulfonium hexafluorophosphate and triphenylphosphine oxide). The suitability of the photo-initiators for the different cross-linking polymers/monomers in poly(vinyl chloride)-based membranes (without extractants) was assessed for the first time, which was followed by optimizing the cross-linking conditions (i.e., membrane composition and duration of UV-irradiation) for all three base polymers studied. The optimum concentrations of photo-initiator and UV-treatment times were different for the different base polymers used, thus highlighting the importance of this study. Aliquat 336 and di-(2-ethylhexyl)phosphoric acid, as the most frequently used PIM extractants, were added to the compositions of the homogeneous cross-linked membranes produced under optimal conditions and the extraction performance of the newly developed cross-linked PIMs was compared with that of their non-cross-linked counterparts in the extraction of SCN^- and Zn^{2+}, respectively. The results showed that all but one of the 13 homogeneous cross-linked PIMs obtained in this study could extract up to 45% more of the corresponding target species than their non-cross-linked counterparts and the remaining one performed similarly to the relevant non-cross-linked PIM. The initial fluxes for the cross-linked PIMs were up to 10 times higher than those of the relevant non-cross-linked membranes and in two cases the fluxes were similar in value. These results demonstrate the potential of cross-linking for enhancing the extraction performance of PIMs.

Keywords: polymer inclusion membrane (PIM); cross-linking; extraction; zinc; thiocyanate

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1. Introduction

The increasing interest in polymer inclusion membranes (PIMs) has established them as environmentally friendly materials for applications in chemical analysis [1] as well as in extraction-based separation processes [2]. The analytical applications of PIMs include their use as the sensing membranes in ion-selective electrodes and optodes [2, 3]. Separation based on the use of PIMs has emerged as a less expensive, safer and environmentally friendlier alternative to conventional solvent extraction of both metallic or non-metallic species [2]. The separation of heavy metals is becoming more important nowadays due to their environmental effects associated with globalisation and industrialisation. Toxic metals are released into the environment in numerous ways. Fossil fuel combustion, sewage waste, vehicle emissions, discarded batteries, mining activities, tanneries, and metallurgy are examples of major sources of heavy metal pollution of aquatic systems [4-7]. Several methods have been reported for the treatment of waters polluted with heavy metals, namely, ion exchange [8], co-precipitation [9], solvent extraction [10], and membrane-based separation [11].

PIMs are a type of liquid membranes composed of a base polymer and an extractant and in some cases they may also incorporate a plasticizer or a modifier. Poly(vinyl chloride) (PVC) [12] and cellulose triacetate (CTA) [13] are the most commonly used base polymers. However, there is a recent trend in using other base polymers, such as poly(vinylidene fluoride) (PVDF) [14] and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) [15, 16]. The base polymer acts as the skeleton of the membrane and holds within its entangled chains the membrane liquid phase, consisting of the extractant (often referred to as carrier) and a plasticizer or a modifier (if used). Aliquat 336 (a mixture of quaternary alkylammonium chlorides with the dominant species being trioctylmethylammonium chloride), di-(2-ethylhexyl)phosphoric acid (D2EHPA), bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos® IL 104), and tetrahydroxycalix[4]arene (Calix[4]arene) are a few examples of PIM extractants [2, 17, 18]. The extractant is usually a complexing agent or an ion-exchanger which forms a complex or an ion-pair with the species of interest and the corresponding adduct is transported across the PIM which involves simultaneous extraction and back-extraction on the corresponding sides of the membrane. PIMs are characterized usually by lower rate of leaching of the membrane liquid phase into the adjacent aqueous phases compared to supported liquid membranes, which are the most frequently used liquid membranes at present. Notwithstanding this advantage, PIM extraction efficiency in terms of amount extracted and rate of extraction needs to be improved further in order to make them suitable for industrial applications [19, 20]. Biofouling is also a major challenge in the membrane bases separation industry.

Different approaches for improving the PIM performance have been reported and they include modification of the membranes by the addition of reduced graphene oxide [21] or the incorporation of a cross-linking polymer in the membrane skeleton [16]. For instance, O'Bryan et al. [16] have demonstrated that a cross-linked PIM could transport thiocyanate across the membrane faster than its non-cross-linked counterpart.

The most efficient method for generating highly cross-linked polymers is based on UV irradiation of a multifunctional monomer in the presence of a suitable photo-initiator [22, 23]. The advantages of photoinduced polymerisation over thermal cross-linking, such as solvent free processing and energy efficiency, make it suitable for the coating industry, photolithography, microelectronics, and the manufacturing of paints, composite materials, dental restorative formulations, and adhesives [24-26].

Different types of monomers including acrylate, vinylether, epoxide, and maleimide have been extensively used for UV-curing in a variety of applications [22, 27-29]. Kara et al. have demonstrated the possibility of using poly(ethylene glycol) dimethacrylate (PEGDMA) beads in heavy metal removal. In their work, PEGDMA was copolymerised with vinyl imidazole to allow the removal of Cd(II), Hg(II) and Pb(II) [30]. Methacrylate based cryogels [31], monoliths [32] and microspheres [33] have also been reported for heavy metal removal. PEGDMA has also been used by us as a cross-linking polymer in

PIMs for enhancing the extraction/transport efficiency of thiocyanate [16] and Zn(II) [34]. In both studies the cross-linked PIMs showed superior extraction/transport performance in comparison with the corresponding non-cross-linked PIMs in addition to providing better long-term stability. Apart from improving the rate of separation, cross-linking with poly(ethylene glycol) (PEG) units could improve the biofouling resistant activity of cross-linked PIMs as PEG is known to have bactericidal properties [35, 36]. Waheed et al. [37] and Hassanien et al. [38] have demonstrated the anti-bacterial property of cross-linked polymer membranes made of PEG and cellulose acetate. Maleimide resins possess high tensile strength and modulus, excellent chemical and corrosion resistance, as well as good stability at elevated temperatures [39]. These advantages increase the applicability of maleimide resins in electronic and aerospace engineering. Vinyl ethers are highly reactive monomers and extensive curing can be achieved in a very short time [27]. The low odour and non-irritating nature of this type of monomers makes them suitable for different UV-curing applications, such as protective coating [40]. Low shrinkage, great impact strength and high adhesion of the UV-cured polymer are additional advantages which make vinyl ethers popular cross-linking polymer [27, 41].

In our previous research we have demonstrated that the cross-linking polymer PEGDMA and the initiator DMPA can be used to prepare successful cross-linked PIMs composed of PVDF-HFP or CTA as the base polymer and Aliquat 336 [16] or D2EHPA [34] as the extractant. However, to the best of our knowledge, other cross-linking polymers or initiators have never been tested for the fabrication of cross-linked PIMs. Hence, in the present study we aimed to explore the applicability of a range of frequently used cross-linking polymers and photo-initiators for the preparation of cross-linked PIMs. The suitability of each photo-initiator studied was examined by fabricating cross-linked PVC-based membrane which contained PEGDMA, poly (ethylene glycol) divinyl ether (PEGDVE), or N-ethyl maleimide (NEM) as the cross-linking polymer and no extractant. This was followed by the optimization of the cross-linking conditions, for the fabrication not only of PVC-based membranes, but also of membranes containing CTA or PVDF-HFP as the base polymer. Cross-linked PIMs, containing either D2EHPA or Aliquat 336, were prepared under the optimal cross-linking conditions established earlier and their extraction performance was compared with that of their non-cross-linked counterparts by using Zn^{2+} or SCN^- as model target species, respectively.

2. Experimental

2.1. Reagents and solutions

Poly(vinylidene fluoride-co-hexafluropropylene) (PVDF-HFP, Aldrich, USA), cellulose triacetate (CTA, Acros Organics, USA) and poly(vinyl chloride) (PVC, Aldrich, USA) were used as base polymers. Poly(ethylene glycol) dimethylacrylate (PEGDMA, Aldrich, USA), poly(ethylene glycol) divinyl ether (PEGDVE, Aldrich, USA) and N-ethylmaleimide (NEM, Aldrich, USA) were incorporated into the membranes as cross-linking polymers. Three different photo-initiators, namely 2,2-dimethoxy-2-phenyl acetophenone (DMPA, Aldrich, Italy), triarylsulfonium hexafluorophosphate salts (TASHFP in 50% propylene carbonate, Aldrich, USA, note: in membranes using TASHFP, the wt% value refers to that in the casting solution) and triphenylphosphine oxide (TPO, Aldrich, USA), were tested for their ability to induce cross-linking in the membranes studied. Analytical grade tetrahydrofuran without stabiliser (THF, VWR) and dichloromethane (DCM, Chem-Supply, Australia) were used to dissolve the PIM components. The extractants D2EHPA (97%, Aldrich, USA) and Aliquat 336 (Aldrich, USA) were used as received. 2-Nitropheny octyl ether (NPOE) (Sigma-Aldrich, Switzerland) was used as a plasticizer in the CTA-based PIMs.

2.2. Membrane preparation

Cross-linked PIMs containing PVDF-HFP, CTA or PVC as the base polymer were prepared by following the procedure described previously [34]. A weighed amount of each polymer was dissolved in either THF (for PVDF-HFP and PVC) or DCM (for CTA) in a glass jar. In the case of PVDF-HFP,

the polymer and solvent mixture was stirred at 50 ºC in a temperature-controlled water-bath until the polymer was completely dissolved and then the solution was cooled down to room temperature. The dissolution of PVC or CTA in THF or DCM, respectively, was performed at room temperature. The extractant D2EHPA or Aliquat 336 was added to the polymer solution which was further stirred until a homogeneous solution was obtained. This was followed by the addition of the cross-linking polymer (PEGDMA, PEGDVE, or NEM) and photo-initiator (DMPA or TASHFP). Since cross-linking polymers and the photo-initiators are light sensitive, the glass jar containing the PIM mixture was covered with an aluminium foil and stirred for 30 min at room temperature. The resultant PIM casting solution (containing PVDF-HFP, CTA or PVC) was cast on a clean and smooth glass plate using a homemade Teflon casting knife [16]. A rectangular PIM (approximately 14 by 12 cm) was formed after slow evaporation of the solvent for approximately 24 h [23]. In the case of CTA-based PIMs, the plasticizer NPOE was also added to the casting solution (10 wt%). The same procedure was applied for the preparation of cross-linked membranes without extractant or plasticizer.

After casting, the membranes were removed from the glass plate, and their optical transparency, flexibility and lack of stickiness were evaluated. Only membranes or PIMs that were flexible, non-sticky and visually transparent, thus indicating homogeneity, were considered as successful and were thus selected to be cross-linked by UV irradiation as described in Section 2.3. The UV treatment step was not applied for the preparation of non-cross-linked PIMs, and moreover no cross-linking polymer or initiator was added to the corresponding casting solutions.

2.3. UV polymerisation

The cross-linking of the successful homogeneous membranes was performed by following the procedure described previously by us [34]. The membranes were placed inside a UV-treatment box containing a UV-lamp (UVP-USA, 8 W, 0.16 A, 230 V) tuned at 365 nm. Any O_2 present inside the UV-treatment box was purged with N_2 for 15 min prior to the start of the UV polymerisation process when UV lamp was turned on. PIMs were irradiated with UV-light for different time periods in N_2 atmosphere, maintained by continuously pumping N_2 through the UV-treatment box.

2.4. Extraction experiments

Circular segments of the cross-linked or non-cross-linked PIMs (3.65 cm diameter) were cut from flat sheet membranes fabricated by using the casting knife method. A homemade membrane holder made of a 3 mm in thickness PVC sheet [34], was used to hold each circular membrane segment inside a glass jar containing 100 mL of an aqueous feed solution while the glass jar was being continuously shaken at 150 rpm on an orbital shaker (Platform Mixer OM 06, Ratek, Australia).

A 30 mg L^{-1} Zn(II) feed solution, prepared from $ZnCl_2$ (Unilab, APS Chemicals, Australia) and adjusted to pH 3 using 1 M HCl solution was used in the Zn^{2+} extraction experiments. During each extraction experiment, 0.5 mL of the feed solution was withdrawn at pre-selected times and the Zn(II) concentration was determined by atomic absorption spectrometry (AAS).

The SCN^- extraction experiments were conducted using a 30 mg L^{-1} SCN^- feed solution, which was prepared from KSCN (VWR, Australia), and the sampling throughout the experiments was performed as described above. After appropriate dilution, the SCN^- concentration in the collected samples was determined by a flow injection analysis system with spectrophotometric detection of the red coloured $[FeSCN]^{2+}$ complex, described by Cho et al. [42]. It is important to note that all membranes used in the SCN^- extraction experiments were conditioned prior to use, by immersing each membrane in 100 mL of 1.0 M $NaNO_3$ solution for 20 h while shaking the solution at 150 rpm on an orbital shaker. This conditioning resulted in exchanging the chloride ion of Aliquat 336 for a nitrate ion [42].

The initial flux (J_0) was calculated by Eq. (1) which is the first derivative of an exponential decay function (Eq. (2)) whose empirical coefficients were determined by fitting Eq. (2) to the transient Zn(II)

or SCN^- concentrations in the corresponding aqueous feed solutions during extraction [43]. A home-made Quick C program was used for conducting curve fitting using a simplex optimization algorithm [43].

$$J_0 = \left(\frac{d\Psi}{dt}\right)_{t=0} = -a_2 a_3 \quad (1)$$

$$\Psi = a_1 + a_2\, e^{-a_3 t} \quad (2)$$

where a_1, a_2 and a_3 are the empirical coefficients and Ψ is the transient Zn(II) or SCN^- concentration in the aqueous feed solution.

2.5. Instrumentation

The cross-linking conditions, such as the UV irradiation time and the effectiveness of the photo-initiators, were monitored using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) (Spectrum 100, PerkinElmer, USA).

An atomic absorption spectrometer (Hitachi Z-2000 Series Polarized Zeeman, Japan) was used for determining the concentration of Zn(II) in the aqueous feed solution samples under the following conditions: Zn hollow cathode lamp (Hitachi, Japan); current, 8 mA; working wavelength, 213.9 nm; burner height, 7 mm; slit width, 0.7 nm; acetylene flow rate, 1.8. L min^{-1}, air flow rate, 15.0 L min^{-1}.

Mass spectrometric measurements (6520 Accurate-Mass Q-TOF LC/MS, Agilent Technologies, USA coupled to an Agilent autosampler, 1200 Series) were performed with electrospray ionization in the positive mode under the following conditions: drying gas flow rate, 7 L min^{-1}; nebuliser pressure, 40 psi; drying gas temperature, 300 °C; capillary voltage, 4000 V; skimmer voltage, 65 V; scan range acquired, 100-2000 m/z. Each analysis involved the injection of 1 µL of sample (feed solution dissolved in acetonitrile (HPLC grade, Sigma, USA)) into the carrier solvent stream of 70% acetonitrile (HPLC grade, Sigma, USA) and 0.1% formic acid (HPLC grade, Sigma, USA), flowing at 0.3 mL min^{-1}.

3. Result and discussion

3.1. Selection of the initiator for the cross-linking polymerisation

Although there are reports in the literature describing the types of initiators that can be used with a specific type of cross-linking polymers [39, 44], to the best of our knowledge, an assessment of the optimal cross-linking conditions and the appropriate initiator to be used in a mixed polymeric system containing a base polymer and a cross-linking polymer have not yet been reported.

In general, cross-linking polymerisation proceeds via two basic pathways, namely, cationic polymerisation or free radical polymerisation. Different types of photo-initiators are required to initiate each of the photo-polymerisation mechanisms [44]. In the present study, three photo-initiators were selected: DMPA, a very efficient and frequently used free radical photo-initiator for methacrylate-based cross-linking [29]; TPO, known to act as a free radical photo-initiator for different types of cross-linking polymers [39]; and TASHFP, commonly used in cationic polymerisation processes [45].

Two cross-linking polymers (i.e., PEGDMA and PEGDVE) and a cross-linking monomer (i.e., NEM) were selected for testing along with the three photo-initiators discussed above. PVC was chosen as the base polymer for the initial assessment of the suitability of the photo-initiators studied because it is readily available, and it is one of the most commonly used base polymers in PIMs. PVC-based membranes were thus prepared using the three cross-linking agents (polymers/monomers) mixed separately with the three different photo-initiators to determine the effectiveness of the photo-initiators in initiating the cross-linking processes in the mixed polymeric membrane systems studied. All these

membranes were composed of a 6:4 base polymer to cross-linking polymer mass ratio and contained 2 wt% photo-initiator. This polymers ratio was selected on the basis of our previous study [34]. After casting the membranes, they were irradiated with UV-light for 15 min and then analysed by ATR-FTIR to assess the effectiveness of the photo-initiator. The results are described in the following sections for each cross-linking polymer.

3.1.1. PEGDVE cross-linking

PEGDVE is a bifunctional vinyl ether oligomer which is very reactive and generally undergoes fast cationic polymerisation in the presence of a photogenerated protonic acid [46]. The degree of polymerisation of PEGDVE in the membranes using the three initiators was assessed by monitoring the change in the transmittance percentage (%T) (Figure 1) of the inverted peak at 1621 cm^{-1} which corresponds to the C=C stretching frequency of the vinyl ether double bond present in PEGDVE [47]. Cross-linking of PEGDVE proceeds via the formation of a new C-C bond and subsequent conversion of alkene to alkane in PEGDVE (i.e., C=C to C-C) (Figure 1SM, Supplementary Material). Thus, the %T at 1621 cm^{-1} increases as the cross-linking process progresses. Figure 1 shows that only TASHFP was effective in photo-initiating the cross-linking of PEGDVE. A small increase in %T was observed for the DMPA initiated membrane, indicating a lower degree of cross-linking. Based on these results, TASHFP was selected as the most efficient photo-initiator for preparing PEGDVE-based cross-linking membranes.

FIGURE 1

3.1.2. PEGDMA cross-linking

PEGDMA has been used in the preparation of cross-linked PIMs previously, and it is known to undergo radical polymerisation upon UV-irradiation [19]. Also, it has been demonstrated by us that the membrane performance improved significantly after cross-linking using DMPA as the photo-initiator [34]. However, to the best of our knowledge, other initiators have not been tested in either PEGDMA-based polymeric membranes or PIMs. Hence, the three different initiators studied were applied for cross-linking a PVC membrane with PEGDMA. The effectiveness of these initiators was assessed by monitoring the change in %T of the ATR-FTIR peak at 1637 cm^{-1} (Figure 2). This peak corresponds to the stretching frequency of C=C bonds in the PEGDMA acrylate groups (Figure 2SM, Supplementary Material), and the consequent shift of the C=O stretching frequency in this group to a higher wavenumber (i.e., from 1716 cm^{-1} to 1728 cm^{-1}) as a result of the loss of conjugation of the C=O moiety with the adjacent C=C moiety after cross-linking [48].

The results shown in Figure 2 indicate that only DMPA and TASHFP were successful in initiating cross-linking via the radical-mediated pathway. As the degree of cross-linking increased, the C=C bonds of the acrylate groups were converted to C-C bonds and subsequently formed new links to acrylate groups of adjacent PEGDMA units via C-C bonding (Figure 2SM, Supplementary Material). Although TASHFP has a preference to act as a cationic initiator, it has been reported that it can induce radical cross-linking as well [49, 50]. In this case TASHFP decomposes in the presence of UV-irradiation thus forming intermediate aryl radicals which may induce radical-assisted polymerisation. Hence, both initiators (i.e., DMPA and TASHFP) were selected for further optimisation studies.

FIGURE 2

3.1.3. NEM cross-linking

Maleimide derivatives and their polymers are well known for their thermal stability as well as their electron withdrawing properties due to the presence of a five membered rigid ring [51]. Maleimide molecules are commonly used for radical assisted cross-linking although it has also been reported that N-substituted maleimide monomers can undergo homo-polymerisation even when they are exposed to

UV-radiation in the absence of an initiator, provided that the monomer contains easily abstractable hydrogen atoms [22]. The extent of cross-linking of NEM using the three photo-initiators studied was assessed on the basis of the IR peak at 698 cm^{-1} as proposed by Decker et. al. [22], and the results are shown in Figure 3. The characteristic peak at 698 cm^{-1} is due to the =C-H bending vibration of the maleimide monomer [52]. It can be observed that only DMPA was effective in cross-linking NEM and was thus chosen for further optimisation studies. This result also supports the radical cross-linking mechanism for the NEM molecule (Figure 3SM, Supplementary Material). The reason why TASHFP was not able to initiate cross-linking could be related to the faster decomposition of the intermediate radical to some other product which suppressed the radical capture by NEM units. The TPO initiator also did not provide an effective cross-linking which could have been most likely due to the lower photon intensity of the UV-light or to some other experimental conditions that may need to be modified (e.g., addition of a modifier such as diallylbisphenol A) [39].

FIGURE 3

3.2. Optimisation of the cross-linking conditions for PVC, CTA and PVDF-HFP-based membranes

The polymerisation reactions used in this study consist of three main steps: initiation, propagation and termination. The initiation reaction depends on the intensity of light as well as the absorption properties of the photo-initiator (i.e., molar absorptivity). The photo-initiator plays a key role in the light-induced polymerisation as it controls both the reaction rate and the depth of cure profile within the sample [25]. The rate of initiation is directly proportional to the quantum yield of formation of the initiating species (i.e., radical or cation). The propagation of the reaction in mixed polymeric systems, with or without an extractant, depends on the spatiotemporal distribution of both the light intensity and the photo-initiator [29] as well as on the nature of the base polymers involved.

The three most commonly used base polymers in PIMs (i.e., PVC, CTA and PVDF-HFP) and the three cross-linking polymers selected in this study (i.e., PEGDVE, PEGDMA and NEM) were used to prepare different membranes without an extractant. Each membrane was optimised in terms of the concentration of the photo-initiator and the UV-irradiation time. In optimising the concentrations of the photo-initiators, selected earlier for further studies (i.e., DMPA and TASHEP), and the UV-irradiation time, consideration was given to minimising the amounts of the photo-initiators used as well as the time of irradiation without compromising the membranes' physical appearance.

DMPA-initiated membranes were prepared using 1, 2 or 4 wt% of the photo-initiator, whereas 2, 4 or 8 wt% photo-initiator was used for TASHFP-initiated membranes because preliminary experiments indicated that the minimal concentration of TASHFP for achieving cross-linking was 2 wt%. The resulting membranes were irradiated by UV-light for 1, 5 or 15 min. If the 15-min irradiation produced a better result than shorter irradiation times, the membranes were irradiated for a further 15 or 30 min to verify if the cross-linking had been completed. All the UV-irradiated (cross-linked) and non-UV-irradiated membranes free of photo-initiator were analysed by ATR-FTIR by comparing the intensities of the characteristic IR peaks at 1637 cm^{-1} (PEGDMA), 1617 cm^{-1} (PEGDVE) and 697 cm^{-1} (NEM), similarly as performed in the previous section.

3.2.1 PVC-based membranes

The optimization of the cross-linking conditions for PVC-based cross-linked membranes is presented schematically in Figure 4. For the PVC-PEGDMA-DMPA membrane, 1% DMPA and 5-min UV-irradiation provided optimal cross-linking conditions. In case of the PVC-PEGDMA-TASHFP membrane, 15-min UV-irradiation produced higher degree of cross-linking than 1 and 5 min, and so the membrane was irradiated for a further 15 or 30 min. This demonstrated that 30-min irradiation was the minimum time required for maximum cross-linking of the membrane using TASHFP as photo-initiator. A possible reason for the need of a longer irradiation time and higher photo-initiator concentration in the case of TASHFP mediated cross-linking could be the partial decomposition of the

TASHFP radical. However, this was not the case when TASHFP was used to initiate the cross-linking of PEGDVE which followed the cationic cross-linking pathway.

In the case of the PVC-PEGDVE-TASHFP membrane, it was noticed that the membrane turned yellow when irradiated for 5 or 15 min irrespective of the photo-initiator concentration. This colouration was probably caused by the by-product formed in the photodecomposition of the photo-initiator [53]. Similar colouration has been reported earlier in case of hydrogel formation during the UV-curing of cross-linking agent [48, 54]. Only the 1-min irradiated membrane did not change its appearance. Comparing the ATR-FTIR spectra of all the 1-min irradiated membranes, the 8 wt% TASHFP membrane was found to exhibit the highest degree of cross-linking. The same result for the PVC-NEM-DMPA membrane was achieved at 2 wt% DMPA and 15-min UV-irradiation. Irradiation for a further 15 and 30 min did not improve the degree of cross-linking.

FIGURE 4

3.2.2. PVDF-HFP-based membranes

The optimization of the cross-linking conditions for PVDF-HFP-based cross-linked membranes is presented schematically in Figure 5. DMPA initiated cross-linking of PEGDMA was comparatively faster with PVDF-HFP as the base polymer than with PVC. This suggested that the transport of the initiating radical across the PVDF-HFP-based membrane was faster than in its PVC-based counterpart. However, cross-linking of the PVDF-HFP-PEGDMA membrane with 2 wt% TASHFP required approximately the same time to reach completion as in the case of the PVC-PEGDMA membrane (i.e., 30 min).

The same yellow colouration, obtained for the PVC-based membrane, was also observed when the PVDF-HFP-PEGDVE-TASHFP membrane was irradiated for 5 or 15 min. To achieve optimum cross-linking without any colouration, 1 min irradiation and 8 wt% TASHFP were required. The optimal conditions for complete cross-linking of NEM were 5-min irradiation and 4 wt% DMPA. This was faster than in the case of the PVC-based membrane though a higher concentration of the photo-initiator was required (Figures 4 and 5).

FUGURE 5

3.2.3. CTA-base membranes

The optimization of the cross-linking conditions for CTA-based cross-linked membranes is presented schematically in Figure 6. Due to the higher viscosity of the casting solution of CTA in DCM, the cross-linking rate in the corresponding membranes was relatively low and therefore in most cases a higher concentration of photo-initiator and a longer UV-irradiation time were required to complete the cross-linking process within 30 min. In the case of DMPA, a 30-min irradiation time and 4 wt% DMPA were required to complete the cross-linking of PEGDMA while in the case of TASHFP an even higher concentration of the photo-initiator (i.e., 8 wt%) was required to achieve the same result if the UV irradiation time was to be kept at 30 min.

For PEGDVE, optimum cross-linking was obtained by using 8 wt% TASHFP and an irradiation time of 15 min. Also, no colouration was observed for the PEGDVE cross-linked membranes. The cross-linked membranes, when NEM was used as the cross-linking monomer, were not successful as NEM crystallised and exuded from the membranes during their overnight drying.

FIGURE 6

3.3. Physical appearance of the membranes after incorporation of different extractants

In the study described earlier, the optimisation was carried out without including any extractant in the membrane composition. Such extractants would have complicated the IR spectra of the cross-linking

agents which were used to monitor the cross-linking process [16]. Therefore, extractants were introduced into the membrane casting solutions to fabricate PIMs only after the optimisation conditions for cross-linking had been established. Hence, PIMs were prepared by using the optimal cross-linking conditions regarding the concentration of the photo-initiator and the UV-irradiation time while keeping the base polymer to cross-linking polymer ratio at 6:4 and incorporating 30 wt% of D2EHPA or Aliquat 336. In the case of PIMs containing CTA as the base polymer, 10 wt% NPOE was added as a plasticizer because otherwise these PIMs were too rigid. The homogeneity of the membranes was visually assessed (Table 1).

TABLE 1

It can be observed that in total 13 successful homogeneous cross-linked PIMs were obtained. All D2EHPA-PVC-based PIMs tested and the D2EHPA-CTA-based PIM with PEGDVE and TASHFP were inhomogeneous with oily surfaces and therefore, were deemed unsuitable for extraction studies. In addition, during the membrane preparation involving Aliquat 336, a white precipitate was formed when TASHFP was added to the THF casting solution containing the base polymer, Aliquat 336 and the cross-linking agent. It was found that the white precipitate was also formed when only Aliquat 336 and TASHFP were dissolved in THF. However, this was not observed when CTA was used as the base polymer. Since the use of CTA involved the use of DCM as solvent rather than THF, it was assumed that the compound forming the precipitate was soluble in DCM but not in THF. This was confirmed by collecting a filtered sample of the white precipitate which dissolved in DCM.

The possible reaction between TASHFP and Aliquat 336 is described by Eq. (3) where TAS^+ and $R_3CH_3N^+$ are the triarylsulfonium and Aliquat 336 cations, respectively, and HFP^- is the hexafluorophosphate anion. This reaction product was confirmed using mass spectrometric analysis in the positive ion mode of a solution of the white precipitate in acetonitrile (Figure 7).

$$TAS^+HFP^- + R_3CH_3N^+Cl^- \rightarrow TAS^+Cl^- + R_3CH_3N^+HFP^- \quad (3)$$

FIGURE 7

The peaks at m/z values of 368, 396, 424, and 452 are characteristic of the four major quaternary ammonium cations of Aliquat 336 [55] while those at m/z values of 278 and 371 correspond to the two arylsulfonium cations (i.e., $C_{36}H_{28}S_3^{2+}$ and $C_{24}H_{19}S_2^+$, respectively) and that exist in TASHFP as received from the supplier. It should be noted that Zhuravlev et al. have also reported the formation of white precipitates of quaternary ammonium hexafluorophosphates [56].

3.4. Extraction experiments

The extraction performance of all homogeneous cross-linked PIMs obtained as part of this study (Table 1) was compared with that of their non-cross-linked counterparts. In the case of the D2EHPA-based PIMs the extracted species was Zn^{2+} since such PIMs have been used successfully in the extraction of this metallic cation [57, 58]. The extraction stoichiometry of Zn^{2+} by D2EHPA, which is present in dimeric form in the PIM (i.e., $(HR)_2$), is described by Eq. (4) [57]. On the other hand, Aliquat 336-based PIMs are capable of extracting the SCN^- ion efficiently [15, 16] and therefore, this anion was used in comparing the extraction performance of the Aliquat 336-based cross-linked and non-cross-linked PIMs studied. The extraction of SCN^- by Aliquat 336 ($R_4N^+Cl^-$ where R refers to an alkyl group) involves an ion-exchange process in which SCN^- replaces the Cl^- anion of Aliquat 336 (Eq. (5) [42]).

$$Zn_a^{2+} + 3/2\,(HR)_{2,m} \leftrightarrows (ZnR_2 \cdot HR)_m + 2H_a^+ \quad (4)$$

$$SCN_a^- + (R_4N^+NO_3^-)_m \leftrightarrows (R_4N^+SCN^-)_m + NO_{3,a}^- \quad (5)$$

where a and m refer to aqueous and membrane phase, respectively.

The extraction results are summarized in Table 2. In each case, extraction was carried out for 6 h using circular PIMs (3.65 cm in diameter) containing 30 wt% of extractant and 10 wt% NPOE in the case of CTA-based PIMs. The amount extracted was then calculated as 'mg' of extracted species per 'g' of PIM. The corresponding extraction curves are shown in Figure 8.

TABLE 2

FIGURE 8

Table 2 shows that all cross-linked PIMs exhibited higher initial fluxes (especially the PVC-based PIMs) than the corresponding non-cross-linked PIMs with the exception of PIM 7 whose initial flux was similar to that of the relevant non-cross-linked membrane (i.e., PIM 10).

All Aliquat 336-based cross-linked membranes extracted a higher amount of SCN^- over a 6 h period than the corresponding non-cross-linked membranes (12 to 45% more), and the PIM, composed of Aliquat 336, NPOE, CTA, PEGDVE and TASHFP (PIM 9) was the best performing Aliquat 336-based membrane (Table 2). In the case of the D2EHPA-based membranes, up to 23% more Zn^{2+} was extracted over 6 h into the cross-linked PIMs compared to the non-crossed-linked ones. Only PIM 17 (i.e., composed of D2EHPA, NPOE, CTA, PEGDMA, and TASHFP, Table 2) showed no improvement in comparison to the amount of Zn^{2+} extracted by the corresponding non-cross-linked membrane. However, its initial flux was twice as high as that of the non-cross-linked membrane.

It has been suggested that the hydration of the hydrophilic functional groups of the cross-linking polymers (e.g., PEG groups in PEGDMA) could lead to the creation of water channels within the membrane assisting the transmembrane transport of the more hydrophilic species such as the ion-pair of the quaternary alkylammonium cation of Aliquat 336 and SCN^- [16, 34]. This could be one of the reasons for the superior extraction and transport properties of the cross-linked Aliquat 336-based PIMs when used for the extraction of SCN^-. However, it can also be expected that structural changes in both the surface and bulk of PIMs created by cross-linking [16, 34] could potentially lead to improvements in their extraction and transport performance even in situations when the transported across the PIM species is hydrophobic, e.g., Zn(II)-D2EHPA complex.

4. Conclusions

PVC, CTA and PVDF-HFP-based cross-linked membranes were fabricated for the first time using the cross-linking agents PEGDMA, PEGDVE or NEM and the photo-initiators TASHFP, TPO or DMPA to select the optimal cross-linking conditions for the base polymers studied. The effectiveness of the photo-initiators listed above was assessed with the PVC-based membranes containing PEGDMA, PEGDVE or NEM as cross-linking agents. The results have shown that both DMPA and TASHFP are effective for initiating cross-linking of PEGDMA while TASHFP is effective for PEGDVE and DMPA for NEM. The concentration of initiator and time of UV irradiation were then studied not only for the PVC-based membranes, but also for the PVDF-HFP- and CTA-based membranes. Different optimal cross-linking conditions were established for each of the three most common base polymers used, thus indicating that the optimal cross-linking conditions are dependent on the base polymer.

The optimal cross-linked conditions resulting in homogeneous membranes were used for the fabrication of PIMs incorporating either D2EHPA or Aliquat 336 as the extractant. These results clearly demonstrated that cross-linking the polymer backbone of PIMs containing either D2EHPA or Aliquat 336 enhanced their extraction performance in terms of the amount of Zn^{2+} or SCN^- extracted and the rate of extraction in comparison with their non-cross-linked counterparts.

It should be emphasized that the optimum cross-linked conditions established for each of the base polymers commonly used in PIMs can be used for the preparation of cross-linking PIMs containing extractants other than D2EHPA or Aliquat 336.

Acknowledgements

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Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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Figure Captions

Figure 1. ATR-FTIR spectra of the PEGDVE membranes containing PVC as the base polymer (6:4 PVC:PEGDVE mass ratio) and 2 wt% of one of the following photo-initiators: (– –) DMPA, (·····) TASHFP, (——) TPO. Membrane (– · –) did not contain a photo-initiator and was not UV irradiated. UV-irradiation time was 15 min. Note: the spectrum of the membrane with TASHFP overlapped with that of the membrane which did not contain a photo-initiator.

Figure 2. ATR-FTIR spectra of the PEGDMA membranes containing PVC as the base polymer (6:4 PVC:PEGDMA mass ratio) and 2 wt% of one of the following photo-initiators: (– –) DMPA, (·····) TASHFP, (——) TPO. Membrane (– · –) did not contain a photo-initiator and was not UV irradiated. UV-irradiation time was 15 min. Note: the spectrum of the membrane with TASHFP overlapped with that of the membrane which did not contain a photo-initiator.

Figure 3. ATR-FTIR spectra of the NEM membranes containing PVC as the base polymer (6:4 PVC:NEM mass ratio) and 2 wt% of one of the following photo-initiators: (– –) DMPA, (·····) TASHFP, (——) TPO. Membrane (– · –) did not contain a photo-initiator and was not UV irradiated. UV-irradiation time was 15 min.

Figure 4. Flowchart representing the optimum cross-linking conditions for PVC-based membranes based on the corresponding ATR-FTIR spectra. (a) base polymer; (b) cross-linking agent (i.e., PEGDMA and PEGDVE polymers and NEM monomer); (c) photo-initiator; (d) optimum concentration of photo-initiator; (e) optimum UV-treatment time. Mass ratio of base polymer to cross-linking agent, 6:4.

Figure 5. Flowchart representing the optimum cross-linking conditions for PVDF-HFP-based membranes based on the corresponding ATR-FTIR spectra. (a) base polymer; (b) cross-linking agent (i.e., PEGDMA and PEGDVE polymers and NEM monomer); (c) photo-initiator; (d) optimum concentration of photo-initiator; (e) optimum UV-treatment time. Mass ratio of base polymer to cross-linking agent, 6:4.

Figure 6. Flowchart representing the optimum cross-linking conditions for CTA-based membranes based on the corresponding ATR-FTIR spectra. (a) base polymer; (b) cross-linking agent (i.e., PEGDMA and PEGDVE polymers and NEM monomer); (c) photo-initiator; (d) optimum concentration of photo-initiator; (e) optimum UV-treatment time. Mass ratio of base polymer to cross-linking agent, 6:4.

Figure 7. Mass spectrum in the positive mode of an acetonitrile solution of the white precipitate formed in the reaction between Aliquat 336 and TASHFP.

Figure 8. Transient concentrations of SCN^- (a, b, c) and Zn^{2+} (d, e) during extraction experiments involving PIMs 1-3 (a); 4-6 (b); 7-10 (c), 11-15 (d); and 16-18 (e). PIM compositions and experimental conditions as in Table 2. Error bars = ±standard deviation (n=3).

Figure 1

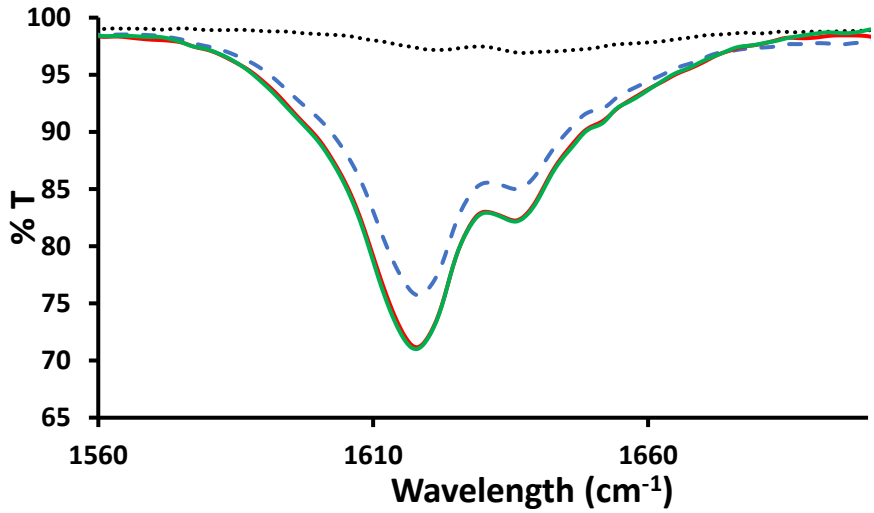

Figure 2

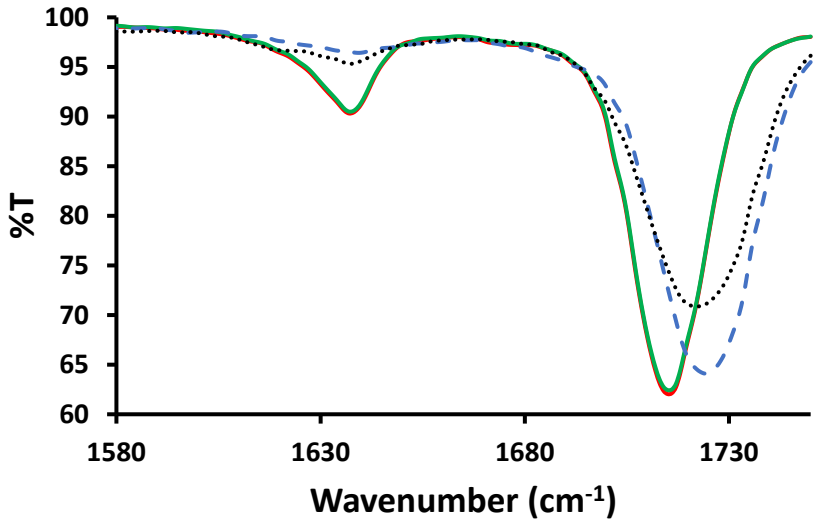

Figure 3

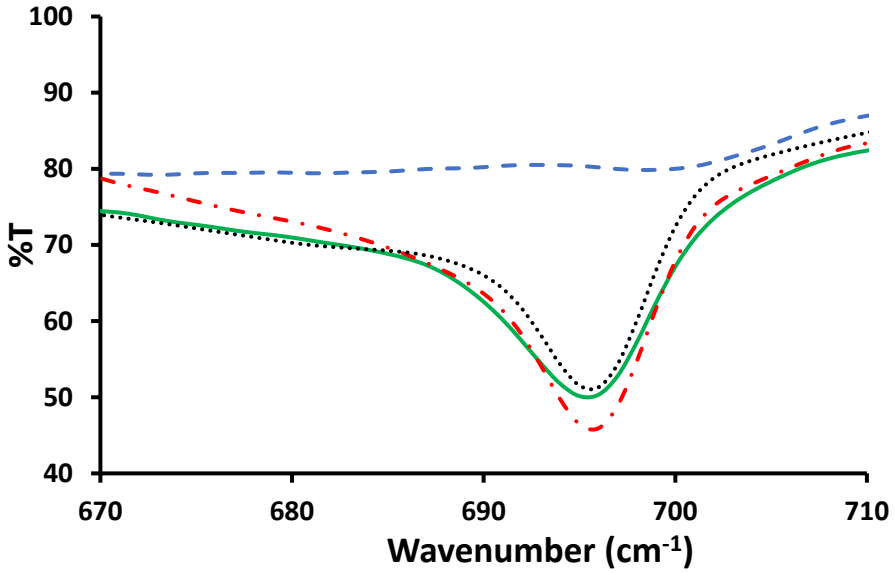

Figure 4

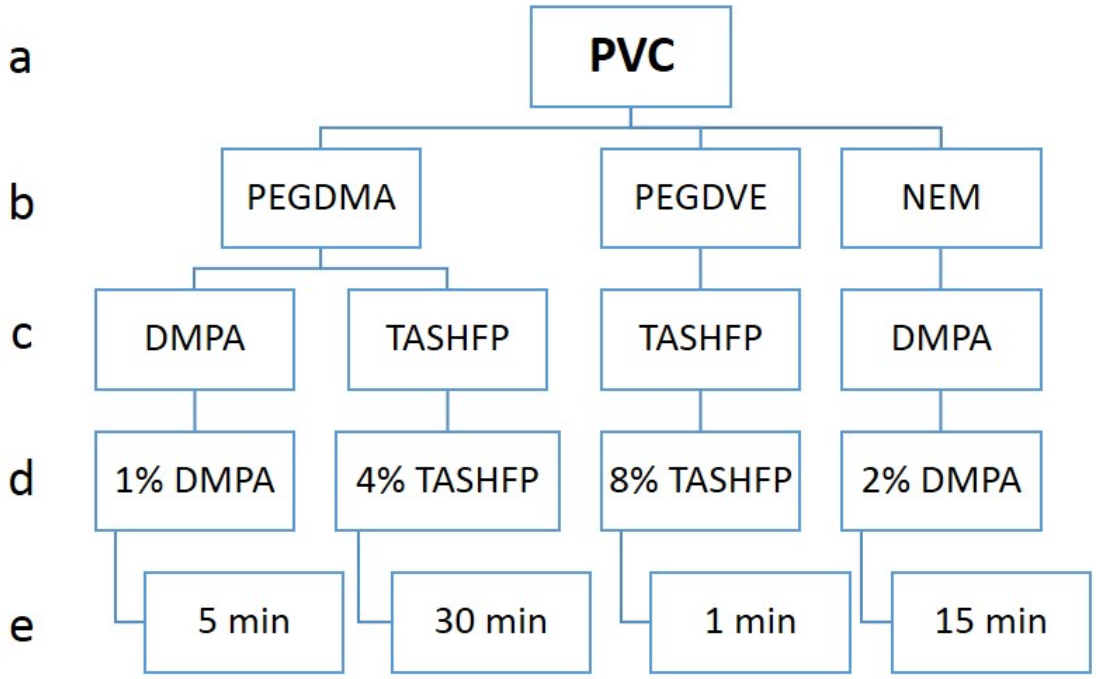
a
PVC
b
PEGDMA
PEGDVE
NEM
c
DMPA
TASHFP
TASHFP
DMPA
d
1% DMPA
4% TASHFP
8% TASHFP
2% DMPA
e
5 min
30 min
1 min
15 min

Figure 5

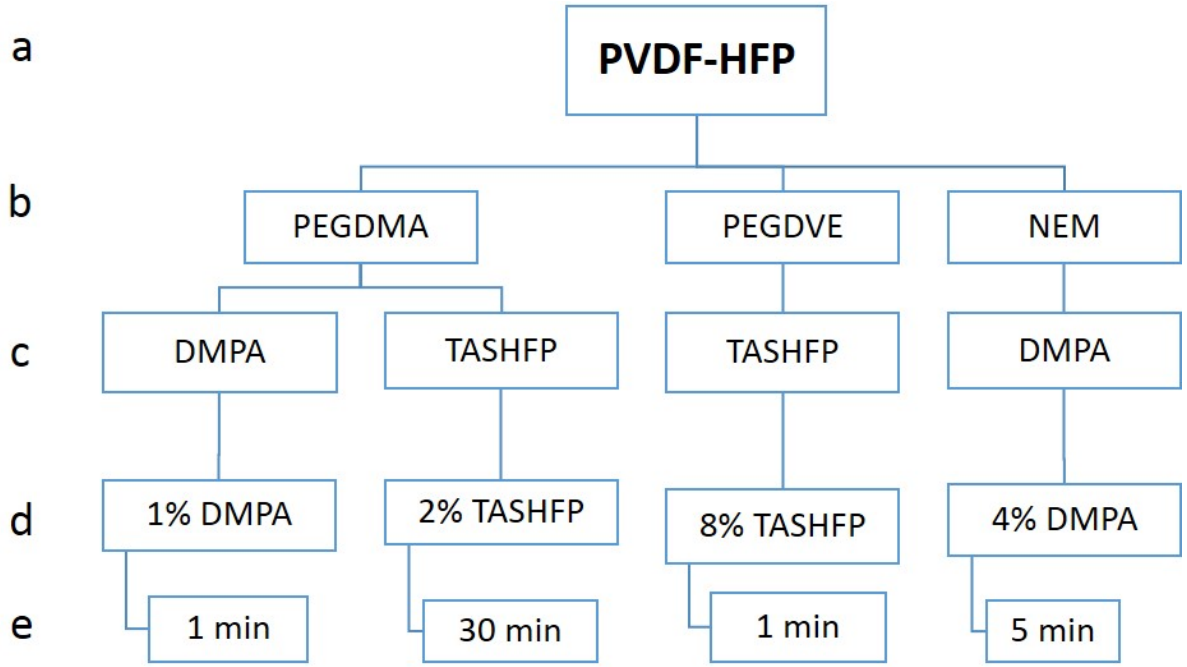
a
b
c
d
e
PVDF-HFP
PEGDMA
PEGDVE
NEM
DMPA
TASHFP
TASHFP
DMPA
1% DMPA
2% TASHFP
8% TASHFP
4% DMPA
1 min
30 min
1 min
5 min

Figure 6

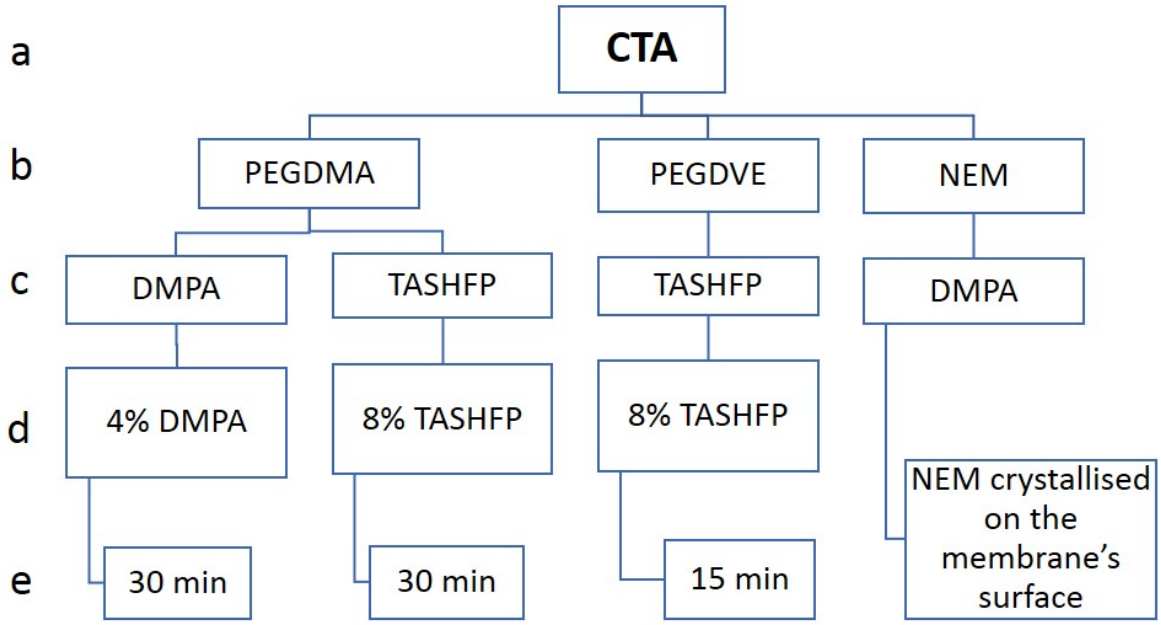
a
b
c
d
e
CTA
PEGDMA
PEGDVE
NEM
DMPA
TASHFP
TASHFP
DMPA
4% DMPA
8% TASHFP
8% TASHFP
NEM crystallised on the membrane's surface
30 min
30 min
15 min

Figure 7

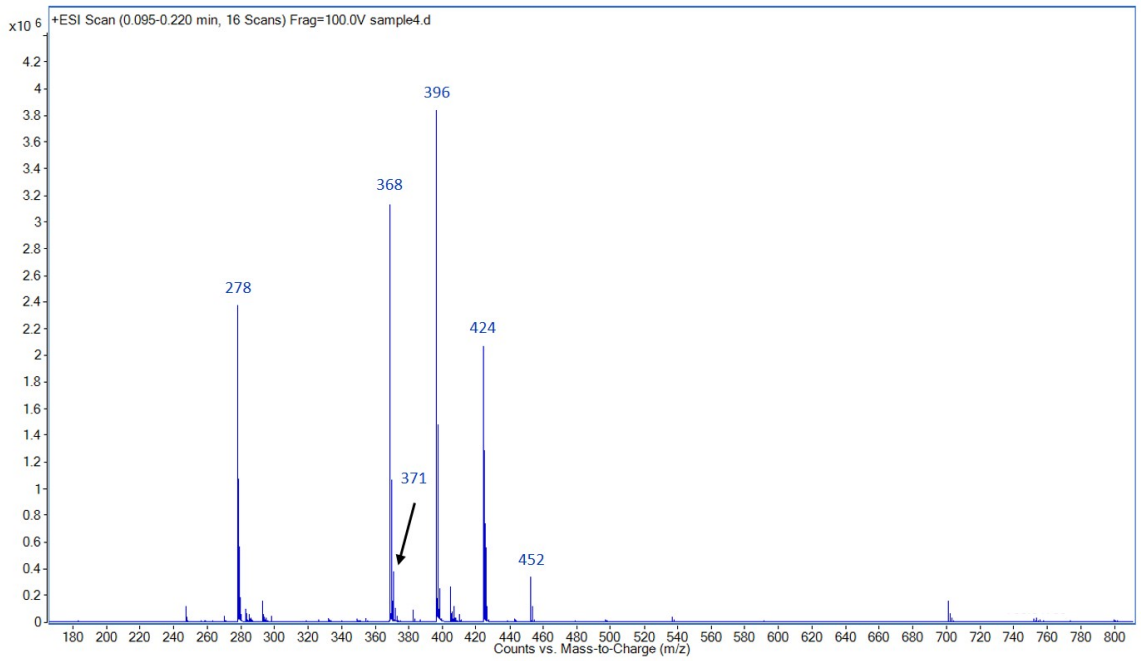
+ESI Scan (0.095-0.220 min, 16 Scans) Frag=100.0V sample4.d
x10 6
4.2
4
3.8
3.6
3.4
3.2
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
396
368
278
424
371
452
180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600 620 640 660 680 700 720 740 760 780 800
Counts vs. Mass-to-Charge (m/z)

Figure 8

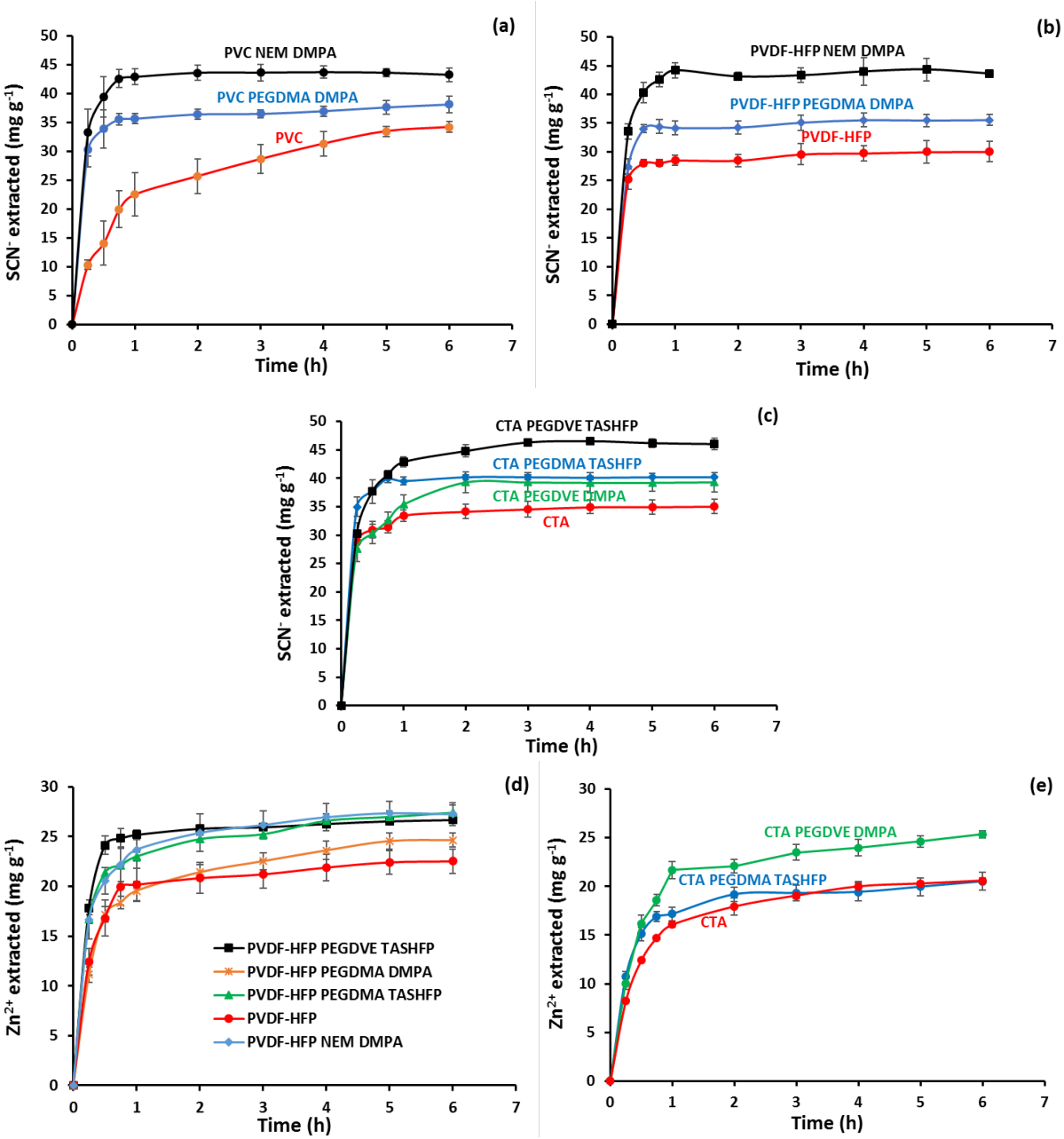
(a)
PVC NEM DMPA
PVC PEGDMA DMPA
PVC
SCN⁻ extracted (mg g⁻¹)
Time (h)
(b)
PVDF-HFP NEM DMPA
PVDF-HFP PEGDMA DMPA
PVDF-HFP
SCN⁻ extracted (mg g⁻¹)
Time (h)
(c)
CTA PEGDVE TASHFP
CTA PEGDMA TASHFP
CTA PEGDVE DMPA
CTA
SCN⁻ extracted (mg g⁻¹)
Time (h)
(d)
PVDF-HFP PEGDVE TASHFP
PVDF-HFP PEGDMA DMPA
PVDF-HFP PEGDMA TASHFP
PVDF-HFP
PVDF-HFP NEM DMPA
Zn²⁺ extracted (mg g⁻¹)
Time (h)
(e)
CTA PEGDVE DMPA
CTA PEGDMA TASHFP
CTA
Zn²⁺ extracted (mg g⁻¹)
Time (h)

Table 1. Physical appearance of PVC, PVDF-HFP, and CTA-based cross-linked PIMs containing 30 wt% D2EHPA or Aliquat 336 as the extractant. CTA-based PIMs also contained 10 wt% NPOE as a plasticizer.

Extractant	Cross-linking agents and photo-initiators				Base polymer
	PEGDMA		PEGDVE-TASHFP	NEM-DMPA	
	DMPA	TASHFP			
D2EHPA	Oily membrane surface	Oily membrane surface	Oily membrane surface	Oily surface	PVC
Aliquat 336	Homogeneous membrane	White precipitate formation in the casting solution	White precipitate formation	Homogeneous membrane	
D2EHPA	Homogeneous membrane	Homogeneous membrane	Homogeneous membrane but very soft before cross-linking	Homogeneous membrane	PVDF-HFP
Aliquat 336	Homogeneous membrane	White solution formation	White precipitate formation in the casting solution	Homogeneous membrane	
D2EHPA	Homogeneous membrane	Homogeneous membrane	Oily surface	Not prepared as NEM crystallised on the membrane's surface	CTA
Aliquat 336	Homogeneous membrane	Homogeneous membrane	Homogeneous membrane		

Table 2. Concentration of Zn^{2+} and SCN^- (± standard deviation, n=3) in circular PIMs (3.65 cm in diameter) of the homogeneous cross-linked PIMs, developed as part of this study (Table 1) after a 6-h extraction period from 100 mL feed solutions containing initially 30 mg L^{-1} Zn^{2+} or SCN^- (×- not present).

PIM ID	Base polymer	Cross-linking polymer	Initiator	Extractant (30 wt%)	Analyte	Plasticizer (10 wt%)	Amount of extracted Zn^{2+}/SCN^- (mg g^{-1})	$J_0 \times 10^6$ (mol m^{-2} s^{-1})
1	PVC	PEGDMA	DMPA	Aliquat 336	SCN^-	×	38.1±1.4	39.14±3.39
2		NEM	DMPA				43.3±2.1	49.54±2.93
3*		×	×				34.1±0.9	4.63±1.53
4	PVDF-HFP	PEGDMA	DMPA	Aliquat 336	-	×	35.5±1.0	44.88±2.69
5		NEM	DMPA		SCN^-		43.6±0.5	52.19±0.90
6*		×	×				30.0±1.7	31.07±3.79
7	CTA	PEGDMA	DMPA	Aliquat 336	SCN^-	NPOE	39.3±1.7	18.76±2.53
8		PEGDMA	TASHFP				40.2±0.2	47.30±4.34
9		PEGDVE	TASHFP				46.1±1.0	35.82±0.39
10		×	×				35.0±1.2	19.94±2.26
11	PVDF-HFP	PEGDMA	DMPA	D2EHPA	Zn^{2+}	×	24.7±0.7	12.29±0.95
12		NEM	DMPA				27.3±1.1	15.14±3.02
13		PEGDMA	TASHFP				27.4±0.8	16.97±0.67
14		PEGDVE	TASHFP				26.7±0.2	24.13±1.33
15		×	×				22.5±1.2	7.82±0.78
16	CTA	PEGDMA	DMPA	D2EHPA	Zn^{2+}	NPOE	25.3±0.4	12.47±0.63
17		PEGDMA	TASHFP				20.5±0.9	13.69±0.41
18		×	×				20.6±0.3	6.54±0.12

*PIMs with compositions identical to those studied by O'Bryan et al. [15]