

EFFECT OF MIX DESIGN ON RHEOLOGY, MICROSTRUCTURE AND SHRINKAGE BEHAVIOUR OF 3D PRINTING CONCRETE

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Abstract

Adopting 3D printing in the construction industry offers a new outlook and unprecedented opportunities, particularly in terms of geometrical freedom of design, reduced waste generation, improved cost efficiency, productivity, safety at construction sites and to some extent, sustainability of construction projects. Even for constructing complex geometries, using 3D printing will drastically minimise (or eliminate) the requirement for formwork while providing architects with further flexibility in design. In addition, robots are readily transportable and deployable on construction sites, particularly in natural disaster-affected areas, distant, isolated or hazardous regions where traditional construction capabilities may be constrained. Therefore, using digital fabrication can result in a substantial decrease in transportation expenses. Furthermore, robots can be deployed in outlying areas where human presence is difficult to sustain, skilled labour is scarce, or human labour costs are prohibitive. Scientists from around the world scaled up 3D printing and brought it into the realm of construction, resulting in the development of extrusion-based 3D printing, often known as construction/concrete 3D printing (C3DP). Although C3DP provides the construction industry with several constructability benefits, it presents particular challenges in terms of material-process optimisation, durability performance and sustainability. A set of very specific fresh-state 3D printing requirements for extrusion-based 3D printing, such as shape stability and buildability (rheological properties), need to be considered for a successful printing project. Furthermore, C3DP technology is a formwork-free process where evaporation of pore water from an early age is inevitable. Moreover, compared to conventional casting, C3DP mixtures often have a higher content of fine aggregate, high volume of paste, relatively lower water-to-binder ratio (W/B), low amount of coarse aggregate, and higher surface area-to-volume ratio (S/V), which result in lower resistance to shrinkage deformation of the printed structure. This thesis is dedicated to the material synthesis of cement-based and geopolymer-based 3D printable mortars. To this end, this research tries to understand and quantify the resilience of free-formed and cast mortars to moisture loss and shrinkage deformation. The shrinkage behaviour of printable mortars was examined under different climatic conditions, namely standard, arid and tropical outdoor 3D

printing environments. The abovementioned concerns have been thoroughly investigated in three experimental studies.

First, a comprehensive analysis has been conducted to determine how the yield stress evolution of the printing material can be controlled and optimised by the water-to-cement (W/C) ratio and a range of admixtures. This study proposed a theoretical framework based on rheological limits of shape stability, buildability and extrudability for implementing slight changes to (optimising) the mixture design to achieve the required quality and efficiency of extrusion-based 3D printing of cementitious mortars across different printing jobs. Experiments were conducted to find correlations between W/C ratio, superplasticiser, accelerator, and retarder dosage with the initial yield stress and structuration rate (A_{thix}) of 3D printable cement-based mortars to be used as controlling factors for optimising the yield stress evolution. Finding a linear relationship between the initial yield stress and superplasticiser dosage demonstrated that a predictive model might be used to adjust the initial yield stress in response to changes in the thickness of printing filament. A new approach was presented for determining the buildability of a mortar with exponential yield stress development by calculating its maximum achievable slope of buildability limit (characteristic buildability slope, Δ_{cb}). It was shown that the characteristic buildability of mortars was linearly correlated with accelerator dosage. A linear model was proposed to modify the accelerator content in response to a variation in the vertical build rate across various printing jobs. It was shown that predictive models could increase the open time for an optimised mixture by up to 33% for a defined print job. The theory suggested that controlling the yield stress evolution could be used as a tool for printing optimisation.

In certain printing projects, a longer interlayer printing gap time may be required due to the changes in the scale and complexity of printing jobs that might adversely affect the long-term durability performance of printed elements due to the evaporation of surface moisture. Moreover, the impaired long-term mechanical and durability performance of printed components is interconnected with the moisture loss behaviour due to the absence of formwork, higher S/V ratio of printed elements and very high cement content in cementitious 3D printing materials. Therefore, the second set of experimental studies aimed to quantify and understand the resilience of free-formed concrete in adverse climatic conditions to serve as a benchmark for future studies on shrinkage mitigating techniques and structural integrity of the printed structure. This

research presents a comprehensive investigation of the effects of different outdoor climatic conditions (24 °C – 50% RH, 35 °C – 85% RH and 35 °C – 45% RH) on the moisture loss, drying and autogenous shrinkage of cementitious 3D printing materials, considering different sand-to-cement (S/C) and surface-to-volume (S/V) ratios of free-formed specimens. Mass loss and length change of mortars that were cured for up to 6 months under 24 °C – 50% RH, 35 °C – 85% RH and 35 °C – 45% RH (free-formed specimens without initial curing) were compared with those under standard conditions (24 °C – 50% RH with 24 hours of sealed initial curing). According to the drying shrinkage results, free-formed specimens subjected to various adverse climatic curing conditions exhibited a 28-day drying shrinkage of up to 30% less compared to conventionally cast specimens under the standard curing environment. However, this study showed that dissipated hydration and pore water evaporation was the reason behind this which resulted in an increased rate of shrinkage evolution at later ages. It was demonstrated that the free-formed specimens are more susceptible to carbonation shrinkage, and printed parts will have a higher shrinkage deformation in the long term compared to conventionally cast specimens. The findings of this experimental work highlight the significance of the post-printing treatment in reducing the long-term shrinkage deformation of 3D printed concrete.

Since many environmental issues are linked with the production of ordinary Portland Cement (OPC), including greenhouse gas emissions, the development of sustainable types of cement for C3DP has recently become the subject of research activities worldwide. Moreover, due to the higher content of fine aggregate in C3DP mixtures, the over-exploitation of land resources, such as natural sand, might increase the environmental impact of the C3DP technique compared to conventional casting. Partial or complete substitution of OPC and natural aggregate with industrial by-products and underutilised aggregates are promising measures that were taken into account to improve the sustainability aspects of C3DP mixtures. Although previous studies successfully developed geopolymer concrete for use in C3DP by optimising the mixture design and rheological properties of geopolymer binders, especially for fly ash (FA) / ground granulated blast furnace slag (GGBS) based geopolymer mortars, the resistance to drying shrinkage of these printable materials have not been investigated so far. Considering the formwork-free nature of C3DP and high volume of paste, as well as the unavoidable need to use thixotropy modifiers in C3DP

geopolymer mixtures, the third set of experimental studies were dedicated to quantifying and understanding the resistance of printable FA/GGBS-based geopolymer mortar prepared with natural sand (NS) and industrial waste aggregate (lead smelter slag, LSS) to drying shrinkage. The effect of using conventional thixotropy modifiers (NC) on the drying shrinkage of geopolymer mortar was investigated. Moreover, the effects of incorporating a novel graphene-based nanomaterial (GO) into printable geopolymer mortar on the rheological properties and shrinkage evolution of printable geopolymer mortar were investigated. Various adverse climatic environments with different temperature-relative humidities (24 °C – 50% RH, 35 °C – 90% RH and 35 °C – 50% RH) were simulated for free-formed specimens by eliminating the initial curing (immediately removing the moulds/formworks).

The effects of adding GO and NC on enhancing the rheological properties of geopolymer mortars were evaluated. It was shown that a very small dosage of NC < 0.5 (wt% of binder) and GO < 0.1 (wt% of binder) improved yield stress development and viscosity recovery capacity of the mortars, which have a direct relationship with the shape stability of printable materials. The results showed that incorporating GO into the mixtures resulted in a higher characteristic buildability rate and viscosity recovery capacity compared to NC. It was found that GO modification improved the rate of dissolution of raw materials and resulted in higher total heat of reaction compared to NC. Moreover, irrespective of being free-formed or conventionally cast, the mechanical strength of printable geopolymer mortars modified with GO for a given curing environment was higher than those modified with NC. It was shown that by simulating the free-formed condition for printable geopolymer mortars under the standard curing environment (24 °C – 50% RH) the 28-day drying shrinkage of optimised geopolymer mortars (irrespective of dosage of GO and NC) increased by approximately 70% compared to their conventionally cast counterpart specimens. This indicates that formwork-free conditions can adversely affect the resistance of printable geopolymer mortars to drying shrinkage. Increasing the temperature of the curing environment to 35 °C in 50% RH reduced the increase in 28-day drying shrinkage of free-formed geopolymer mortars. When the relative humidity increased to 90% (at 35 °C) to simulate a high temperature-high humid environment, the increase in 28-day drying shrinkage of free-formed mortars was reduced to approximately 40% compared

to their cured counterparts under free-formed condition and the standard environment (24 °C – 50% RH). The findings of this study provide a baseline for future research on the influence of different curing processes (internal/external curing) on shrinkage reduction (uniform/nonuniform) of cementitious and geopolymer mortars intended for extrusion-based concrete 3D printing.

Declaration

This is to certify that:

- i. The work contained in this thesis has not been previously submitted to meet requirements for an award at this or any other higher education institution. The thesis comprises only my original work towards the PhD;
- ii. Due acknowledgement has been made in the text to all other material used;
- iii. The thesis is fewer than 100,000 words in length, exclusive of tables, maps, bibliographies, and appendices.

Signature: Mohsen REZAEI SHAHMIRZADI

Date: 25 August 2022

Preface

I hereby confirm that the works provided in this dissertation are based on my original research undertaken throughout my PhD candidature at the University of Melbourne (April 2018 - August 2022). I was the researcher and was responsible for all of the work in this dissertation.

The experimental work was conducted with help from other researchers and organisations. Dr Jinghan Lu (MTS universal testing, geotechnical and concrete laboratory), Mrs Laura Juke (calorimetry testing, geopolymer and mineral processing group), Dr Anders Barlow and Dr Ranjeet Singh (x-ray characterisation and nitrogen adsorption-desorption analysis, materials characterisation and fabrication platform), and Dr Alex Duan (thermogravimetry analysis, trace analysis for chemical, earth and environmental sciences platform) supported me for running some of the experiments and characterisation analysis.

The works in Chapter 4 in this thesis has been published in journal. Chapter 3 and Chapter 5 are ready to be submitted. My PhD supervisors, Prof Tuan Ngo, Dr Alireza Kashani and Dr Aliakbar Gholampour supervised my works and contributed to the published/to-be-submitted articles. My co-authors, Dr Alireza Kashani and Dr Aliakbar Gholampour, helped me conduct my experiments and supported revising and evaluating of the published/to-be-submitted articles. The amount of my contribution towards each published chapter is listed below.

Chapter 1: Unpublished material, not submitted for publication

Chapter 2: Unpublished material, not submitted for publication

Chapter 3: Manuscript is ready to be submitted

- I performed all the experiments and prepared the manuscript drafts (contribution: 90%).
- Prof. Tuan Ngo (contribution: 5%), Dr. Alireza Kashani (contribution: 5%) provided the initial project direction and revised the manuscript.

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- I performed all the experiments and prepared the manuscript drafts (contribution: 85%).
- Prof. Tuan Ngo (contribution: 5%), Dr. Alireza Kashani (contribution: 5%) and Dr Aliakbar Gholampour (contribution: 5%) provided the initial project direction and revised the manuscript.

Chapter 5: Manuscript is ready to be submitted

- I performed all the experiments and prepared the manuscript drafts (contribution: 90%).
- Prof. Tuan Ngo (contribution: 5%) and Dr. Aliakbar Gholampour (contribution: 5%) provided the initial project direction and revised the manuscript.

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Chapter 1: Introduction

This chapter outlines the background (Section 1.1), problem statement and motivation (Section 1.2) of the research, and its aims and objectives (Section 1.3). Section **Error! Reference source not found.** describes the layout of the thesis and scope of this research.

1.1 RESEARCH BACKGROUND

The Digital Revolution has been rapidly developing worldwide, resulting in the emergence of the Fourth Industrial Revolution (4IR), also known as Industry 4.0. Throughout the 4IR, the global production and supply network has been undergoing significant alterations as a result of the growing automation of conventional manufacturing and traditional industrial fabrication processes, employing smart technologies including robotics, quantum computing, machine-to-machine communication, Artificial Intelligence (AI), Internet of Things (IoT), Additive Manufacturing (3D printing), nanotechnology and many others [1]. This interconnection promotes automation and self-monitoring, facilitating the deployment of intelligent robots that can evaluate and identify issues without human intervention. It was anticipated that the increasing growth rate of 4IR relative to the previous technological revolutions would involve the majority of industry sectors globally.

The construction industry is lagging behind in terms of exploiting the advantages of state-of-the-art technology in conventional construction methods. Despite all the advancements made to date, conventional construction methods remain detrimental to the environment due to the emission of harmful greenhouse gases and the generation of an excessive quantity of discarded solid materials that cannot be reused. By virtue of the recent advancement in robotics technology and computer science, 3D printing has been introduced to the manufacturing sector via a process called CAD/CAM - Computer-Aided Design and Manufacturing - in which objects are designed on the computer, without direct human intervention, and sent to the production machinery that automatically fabricates the products [2]. 3D printing has been successfully implemented in aerospace, automotive and biomedical fields, while the construction

industry still needs to streamline the construction process by benefiting from the experiences gained in manufacturing sectors.

According to various established statistics, aside from being slow, the way that the construction industry stands today is still wasteful, emits various harmful emissions, and generates an excessive quantity of discarded formworks and solid materials that are not reusable [3–6]. Approximately 40% to 50% of overall construction project expenditures and about 60% to 70% of total construction time are accounted for temporary structures such as formwork when using the conventional construction method [7]. Moreover, construction is the most hazardous profession, even more dangerous than mining and agriculture. According to the United States Department of Labour, in 2019, out of 5333 worker fatalities in the private industry, about 20% were in the construction sector [8]. Even though more restrictive legislations compel the implementation of stronger safety standards in Australia, the fatality and injury rate in the Australian construction sector is almost 14% [9]. In addition, the construction industry accounts for 5-8% of global CO₂ emissions mainly as a result of the decomposition of limestone during energy-intensive Ordinary Portland Cement (OPC) production [10].

Adopting 3D printing in the construction industry has the potential to improve the cost efficiency, productivity, safety and, to some extent, sustainability of construction projects [11,12]. Digital fabrication in construction will significantly reduce (or remove) the need for formwork while offering freedom of design to architectures, thereby reducing the construction times and costs even for more intricate geometries [11]. Automation in construction can optimise material consumption by reducing the amount of waste produced during construction practices [13]. Robots may be used in distant locations and hazardous environments where human access is limited or skilled human resources are insufficient or expensive, thus increasing the safety at work [14]. Multi-robot systems may be used in construction projects, and several 3D printers can operate simultaneously on the same construction, resulting in significant reductions in construction time and costs [15].

Scientists from around the world scaled up 3D printing processes and brought them into the realm of construction. Incorporating digital fabrication into the construction industry resulted in the development of extrusion-based construction 3D printing, often known as concrete 3D printing (C3DP) [16]. This new fabrication

technique is defined as a construction process of a structure with an intricate architecture by continuous deposition of printable materials, primarily a cementitious mortar, layer-by-layer to build a vertically standing multi-layer structure [6,17]. In order to reveal the full capacity of C3DP, having a better understanding of the relationships between design, construction materials, 3D printing process, and final printed product quality and durability would be necessary. Consequently, various studies have been conducted, and developments are ongoing by research groups and industry stakeholders to address some of these concerns in C3DP technology. This includes developing printable materials (concrete) that must simultaneously attain appropriate printing characteristics such as extrudability, shape stability, buildability performance during the printing process, and high mechanical strength and appropriate durability properties in the long term. The 3D printing construction materials must be engineered to pass through the delivery system without any clogging or discontinuity (extrudability). Simultaneously, the printing material must maintain properties to preserve its shape dimensions as per nozzle geometry under its own weight after deposition (shape stability). Furthermore, the deposited filament must develop sufficient strength and tolerate the weight of subsequent layers to avoid strength-based or stability failure (buildability performance). Even though a great deal of work has been done, there is still potential for further improvement in the mixture optimisation of 3D printing concrete.

Despite the progress made to address the additional material property requirements imposed by C3DP, there are also some challenges intrinsic to the concrete mixture design that demand more consideration when C3DP is employed. Moreover, shrinkage strain development (dimensional stability) and shrinkage cracking are significant issues that can be exacerbated when the structure is built using the C3DP technique. Since C3DP is a formwork-free process, printed materials are exposed to an open atmosphere after the deposition. This will increase the moisture escape from the printed products, leading to higher porosity in 3D printed structures, which can cause durability-related issues. Moreover, using coarse aggregate in 3D printing materials is restricted through the limitation of pumping and extrusion systems, making the printed structure more prone to higher shrinkage strains. The abovementioned concerns are some of the challenges that still need to be addressed to

pave the way for large-scale industrial implementation of C3DP in future construction projects.

1.2 PROBLEM STATEMENT AND MOTIVATION

Traditional construction techniques such as precast or cast-in-situ utilises formwork that restricts concrete to specific geometries (typically rectilinear). Therefore, in conventional casting, the most critical requirement for concrete is to reach a flowability limit that can fill the formwork and the gaps between reinforcements uniformly. The flowability of concrete is characterised using traditional standard procedures such as flow table, slump, and V–funnel tests. The obtained results from these tests, coupled with the hardened-state mechanical strength (such as compressive and flexural) and durability-related properties (such as drying shrinkage strain), are generally adequate to design concrete according to construction codes, as well as design and engineering requirements. Therefore, the optimisation of additional rheological parameters such as yield stress development or thixotropy properties are typically indirectly considered in flowability examination (or not explicitly needed to be investigated) to design concrete when conventional construction is used.

In contrast to conventional methods, C3DP is a free-formed (FF) construction process in which complete control over various properties of a printing material is essential for a successful print. These properties include extrudability (pumpability), shape stability and buildability (see Section 2.4). These printing requirements are competing parameters and need to be balanced carefully to maximise the vertical build rates of the printing job, resulting in a faster construction process. Moreover, the overall quality of printed products and the efficiency of the construction job depend on these specific material requirements. Comparing the C3DP with conventional casting, it is evident that conventional workability tests are not solely sufficient to design a 3D printing concrete, and the rheological properties of concrete that are designed for C3DP should be studied in more detail. A range of theoretical models and experimental approaches have been suggested in the literature to determine the optimal vertical build rate and the time at which failure (strength-based or stability-based) would occur for material-process combinations in C3DP [18–24]. However, there is still a lack of agreement on which quantitative material properties and related experimental procedures are suitable for buildability analysis. In order to accurately

examine the buildability of the 3D printing material, a specific framework for characterising the behaviour and strength of concrete in its fresh condition is still required.

Using the previous conceptual frameworks [18,21,22], an urgent need exists for a simple and applicable model based on finding the optimal mixture design that satisfies the abovementioned requirements. This can be considered as a significant contribution to C3DP since it is expected that the vertical build rates in C3DP jobs are likely to change frequently, for instance, when the scale or resolution of a print job is altered. By changing the scale of construction projects, new material properties or printing requirements are needed. Consequently, it is essential to determine if concrete printing mixtures can be modified in a predictable manner to achieve optimum material-process performance in response to the various construction printing jobs. To achieve this, a possible solution is to use different types and ratios of chemical admixture and additives to modify the critical rheological parameters, including yield stress evolution and flowability of construction materials, and thereby yield the optimal 3D printing concrete mixture. Some recent studies tried to address this need by adjusting the ratios of additives such as high-range-water-reducer, accelerator and retarder. However, further studies are still required to consider a broader range of additives, as well as other critical parameters, such as the water-to-binder ratio.

Given the importance of C3DP mixture optimisation for achieving the desired printing quality, it is worth considering that the C3DP mixture proportions vary significantly from conventional cast-in-situ concrete. A range of additives and admixtures with different ratios (depending on the capacity of the pumping unit and other 3D printer parameters) are typically used in C3DP mixtures. In addition, using coarse aggregates is limited due to the difficulties with extrusion and material delivery. Hence, only fine aggregates with a maximum particle size of 2-4 mm are used in a typical C3DP mixture. However, there are a few recent studies which used coarse aggregates in C3DP [25,26]. Besides, the aggregate-to-binder ratio (S/C) in C3DP is typically between 1.0 and 1.6 compared to 4.0 to 6.0 in conventional casting [27]. In C3DP, the water-to-binder ratio is typically less than 0.4, while it usually varies between 0.4 and 0.6 in conventional casting (except for the high-performance concrete). All the abovementioned variations between the concrete mixture in C3DP and conventional casting pose significant concerns regarding the higher vulnerability

of 3D printing mixtures to different types of shrinkage (autogenous, drying and carbonation) development. To date, only a few studies have explored the shrinkage evolution in C3DP mixtures considering the effect of mixing proportions. Therefore, further studies are required to investigate the effects of such parameters (e.g. S/C ratio) on various shrinkage types and their evolution in the long term.

In addition to the abovementioned variations in the mix design, it is worth noting that cement-based C3DP mixtures require a higher OPC paste volume in their mixture compared to conventional cast concrete [28]. Moreover, in C3DP mixtures, fine aggregate content is generally higher and using coarse aggregate is limited compared to conventional concrete [29], which also results in a substantial likelihood of reduced durability [30]. Therefore, the environmental effect of using C3DP in the building industry has become a contentious issue regarding its large OPC consumption and over-exploitation of abiotic resources such as natural sand [30–32]. Recycled or waste (by-product) materials can be vastly used in C3DP concrete as a solution to address these issues and to substantially promote sustainable and cost-effective extrusion-based 3D printing in the construction industry. A few studies recently attempted to develop waste materials-based concrete for C3DP to improve its sustainability and lower the embodied carbon of 3D printing mixes. Two approaches have been mainly taken to develop waste-based concretes for C3DP by utilising waste or recyclable materials: i) as a primary cementitious material (e.g. geopolymer binder as an alternative to OPC or as a supplementary cementitious material in OPC-based concrete) [33–36], and ii) as the fine aggregate (recycled aggregates-based concrete) [37,38]. Most of the previous studies have explored Fly ash (FA) and ground granulated blast furnace slag (GGBS) -based geopolymer concrete for C3DP. Researchers investigated the rheological properties and printable qualities of FA/GGBS geopolymer concrete by incorporating admixtures (e.g. nanoclay) to address the challenges of the absence of colloidal interaction and thixotropy properties which is one of the main issues with geopolymer binders [33,39,40]. Therefore, the main aim was to find optimal printable mixtures (buildability) by adjusting rheological properties and mechanical properties. However, to date, no research has been conducted on the development of shrinkage in geopolymer-based concrete designed for C3DP. Moreover, available studies did not consider the effect of thixotropy

modifier admixtures on the water loss and shrinkage development of concrete in C3DP.

Aside from the influence of the mixing ratios (e.g. W/C, S/C) of C3DP mixtures on the shrinkage evolution, free-form construction also faces some challenges arising from rapid water evaporation, which can exacerbate the shrinkage development and subsequent cracking in C3DP. Over the previous two decades, our understanding of shrinkage in concrete structures and its numerous causes has progressively increased. Shrinkage strain development has different mechanisms, which depend on mixture design, the moment of occurrence, initial curing procedure (free-formed or in formwork), temperature and relative humidity. Shrinkage development in concrete has evident detrimental effects on durability, load-bearing capacity and aesthetics of structures. It may result in fissures and cracking, promoting the ingress of gases and moisture, corrosion of reinforcement, and carbonation, thereby notably reducing the strength (predominantly tensile capacity) and service life of a structure [41–43]. Shrinkage is controlled and monitored in conventional construction via different shrinkage mitigation techniques. Active or passive curing procedures [44,45] were followed to minimise the adverse effects of shrinkage development on the mechanical strength and durability of the structures. Examples of concrete components susceptible to significant levels of shrinkage strain include slabs, roadways and bridge decks. Due to the high surface area to volume ratio (S/V) of these concrete parts, they are more susceptible to shrinkage when placed in harsher environments (e.g. high temperature and low humidity) without appropriate curing.

Concrete elements made by the C3DP technique are even more vulnerable to shrinkage development than ordinary cast concrete components. Firstly, since C3DP is a formwork-free process, freshly deposited filaments are more exposed to the open atmosphere after the deposition. Therefore, shrinkage development can occur more significantly in printed parts due to the higher surface-to-volume ratio and accelerated pore water evaporation, which causes a negative pore pressure in the microstructure resulting in three-dimensional volume contractions. Secondly, with the lower rate of bleeding in C3DP, which is related to the higher amount of fine aggregate and lower W/C ratios compared to conventional concrete, there is a limited bleeding water layer on the surface of the construction element to act as a preventative evaporation barrier, resulting in a higher rate of water loss in C3DP mixtures. In addition to the fact that

changes in the environmental variables can significantly influence the water loss from printed specimens, they also impact hydration and microstructure development of C3DP. For instance, higher temperatures increase the evaporation of water whilst accelerating the hydration response simultaneously, resulting in microstructure alteration, higher permeability in the long term, and a high proportion of unreacted or partially reacted particles [27]. The microstructure of C3DP mixtures attempts to restrain the deformation induced by negative pore pressures, resulting in capillary tensile stresses in the system. If the tensile stress development exceeds the tensile stress capacity of 3D printing concrete, crack propagation occurs, leading to failure in the printed structure. Further investigation on the effect of both climatic parameters and formwork-free condition (a larger surface area exposure compared to conventional casting) on the evolution of shrinkage of 3D printing materials, as well as their influence on the degree of hydration and other mechanical and durability-related properties, is deemed necessary.

1.3 AIMS AND OBJECTIVES

The abovementioned issues motivated the research on the effect of mix design on rheology, microstructure and shrinkage behaviour of 3D printing concrete in both OPC and geopolymer binder systems. The main aim of this research is to propose a theoretical framework, based on yield stress-related limits, for optimising the material-process interactions in extrusion-based 3D printing and then identify the effect of free-form curing and different environmental conditions on the pore water evaporation, shrinkage development, microstructure and strength of mixes. This study encompasses the following objectives:

(1) Optimising cement-based mortar's mixture design for C3DP by considering rheological limits

- To propose a theoretical framework based on the yield stress-related limits by which the changes in the printing job's scale and complexity can be used to optimise the mixture design and obtain the necessary printing qualities for the new printing job.
- To achieve this, experiments are conducted to investigate how the yield stress evolution in cement-based mortars can be controlled by optimising the mixing ratios and admixtures.

(2) To study the shrinkage behaviour of cementitious 3D printing materials by considering the effects of temperature and relative humidity

- To design 3D printing cementitious mortars with different S/C ratios following the yield stress-related limits provided earlier in this research.
- To evaluate the printing mixture's shrinkage behaviour (autogenous and drying) and investigate the shrinkage mechanism in standard conditions. Specimens are conventionally cast and cured at different moistures and air conditions with different sizes according to ASTM and BS-EN standards. The effect of high cement content and low W/C ratio are investigated.
- To measure short and long-term drying shrinkage of free-formed (3D printed) specimens cured in different outdoor 3D printing weather conditions (different weather zone with high and low temperatures and relative humidity) by removing the mould immediately after the initial setting. The results are compared with that of conventionally cast specimens. The effect of S/C in the mixtures and S/V of filament are considered.

(3) To analyse the shrinkage behaviour of geopolymer 3D printing mortars with consideration on the effects of mixture nanomodification and environmental conditions

- To design 3D printing geopolymer mortars following the yield stress-related limits. Different controlling factors, including binder composition, activator modulus and mixing ratios (activator-to-binder) are modified to optimise rheology of geopolymer mortars. The effect of substituting natural sand with underutilised aggregates (lead smelter slag or black sand, LSS) on the fresh and hardened state properties is investigated.
- To further improve the rheological properties of geopolymer mortars by incorporating graphene oxide (GO) and comparing its effects on yield stress and thixotropy in the C3DP geopolymer mortars.
- To determine the drying shrinkage development in geopolymer-based free-formed (3D printed) specimens cured in different environmental conditions and by removing the mould immediately after the initial setting. The results are compared with that of control specimens prepared with conventional

casting. The effect of adding thixotropy modifiers to the geopolymer binder and using lead smelter slag on the drying shrinkage in free-formed and cast specimens are compared.

1.4 THESIS STRUCTURE

There are six chapters in this thesis as outlined below. Three experimental chapters are in the form of published or ready-to-be-submitted journals to follow the PhD by publication structure of the University of Melbourne.

Chapter 1 - Introduction

This chapter briefly introduces 3D printing in the construction industry its benefits and challenges. The research problem and primary objectives of the thesis are defined in this chapter.

Chapter 2 - Literature review

This chapter summarises the relevant studies on mixture optimisation and production of 3D printing cement-based and geopolymer-based mortars, including those prepared with underutilised aggregate. A literature review on the effect of different additives and geopolymer admixtures (i.e. nanoclay, graphene oxide) is provided in this chapter. This chapter also reviews and summarises previous research on shrinkage behaviour and durability-related properties of 3D printed structures.

Chapter 3 - Rheological limits in optimising cement mortar mix design for 3D printing: Effects of water and admixtures

This chapter proposes a theoretical framework based on rheological limits to optimise mortar formulations for 3D printing applications. The theory suggested that controlling the yield stress evolution could be used as a tool for printing optimisation. The effect of different parameters and admixtures, i.e. water to cement ratio, superplasticiser, accelerator, retarder, on yield stress development is discussed. The methodology presented in this research provides a framework for implementing

changes to the mix design to achieve the required quality and efficiency of extrusion-based concrete 3D printing.

Chapter 4 - Shrinkage behaviour of cementitious 3D printing materials: Effect of temperature and relative humidity

This chapter describes the first comprehensive investigation of the effects of different outdoor environmental conditions, i.e. relative humidity (RH) and temperature on the moisture loss, drying and autogenous shrinkage of cementitious 3D printing materials, considering different sand to cement (S/C), and surface to volume (S/V) ratios of free-formed specimens. Mass loss and length change of mortars that were cured under standard conditions (24°C-50%RH with 24 hours of sealed initial curing) were compared with those at 24°C-50%RH, 35°C-85%RH and 35°C-45%RH (free-formed specimens without initial curing) to investigate the effect of outdoor printing environment and the absence of formworks on the deformations caused by shrinkage.

Chapter 5 - Drying shrinkage behaviour of geopolymer mortars for use in extrusion-based construction 3D printing: Effect of LSS aggregates, graphene oxide and nanoclay at different environmental conditions

This chapter describes the rheological, mechanical and shrinkage properties of geopolymer mortars formulated with lead smelter slag as fine aggregate for extrusion-based 3D printing. The rheological parameters (yield stress evolution and viscosity capacity) that are directly related to the printing properties, such as flowability (extrudability) and the stability of the layered structure (buildability), were tested in LSS geopolymer mortars. Due to the lack of colloidal interaction in alkali-activated binders, which is responsible for sufficient shape stability and extrudability, the effect of adding graphene oxide (GO) and nanoclay (NC) on the improvement of yield stress and viscosity recovery properties are presented in this chapter. Moreover, improvement in viscosity recovery and hydration reaction after replacing GO with NC are discussed in this chapter. The drying shrinkage and microstructure of the free-formed and conventional casting (control) specimens, incorporated graphene oxide,

nanoclay, and lead smelter slag (versus natural sand), are compared at temperatures and relative humidities of 24°C-50%RH, 35°C-50%RH and 35°C-90%RH.

Chapter 6

This chapter summarises the key results and proposes directions for further study in this area.

Figure 1.1 illustrates the research methodology utilised for this thesis to measure the drying shrinkage strain of cement and geopolymer-based mortars for construction 3D printing after optimising their printing qualities and rheological properties. The novelty of this PhD research is that, for the first time, the shrinkage development in the formwork-free process of extrusion-based concrete 3D printing is simulated by preparing free-formed specimens which were tested under different outdoor drying environmental conditions. Moreover, the effect of parameters that are essential in higher shrinkage strain of 3D printed elements as opposed to conventional casting, including low aggregate to binder (S/C) and water to binder (W/C) ratio, as well as the high surface area to volume ratio are evaluated. This research also investigated the effect of thixotropy modifiers (nanoclay and graphene oxide) on the shrinkage development of geopolymer-based mortars prepared for 3D printing. Moreover, the effect of LSS recycled aggregate on the drying shrinkage of geopolymer-based 3D printing mixtures is investigated. The findings of this study will contribute toward addressing durability-related problems in extrusion-based concrete 3D printing, and the results of this research will serve as a benchmark for future studies on the influence of shrinkage on the structural integrity of printed structures.

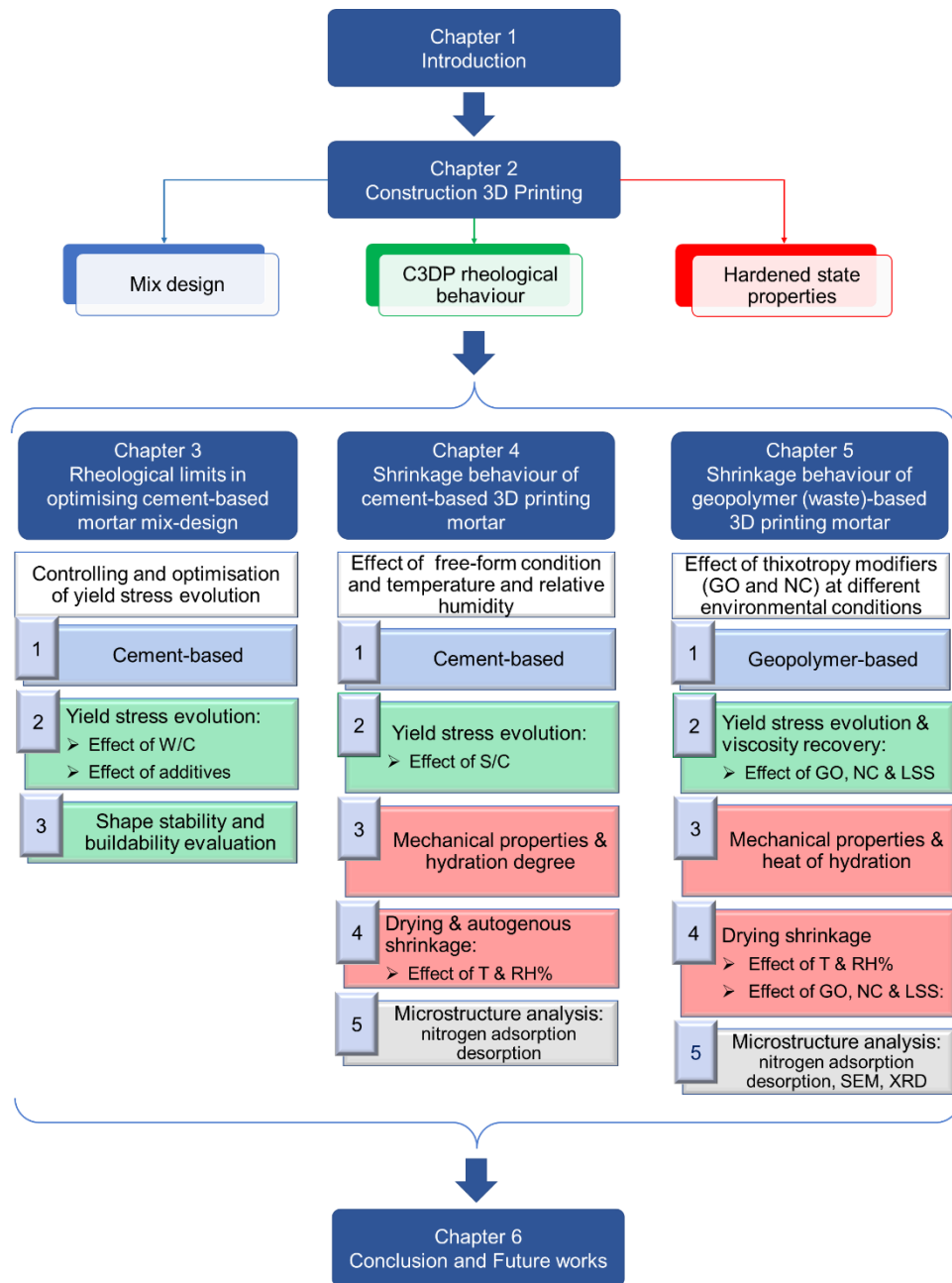


Figure 1.1. Thesis research methodology and chapter structure.

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Chapter 2: Literature Review

This chapter begins with a background and review of the market potential for 3D printing in the construction industry (Sections 2.1 and 2.2). Afterwards, a literature review on the following topics is provided:

- [Definition of digital construction and concrete 3D printing (C3DP)] (Section 2.3) introduces different methods of construction scale 3D printing;
- [Characterisation of concrete for 3D printing] (Section 2.4) discusses the concrete fresh-state properties required for extrusion-based 3D printing;
- [Mixture design and effect of raw materials optimisation] (Section 2.5) reviews the mix-design of C3DP mixtures prepared with ordinary Portland cement (OPC) (Section 2.5.1) and alkali-activated binder (Section 2.5.2) and discusses their fresh and hardened state properties for extrusion-based 3D printing;
- [The natural and underutilised fine aggregate for Concrete 3D Printing] (Section 2.5.3) reviews the effect of using natural fine aggregate and its substitution with underutilised fine aggregate on 3D printing properties of printable concrete;
- [Nanomaterials in C3DP mixtures] (Section 2.5.4) reviews the experimental research carried out on nanomodification of 3D printable concrete using conventional (nanoclay) and novel (graphene oxide) rheology modifiers on fresh state properties, mechanical strength and shrinkage deformation of 3D printable concrete;
- [Structural build-up in concrete for 3D printing] (Section 2.6) reviews the recently developed models for in-print strength-based and stability failure of 3D printable concrete;
- [Durability in concrete 3D printing] (Section 2.7) reviews the definition of different types of shrinkage and discusses current research on shrinkage evolution and the measures taken to control it in the formwork-free nature of C3DP.

2.1 INTRODUCTION

Additive manufacturing, or more commonly these days, 3D printing, has become popular in recent decades for its ability to produce cost-effective prototypes and bespoke parts and products. Some consequences of this disruptive and revolutionary technology are that design and development cycles have been simplified and shortened, the gap between design and engineering is being bridged, and communication and collaboration between stakeholders have been improved [1]. A diverse range of industries, including the automotive, aerospace, biomedical engineering, consumer goods, food and art sectors, have already found a wide range of applications for this technology [2]. More recently, the construction industry has started to explore the potential applications and benefits of 3D printing and research in this area is becoming increasingly popular [3]. The freeform nature of additive manufacturing differs significantly from traditional construction methods, and the scale required for the industry is much larger than that of previous applications. For these reasons, there is a need to fundamentally understand the relationships between design, material, process and product to assist in the adoption of this technology [3].

2.2 MARKET POTENTIAL FOR 3D PRINTING IN THE CONSTRUCTION INDUSTRY

The construction industry is currently shifting toward adopting cutting-edge technologies, something it has largely resisted for years now and for which it has been the subject of much criticism [4]. Over the last fifty years, there has been a stagnation in labour productivity [1]. The reasons for this are numerous but include factors such as contractor's resistance to change (primarily due to long payback periods), high turnovers making it hard to implement new methods and poor data interoperability [1]. However, the emerging acceptance of building information modelling (BIM) is a massive step forward and may also help facilitate further advances, like automated manufacturing processes [5].

There are many benefits that automation can bring to the construction industry. Lim et al. [5] suggest some of these are: a reduction in the labour force to increase safety; a reduction in on-site construction times; a reduction of production costs; and an increase in architectural freedom. To this extent, it is expected that additive manufacturing has a role to play in large-scale construction applications [5]. With tools like BIM bringing architecture and engineering closer together, there is a desire to

explore construction methods capable of economically producing avant-garde designs [6]. 3D printing, to a limited extent at the moment, has the ability to achieve this goal.

When considering construction scale 3D printing, concrete is the obvious choice since it is ubiquitous as a building material and is initially plastic, which allows it to be pumped and extruded. The fact that 3D printing is inherently freeform means that there is an opportunity for new concrete architectures to be constructed that were previously either not possible or were prohibitively expensive. Figure 2.1 shows that up to 50% of the total cost of a new concrete construction project can be spent on formwork and the associated labour [7,8]. This is the primary reason the industry has been confined to building in simple geometries. The 3D printing technique also supports the production of parts with structurally efficient forms that allow for the incorporation of additional functionality [9].

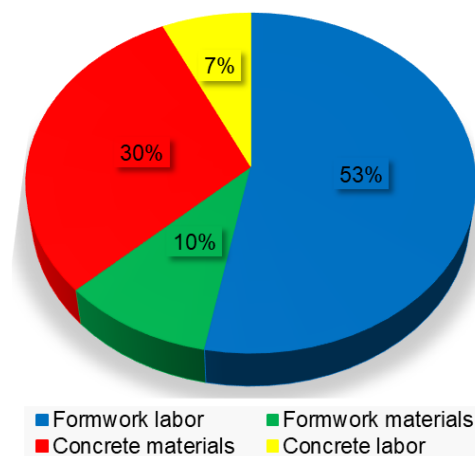


Figure 2.1. Typical cost allocation for a construction project [8].

While there are many hurdles to overcome, the benefits that freeform construction and automation can offer are substantial. The shift toward sharing information and collaborating using BIM is an important step in realising these benefits since much of the digitisation necessary for printing and automation will be accessible through this software [10]. Figure 2.2, adapted from Paul et al. [7], shows the steps necessary to produce a 3D printed product. The software stages on the left have already been integrated into BIM packages by some developers, meaning that any suitable object within the model is essentially ready to print [10]. This has obvious benefits from a streamlining perspective, and the uptake of this type of software is

likely to encourage further adoption of automation and additive manufacturing processes [5].

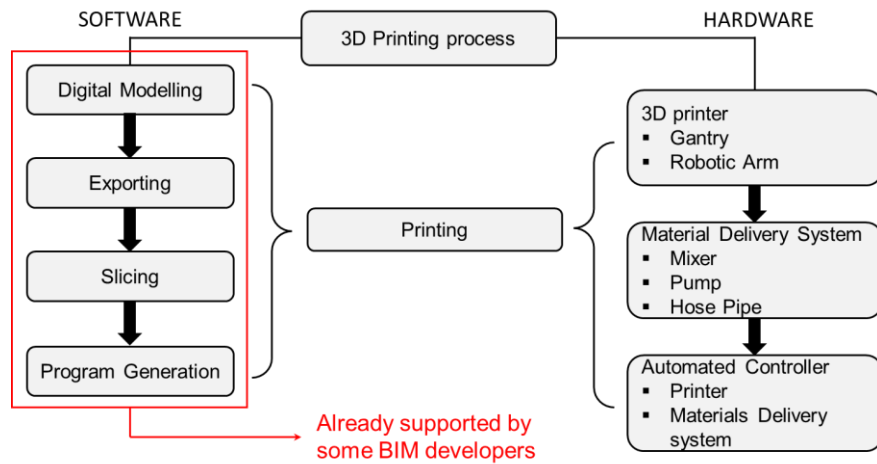


Figure 2.2. The process of 3D printing for construction [7].

2.3 DIGITAL CONSTRUCTION - CONCRETE 3D PRINTING (C3DP)

2.3.1 Methods of Construction Scale 3D Printing

Construction 3D printing techniques can be classified into two general forms: powder printing (e.g. D-shape) and extrusion printing (e.g. Concrete Printing and Contour Crafting) [11,12]. These techniques differ based on the application and printable material [5]. These techniques are developed to print a structure layer by layer via injecting a binder or extruding cementitious material from a nozzle mounted on a robotic arm. A summary of both systems is presented below.

Powder-Based 3D printing

Developed by Enrico Dini, the D-shape process uses dry sand sequentially placed and compacted to the desired thickness before gantry-mounted nozzles deposit a binder in the local areas to be solidified [5]. As shown in Figure 2.3 (a, b), The surrounding sand bed acts as support material for the solidified part, and once the layer-by-layer printing process is complete, the remaining sand is removed, and the printed part is revealed [12]. Because of the support material, D-shape technology allows accurate 3D printed parts with complex geometries. This is a distinct advantage over contour crafting and concrete printing, which are unable to print significant overhangs without support structures being added through outside intervention [12]. The end product of D-shape printing (Figure 2.3 (c, d)) is strong and similar to sandstone, however, due to the large amounts of sand that need to be placed during printing, the

technology is more suitable for off-site fabrication, and the production of very large parts is impractical and time-consuming [13].

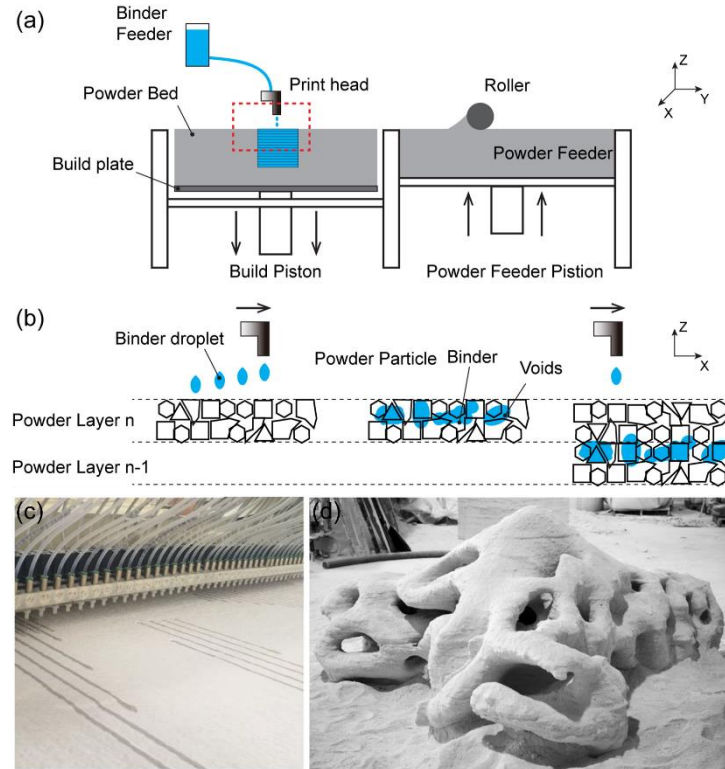


Figure 2.3. Powder-based 3D printing process: (a) inkjet printing system, (b): powder/binder interaction [11] (c, d): DS 3×3ACADEMY particle-bed 3D Printer, print product in D-shape before powder recycling [14].

Extrusion-Based 3D printing

In recent years, two methods of contour crafting and concrete printing have been developed based on the extrusion of construction materials which are similar in many ways. Both are based on extruding a strand of printing material, mostly concrete, in order to fabricate a vertically standing multi-layer product [12]. Contour crafting was developed in the mid-1990s in California, USA, by Behrokh Khoshnevis [15]. Valuable development has been done on contour crafting by Xtree in France, the Chinese company Winsun, and the University of Loughborough, England [5]. All attempts envisage that the construction of buildings with various geometry can be achieved in a single run via this method [13]. The contour crafting technique has often been used to create parts by essentially printing a formwork, which can be back-filled with suitable material and reinforcement if desired. Generally, thick layer heights are used in contour crafting, and this method's print speed is fast [12]. Contour crafting is distinguished by using trowels assembled on the nozzle during printing, achieving

extremely smooth and precise exterior surfaces. Figure 2.4 shows the contour crafting process, the nozzle assembly and a final hollow wall product constructed by the contour crafting technique.

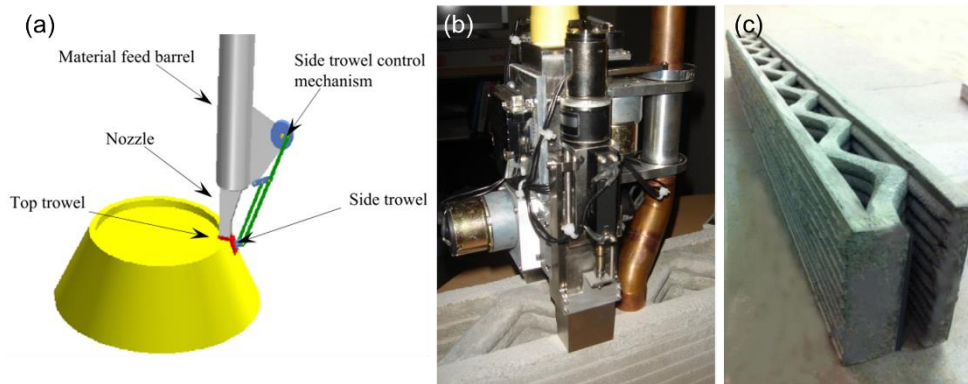


Figure 2.4. Contour crafting process (a) [16], an advanced nozzle for contour crafting is used to create a hollow interior wall (b), a concrete wall made by a contour crafting machine (c) [17].

Correspondingly, the concrete printing method was developed at Loughborough University in a project similar to contour crafting [12]. In concrete printing, the concrete extrudes vertically down, and the product is built layer by layer from the bottom to the top. In both methods, there is no need for exterior support material, making engineers capable of incorporating functional voids into the print product and giving them higher flexibility in designing intricate shapes [13]. In the concrete printing technique, smaller resolutions are achievable by adjusting the printer nozzle size, giving greater control of internal and external geometries [5]. Moreover, the final printed part has a ribbed exterior surface. Concrete printing generally consists of design and material preparation, delivery system and printing process. Printers in construction scale are designed in different dimensions. For example, at Loughborough University, the frame dimension for the printer is $5.4 \text{ m} \times 4.4 \text{ m} \times 5.4 \text{ m}$ with a movable print head that can move up to 83 mm/s [4]. Figure 2.5 shows some noteworthy examples of recent projects used gantry and robotic arm printers in large-scale C3DP.



Figure 2.5. COBOD BOD 2 gantry printer (a) used to build a two-story 160 m² 3D printed residential building in Europe (b) [18]; Cybe mobile robotic arm 3D printer (c) used to build self-contained toilet units (d) in Japan [19]; Apis-cor printers in polar coordinates (e) used to build a two-story 640 m² world largest 3D printed building (f) [20].

2.4 CHARACTERISATION OF CONCRETE FOR 3D PRINTING

Due to the freeform nature of 3D printing, the fresh properties of concrete required for extrusion-based techniques, like contour crafting and concrete printing, need to be significantly different to those developed for traditional cast situations. These new material requirements are related to the processes specific to 3D printing and have been identified and detailed by several authors [1,4,5,21]. The four main material characteristics of wet-process, extrusion-based additive manufacturing are:

1. Pumpability – is defined by the reliability and ease with which the material passes through the delivery mechanisms [1].
2. Extrudability (also reported by Kazemian et al. [4] as “print quality”) – is defined as the ease and reliability of depositing material without incurring

discontinuities [1,22,23]. Figure 2.6 shows examples of proper extrudability of alkali-activated concrete [21,24].



Figure 2.6. Suitable extrudability (no filament breakage or discontinuity) of (a) cement-based [21] and (b) FA-GGBS based [24] 3D printing concrete mixtures.

3. Buildability (also reported by Kazemian et al. [4] as “shape stability”) – is defined as the resistance of the printed material to deformation under loads [21]. Figure 2.7 shows examples of printed layers' acceptable/unacceptable shape stability and buildability, respectively.

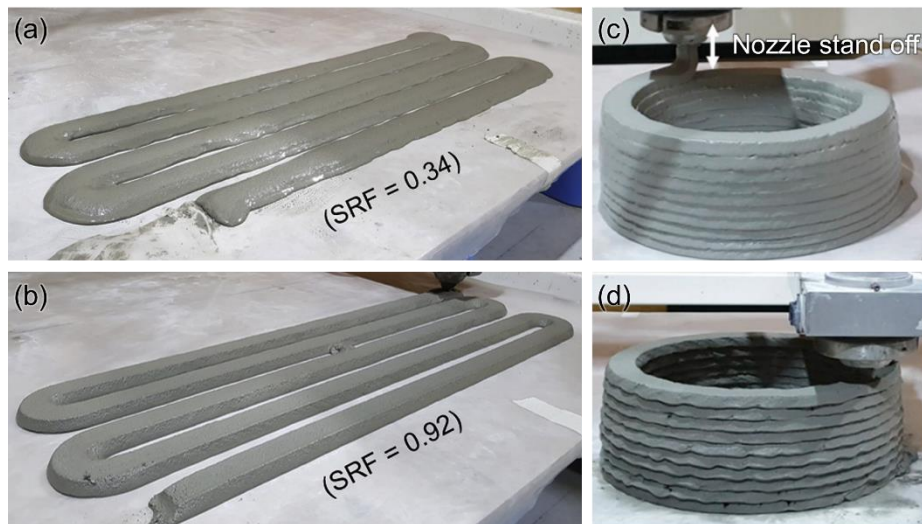


Figure 2.7. (a, b): Shape stability (shape retention factor (SRF) of 1.0 is the ideal value) and (c, d): buildability of geopolymer printed layer. Nozzle stand-off distance represents low buildability[25].

4. Open time (also reported by Kazemian et al. [4] as a “printability window”) – is defined as the period of time where the above qualities remain consistent

within predefined tolerances [1]. Figure 2.8 shows the time frame when extrudability is lost to measure the printing window.

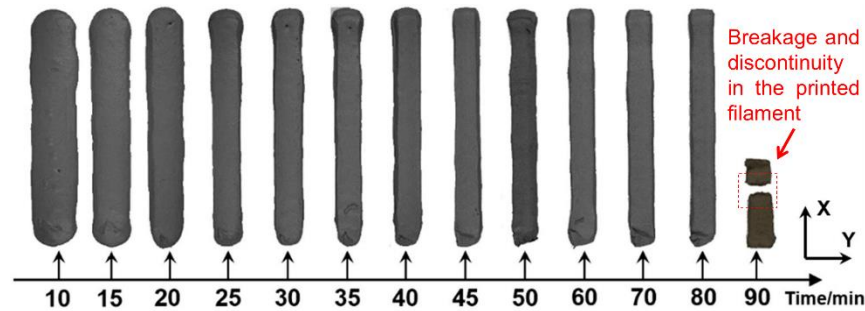


Figure 2.8. Open time is recorded as the timeframe between the end of mixing and a time when breakage or discontinuity occurs in the printed filament [21].

The above properties will need to be adjusted depending on the mix design, delivery system and deposition device and need to be tailored for job-specific requirements like layer height, print speed and vertical build rate [5]. In all cases though, the rheology of concrete for 3D printing must allow for pumping and extrusion through a printing nozzle but also have sufficient capacity to resist deformation immediately after printing and when subsequent layers are added [1,22,23].

2.5 CONSTRUCTION 3D PRINTING MIXTURE DESIGN AND EFFECT OF RAW MATERIALS OPTIMISATION

Concrete printing jobs vary significantly in scope and resolution and can range from relatively small parts to entire walls or even systems of walls and columns. As a result, the delivery system and job parameters can differ depending on the application. Therefore, it is desirable for the concrete mix used in each situation to be tailored specifically for the job type. The mixture design will strongly influence the viability and efficiency of the printing process and determine the printed parts' final strength and durability. While, as stated, concrete mixes will vary due to system parameters and job type, they are generally characterised by the following attributes:

- Low or no slump – a requirement due to the need for resistance to deformation while printing [4].
- Small aggregate size – since printing nozzle dimensions are relatively small, larger aggregates could cause blockages [12].
- Use of admixtures – superplasticisers, accelerators, retarders and viscosity modifying admixtures are all common additions to printing mixtures to control the fresh and hardened properties [22,23].

Furthermore, it is desirable for mixes to have a low water-to-binder (W/B) ratio to maximise the final strength [22,23]. While this is true for concrete in most applications, it is particularly relevant in 3D printing since printed parts lack the steel reinforcement of cast concrete and also suffer from weak zones where layer-to-layer adhesion can be underdeveloped [22,23,26,27].

There are a particular set of inter-related dichotomies that require balancing when considering concrete mix design for 3D printing. Firstly, in order to maximise the final compressive strength of the printed part, it is desirable to reduce the W/B ratio as much as possible, however, this results in a less workable material that could be unsuitable for pumping and extruding [28]. In addition, the mix must flow freely through delivery devices but, after being extruded, must support its weight and the weight of subsequent layers without significant deformation occurring [28]. Lastly, after being deposited, the mix should be set as fast as possible to increase buildability but not so fast that the interlayer adhesion is compromised [28]. The balance of each of these trade-offs will be highly dependent on the job type and machine parameters.

C3DP mixtures' desirable characteristics can only be achieved through careful material selection. In order to meet the fresh-state requirements of C3DP mixtures, various types of cement, mineral additives, chemical admixtures, and aggregates have been used. The following sections review the cement-based and alkali-activated binder systems, aggregate types used, and novel nanomaterial used in C3DP technology.

2.5.1 Cement-Based 3D Printing mortar

Compared to the conventional concrete, the cement-based C3DP mixtures are designed with higher proportion of binder and fine aggregate (no coarse aggregate) and decreased water content (low water to cement ratio) to meet the printability requirements such as a high early age yield stress, high green strength, improved shape stability capacity and rapid setting.

As shown in Table 2.1, which summarises the optimum mixture design of cement-based printable mixtures from recent studies, cement-based C3DP mixtures typically consist of more than 70% OPC in the binder as well as other supplementary cementitious materials such as fly ash (FA), ground granulated blast furnace slag (GGBS) and silica fume (SF) at lower ratios [29]. The typical W/B ratio is within the range of 0.3 to 0.4, while the sand-to-binder (S/B) ratio for most research falls between

1.2 and 2.0. Besides, researchers used chemical admixtures such as high range water reducer (HRWRA), viscosity modifying agent (VMA), accelerator (Acc), retarder (Ret), and nanomaterials (such as nanoclay: NC) in C3DP mixtures to modify the required printing properties.

Table 2.1. Cement-based 3D printable mixtures [29].

Concrete type	Ref	Binder type	Binder proportions				W/B	Aggregate size & ratio		Admixture & additives (%wob)		
			OPC	FA	SF	GGBS		S/B	D _{max} (mm)	HRWRA	VMA	Other
Cement-based mix	[30]	OPC	1	-	-	-	0.41	1	0.1	0.3	-	-
	[31]	OPC	1	-	-	-	0.36	2	2	0.15	-	-
	[32]	OPC	1	-	-	-	0.35	1	1.2	0.1	-	-
	[33]	OPC	1	-	-	-	0.42	1.7	2	0.7	-	-
	[34]	OPC	1	-	-	-	0.39	1	1.2	0.18	0.1 2	-
	[35]	OPC	1	-	-	-	0.36	1.5	2	-	-	-
	[36]	OPC	1	-	-	-	0.35	1.18	2	0.2	-	CSA = 0.7
Cement-SCM blended mix	[37]	OPC, FA, SF	0.7	0.2	0.1	-	0.28	1.38	0.2	1	0.2	-
	[22]	OPC, FA, SF	0.7	0.2	0.1	-	0.28	1.5	2	0.5 - 2.0	-	Ret = 0 - 2.0, Acc = 0 - 5.0
	[38]	OPC, FA, SF	0.26	0.26	0.48	-	0.42	1.54	2	2.0 - 3.0	-	-
	[39]	OPC, SF, NC	0.96	-	0.02	-	0.35	1	1	0.26	0.0 1	NC = 2
	[7]	OPC, FA, SF	0.41	0.39	0.1	-	0.4	1.7	1	1	-	-
	[40]	OPC, FA, SF	0.7	0.2	0.1	-	0.49	1.7	2.36	-	-	-
	[41]	OPC, FA	0.8	0.2	-	-	0.32	1.5	-	0.08	0.2 5	-
	[42]	OPC, SF	0.9	0.1	-	-	0.4	1.25	1.5	0.26 - 0.40	-	-
	[43]	OPC, FA, SF	0.59	0.23	0.17	-	0.3	2.5	8	0.84	-	-
	[44]	OPC, LS	0.75	-	-	-	0.36	1.55	2	0.5	0.2	LS = 25
	[45]	OPC, GGB S, FA	0.55	0.15	-	0.3	0.31	1.18	-	1.2	0.6	-

[46]	OPC, FA, SF	0.7	0.2	0.1	-	0.26	1.5	-	1	-	Ret = 0.5
[47]	OPC, FA, SF	0.7	0.2	0.1	-	0.45	1.41	4.75	0.7	-	-
[48]	OPC, FA, SF	0.7	0.2	0.1	-	0.32	1.5	2	0.17	-	-
[4]	OPC II, SF	0.9	-	0.1	-	0.43	2.3	2.36	0.15	-	NC = 0.3
[49]	OPC, FA, SF	0.7	0.25	0.05	-	0.35	0.75	1	0.3	-	NC = 0.5

OPC: Portland cement, FA: Fly Ash, SF: Silica Fume, GGBS: slag, CSA: calcium sulfoaluminate HRWRA = high-range water-reducing agent, VMA: viscosity modifying agent, Acc: accelerator, Ret: retarder, NC: nanoclay, LS: limestone, wob: weight of the binder.

Using higher OPC and fine aggregate proportions are inevitable requirements for C3DP mixtures, which can cause an increase in the heat of hydration and autogenous and drying shrinkage evolution [50]. Further research is needed to measure the effect of higher OPC content and lower W/B ratio of printable mixtures as well as the formwork-free nature of C3DP practice on shrinkage deformation, especially autogenous and drying shrinkage of the printed structure.

2.5.2 Alkali-Activated 3D Printing mortar

The most energy-consuming and pollutant-emitting aspect of OPC-based concrete is generally its binder system. Figure 2.9 depicts the binder proportion of several OPC-based 3D printing concrete formulations described in the literature (incorporated with various supplementary cementitious materials, i.e., FA, GGBS, SF, and so on).

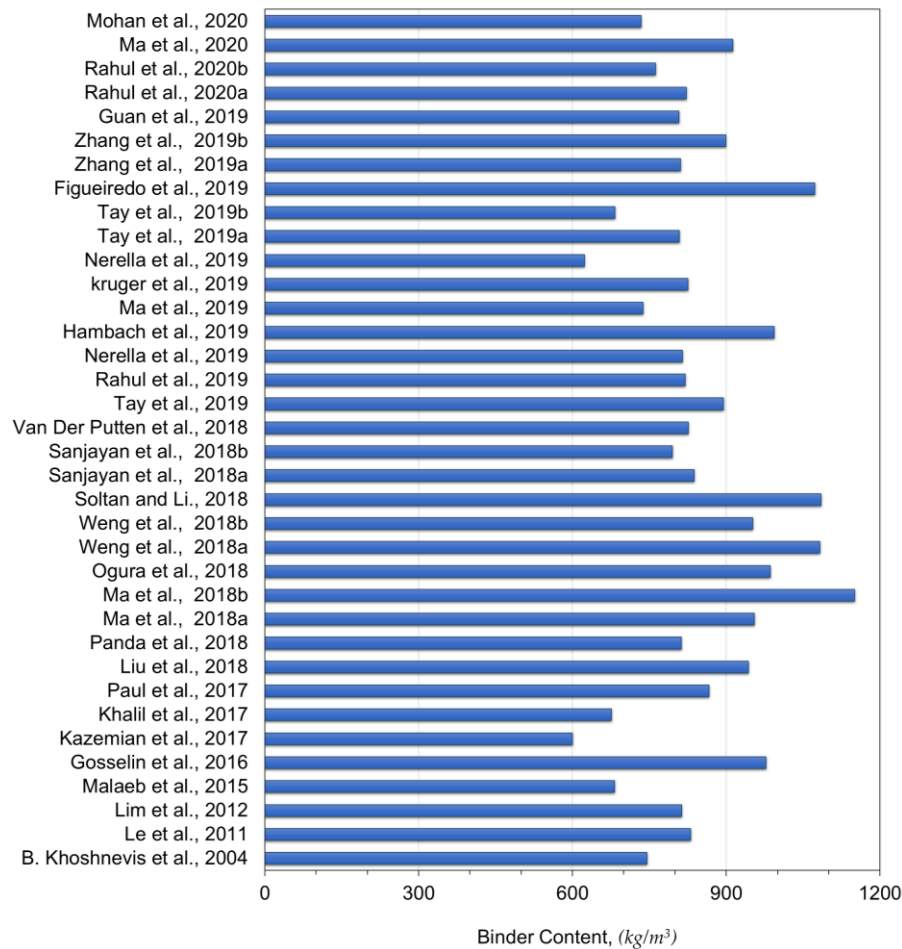


Figure 2.9. Comparison of binder content in cement-based printable mixtures used for C3DP [4,5,7,12,16,21,22,26,28,36,38–41,48,51–72].

In conventional casting concrete, the binder content of the mixtures is usually within the range of 300 to 400 kg/m³ [51]. However, the binder proportion in OPC-based 3D printing concrete is at least 40% higher and generally at an average of approximately 850 kg/m³ [4,5,7,12,16,21,22,26,28,36,38–41,48,51–72]. Therefore, considering the higher proportion of OPC, which its production is high energy-consuming and pollutant-emitting, C3DP technology is not still an eco-friendly and sustainable technology compared to the conventional casting.

Numerous research has been conducted to find an alternative for OPC to enhance the sustainability of the C3DP. The 3D printing concrete was designed with Alkali-activated binder [24,25,73–85], magnesium phosphate cement [86], and calcium sulfoaluminate cement [87–90]. However, due to alkali-activated materials' superior properties, FA-GGBS-based geopolymer is the most widely used alternative material for OPC. Typically, materials with thixotropic properties, high yield stress and low viscosity are the most appropriate materials for concrete 3D printing. However, it has

been reported that, as opposed to the cement-based binder systems [91], the geopolymer-based binder system lacks the colloidal interaction between raw materials particles [92]. This can translate that the yield stress development in geopolymer-based concrete is controlled by the percolation of aluminosilicate gel formed between precursors particles. Therefore, some studies have been conducted to address this limitation by incorporating thixotropic agents such as nanoclay (NC) and silica fume (SF). These studies proved that geopolymer mixtures could be tailored to obtain suitable buildability and mechanical properties for C3DP [75]. Panda et al. conducted the first comprehensive research on the mixture design of 3D printing geopolymer-based mortar [78]. Critical 3D printing fresh-state properties, including shape retention, buildability, and extrudability, were tested for mixtures with various FA-GGBS binder ratios to find the optimum value. Five mixtures with the sand-to-binder (S/B) ratios of 1.0, 1.2, 1.4, 1.6 and 1.8 at constant binder composition of FA : GGBS : SF of 0.78 : 0.14 : 0.08, activator-to-binder (AB) ratio of 0.42, and liquid to binder ratio of 0.5 were investigated. The appropriate yield stress range in terms of the optimum extrudability was found between 600 and 1000 Pa. They have reported the shape retention coefficient in the range of 0.85-0.90 and open time of around 10 to 15 minutes. To induce some thixotropic effect in the mixture and enhance the buildability of the geopolymer mixture they have modified the optimum mixture (S/B = 1.4) by addition of 1.2% NC (nano attapulgite).

In another study, Panda et al. [25] investigated the rheological properties of FA-GGBS-based geopolymers to evaluate their suitability for C3DP by controlling various mixing parameters, including activator modulus ($MR = \text{SiO}_2/\text{K}_2\text{O}$ molar ratio), activator-to-binder (AB) ratio, water-to-solid (WS) ratio and inclusion of NC as a thixotropic agent. The results showed that for FA : GGBS binder composition of 0.85 : 0.15, the optimum AB and WS were 0.35 and 0.30, respectively [25]. Yield stress and apparent viscosity of the mixtures decreased when WS increased, which was attributed to the reduction of interparticle friction and alkali ion concentration, respectively [25]. Moreover, they reported that increasing MR resulted in higher yield stress and apparent viscosity due to the enhancement of activator viscosity [25]. Although the NC inclusion enhanced the rheological parameters of geopolymer mixtures, the results indicated that 0.5% NC inclusion resulted in a 17% reduction in compressive strength [25]. These results were contrary to the previous findings that

the space-filling ability of NC can improve the flexural strength of geopolymer mixtures [93].

In another research by Zhang et al. [56], the effect of Si/Na ratio in alkali activator on the structural rebuilding and yield stress development of geopolymer paste was investigated. The results have shown that Si/Na ratio was negatively correlated with the yield stress development and viscosity of geopolymers [77]. Increasing the Si/Na resulted in lower viscosity and yield stress development rate. Consequently, reducing the alkali activator's Si/Na ratio enhanced the structural rebuilding properties of geopolymer paste [77]. Alghamdi et al. [79] examined the extrudability and buildability of FA-based 3D printable geopolymer incorporated with a minor proportion of limestone, OPC and GGBS. The mini-slump and yield stress measured for mixtures and a printability window have been defined. The lower and upper bound of yield stress for printable mixes were found at 150 Pa and 700 Pa, respectively. Printable mixtures also showed mini-slump values lower than 20 mm [79]. It is believed that using geopolymer binders reduces the carbon emission related to OPC production in 3D printing mortars.

Although the rheological aspects of using geopolymer binders as an alternative for OPC in 3D printing mixtures have been studied to some extent, further experimental studies are needed to investigate the durability-related properties of geopolymer-based 3D printing mixtures, including the effect of outdoor 3D printing environment (formwork-free and open-to-atmosphere condition) and thixotropic agents on the shrinkage development of 3D printing geopolymer mortars.

2.5.3 The natural and underutilised (by-products, recycled or waste) fine aggregate for Concrete 3D Printing

Natural aggregate

One of the main differences between conventional casting and C3DP is the limitation in using coarse aggregate in C3DP mixtures [94]. The reason behind this is the critical requirement for extrudability and buildability and avoiding any blockage of the delivery piping system [95]. Considering the printing nozzle size limitation, which is typically set for approximately 0.1 of the diameter of the printing nozzle (generally between 20 mm and 40 mm), the maximum diameter of aggregate in extrusion-based 3D printing is generally limited to 4 mm [22,94,96,97]. Due to this limitation in using coarse aggregate, low water and high binder content, C3DP

mixtures are prone to higher plastic, autogenous and drying shrinkage [50,98]. However, higher S/B ratios reduce binder content, shrinkage cracking and total heat of hydration [99].

The impact of aggregate properties and morphology on the behaviour of printed concrete has been examined by researchers. In a research published by Zareian and Khoshnevis [100], the influence of aggregate size on the mechanical performance of 3D printing concrete was investigated. They have designed four different 3D printing mixtures to meet the rheological properties requirement for C3DP, using aggregates with a maximum particle size of 2.38, 4.76, 6.35 and 12.7 mm. They have reported that the 14 and 28-day compressive strength of mixtures containing aggregate with smaller maximum particle size improved by up to 141% at a constant S/B ratio of 1.5. In another study by Chen et al. [101], 3D printing concrete containing aggregates with the maximum particle size of 20 mm and different S/B ratios were designed and tested for flowability, shape stability, buildability and mechanical strength performance. Their results have shown that increasing the particle size of fine aggregate in 3D printing mixtures decreases the printing qualities and increases the porosity in the printed structure.

In general, fine aggregates with a larger maximum particle size (within the acceptable range) and a broader particle size distribution leads to increased packing density and improved 3D printing properties (i.e. flowability) [96]. Zhang et al. [39] examined the influence of fine aggregate content (effect of S/C ratio) on different rheological parameters of a 3D printing concrete. The apparent viscosity, yield stress and thixotropy of mixtures with S/C of 0.6, 0.8, 1.0 and 1.2 were measured at different open times after mixing. According to their findings, the S/C ratio was directly correlated with the initial viscosity and initial yield stress, whereas it was inversely correlated with initial thixotropy properties. They have reported that raising the S/C ratio by twofold increased the apparent viscosity and yield stress by approximately 16% and 130%, respectively. However, according to their findings, increasing S/C did not have a tangible effect on reducing the drying shrinkage of printable mixtures. A similar trend was observed by Mohan et al. [102], where a 40% increase in fine aggregate content (S/C of 1.0 to 1.4) increased the yield stress and viscosity by 22% and 152%.

As discussed in this section, based on the available literature very limited number of studies investigated the effect of S/C on the durability-related properties of 3D printable concrete. Considering the fact that compared to conventional and self-consolidating concrete, 3D printable concrete mixtures contain a higher binder and fine aggregate content, and using coarse aggregate in C3DP mixtures is restricted, further investigation of the effect of the S/C ratio on the shrinkage deformation (autogenous and drying) of 3D printable mixtures is required.

Underutilised aggregate

Another important consideration in designing C3DP mixtures is using alternatives for non-renewable resources such as natural sand (NS) and silica sand as fine aggregate. To date, several studies have been carried out on using waste materials, industrial by-products, and recycled aggregates in C3DP mixtures [103]. However, further experimental investigations are still required to address the deficiencies in the literature, especially in terms of durability-related properties such as shrinkage risks. It is well known that partial or complete replacement of these materials with natural sand can contribute to improving the economic and ecological sustainability of C3DP technology. In addition, research showed that the overall performance and dimensional stability could be improved by using waste/recycled aggregates in C3DP mixtures.

Recent research by Bai et al. [104] investigated the effect of using underutilised and waste solids, including desert sand, ceramsite sand (artificial foundry sand), and recycled concrete, on fresh properties of 3D printing concrete, such as flowability and buildability as well as hardened-state properties including mechanical strength and shrinkage properties. They have shown that underutilised aggregates improve the structural build-up performance and inter-layer bonding of printed structures, whereas aggregate types adversely affect the shrinkage development in 3D printed parts. Ma et al. [21] conducted the first research on substituting different ratios (0% to 50%) of copper mine tailing with natural sand in C3DP mixtures to determine the optimum ratio in terms of favourable fresh-state 3D printing properties. They have found that increasing the substitution ratio by more than 30% decrease the buildability, whereas the highest 28-day compressive strength was achieved for 40% substitution. In another experimental work by Álvarez-Fernández et al. [105], the effect of partial replacement of silica sand with mine tailing on buildability and rheological properties of C3DP mixtures was investigated. Their findings demonstrated that the substitution of silica

sand with recycled material at 20% led to the optimum buildability and mechanical properties for C3DP. Ding et al. [106] investigated the effect of substituting 25% and 50% river sand with recycled sand crushed from waste concrete on fresh-state strength and elastic modulus of 3D printing concrete. They have found that the recycled sand replacement enhanced the buildability performance and reduced the printing open time window. They have reported that recycled sand replacement improved the compressive strength and elastic modulus after the setting at approximately 90 min, while it had slightly increased these properties before 90 min. Xiao et al. [107] have shown that by adjusting the printing parameters, printing mortars including 25% recycled sand can be well-matched with C3DP systems. They have found that partial replacement (by 25%) of recycled sand with natural sand in C3DP mixtures increased the yield stress by 3% and reduced flowability by 7%. They have reported that since no evident decrease occurred in the hardened state overall mechanical performance of C3DP mortars with 25% recycled sand, it is applicable to replace natural sand with recycled sand in C3DP.

The first study on using unsorted recycled glass as fine aggregates in C3DP mixtures was conducted by Ting et al. [70], in which they investigated the effect of substituting recycled glass for river sand with approximately identical particle size distribution on mechanical strength performance and flowability properties. Their findings demonstrated that incorporating recycled glass sand into the mixtures adversely affected the yield stress and buildability. Moreover, they have found that the compressive, flexural and splitting tensile strength of the recycled glass C3DP mixtures were 50%, 30% and 80% lower than that of river sand mixtures, respectively. The observed reduction in mechanical strength was attributed to the weaker bonding between aggregate particles and cement matrix at the interfacial transition zone (ITZ). These results were in line with the findings of Ding et al. [108], who investigated the effect of replacing recycled sand with natural sand at a 50% replacement ratio. They have reported that the flexural strength of 3D printed specimens was reduced between 33% and 50% for recycled sand mixtures. This phenomenon was associated with the differences in morphology and microstructure of recycled and natural sand. Ding et al. [108] reported that using recycled sand reduced the compactness of the microstructure and resulted in a higher amount of microcracking in ITZ between aggregate and cement matrices of 3D printed specimens.

Cuevas et al. [109] developed 3D printed lightweight concrete using the expanded thermoplastic microsphere and substituting 50% and 100% waste glass for natural aggregate. They reported that 100% replacement of the waste glass with natural aggregate in C3DP mixtures would be possible if minor mixture modifications were applied. They reported that incorporating the recycled glass reduced the printed mixture's initial and final setting time. Moreover, mixtures containing waste glass exhibited approximately 38% lower thermal conductivity. Mixtures with 0%, 50% and 100% recycled glass, which was modified with 0.03 wt.% (by weight of cement) expanded thermoplastic microsphere, exhibited 18%, 1% and 26% lower yield stress compared to their corresponding unmodified mixtures, respectively. However, according to their findings, expanded thermoplastic microspheres modification improved plastic viscosity, shape retention, and buildability performance of 3D printed lightweight concrete. Rahul et al. [41] developed a lightweight, printable concrete by using lightweight expanded clay aggregate with a maximum particle size of 10 mm in place of silica sand. It was determined that a 30% replacement of fine aggregate with lightweight expanded clay did not adversely affect extrudability and printability. Increasing the quantity of lightweight aggregate by more than 30% led to segregation in the piston pump during concrete extrusion. Sambucci et al. [110] developed a 3D printable rubber-cement composite using recycled tyre powder (0.5 – 1.1 mm) and granules (2.5 – 3.7 mm). According to their findings, complete replacement of recycled rubber powder with fine natural aggregate can reduce the density by up to 30%, resulting in a lightweight 3D printing concrete appropriate for dead load reduction of the structures. They also found that substituting recycled rubber enhanced the sound and thermal insulation performance while significantly reducing the compressive and flexural strength. Craveiro et al. [111] developed functionally graded lightweight printed wall with enhanced thermal insulation performance by substituting 10 % natural aggregate (basalt and river sand) with cork granules. Their findings indicated that modified mixture with cork reduced the thermal conductivity by 12%.

Lead Smelter Slag (LSS) as fine aggregate

To some extent, the C3DP is not still an environmentally benign technology from a material utilisation standpoint since it requires a large proportion of energy-intensive and high embodied carbon components in the mixture. As discussed in Sections 2.5.2 and 2.5.3, using alkali-activated binder as an alternative for OPC and using

underutilised aggregates such as waste/recycled aggregate and glass sand (GS) as fine aggregate are being considered as solutions for decreasing the environmental impact associated with C3DP technology. This allows to improve the sustainability of C3DP and reduce the embodied carbon in the C3DP mixtures. Moreover, this can contribute to reducing environmental deterioration due to the over-exploitation of non-renewable natural resources, including natural sand (NS). Besides the fact that the reprocessing of recycled aggregate in the construction sector has been recently targeted, utilising industrial by-products in the construction industry as a substitution for natural aggregate, especially in C3DP, will be a promising step forward in resolving the problem of natural aggregate shortage and environmental deterioration.

As discussed in the previous Section (2.5.3), existing studies have shown that underutilised aggregate, the abundant waste products currently being landfilled, exhibit properties that make them suitable for use in structural concretes and 3D printable mixtures. However, concrete incorporated with recycled aggregates is often claimed to have low mechanical characteristics and significant shrinkage strain [112,113]. Therefore, to improve the sustainability of C3DP by taking advantage of the capabilities of alternative aggregates (recycled or waste aggregate) in the 3D printable concrete mixtures while not sacrificing the mechanical performance and dimensional stability of the printed structure, more research is required to find the most appropriate replacement for natural aggregate in C3DP mixtures.

Lead smelter slag (LSS), also known as black sand, is an industrial waste (by-product) from the metallurgical industry produced during pyrometallurgical processing of lead concentrates and lead wastes that exhibited promising mechanical strength and shrinkage performance when used as a substitution for natural aggregate in cement-based and geopolymer-based concrete and mortars [114]. This section will review previous studies on the properties of LSS in concrete that exhibited the potential of LSS to be used in the complete replacement of natural fine aggregates.

With the global growth observed in lead production from 2009 to 2016 [114,115], the total production of LSS reached approximately 5.5 million tons in 2016 [114], primarily dumped in landfills. LSS ranges in colour from black to red (mostly dark black) since it often has a high iron oxide concentration. LSS is a granular substance with a specific gravity ranging from 2.65 to 3.79 and has a unit weight that ranges from less than 2.5 g/cm³ to as high as 3.6 g/cm³ [116]. As shown in Figure 2.10,

LSS is characterised as glasslike, angular, and sharp-cornered (cubical) particles [117]. LSS is porous by nature, and its water absorptions can be slightly higher than the natural sand [116].

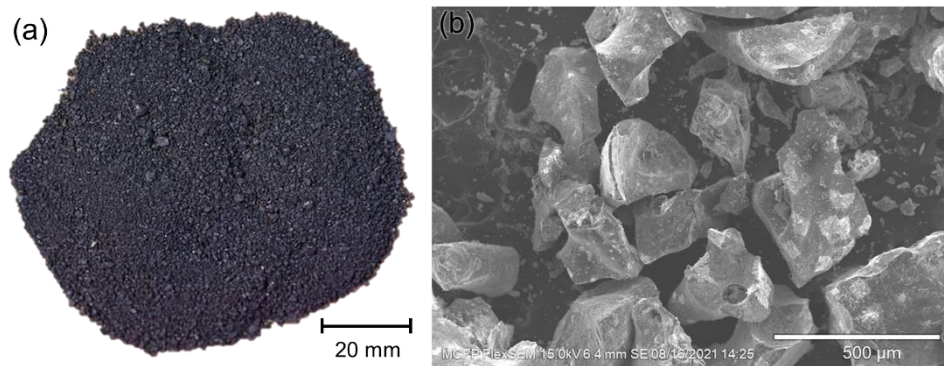


Figure 2.10. Particle size: (a), and surface morphology: (b) of LSS particles.

Despite the availability of LSS and its potential for reuse and recycling, most research has focused on the characterisation, stability and the implication for proper disposal of LSS [118–121]. Several studies were conducted on using LSS in road constructions and cement-based concrete and mortars. However, few studies investigated the effect of using LSS in alkali-activated concrete.

The similarity between LSS and natural aggregate's physical and mechanical properties made it a suitable substitution for natural aggregates [114,122]. Atzeni et al. [123] conducted the first research to prove that LSS can be used in partial or complete replacement of fine aggregate in cement-based concrete. Further studies by Alwaeli [124] and Saikia et al. [125,126] showed that the mechanical performance of cement-based concrete and mortar produced by LSS was higher than those produced by conventional aggregates.

Given the availability of the LSS and considering its composition, which is mainly consisted of silica (SiO_2) in an abundant quantity (15 – 43%) and aluminium, calcium and iron oxide in smaller quantities (2 – 30% Al_2O_3 , 3 – 23% CaO and 1.7 – 6.2% Fe_2O_3) [127], LSS is potentially appropriate for the use in structural and non-structural alkali-activated concrete and mortar production [114]. Recently few studies reviewed the effect of using LSS on the mechanical and durability properties of alkali-activated concrete and mortars [122,128,129]. Albitar et al. [122] conducted the first research on using LSS in alkali-activated concrete to study the effect of its substitution with fly ash as a binder and washed natural aggregate as filler on the mechanical

performance and shrinkage properties. According to their findings, complete replacement of LSS with natural sand and partial replacement of LSS up to 75% with FA as binder in alkali-activated concrete resulted in improvement of (or at least identical) mechanical performance of LSS-based alkali activated concrete compared to that of NS-based alkali-activated concrete. They also reported that the drying shrinkage strain of alkali-activated concrete using high volume of LSS as binder was lower than that of FA-based alkali-activated concrete. Gholampour et al. [128] conducted the first comprehensive study on fresh and hardened state properties of FA-GGBS based mortars prepared with LSS as fine aggregate and compared them with NS-based geopolymer mortars [128]. They have used NS and LSS aggregates with maximum particle size of 2.13 and 1.91 mm, respectively. Four proportions of 100% FA, 80% FA – 20% GGBS, 50% FA – 50% GGBS and 100% GGBS was used as binder. Mixtures were activated using sodium hydroxide and sodium silicate solutions. According to their findings, 100% replacement of LSS with NS increased the compressive strength of all mixtures except 100% GGBS by up to 8%. However, the 100% GGBS mixtures prepared by LSS also exhibited 28-day compressive strength of 73.9 MPa which was only 0.9% lower than that of the mixture prepared with NS (74.6 MPa). They have also reported that for a given binder type, the direct tensile strength of the LSS and NS alkali-activated mortar followed similar trends to those of compressive strength. According to their findings, substitution of LSS with NS for a given binder proportion reduced the drying shrinkage of alkali activated mortars at any given curing ages under the ambient curing environment. This phenomenon has been attributed to the honeycomb surface morphology and higher water retention capacity of the LSS aggregate.

Considering the fact that using LSS in alkali-activated mortars improves their mechanical performance and increases their resistance to drying shrinkage deformation, replacing LSS with NS in C3DP mixtures or other type of underutilised aggregate in waste-based C3DP mixtures might be a potential solution to address the problems with the poor mechanical properties and higher drying shrinkage of waste-based alkali-activated mortars, especially in the open-to-atmosphere condition of C3DP. Therefore, it is of particular importance to understand the rheological, mechanical and shrinkage behaviour of LSS-based alkali-activated concrete for use in extrusion-based C3DP technology.

2.5.4 Nanomaterials in C3DP mixtures

When designing a 3D printable mixture, several fresh state properties, including shape stability, buildability, thixotropy and final (hardened) properties such as bulk density, interlayer bonding, mechanical performance, durability, and shrinkage need to be considered [94]. These properties are significantly dependent on the composition of the mixture and the printing process [130]. Several studies have been done on using nanomaterials to modify 3D printable concrete mixtures to improve their fresh state and hardened state properties, as well as the microstructure [131]. This is well-known that incorporating nanomaterials into cement-based and alkali-activated mixtures promote the rate of reaction [132,133] and hydration degree [134,135], and it provides preferential nucleation sites [132,136] for hydration products precipitation and growth [137]. Moreover, due to the formation of various hydrated products, incorporating nanomaterials into concrete mixtures can enhance their mechanical performance [130].

The use of nanomaterials in alkali-activated binder systems is of increasing significance compared to the OPC binder system. Unlike OPC systems in which colloidal reaction (due to the van der-Waals forces) contributes to the development of yield stress by the formation of a percolated rigid network between cement particles [91], the yield stress evolution in geopolymer paste at early ages is exclusively governed by percolation of an aluminosilicate gel between the precursors, and there is no colloidal interaction between the geopolymer precursors particles [78,92]. This means that alkali-activated binders lack thixotropy property; instead, the hydrodynamic interaction observed in geopolymer mortars is correspondent to the viscous nature of the alkali activating solution. Therefore, the incorporation of nanomaterials, such as NC and graphene-based nanoparticles, into alkali-activated binders can contribute to the Geopolymerisation reaction by offering more nucleation sites or a higher rate of dissolution of raw constituents [138,139].

Among an extensive range of nanomaterials that are used in concrete technology, (NC) was typically used in C3DP mixture for modification of rheological parameters to enhance shape stability and buildability properties by increasing the flocculation rate and the static yield stress of the mixtures [131]. Moreover, some recent research also showed the great potential of graphene-based nanomaterials to improve the favourable fresh and hardened state properties of both cement-based and alkali-

activated concrete mixtures that are appropriate for use in C3DP. Within the scope of this research and based on the available studies in this area, the following sections will review the recent studies conducted on the C3DP mixture's nano-modification effect of NC and graphene-based nanomaterial (GBN) on their fresh and hardened state properties.

Nanoclay

According to its morphology and chemical composition, NC can be classified into three common groups: kaolinite, montmorillonite and attapulgite [137]. Researchers have mostly used highly purified attapulgite clay, a magnesium aluminium silicate clay, to improve the green-state properties of 3D printable mixtures [4,25,78,131,140,141]. Unlike montmorillonite and kaolinite, attapulgite particle has acicular (rod-shaped) geometry rather than flake-like structure, enabling them to have a water retention capacity of up to 200% of their own weight [142]. The high specific surface area of NC and its huge water-absorption capacity can reduce the free water content of mixtures, resulting in higher yield stress and viscosity [141]. The rod-shaped structure of NC particles can usually be obtained under shearing or in solution form. In their rod-shaped structure, NC particles generally have an average length, diameter and specific surface area of 1.75 μm , 3 nm and 150 m^2/g , respectively [137]. Among all NC types, attapulgite NC has been the most commonly investigated as a rheological properties modifier in cement-based and alkali-activated concrete [137].

Kazemian et al. [143] reported that 0.3% nano-attapulgite inclusion in the cement-based 3D printable mixture increases the shape stability. They studied the green strength of the printable mixture using the fresh cylinder stability test and measured the visible displacement of two consecutive layers. Moeini et al. [144] compared the effect of nanomodification on the fresh state properties and green strength of cement-based printable mortars with 0.5% NC and 1% viscosity-modifying agent (VMA). They reported that NC incorporation increased the rigidity of the mixture and resulted in a brittle fracture. However, VMA modification showed a plastic deformation-like failure under compression.

Zhang et al. [54] developed a cement-based 3D printing mortar and investigated the effect of substituting 2% NC and silica fume (SF) with cement on the rheological properties (yield stress, viscosity and thixotropy), buildability, and heat of hydration. They have reported that the incorporation of NC increased the yield stress, structural

rebuilding and buildability of the mixture at a higher rate compared to silica fume (SF). In addition, their results showed that the inclusion of NC and SF increases the hydration rate and total heat of hydration. However, the magnitude of the increase in the rate and total heat of hydration associated with the NC mixture was lower than that of the SF mixture.

Chougan et al. [145] investigated the effect of nano-attapulgite modification on the yield stress, shape stability and structural build-up properties of alkali-activated 3D printing mortars. Their findings show that nano-attapulgite replacement with the binder increased the properties mentioned. Substitution of 1% nano-attapulgite resulted in optimum printing properties in alkali-activated concrete.

Panda et al. [56] investigated the effect of incorporation of 0.1, 0.3 and 0.5% (by mass of binder) NC on the static yield stress, viscosity properties (apparent viscosity and viscosity recovery), mechanical strength and microstructure of high-volume fly ash 3D printing mortar. They reported that the static yield stress and apparent viscosity properties were positively correlated with the NC content in the mixtures. They also showed that the initial yield stress and the static yield stress development rate increased after the incorporation of 0.5% NC. According to their findings, the inclusion of NC did not significantly enhance the compressive strength, while a reduction in tensile bonding strength of printed specimens with the interlayer printing time interval of 5 and 30 min was observed. Panda et al. [78] also conducted another research on the development of FA-GGBS-based geopolymer mortar and added 1.2% NC by mass of binder to enhance the yield stress, viscosity recovery and buildability properties of the optimum mixture. Panda et al. [25] also studied the effect of incorporating 0.5% NC into 85% FA – 15% GGBS 3D printing geopolymer mortar on the static yield stress, apparent viscosity and viscosity recovery properties, as well as heat flow behaviour and compressive strength of the mixtures. They investigated the effect of changing activator-to-binder (AB) and water-to-solid (WS) ratios variables on the rheological properties and concluded that adding NC increases the fresh state 3D printing properties. However, the rate of increase at lower AB (0.35) and WS (0.3) ratios was more significant.

The above research studies suggest that the inclusion of NC in cement-based and geopolymer-based 3D printable mixtures is beneficial for optimising materials printing requirements by adjusting rheological properties, especially by improvement of the

shear-thinning behaviour and increasing the early structural build-up properties. However, some shortcomings with incorporating NC in the mixtures have been observed, including insufficient green strength development and excessive stiffness that leads to brittle behaviours. According to the reviewed literature, the effect of adding NC in printable mixtures was investigated at an addition level of up to 2%. Previous studies [137,146] reported that the 2% NC incorporation level is the upper threshold for attaining the best NC dispersion in the mixtures. Beyond this limit, due to the agglomeration of the NC particles, the shrinkage deformation of NC modified mixtures, i.e. autogenous and drying shrinkage, might raise significant issues which also can reduce the mechanical strength development of the mixture [146]. It is worth noting that even for the NC incorporation level of less than 2%, to the best of our knowledge, there is still no research on the drying shrinkage evolution of NC-modified 3D printable mixtures, especially in an alkali-activated binder system. Besides, there is still a lack of consensus on the results of the mechanical strength of NC-modified 3D printing mixtures. For instance, Panda et al. [25] reported a decrease in the compressive strength with 0.5% NC-modification of alkali-activated mortar, while Chougan et al. [145] observed an increase in the mechanical strength at an NC incorporation level of 1%. Therefore, further research is needed to investigate the effect of NC-modification on the shrinkage evolution of 3D printing mixtures.

Graphene-based nanomaterials (Graphene oxide: GO)

Graphene-based nanomaterials (GBN) have recently gained significant research interest in cement-based and alkali-activated concrete [130,131]. GBNs' tensile strength and elastic modulus are approximately 130 and 1000 GPa, respectively [147]. Since the graphene derivatives have a high specific surface area, nano-scale particle size, and can act as filler, they can have strong physical interactions and chemical bonds with cement-based and alkali-activated materials, leading to improvements in rheological properties (yield stress, thixotropy, etc.), compressive, and flexural strengths of cement- or alkali-activated composites [147–153]. The abovementioned characteristics make them an excellent choice for modification of cement-based and alkali-activated mixtures for C3DP. Among several graphene derivatives, nano-graphite platelets (NGP), graphene nanoplatelets (GNP), graphene oxide (GO), and reduced graphene oxide (rGO) have been recently used as relatively novel and advanced additives in cementitious mixtures, especially in C3DP. Rather than the

enhancement of rheological and mechanical properties [148], It has been recently established that the incorporation of GBNs (i.e. GO, rGO and GNP) into alkali-activated materials can also reduce the drying shrinkage evolution of nano-modified composites [129,154].

Implementing GBNs modification into 3D printable mixtures has been rarely studied due to the relatively modern nature of C3DP technology. This section will review the recent literature on GBN-modified 3D printable mixtures as well as some research on conventionally casted mixtures to assess the potential benefits using GBN can offer on fresh properties, mechanical performance and shrinkage strain control in alkali-activated mixtures.

Chougan et al. [155] developed FA-GGBS alkali-activated mortars for 3D printing by changing the proportion of GGBS at constant FA and SF contents. They investigated the effect of NGP-modification with NGP additions of 0.1, 0.3, 0.5 and 1.0% (by wt% of binder) on rheological parameters and mechanical performance of the optimum mixture. According to their findings, mortar with the binder proportion of FA : GGBS : SF of 0.65 : 0.25 : 0.15 showed the optimum flowability and extrudability, with an initial setting time of 35 min and a printing window of 20 min. Their results indicated that the inclusion of NGP at 0.3% and 1.0% into the optimum mixture increased rheological parameters. The highest improvement in fresh properties was observed for a 1.0% NGP-nanomodified mixture with a 96% and 56% increase in yield stress and plastic viscosity, respectively. Their findings on the 7-day mechanical performance of nanomodified mixtures exhibited that the flexural strength was positively correlated with the NGP incorporation ratios reaching the maximum strength of 15.3 MPa at 1.0% NGP dosage. This can be attributed to the crack-bridging and crack-blocking properties of GBNs in the geopolymer matrix [156]. Although the compressive strength of nanomodified mixtures did not follow the increasing trend similar to that of flexural strength, specimens with 0.1% and 1.0% NGP showed an increase of approximately 18% and 14% compared to those of neat specimens.

The first attempt for 3D printing of GO-modified geopolymer composite was successfully carried out by Zhong et al. [157]. They have incorporated 4%, 5%, 10%, and 20% (by wt% of aluminosilicate precursor) GO into the geopolymer ink to enhance the rheological properties of the mixtures. Their results showed that incorporating GO increased the storage and loss modulus of the geopolymer ink by up

to 200%. According to their findings, adding 4% GO increased the shear yield stress of the geopolymer mixture from 4 Pa to 2000 Pa. They have suggested a mechanism for the improvement observed in the deformation behaviour of GO-modified geopolymer ink. They attributed the improvement of elastic deformation of GO-modified mixtures to the formation of GO-water-aluminosilicate microstructure, which can tolerate higher elastic deformation. They have also reported that compressive strength and elastic modulus of printed GO-modified geopolymer ink increased with the increase of GO dosage from 4 to 10%. However, these properties were reduced at the 20% GO incorporation rate due to the aggregation of the GO particles. Zhou et al. [158] conducted similar research on geopolymer ink modified with GO but investigated the effect of GO particles' lateral size on the fresh properties of GO-modified geopolymer ink. Their results showed that GO particles with larger lateral geometry increased GO-modified geopolymer ink's storage and loss modulus more significantly than small GO-modified and neat geopolymer ink. Therefore, they can make the geopolymer ink more appropriate for 3D printing. Nevertheless, in terms of mechanical strength and elastic modulus development, using a smaller size of GO particles resulted in a better performance.

GO can be efficiently and economically synthesised in high quantities, and more significantly, the hydrophilic functional groups bonded onto GO nanoparticles make it extremely water-soluble, contributing to a more intense interaction with the matrix materials [129,131,156]. Therefore, it gained greater attention for use in cementitious nanocomposites. However, using GO in alkali-activated materials was also restricted to a few studies [129,154,159,160].

Liu et al. [159] investigated the effect of adding GO and rGO into FA-based geopolymer mortars on the mechanical performance, microstructure and hydration degree. They have found that GO-nanomodification can increase the dissolution rate of amorphous phases of FA particles and accelerate the Geopolymerisation reactions. Moreover, they have reported that the inclusion of GO and rGO reduced the porosity of the geopolymer mortar. Furthermore, they showed that the flexural strength of 0.3 wt% GO- and 0.1 wt% rGO-modified geopolymer mortars was enhanced by 25% and 10% compared to that of neat mortar. In similar research, Saafi et al. [160] also found a significant enhancement of mechanical properties of geopolymer pastes that were cured at 60 °C. According to their findings, GO's hydrophilic functional groups were

reduced in the alkaline environment of the geopolymer mixture, resulting in the formation of rGO nano particles. They have reported that the crack-bridging characteristics of rGO nanoparticles at the interface of rGO-geopolymer gel contributed to the improvements of mechanical properties. Align with these findings, Long et al. [138] reported that incorporating rGO nano particles into the GGBS-based geopolymer mortar can significantly increase the concentration of OH^- ions in the system resulting in the reduction of Ca^{2+} ion concentration in its vicinity and accelerating the GGBS dissolution. Besides, since the rGO provides preferential nucleation sites for C-S-H and C-A-S-H formation [161], the presence of rGO in the mixtures contributed to obtaining a higher hydration degree.

Ho et al. [129] have recently investigated the effect of GO-nanomodification of FA-GGBS-based mortar prepared with NS and LSS as fine aggregate on its fresh-state properties, mechanical performance and durability properties. According to their findings, adding 0.05 wt% and 0.1 wt% (by weight of binder), irrespective of the FA-GGBS binder proportions and types of aggregate, increased the compressive and tensile strength of nanomodified mixtures compared to their corresponding neat geopolymer mortar. The increase in the mechanical performance was attributed to the reduction of GO nanosheets and the formation of rGO in the nanomodified mixtures, which controlled the crack propagation in the microstructure. Moreover, the 28-day drying shrinkage deformation of 0.5% and 0.1% GO-modified mixtures prepared with LSS reduced by 22% and 28%, respectively. The observed shrinkage-reducing behaviour was attributed to the microstructure's densification and the crack propagation control with GO-modification.

The above studies suggest that the inclusion of GBN, especially GO, in alkali-activated mortars is beneficial for optimising materials printing requirements by adjusting rheological properties and increasing the early structural build-up properties. Moreover, as discussed, the inclusion of GO/rGO into alkali-activated paste or mortars can offer a higher rate of dispersibility (compared to other non-graphene-based nanomaterials), higher rate of geopolymerisation reaction, higher mechanical strength, lower microstructural porosity and lower drying shrinkage deformation. Therefore, using GO/rGO in alkali-activated mortars can be considered a feasible solution to address the deficiencies that using NC additives may have for nanomodification of 3D printable alkali-activated mortars, especially in terms of agglomeration issues and the

drying shrinkage strain (hardened state properties). However, some challenges of using GO/rGO in 3D printable geopolymer mortars still need further study. This includes drawing a comparison between the improvement of the rheological properties (i.e. yield stress evolution and viscosity recovery capacity), mechanical performance and microstructure modification by incorporating GO and NC. Moreover, an in-depth research is needed to compare the evolution of drying shrinkage in 3D printable alkali-activated mortars modified with NC and GO, considering the free-formed nature of C3DP technology and different curing environment.

2.6 STRUCTURAL BUILD-UP IN CONCRETE FOR 3D PRINTING

Since the material requirements for printable mixtures, as discussed in Section 2.4, have competing properties, the desired material qualities for extrusion-based 3D printing can be presented by considering the balance of these material requirements. Firstly, the concrete must flow easily (low yield stress) enough so that it can be pumped and extruded (pumpability/extrudability) [162]. However, a minimum yield stress level (initial yield stress) is required immediately after deposition for the filament to hold its shape (shape stability) [4]. Furthermore, the printed concrete filaments must quickly gain strength to withstand the pressure from subsequently placed layers (buildability), but not at a rate that compromises pumpability and extrudability [30,162].

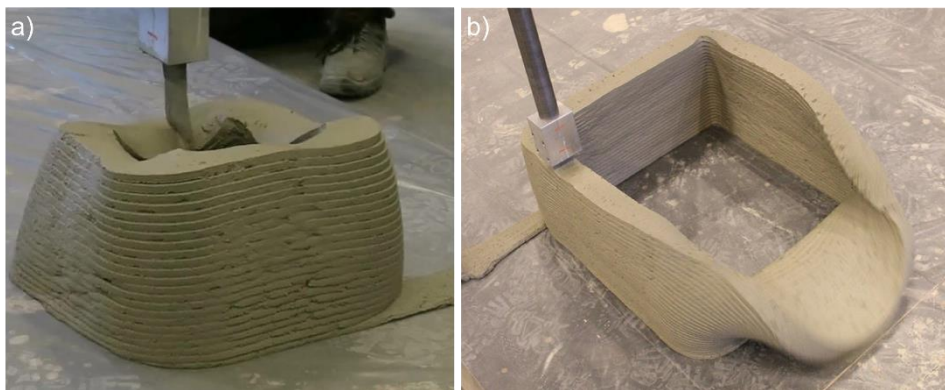


Figure 2.11. In-print failure mechanisms in extrusion-based C3DP: a) material failure, b) loss of stability [163].

Due to its formwork-free nature, 3D printed elements may fail during the construction process (in-print failure) by extrusion-based 3D printing. Given that the printing material's strength at early ages (several minutes after deposition until the first few hours) is low compared to its self-weight, printing material's buildability is a

critical property in determining whether or not a mixture is suitable for printing [5,22]. Based on the range of properties and processes involved in refining the buildability concept, the failure of extrusion-based 3D concrete printing elements during the printing process is attributed to two mechanisms: i) material failure (strength-based failure) and ii) stability failure. Figure 2.11 shows examples of each failure mechanism.

Stability failure is the loss of equilibrium of forces and moments that causes elastic deformations or displacements. However, material failure happens when the plastic yielding (leads to materials flow) or fracture occurs in the freshly printed element since the applied loads on the element exceed the mixture's strength at an early stage [163,164].

Prediction models for printed elements failure during cementitious material printing have been established in some previous studies until now [2,30,51–53,69,165–171]. These studies considered the load exerted by the printed element's self-weight as the primary load source responsible for the failure. Although various additional types of loading are plausible in C3DP (Figure 2.12), including horizontal drag from filament deposition, eccentric loading because of filaments misalignment, and non-vertical pressure from back-fill materials, considering the self-weight as the primary loading source allowed researchers to develop reasonably simple equations to define a relationship between the printing materials' strength and building element's height.

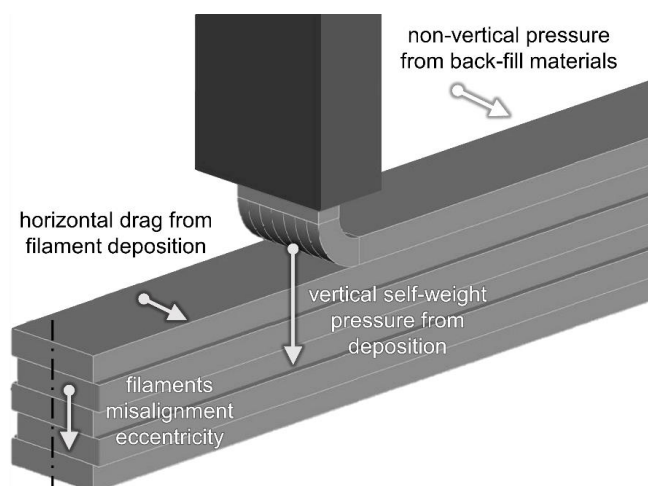


Figure 2.12. Self-weight and additional potential in-print loads are exerted on a wall [164].

Generally, a linear correlation [165,166,169,170] is considered appropriately accurate [164]. However, bi-linear [69], exponential [30,171] and exponential-decaying [2] correlations have been developed to enhance the accuracy of the models [164]. Within the scope of this research which will be limited to the rheology-based models, a summary of some fundamental approaches is provided. It is worth noting that, although recent research works addressed the buildability issue both from a fluid and solid mechanics point of view and for both approaches, the time-dependency has been taken into account, there is still a lack of agreement on which quantitative material properties and associated experimental procedures are suitable for buildability analysis.

Di Carlo et al. [168] conducted the first investigation on fresh concrete structural properties, using the uniaxial compression analysis to evaluate the load-bearing capacity of green mortar by analysing the stress-strain curves at early ages. According to their findings, printable mortar developed a green strength within the range of 5.5 kPa and 88.3 KPa and elastic modulus of 80 kPa and 1241 kPa at different time intervals from 11 min to 5 hr. They have reported that the Drucker-Prager plasticity model was adequate for predicting materials behaviour using the finite element method (FEM).

A study by Perrot et al. [30] looks more closely at one of the concrete mixture design dichotomies mentioned earlier in this section. Namely, that the time gap between deposited layers must be long enough to provide the required strength to support the weight of subsequently placed layers but also short enough to ensure adequate bonding between layers and to minimise build times [30]. It can be inferred then, that the optimised time gap between layers should be the minimum time it takes to ensure structural stability during construction [30]. For this stability to be maintained, it can be stated more explicitly that the stress induced by the self-weight of the structure at any time must be smaller than some critical stress in the fresh concrete, which would induce flow or deformation [30]. Furthermore, this critical stress is linearly related to the yield stress of the concrete by a geometric factor related to the form of the built structure [30]. Equation 2.1 shows the vertical stress acting on the first printed layer (critical layer) as a function of time [30].

$$\sigma_v = \rho gh(t) = \rho gRt \quad \text{Equation 2.1}$$

Where ρ (kg/m³) is the density of the concrete, g (m/s²) is the acceleration due to gravity, h (m) is the vertical height, t (s or min) is time, and R (m/s or m/min) is the build rate or height per unit time. For structural stability to be maintained during printing, it is essential that σ_v (Pa) be less than the stress required to induce flow or deformation in the critical layer (σ_c) at all times. Perrot et al. [30] asserted that this critical stress is linearly related to the yield stress of the first deposited layer by a geometric factor.

$$\sigma_c(t) = \alpha_{geom} \cdot \tau_y(t) \quad \text{Equation 2.2}$$

Where $\sigma_c(t)$ is the critical stress as a function of time, $\tau_y(t)$ is the yield stress as a function of time, and α_{geom} is a dimensionless geometric factor related to the form of the built structure [30]. Furthermore, it was shown that the yield stress development of concrete is linear for an initial period and can be described by:

$$\tau_y(t) = \tau_{y,0} + A_{thix} \cdot t \quad \text{Equation 2.3}$$

Where $\tau_{y,0}$ is the initial yield stress, and A_{thix} (Pa/s or Pa/min or Pa/h) is the structuration rate or the constant rate of increase in yield stress over time at rest [30]. Moreover, Perrot et al. [30] proposed another yield stress evolution model that describes a smooth transition from linear to exponential evolution:

$$\tau_y(t) = \tau_{y,0} + A_{thix} \cdot t_c (e^{t_{rest}/t_c} - 1) \quad \text{Equation 2.4}$$

Equation 2.4 describes the transition to an exponential structuration rate where t_c is a characteristic time that should be chosen to obtain the best fit with experimental data. It has been shown that the yield stress development of fresh concrete (up to approximately 1 hour) is linear and that the specific values can be obtained by simple laboratory tests using a rheometer [30]. Using this information, it is then possible to predict the time of failure during printing based on the layer height and deposition rate (vertical height as a function of time) according to the following equation [30]. Figure 2.13 shows the results of their predictions based on this theory. They tested a cement-based mortar mixture prepared with kaolin clay aggregates to validate the proposed model. The mixture showed a linear stress growth rate of 54 Pa/min (A_{thix}) for the first 40 min, and its yield stress increased from approximately 4000 Pa at 0 min to 6300 Pa at 40 min. After 40 min, the mixture showed an exponential development in the yield

stress. As shown in Figure 2.13, the validating trials closely correlated with the anticipated failure times.

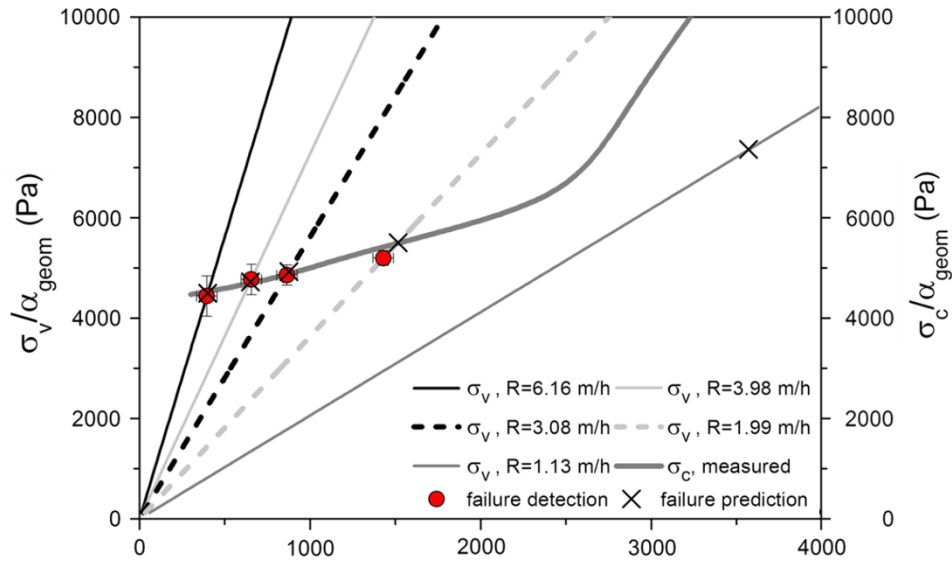


Figure 2.13. Failure is predicted to occur when the time-dependent vertical stress σ_v reaches the time-dependent critical stress σ_c . The actual failure was observed to be in very close agreement with the predicted values [30].

Wangler et al. [169] redefined the similar method by removing the geometry parameter and employing the von Mises yield criterion by considering a coefficient of $\sqrt{3}$ in the buildability equation as follows:

$$\tau_y(t) \geq \frac{\rho g h(t)}{\sqrt{3}} \quad \text{Equation 2.5}$$

Wolfs et al. [166,170] developed a numerical model using FEM in which both strength-based and stability failures were considered simultaneously. The model was based on the Mohr-Coulomb criterion and required five essential time-dependent (up to 90 min after deposition) characteristics of 3D printable concrete as input data. The uniaxial compression and direct shear tests were conducted to measure Young's modulus $E(t)$, Mohr-Coulomb's cohesion coefficient $C(t)$, Poisson's ratio ν , angle of internal friction $\phi(t)$, and dilatancy angle $\psi(t)$. Their results showed that both $E(t)$ and $C(t)$ increased linearly with the concrete age. However, the rest remained constant within the measurement time frame. They have concluded that the developed numerical model was appropriate to predict the failure mode qualitatively. However, the overestimation of the printing material's properties due to the compaction of the samples during the compression test and neglecting the material's imperfections during

the actual 3D printing process resulted in the overestimation of the stability and strength-based failures of the printed element.

Roussel [171] used the solid mechanic's concepts and redefined the stability failure criterion to develop a mixed failure prediction model together with the rheology strength-based failure (Equation 2.5). According to their research, to avoid stability failure in the printed element, the elastic Young modulus should be above its critical value as stated in Equation 2.6:

$$E_c(t) \geq \frac{3\rho g h(t)^3}{2\delta^2} \quad \text{Equation 2.6}$$

Considering the relationship between the yield stress, critical shear strain, and shear modulus in $\tau_c = G \cdot \gamma_c$, as well as the relationship between Young modulus, shear modulus, Poisson's ratio in $E = 2G \cdot (1 + \nu)$, the transitional height, can be calculated as:

$$h(t) = 2\delta \cdot \sqrt{\frac{1+\nu}{3\sqrt{3} \cdot \gamma_c}} \quad \text{Equation 2.7}$$

Using the proposed mixed methodology, it was expected to find the transition height ($h(t)$) where below that height the strength-based failure and above that the stability failure is the dominant failure mode.

Kruger et al. [69] continued the development of the strength-based failure mechanism devised by Perrot et al. [30], Wangler et al. [169] and Roussel [171] by proposing a bilinear structuration rate instead of a linear one. They included the chemical and physical properties into the developed model by considering the re-flocculation parameter (R_{thix}) and structuration rate (A_{thix}). They have shown that the rate of re-building the static yield stress after extrusion (R_{thix}) is a critical buildability parameter in terms of the thixotropic behaviour of 3D printable mixtures compared to the A_{thix} .

Although an extensive range of studies was conducted on the in-print failure of 3D printing concrete, several aspects of it still remain unexplained. Most recent studies mainly focused on the assessment of 3D printable mortar's buildability by identifying the failure boundary, i.e. the maximum buildability rate (height of the object or number of layers) to avoid material or stability failure, or identifying the in-print failure mode that occurs first.

However, there is still a gap in the research work on using the same rheological material failure conceptual framework to find the optimal mixture based on a given vertical build rate, as opposed to finding the optimal vertical build rates based on a given mixture. Although changing the printing window limits, such as the buildability limit by modifying the printing speed and layer height, can be a more straightforward solution than modifying the mixtures to fit within a specific printing window, this has its own limitation.

The significance of such a different approach is when equipment-related limitations exist, or a specific setting for the 3D printing project is needed. For instance, when only the batch mixing printing process can be utilised or it is the preferred method or the access to instantaneous mixing (mixing in the nozzle) printer owing to its initial and operating expenses is impossible, or when the range of printing speed is limited due to the printer capabilities constraints. Moreover, there might be some constraints on the setting of a 3D printing project, where modifying the filament height or shape is not allowed due to the required printing resolution or when reducing the printing speed is not allowed since it affects the overall print time and might result in the formation of cold joints. The 3D printable mortar modification can be a solution to address these challenges and obtain the best performance possible in various 3D printing jobs. Therefore, one aspect that needs further research is how the yield stress evolution of mortars can be controlled for optimisation where 3D printing with no instantaneous mixing (mixing in the nozzle) procedure can be utilised.

Overall having more tools for optimisation of the 3D printing process is preferable to attain the best performance in different 3D printing jobs.

2.7 EFFECT OF CONCRETE 3D PRINTING-RELATED PARAMETERS ON SHRINKAGE DEVELOPMENT

Considering the C3DP technology and 3D printable mixtures characteristics, including being a formwork-free process, restriction on maximum aggregate size, minimum bleeding moisture (low W/C), a high surface-to-volume ratio and substantial fine aggregate proportion, the 3D printing concrete is particularly prone to a higher risk of shrinkage development (mainly plastic and drying shrinkage) than conventional concrete. Moreover, the low W/C ratio in C3DP mixtures increases their susceptibility to autogenous shrinkage development. Figure 2.14 summarise the effective parameters for shrinkage development in 3D printable concrete.

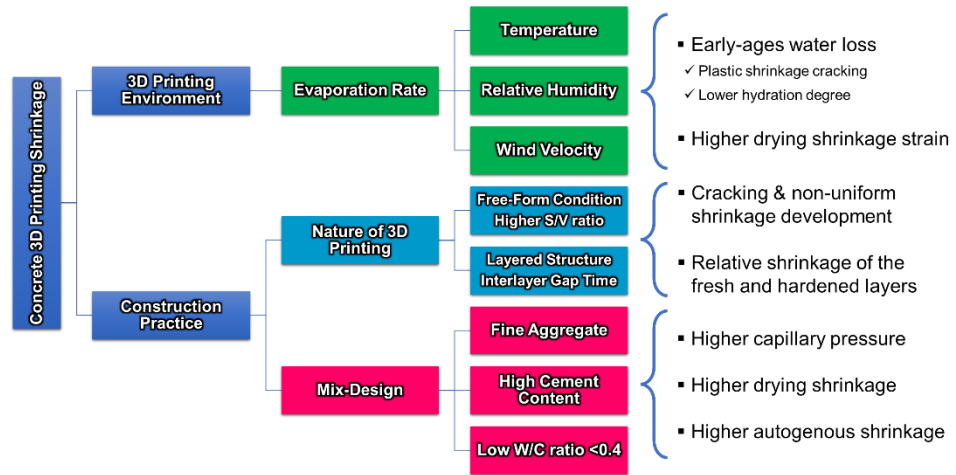


Figure 2.14. effective parameters on the shrinkage development in 3D printable concrete.

This section provides an overview of the most commonly recognised forms of shrinkage. In addition, a comprehensive literature review of all recent shrinkage-related C3DP research is presented.

2.7.1 Shrinkage in Concrete 3D Printing

Concrete components face several challenges due to inevitable volumetric variation throughout their lifespan. The unfavourable deformations affect both the element's geometry and mechanical characteristics. Shrinkage may cause (tensile) strains and cracking in printed elements, especially when the deformations are restrained. Figure 2.15 shows examples of shrinkage cracking, cold joint interfaces and signs of interlayer capillary water absorption due to the formwork-free nature of 3D printing and early age pore water evaporation in 3D printed elements.

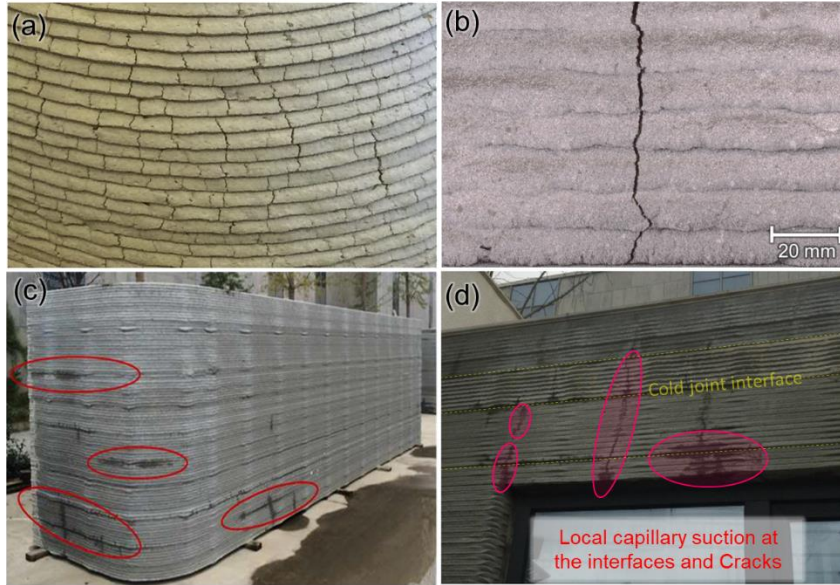


Figure 2.15. (a): Excessive plastic shrinkage cracking [172], (b): crack propagation of a 3D printable mixture under a moderate evaporation condition [98], (c, d): interlayer capillary water absorption due to higher interlayer porosity and cold joint formation [33,57].

Shrinkage may be divided into three main categories according to its active mechanism: chemical and carbonation shrinkage caused by cement hydration and carbonation of hydrated products, respectively; autogenous shrinkage caused by self-desiccation process, and plastic (first-day) and drying shrinkage caused by pore water evaporation [173–175]. Although different shrinkage types may not be interconnected theoretically, given that the various shrinkage types coincide and the measurement techniques are error-prone and arduous, it is rather difficult to distinguish each type in practice.

2.7.2 Plastic Shrinkage

Plastic shrinkage is, in fact, a contraction that occurs in plastic cement paste due to the capillary pressure induced by evaporation from the surface of the concrete or the water absorption by the surface of underneath dried concrete [176]. Free (unrestrained) shrinkage occurs if the induced capillary pressure can freely deform the concrete. Suppose the dimensional contraction due to the capillary pressure is limited by internal restraint, formwork, or reinforcement [177,178]. In that case, the shrinkage is restrained, and the volume reduction associated with it leads to tensile stresses within or on the surface of the concrete element, which can reach the tensile stress capacity of the concrete, leading to cracking from the time of placement until the end of the first day [178,179]. Water can be absorbed into the ground or substrate of concrete

(previously printed layers in case of C3DP), reducing the amount of bleeding water and sharply intensifying concrete settlements [98]. It is worth noting that the higher the binder (cement) and the less the volume of the aggregates in the concrete, the greater the shrinkage in the plastic state [98]. Figure 2.16 shows a schematic of the mechanism of capillary pressure increase in a drying mixture [180].

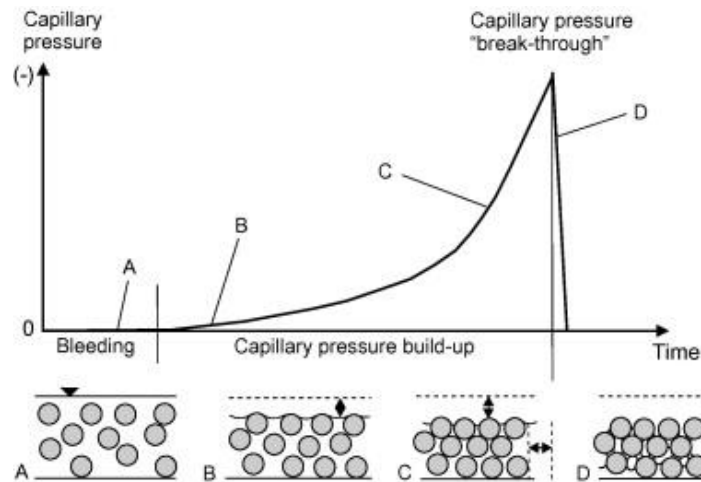


Figure 2.16 Capillary pressure build-up in a drying mixture [180].

The atmosphere condition parameters such as the air temperature, relative humidity and wind velocity in the construction site and the mixture temperature affect the water evaporation rate. The higher temperature and lower humidity are the main reasons for rapid pore water evaporation.

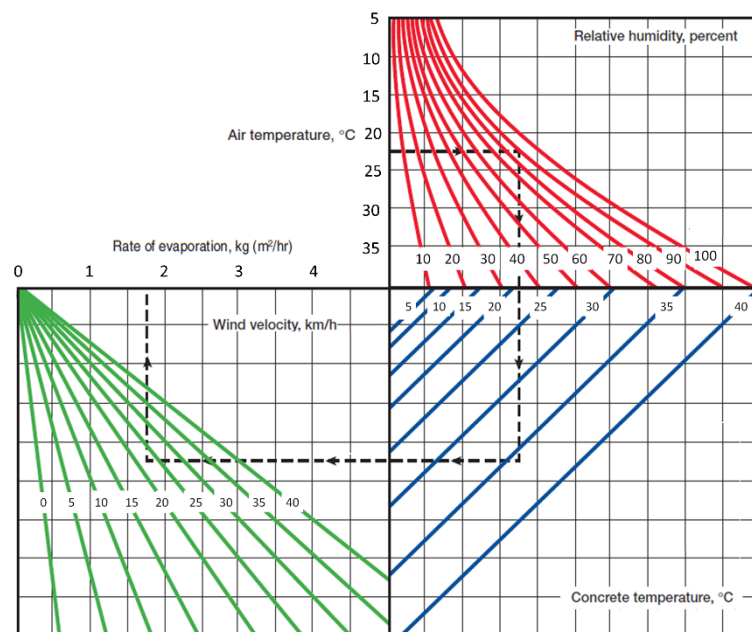


Figure 2.17. The nomograph of evaporation rate calculation based on weather and mixture conditions [181].

Figure 2.17 shows the nomograph for finding the evaporation rate considering the printing environment's air temperature, relative humidity, wind velocity and the mixture temperature variables [181]. The evaporation rate in the nomograph in Figure 2.17 is from a water surface. Unlike conventional casting, since the surface of the printed concrete is likely unsaturated; usually, the concrete surface is not covered by a thin layer of water, or the surface is not fully saturated immediately after the deposition. Thus, It is expected that the evaporation rate would be significantly lower in C3DP. This topic has been recently investigated for 3D printable concrete and will be further discussed in Section 2.7.5.

2.7.3 Chemical and Autogenous shrinkage

The chemical shrinkage is defined as the concrete volume contraction resulting from the hydration/reaction process [182]. This is because the volume of hydrated cement (OPC) in cement-based or reacted products (fly ash, slag, etc.) in geopolymer-based concrete is lower than that of the raw constituents [182]. The chemical shrinkage quantity is directly related to the age of the product and increases as time passes.

Chemical shrinkage in concrete is a process that occurs as a result of the ongoing hydration of cement. Initially, as the cement particles absorb water and expand, a paste is formed that binds the aggregates together. However, as the concrete continues to harden, the paste begins to lose water through autogenous shrinkage, which can lead to cracking and reduced strength. After about 40 days, the shrinkage rate decreases significantly and reaches a steady-state. The plasticity of the paste is reduced and the paste volume can no longer change. However, hydration and chemical shrinkage continue through the formation of empty voids within the paste structure at the microscale [181]. This change in volume is primarily internal and does not significantly affect the external dimensions of the element. However, chemical shrinkage can impact the concrete's ability to bear structural loads due to the presence of small cracks and voids within the microstructure. To minimize chemical shrinkage, it is important to optimize the water-cement ratio and properly cure the concrete to maintain its moisture content. Additionally, incorporating supplementary cementitious materials such as fly ash or slag can also help reduce chemical shrinkage [181,182].

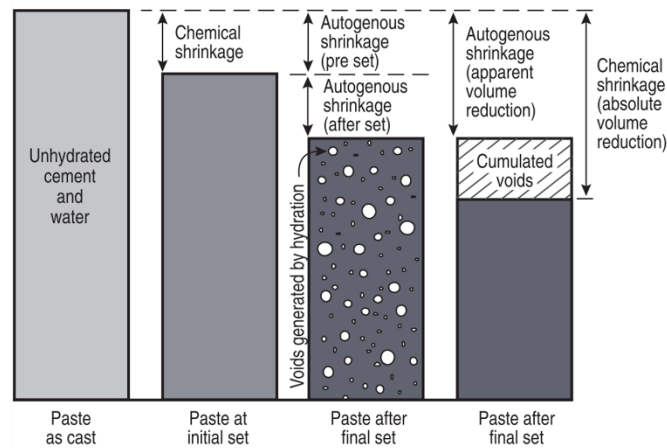


Figure 2.18. The proportion of different chemical and autogenous shrinkage of a cement paste at different aging time, not to scale [181].

Autogenous shrinkage is a specific type of shrinkage in which the main reason for the uniform volume reduction is water consumption within the concrete. The main factor that causes autogenous shrinkage is the chemical reaction [183–185]. Autogenous shrinkage in concrete is a phenomenon that occurs as a result of the ongoing hydration of cement. The bleeding process provides the necessary water film on the surface for the cement hydration reaction to begin, but autogenous shrinkage can also occur as the cement continues to hydrate, regardless of the presence of surface water. As the cement particles absorb water and expand, a paste is formed that binds the aggregates together. However, as the concrete continues to harden, the paste begins to lose water through autogenous shrinkage, which can lead to cracking and reduced strength. The self-desiccation of the paste due to the consumption or evaporation of water leads to a decrease in the paste volume and can cause capillary tension in the internal pore network. The risk of autogenous shrinkage increases as the water-cement ratio decreases and proper curing techniques should be used to maintain the moisture content in the concrete. Additionally, using supplementary cementitious materials such as fly ash or slag can also help to reduce the risk of autogenous shrinkage [174,181,183,186,187]. An increase in the amount of binder paste and a reduction of the W/B ratio can result in higher autogenous shrinkage [174,184]. Due to the stiffness of the hardened paste, the visible volume contraction of autogenous shrinkage is much lower than the absolute volume reduction of chemical shrinkage. Figure 2.18 illustrates a schematic of the relationship between autogenous and chemical shrinkage [181]. The low W/B ratios and high quantity of binders predispose printed concrete to significant autogenous shrinkage [183,188].

2.7.4 Drying Shrinkage

Drying shrinkage is a contraction in the volume of hardened concrete as it loses water through evaporation. When concrete elements are exposed to an environment with a relative humidity of less than 100%, water in the cement paste and large pores of the specimen start to evaporate. The water that is not chemically or physically bonded to the hydrated cement, known as free water, does not initially lead to a reduction in volume. However, as the drying continues, water is lost from the small pore networks and gel pores, causing a decrease in vapor pressure within these pores. This decrease in vapor pressure leads to an increase in tensile stresses in the remaining capillary water, which in turn induces compressive stresses in the surrounding concrete to counterbalance these tensile stresses. As a result, the concrete shrinks [189]. Additionally, shrinkage also occurs due to the evaporation of gel water which changes the surface energy of the solid part of the concrete [181,189].

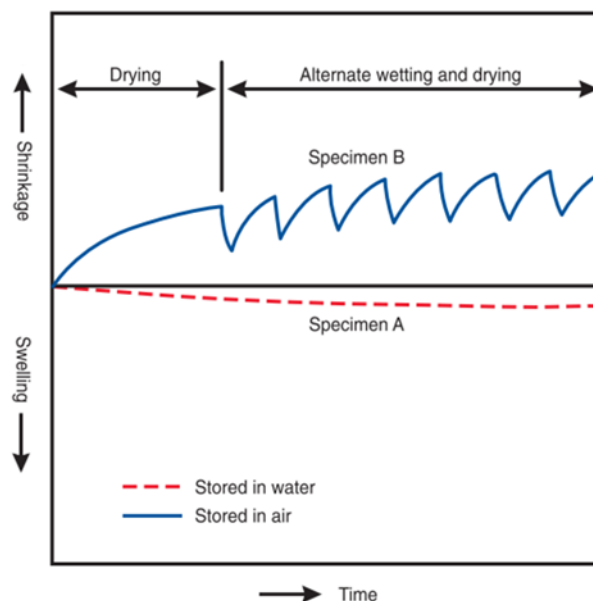


Figure 2.19. Volume changes in cyclic moist and dry curing condition [181].

Concrete starts to reach an equilibrium state when exposed to its service environment. Based on the service environment condition (wet or dry), moisture can flow from the environment to the concrete or vice versa. The result of moisture flow from the environment to the concrete is a volume increase or swelling, whereas Moisture flows from the concrete to the environment, leading to volume contraction. Figure 2.19 demonstrates a schematic graph of volume reduction and increase in concrete due to alternate cyclic drying and wetting. A small portion of this drying

shrinkage can be retrieved on subsequent moistening, and a significant part is irreversible [181].

Drying shrinkage is influenced by various factors, which can be broadly categorized into mix-design and curing conditions parameters (Figure 2.14). Mix-design factors pertain to the composition of the mix, such as the type of binder, aggregate, chemical additives, and water-to-binder ratio [190–193]. Curing conditions include factors such as temperature, air velocity, relative humidity, and the dimensions of the specimens [193,194]. The most important variable in drying shrinkage is the total water content [181,193]. Figure 2.20 demonstrate the positive, relatively linear correlation between the amount of water and the drying shrinkage in fresh concrete.

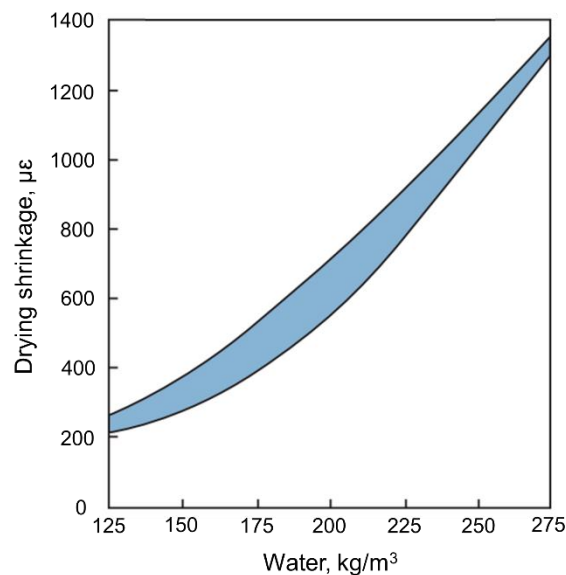


Figure 2.20. Effect of water content on drying shrinkage; The shaded area represents several mixtures with various water content (per unit volume of concrete).

The drying shrinkage rate also depends on the climatic parameters, i.e. wind velocity, curing temperature, and relative humidity. Concrete exposed to lower relative humidity and higher temperature mostly will experience a more significant drying shrinkage than if subjected to a wet and low-temperature condition [181,189,195].

2.7.5 Current research on moisture loss and shrinkage development in concrete 3D printing

Regarding relevant C3DP literature, a limited number of studies investigated the effect of C3DP characteristics, including a higher likelihood of pore water evaporation, coarse aggregate utilisation limitation, etc. This section presents a summary of the very recent studies on different types of shrinkage development in 3D printable concrete.

Previous research has shown that printed elements' structural integrity, volumetric stability and mechanical strength depend on the moisture loss and water transport properties of 3D printing concrete [23,57,59,84,196,197]. Sanjayan et al. [59] evaluated the bonding strength of two consecutive layers of a C3DP mixture with a filament dimension of $250 \times 25 \times 15 \text{ mm}^3$ and a printing interlayer gap time of 20 min under the outdoor printing environment of 24°C and 65% RH. As shown in Figure 2.21, they have observed that 20 min after the deposition, evaporation of 160 mg surface moisture resulted in 50% lower interlayer bonding strength.

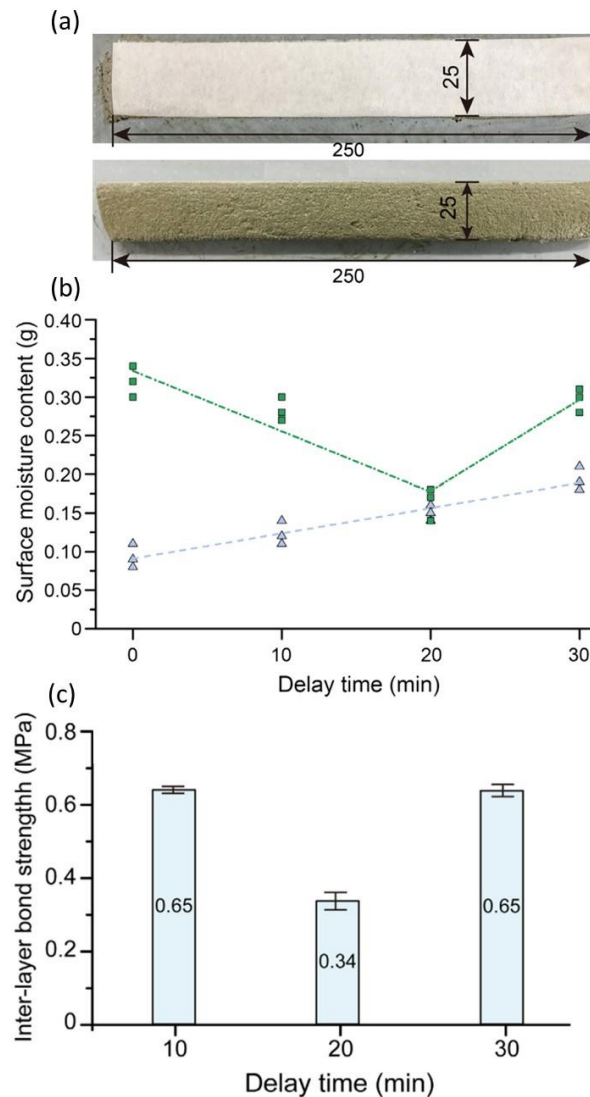


Figure 2.21. (a) Surface water evaporation measurement method, (b) surface moisture evaporation quantities of extruded filament and cast specimen and (c) bonding strength of two consecutive layers after the loss of surface moisture[59].

Nerella et al. [57] investigated the effect of layer-interface quality (between individual layers) on interlayer bonding performance of 3D printed concrete specimens constructed with varying time intervals between succeeding layer depositions. Their

close macro and microscale evaluation revealed that three potential mechanisms might be responsible for the reduction of interlayer bonding: i) higher porosity in the core material, ii) air entrapment, and higher amount of large pores or microcracks at the interface and iii) plastic and drying shrinkage cracks of printed materials. They have reported that non-uniform water evaporation due to the deposition of printing filament at varying printing time intervals (in the case of prolonged printing interval time) leads to non-uniform shrinkage, resulting in weak interfacial bonding strength between deposited layers. Their reported results were in line with the findings of previous studies by Beushausen and Alexander [198] and Amba et al. [199], who investigated the performance of bonded concrete/mortar overlays in terms of crack-resistance and debonding. They have reported that the differential volume variation between the substrate and the overlay is the primary failure mechanism of overlay debonding.

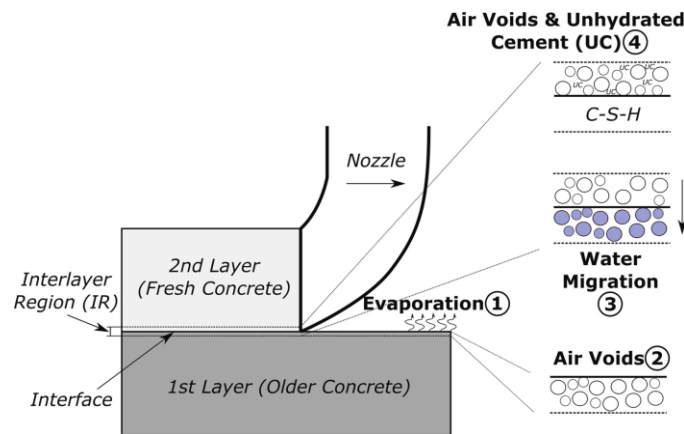


Figure 2.22. Moisture loss from the surface of previously printed filament (1st layer) leaves air voids and porosity in the interlayer region, which are filled with the capillary water from the freshly deposited layer (2nd layer), resulting in partial hydration of cement, higher porosity and permeability in the interlayer region [196].

Kruger and Van Zijl [196] summarised the prominent lack of fusion mechanisms. They defined the loss of surface moisture and air entrapment in the interface region as the most critical potential mechanism for weak bonding strength between printed layers. According to their detailed review, moisture loss from the free surface of the printed filament after deposition, which is controlled by printing environment temperature, relative humidity and wind velocity, results in a drier and more rigid surface, decreasing the remixing and rebinding of the subsequent printing filament to the previously printed layer, leading to weaker interlayer bonding. In this condition, the previously printed layer absorbs water from the freshly printed top layer, forcing more air to the interlayer region and leaving more porosity in the filament in

the vicinity of the interlayer region [200,201]. Therefore, poor physical interlayer bonding is achieved. As a further consequence of the higher evaporation rate in C3DP technology, hydration of the raw constituents (i.e. cement, supplementary cementitious materials, FA, GGBS) is adversely affected in the filament and at the interlayer region, resulting in higher amounts of nonreacted precursors or partially reacted products [202,203]. This phenomenon also contributes to the weak interlayer bonding given the water transportation from the top wet layer to the dry previously deposited layer. The surface moisture loss mechanism (pore water evaporation, water transport and lower hydration degree) in the concept of C3DP is illustrated in Figure 2.22.

As previously discussed, the higher evaporation rate in C3DP, which is controlled by curing (drying) environment parameters, results in higher shrinkage deformation and early-ages moisture loss. To date, only a limited number of studies have investigated the effect of these parameters on the shrinkage strain development in C3DP. The first investigation was conducted by Le et al. [23] to examine the drying shrinkage of the printable concrete containing FA and SF. The shrinkage development was studied for the mould cast $75 \times 75 \times 229 \text{ mm}^3$ beams specimens of the 3D printable concrete prepared according to the BS-EN 12617-4:2002 [204] under three curing conditions of thoroughly water-immersed, covered in damp hessian under the ambient outdoor environment (100%RH and 15–25 °C) and standard climatic weather of 20 °C – 60% RH for six months. As shown in Figure 2.23, Le et al. [23] found that the ultimate drying shrinkage of C3DP mixtures reach 180, 570, and 855 $\mu\epsilon$ after six months for the abovementioned curing conditions, respectively.

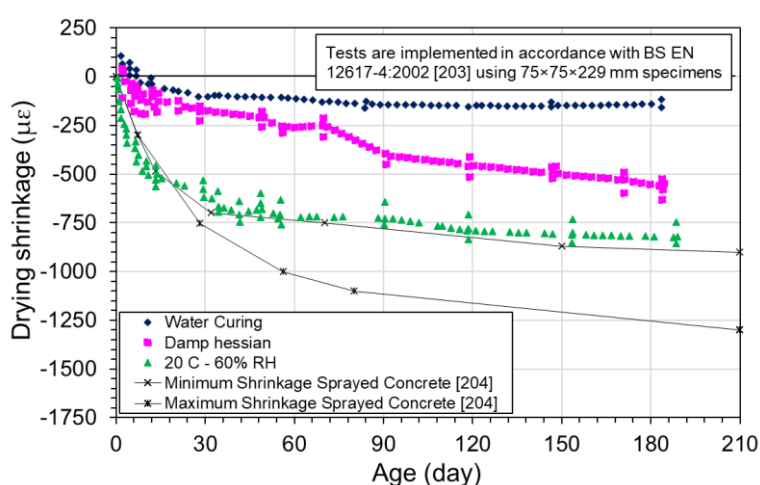


Figure 2.23. Drying shrinkage measurement in accordance with BS EN 12617-4:2002 [204] of printing concrete cured in different initial curing conditions [23] compared to minimum and maximum shrinkage limits of sprayed concrete [205].

Zhang et al. [39] conducted the first experimental research on measuring printed specimens' drying shrinkage deformation. They measured the drying shrinkage of $100 \times 100 \times 400 \text{ mm}^3$ beam specimens cut from a printed element under the standard curing environment of $20 \pm 2^\circ\text{C} - 50 \pm 5\% \text{ RH}$ for three months. As shown in Figure 2.24, they have reported that the specimens exhibited 280 – 330, 605 – 614, 715 – 744 and 807 – 840 $\mu\epsilon$ in 3-day, 15-day, 56-day and 70-day, respectively. They have also reported that the effect of increasing the S/C ratio from 1.0 to 1.2 on the drying shrinkage reduction was negligible. The abovementioned studies [23,39] compared their drying shrinkage results with that of sprayed mortars under the curing condition of $20^\circ\text{C} - 50\% \text{ RH}$. This indicated that the drying shrinkage of 3D printable concrete that was initially cured under the wet conditions (according to the international standards) exhibited lower drying shrinkage strain compared to the sprayed mortars (at the same age), which ultimately developed approximately 800 - 1200 $\mu\epsilon$ shrinkage deformation [205,206].

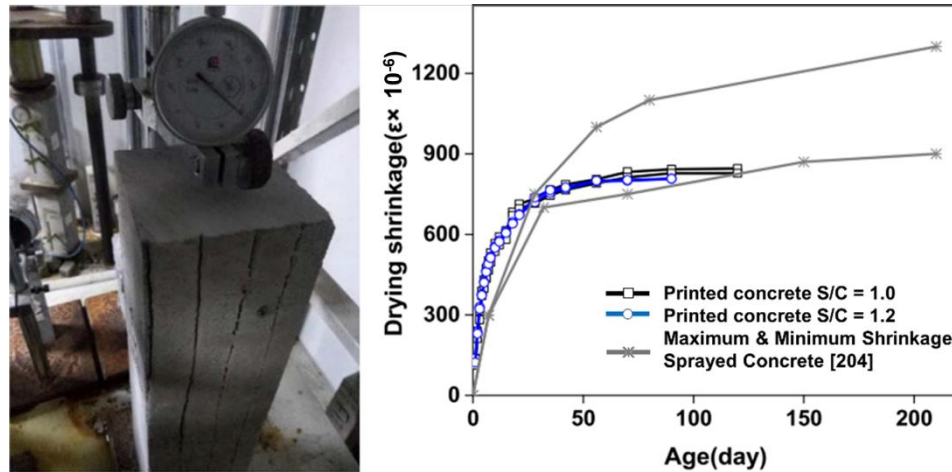


Figure 2.24. Test setup and drying shrinkage evolution of 3D printable concrete with various S/C ratios under $20 \pm 2^\circ\text{C} - 50 \pm 5\% \text{ RH}$ [39] compared to upper and lower shrinkage limits of sprayed concrete [205].

Moelich et al. [98] conducted the first comprehensive investigation on the plastic shrinkage cracking in 3D printed concrete originated from early age moisture loss due to the free-formed nature of C3DP, lower W/B ratio and aggregate-to-binder ratios, and higher amount of fine aggregate in 3D printable concrete. They have used the digital image correlation (DIC) technique to measure the unrestrained and restrained shrinkage deformation. Based on the results of unrestrained shrinkage, they have found that the rate of shrinkage strain gain, and the ultimate shrinkage strain values measured under the moderate evaporation rate ($25^\circ\text{C} - 60\% \text{ RH} - 13 \text{ km/h}$) were significantly

higher for 3D printed concrete compared to the conventional concrete. To evaluate the shrinkage development in 3D printing, they printed single-layer, and triple-layer specimens with different filament lengths of 200 mm and 300 mm, as shown in Figure 2.25 (a, b). Specimens were monitored for length changes from the top (single and triple-layer) and side (triple-layer) for the first 2.5 h after the deposition. This has enabled the researchers to investigate the effect of various surface-to-volume ratios (15% for single-layer and 8.3% for triple-layer) and bottom-layers constraint on the shrinkage development of freshly printed filaments.

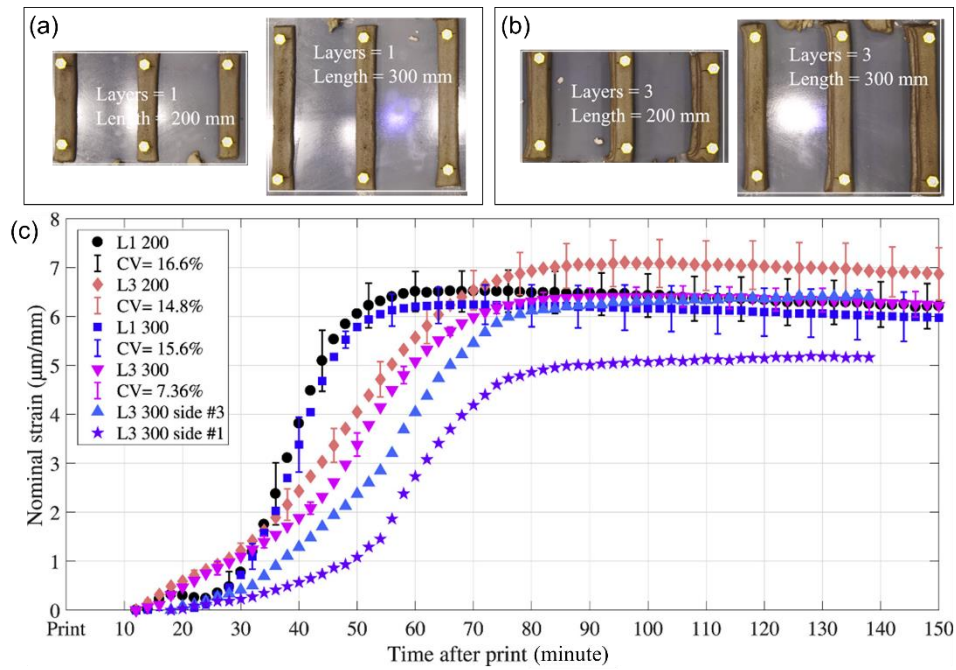


Figure 2.25. (a, b) Single-layer (L1) and triple-layer (L3) printed shrinkage specimens with lengths of 200 and 300 mm, (c) Variations of shrinkage deformation versus age after deposition; Shrinkage deformation of L3 – 300 specimen was also recorded from the side where #3 and #1 referred to the top and bottom layer, respectively [98].

As shown in Figure 2.25 (c) [98], the rate of shrinkage development for single-layer (L1 with S/V of 15%) specimens was higher than for triple-layer (L3 with S/V of 8.3%) specimens. The ultimate free shrinkage strain occurred earlier for the single-layer specimens at around 50 min compared to the triple-layer specimens at approximately 80 min after the deposition. The ultimate shrinkage deformation of the specimens was in the range of 6300 – 7100 $\mu\epsilon$. Moelich et al. [98] also observed that the shrinkage deformation could be transferred between layers resulting in interlayer slip.

Besides the shrinkage measurement for C3DP mixtures, a few studies recently investigated shrinkage mitigation techniques [7,50,197,207]. Kim et al. [207] showed the feasibility of using styrene-butadiene rubber (SBR) to decrease the drying shrinkage of the cementitious 3D printable concrete. They performed the drying shrinkage measurements according to ASTM C596-01 [208] and showed that the shrinkage strain of mixtures with an SBR-to-cement ratio of 0 – 0.2, cured at 23 °C - 60% RH, decreased by approximately 56% after 28 days (Figure 2.26).

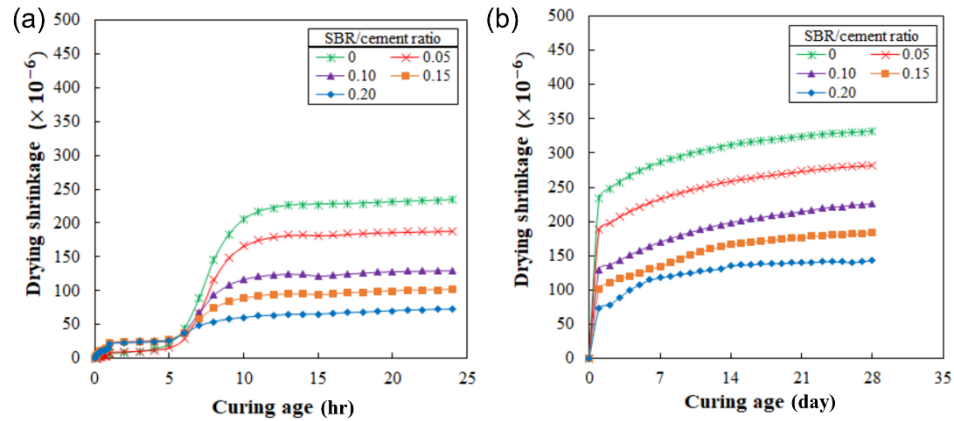


Figure 2.26. Drying shrinkage evolution of cement-based 3D printable mixtures modified with various SBR/cement ratios during the first day: (a), and after 28 days of curing: (b).

Federowicz et al. [50] studied the effectiveness of various initial curing methods, especially incorporating shrinkage reducing admixtures (SRA), on the drying shrinkage evolution of C3DP mixtures. They have examined the 7-day shrinkage development of 3D printed layers under varying curing procedures of open-to-atmosphere curing, foil-sealed curing, and internal curing with SRA-modification under the standard weather condition of 20° C and 50% RH. According to their findings, the 7-day free shrinkage deformation of the open-to-atmosphere specimens was approximately 385% higher than the foil-sealed specimens. Moreover, they have reported that 2% and 4% SRA-modification of C3DP mixtures reduce the 7-day ultimate free shrinkage by approximately 4% and 20%, respectively.

Van Der Putten et al. [197] investigated the effect of internal curing with superabsorbent polymers (SAP) on autogenous and drying shrinkage development and associated early-age crack formation of 3D printable concrete. They have reported that the SAP incorporation into the mixtures reduces printed concrete's shrinkage by up to 200%.

Regarding the effect of coarse aggregate constraint on shrinkage strain of C3DP mixtures, Rahul et al. [209] studied the influence of using natural and recycled coarse aggregates with a maximum particle size of 10 mm and substitution ratio of 30% with the fine aggregate on the autogenous and drying shrinkage behaviour of 3D printable mortar. Following the ASTM C596-01 [108], measurements were conducted for the $40 \times 40 \times 160 \text{ mm}^3$ mould cast specimens under a moderate climatic atmosphere of 20 °C and 60% RH. Their results have shown that the restraining effect of coarse aggregate inclusion in the mixtures contributed to the reduction of the 31-day total free-shrinkage by 16% and 11% for natural and recycled aggregate, respectively. Moreover, they have reported that due to the higher water absorption capacity of recycled aggregate (possibility of internal curing), the addition of recycled aggregate resulted in significant reductions (approximately 60%) in autogenous shrinkage.

2.8 SUMMARY AND IMPLICATIONS

The in-print failure of 3D printing concrete has been studied extensively, yet certain parts of it need further investigation. As discussed in Sections 2.4 and 2.6, to avoid material or stability failure or to identify the in-print failure mode that occurs first, most recent studies have primarily focused on assessing the buildability of 3D printable mortar by predicting the optimal vertical build rate for a given mixture composition. However, in contrast to prior research identifying the optimal mixture based on a certain vertical construction rate has not been thoroughly examined. The significance of this distinct approach is when a particular configuration is required for the 3D printing job, or equipment-related limits exist. When the scale of the printing project is large in such a way that it limits the reduction in the printing speed to avoid the formation of cold joint and the increased overall print time; or when changing the filament height and size is not preferred due to required printing resolution; or when there are equipment-related limitations such as where only the batch mixing printing machine can be utilised or modifying the printing speed is restricted due to the printer capabilities constraint, the best performance in 3D printing operations can be achieved via modification of 3D printable mixture as a solution to these issues and obstacles. Therefore, further study is needed on how to regulate the yield stress development of mortars for optimisation where 3D printing with no instantaneous mixing (mixing in the nozzle) procedure can be utilised. This topic is further investigated in Chapter 3.

Many technical concerns remain unanswered in the field of 3D printing, despite the significant growth in knowledge over the last few years. As previously discussed (Section 2.7), the formation of so-called cold-joints in the interlayer region is one such issue, resulting in weak interlayer bonding and adversely impacting the mechanical performance and durability of 3D printed components in the long run. It has been recently identified that one of the significant mechanisms behind this is the moisture loss and migration from the surface of the printed element and between the layers, respectively. Printed concrete's durability-related properties, especially its shrinkage deformation, depending on the moisture transport between the printed elements and its printing environment. For several reasons, printed elements are prone to different types of shrinkage deformation and cracking. Firstly, C3DP technology is a formwork-free process where evaporation of pore water from an early age is inevitable. Secondly, the higher content of fine aggregate and relatively low W/B ratio in the mixtures offer the minimum protection against pore water evaporation due to the reduced bleeding rate. Thirdly, although incorporating the coarse aggregate may offer higher dimensional stability and decrease the shrinkage deformation, the rheological requirements of C3DP necessitate avoiding using coarse aggregate in 3D printable mixtures. Fourthly, due to the high content of binder and fine aggregate in 3D printable mixtures and low W/B ratio, higher level of capillary pressure and self-dessication is expected in the microstructure, resulting in increased autogenous shrinkage deformation. Finally, since printed components have a higher surface area-to-volume ratio (S/V) because of their slender wall construction, the rate of surface water evaporation might be higher, resulting in more significant shrinkage deformation. This topic is further discussed in Chapter 4 for the cement-based 3D printable mixtures considering the abovementioned variables (e.g. S/C and S/V) and different outdoor curing environments (various temperature and relative humidities). This topic also is investigated for the alkali-activated concrete in Chapter 5.

As discussed in 2.5.1 and 2.5.2, the binder content in C3DP mixtures is approximately 40% higher than that of conventional concrete. Considering the fact that OPC production is still the most energy- and pollution-intensive aspect of OPC-based concrete, C3DP technology is still not an eco-friendly technology compared to conventional casting. C3DP's sustainability challenges may be addressed in two ways: by adopting an alternative waste-based binder for OPC and by substituting

underutilised fine aggregate with natural fine aggregate (partially or fully). Alkali-activated concrete, especially FA-GGBS-based binders, is the most widely used alternative binder for OPC. Previous studies (discussed in Section 2.5.2) successfully developed C3DP mixtures with alkali-activated binders (typically FA-GGBS-based at specific proportions). However, the alkali-activated binders do not have colloidal interactions between their particles compared to the OPC system. Therefore, as discussed in Sections 2.5.2 and 2.5.4, the focus of the studies on alkali-activated 3D printing concrete was mainly the improvement of thixotropy properties, i.e. viscosity and yield stress recovery by incorporating a widely used thixotropy modifier known as nanoclay (NC) and graphene oxide (GO). Although the rheological aspects of using alkali-activated binders in C3DP mixtures and the influence of nanomaterials as a rheology modifier have been studied to some extent (Sections 2.5.2 and 2.5.4), no studies have been conducted on the effect of various curing environment (temperature and relative humidities) and the impact of nanomodification on the drying shrinkage evolution of alkali-activated 3D printable concrete so far (Section 2.7.5). This topic is further discussed in Chapter 5 for the alkali-activated 3D printable mixtures considering different outdoor curing environments (various temperatures and relative humidities).

The second approach to address the sustainability challenges of C3DP is substituting non-renewable resources, i.e. natural fine aggregate, with underutilised fine aggregate in C3DP mixtures. To date, several studies (Section 2.5.3) have been carried out on using waste aggregate, industrial by-products, and recycled aggregates in C3DP mixtures. Most existing studies have shown that the partial substitution of underutilised aggregate is possible and results in enhanced or equal printability properties (yield stress development, buildability) compared to conventional mixtures with natural aggregate. However, it is often reported that C3DP mixtures prepared by underutilised aggregates exhibit poor mechanical performance and a considerable drying shrinkage strain. Lead smelter slag (LSS), also known as black sand, is a by-product of metallurgical processes and its compositions and physical properties make it a suitable replacement for natural sand in alkali-activated concrete. Previous studies found that using LSS in alkali-activated mixtures showed higher compressive strength and lower drying shrinkage deformation than natural aggregate.

Therefore, to improve the sustainability of C3DP by taking advantage of the capabilities of alternative aggregates (recycled or waste aggregate) in the 3D printable concrete mixtures while not sacrificing the mechanical performance and dimensional stability of the printed structure, more research is required to find the most appropriate replacement for natural aggregate in C3DP mixtures. Therefore, it is particularly important to understand the rheological, mechanical and shrinkage behaviour of LSS-based alkali-activated concrete for use in extrusion-based C3DP technology to address the sustainability and durability-related challenges of C3DP simultaneously. This topic is further discussed in Chapter 5.

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Chapter 3: Rheological limits in optimising cementitious mortar mix designs for 3D printing: Effects of water and admixtures

The free-form and additive nature of extrusion-based concrete 3D printing facilitates the production of unique designs. While this is seen as one of the fundamental advantages of the technology, it presents certain challenges from a material-process performance standpoint. There is a set of very specific rheological requirements for extrusion-based 3D printing. When the scale or complexity of a printing job is changed, new rheological requirements also need to be considered. This chapter proposes a theoretical framework, based on yield stress-related limits, for optimising the material-process interactions in extrusion-based 3D printing. Furthermore, experiments showed how the yield stress evolution of the printing material can be controlled and optimised by water to cement ratio and a range of admixtures. The methodology presented in this research provides a framework for implementing changes to the mix design to achieve the required quality and efficiency of extrusion-based 3D printing of cementitious mortars.

3.1 INTRODUCTION

Extrusion-based three-dimensional concrete printing (3DCP) refers to an additive extrusion process of a cementitious mortar through a nozzle and along a predefined material deposition path without any formwork or subsequent vibration [1–4]. The interest from industry and academia in concrete 3D printing has increased sharply over the past few years. As a result, these technologies are being considered more seriously as legitimate construction techniques. Among the recently completed projects, there are a variety of dwellings [5,6], a 2-story office building [7] and similar structures, such as urban furniture, footbridge, staircase, art installations, and a telecommunication tower [8–14]. A report by Kashani [15], provided a detailed description of the adoption of 3D printing in the construction industry by showcasing some of the exciting projects around the world. With a consistent flow of exciting new projects appearing, concrete 3D printing is becoming a hot topic.

There are numerous advantages that concrete 3D printing can provide over traditional construction methods. A high degree of automation offers an efficient building process and creates a much safer working environment [16,17]. Furthermore, the technology removes the need to construct complicated and costly formwork, which greatly simplifies preparation activities [18]. Formwork and the associated labour can account for up to fifty percent of the build price for a concrete structure [19]. In order to keep costs down, formwork geometries are therefore kept as simple as possible. Being freeform, 3D printing technology allows for interesting designs and structurally efficient shapes to be constructed without any added complexity [3,18,20–22].

Despite the advantages of concrete 3D printing, there are still several hurdles to overcome. The challenges are interdisciplinary and cover a broad range of fields including structural engineering, robotics, mechatronics, programming, mechanical engineering and materials science [2,16,17,23–27]. This chapter addresses the materials aspect and aims to show how the rheology of cement printing mortar can be modified to optimise printing mixtures for 3D printing process requirements.

The focus of this research is extrusion-based concrete 3D printing, which has very specific material requirements that need to be balanced carefully [16,28]. The characterisation of concrete for this purpose is quite different to that of traditional precast or cast-in-situ concrete. As such, researchers have developed a new vocabulary around fresh concrete properties for 3D printing as summarised below.

Pumpability: the reliability and ease with which the material can be pumped through the delivery mechanisms during extrusion [1,16,29].

Extrudability: the ease and reliability of depositing a material without incurring discontinuities in the extruded filaments [1,20,29].

Shape-stability: the ability of printed concrete filaments to hold their shape immediately after extrusion [17].

Buildability: the ability of printed concrete layers to resist deformation under the vertical pressure exerted from subsequently deposited layers [1,16,18].

Open time: defined as the period of time in which the material can be successfully used for printing given the requirements listed above [1,18,29].

Since these material requirements have competing properties, the desired material qualities for extrusion-based 3D printing can be presented by considering the balance of the above material requirements. Firstly, the concrete must flow easily (low yield stress) enough so that it can be pumped and extruded (pumpability/extrudability) [16]. However, there is a minimum yield stress required immediately after deposition for the filament to hold its shape (shape stability) [17]. Furthermore, the printed concrete filaments must quickly gain strength to withstand the pressure from subsequently placed layers (buildability), but not at a rate that compromises pumpability and extrudability [16,19]. Depending on the printing process and material delivery system, the open time can vary. For instance, using an in-line mixing delivery mode allows printing mortars with the shortest open time [30]. Furthermore, with an inline mixing delivery system, it is possible to add accelerator at the nozzle to increase early strength without affecting open time, pumpability and extrudability [31]. However, If the accelerator is added at the nozzle immediately before printing, it may not be as evenly distributed throughout the concrete mix, leading to uneven curing and potentially weaker areas in the final structure. On the other hand, if the accelerator is added during the mixing process, it is more likely to be evenly distributed and result in a stronger and more consistent final product. Additionally, adding the accelerator during mixing allows for better control over the amount of accelerator used, whereas adding it at the nozzle may result in an unpredictable amount being used. Moreover, the bond strength between deposited layers is increased when adjoining filaments are wet (fresh material state) [32]. The longer elapsed time between layer depositions

affects the interlayer bond strength and results in the formation of "cold joints" [33,34]. This study aims to develop an understanding into how the optimal material-process performance can be achieved based on these competing requirements.

Printable mortars have a transitory characteristic which evolve from a highly viscous fluid (immediately after mixing) into highly pliable solid (just before initial setting). The material requirements for cement mortar 3D printing relate to this evolution of the strength and flow characteristics over time. Cement mortar starts to gain strength almost immediately after mixing which coincides with a loss of flow-ability. Considering this feature of the printing materials a range of different theoretical models and experimental approaches have been suggested in the literature to determine the appropriateness of material-process combination for 3D printing. Recent research works addressed the issue both from a fluid and solid mechanics point of view, and for both approaches the time-dependency has been taken into account [31]. There is still lack of agreement on which quantitative material properties and associated experimental procedures are suitable for buildability analysis.

First attempts in studying the structural properties of fresh concrete were done by Di Carlo et al [35] through solid mechanics approach with unconfined uniaxial compression experiments. Kazemian et al. [17] defined a cylinder stability test for a rapid comparison to assess the impact of mixture compositions on constructability. To determine if a mixture is accepted or rejected, they assessed the buildability using measurements of deformations in each layer of two to five printed layers. Perrot et al. [19] presented another approach based on fluid mechanics to predict the static yield stress development with resting time after mixing. The static yield stress in fresh concrete is the amount of stress required to induce inelastic deformation or flow [36]. It will be shown that this single measure, under certain conditions, can be related to the properties of pumpability, extrudability, shape stability, buildability and open time. As a result, the yield stress evolution curves can be used to classify the suitability of the concrete for a given printing job. Wangler et al [37] redefined the buildability requirement for concrete 3D printing based on the similar approach of rheological yield stress using the von-Mises plasticity criterion to predict the failure stresses for deformation or collapse of fresh concrete during the printing process. Kruger et al. [38,39] developed a buildability model to identify maximum vertical build rate considering the print speed and extrudate layer's height. They verified the proposed

model by printing a 500 mm height 3D concrete printed wall. The static and dynamic yield stress evolution curves were utilised as input for their model and optimum layer height and print speed of 8 mm and 87 mm/s was reported for a successful printing.

A study by Perrot, et al. [19] used the yield stress evolution of a printing mortar to assess the time at which strength-based failure would occur. Different failure times were reported based on various theoretical vertical construction rates. This is essentially an assessment of mortar buildability. Using the same conceptual framework, the research presented here uses a similar type of failure by finding the optimal mixture based on a given vertical build rate, as opposed to finding the optimal vertical build rate based on a given mixture. This is seen as an important distinction since it is the vertical build rates that are likely to change frequently (for example when the scale or resolution of a job is altered). As a result of these changes, new material properties or printing requirements (e.g. printing speed, layer size, and flow rate) will be required. Therefore, it is pertinent to understand whether predictable mortar modifications can be made for optimal material-process performance, in response to these types of changes.

The use of chemical admixtures, including superplasticiser, accelerator, and retarder to adjust the yield stress evolution and workability of cement mortar systems for structural application is another technique for optimising the concrete material for 3D printing [20,40]. Using various chemical admixture types and ratios was the subject of a few recent studies. However, only limited studies were conducted on the effect of water-to-cement ratios. This research also seeks to understand whether modifications can be made to cement mortar mix design in order to maintain material-process optimisation in response to process specific changes.

Two methodologies were employed as part of the research program. Firstly, developing a theoretical framework aimed at optimising 3D printing mortars using yield stress development over time. Following this, an experimental program was undertaken to determine how such an optimisation could be achieved, primarily by adjusting mix designs for the purpose of controlling yield stress evolution. The results of this study provide a fundamental understanding of the effects of admixtures and water to cement ratio on rheological requirements of cement mortar for extrusion-based 3D printing.

3.2 THEORETICAL FRAMEWORK

Under certain conditions, the mortar requirements specific to extrusion-based 3D printing can be related to the material yield stress [20,28,33,41]. Specifically, the pumpability/extrudability, shape stability and buildability of a mortar can be defined by analysing the yield stress development in the material over time. This is an important point in the context of the following theory such that the relationship between each characteristic and yield stress can be established.

3.2.1 Pumpability and Extrudability

Pumpability and extrudability are grouped together because either characteristic will represent an upper limit for the yield stress of a material for 3D printing. Since most cement mortars behave as a visco-plastic Bingham (or sometimes Herschel–Bulkley) materials, they will flow only when subjected to stresses higher than the yield stress (τ_y) [41]. The internal structure of cementitious materials will start building up through a flocculation, dissolution and reaction processes after mixing and throughout the printing process [41]. As a result, the yield stress increases, and the material simultaneously stiffens and loses the ability to flow. Therefore, it is possible that during printing, the yield stress will increase to a value at which the pump can no longer deliver the mortar to the extrusion point (loss of pumpability) [20]. Alternatively, prior to the loss of pumpability, the increased stiffness could result in discontinuities in the extruded filament causing loss of extrudability [20]. When either of these situations occur, the yield stress has reached an upper limit where printing is no longer possible.

The yield stress value at which a loss in pumpability or extrudability occurs is highly dependent on the pumping/extrusion system being used. Parameters like pump type and power, hose diameter, length and its internal friction, as well as nozzle shape and size will have a significant effect on how materials with a higher yield stress can be printed using that system. Suggestions in the literature on the upper limit of yield stress for a cementitious material for 3D printing range significantly. Values as low as 0.9 kPa were reported by Le, et al. [20] for their system while Paul, et al. [28] reported a yield stress as high as 13 kPa for their printing mixture.

Roussel [41] points out that it is not always appropriate to use yield stress as a measure of pumpability. In some situations, the capacity to form a 'lubrication layer'

between the concrete and delivery pipe is reported to be more important than yield stress or viscosity [41,42]. Also, where significant shearing occurs near the nozzle, Roussel [41] suggests that the pressure gradient is mostly related to the plastic viscosity and not the yield stress. Considering these scenarios, it is apparent that using yield stress as a single measure to judge the pumpability and extrudability of a mortar can be problematic, particularly when comparing different material-system configurations.

Giving due consideration to the above limitations presented by Roussel [41], yield stress was considered as an appropriate measure of pumpability since the material-system interactions were not expected to change significantly within the context of this research. Here, the experimental section assesses the effect of only relatively small changes in mix design on the yield stress evolution behaviour. Also, as previously stated, it would be expected that the yield stress at which pumping becomes untenable will vary significantly between systems. However, in the confines of a given printing setup and by only making subtle changes to the material, it is expected that the measure of yield stress will be proportional to the pumpability. This claim is supported by Le, et al. [20] who presented upper and lower limits of yield stress as a measure for printability. The upper bound is a limit at which the material becomes too stiff to print with.

3.2.2 Shape Stability

Shape stability refers to the ability of the cementitious filament to resist deformation after extrusion has taken place [17]. Layer heights (h_0) for extrusion-based cementitious printing can vary significantly depending on the printing system being used. Generally, this range is 6 mm to 50 mm [33]. In many cases, the layer height is proportional to the size of the nozzle opening, which restricts the size of aggregate that can pass during extrusion. This study focuses on the rheological behaviour of mortars, for which layer heights are typically 10 mm to 30 mm. In all cases, it is expected that the initial gravity-induced stresses that the filament should sustain during deposition (before printing successive layers) will be predominately shear [41]. In order to resist deformation under these stresses, the deposited filament must already have, or quickly develop, a high enough initial shear yield stress (τ_{y0}) [41]. The flocculation process of cementitious particles at low shear rates, as a result of the chemical or physical bonding of particles, is where the initial yield stress starts developing [41]. To ensure the shape

stability of each filament, the yield stress needs to be in the order of ρgh_0 , where ρ is the density of the mortar, g (9.81 m/s^2) is the acceleration due to gravity and h_0 (m) is the height of the extruded filament [41]. For example, considering the mortar density of 2070 kg/m^3 in this study, the shape stability limit will be in the range of 203 Pa and 610 Pa for layer heights of 10 mm and 30 mm, respectively.

Roussel [41] suggests competition is developing between the characteristic flocculation time and spreading time directly after a deposition where the printing material is sheared in the nozzle. Furthermore, the printing speed can cause inertial stress in the deposited filament in the order of hundreds of Pascals [41]. Since this value is similar to that of the initial yield stress required, it is possible that the filament shape may be affected by these forces [41]. However, in most cases inertia forces are weak enough to be neglected and, most likely, the gravity-induced stress and yield stress will determine the shape of the deposited layer [41].

Figure 3.1 illustrates the concepts of pumpability/extrudability and shape stability limits as they relate to the yield stress evolution of a mortar. Represented so far is an upper and lower bound on the material yield stress for printing. It is worth noting that the yield stress at zero time can be lower than "shape stability limit", however, the open time only starts when the yield stress exceeds the shape stability limit (which means the start time of printing can be delayed accordingly). The numerical values of these limits are notional and are provided so the theory can be explained. As mentioned, they are highly dependent on the printing system being used.

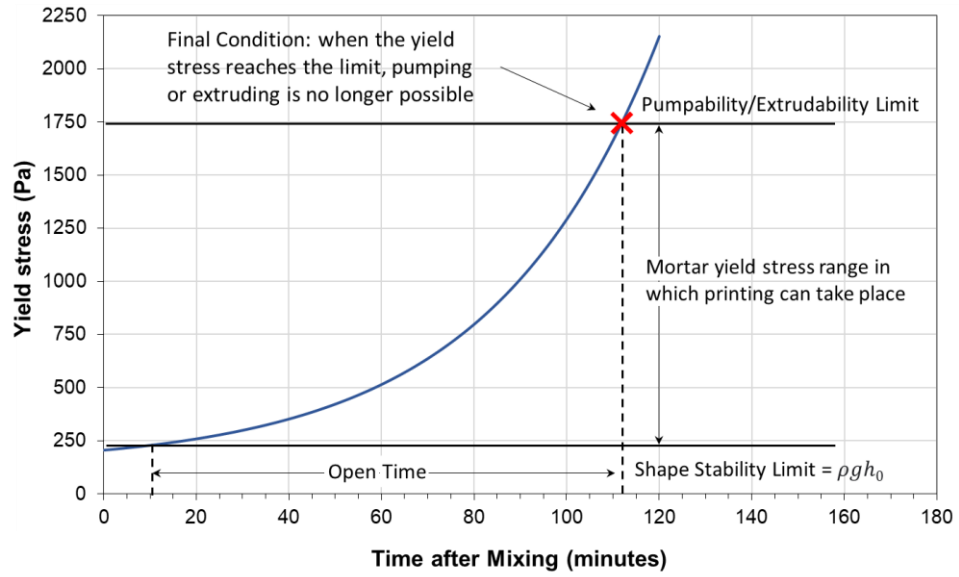


Figure 3.1. A schematic description of pumpability/extrudability, open time, and shape stability limits in the context of yield stress evolution for extrusion-based 3D printing.

3.2.3 Buildability

Buildability is defined as the ability of printed layers to resist deformation under the pressure exerted by subsequently deposited layers [1,16,18]. In essence, if the printing material gains strength quickly, it can support a faster rate of subsequently placed material (higher buildability). On the other hand, a slow rate of strength development will only be able to support a slower vertical build rate (lower buildability). The basis for using yield stress as a buildability limit relies heavily on the work done by Perrot, et al. [19] and Roussel [41]. A study by Perrot, et al. [19] used the yield stress evolution of a mortar to predict the time at which printed structures would fail during the printing process. The failure is attributed to a strength-based deformation in lower layers that could not support subsequently added material (a requirement in freeform additive manufacturing). The predicted time of failure was calculated from the yield stress evolution of the mortar and the vertical build rate [19]. Using a similar concept applied in a different context, this study aims to avoid the same type of failure by controlling the yield stress evolution of the mortar based on the vertical build rate of a given printing job. This has the effect of preventing failure in a different way. It is expected that changes to printing form, scale or complexity from one printing job to another may result in different vertical build rates ($\dot{H}$, typically expressed in units of length per unit time, e.g., m/s, m/h, or mm/min). When the vertical build rate changes, the pressure build-up on lower layers also changes and the rate at which the material gains strength may need to be adjusted.

The 3D printing layering process discussed here causes a progressive build-up in vertical pressure and, intuitively, the maximum pressure applied occurs in the bottom layer. As the printed filaments are sequentially placed, the structure becomes taller and slenderer in nature, producing predominately extensional stresses in the lower layers [41]. This means the yield stress value in the critical layer (generally the first deposited layer) must be greater than $\rho gh/\sqrt{3}$ (Pa) to resist gravity-induced stresses, where h (m) is the height of the structure above the critical layer, g (m/s²) is acceleration due to gravity, and ρ (kg/m³) is the density of concrete [41]. In layer-wise construction, h is a function of the vertical build rate and time ($h = \dot{H}t$). Considering the yield stress in the critical layer should remain above $\rho gh/\sqrt{3}$ at all times, the concept can be described mathematically by the following equation [41]:

$$\tau_y(t) > \rho g \dot{H} t / \sqrt{3} \quad \text{Equation 3.1}$$

Equation 3.1 assumes that the critical layer is printed at time $t = 0$, immediately after mixing. While this may not always be the case, simple modifications can be made to account for such changes. It is also prudent to point out that the left-hand side of Equation 3.1 is a material property, and the right-hand side is largely dependent on print process parameters, namely the vertical build rate. More specifically, $\dot{H}$ (Equation 3.2) is a function of the contour length of each layer (l_c , expressed in units of length, e.g., m or mm), the linear velocity of the deposition nozzle (v_n , expressed in units of length per unit time, e.g., m/s, m/min, mm/s, or mm/min) and the layer height (h_0 , expressed in units of length, e.g., m or mm), parameters that are all known before printing begins.

$$\dot{H} = \frac{h_0}{(l_c/v_n)} \quad \text{Equation 3.2}$$

Since Equation 3.1 states a condition that the yield stress evolution must stay above $\rho g \dot{H} t / \sqrt{3}$, this term can be viewed as a limit and plotted alongside the pumpability/extrudability and shape stability limits. Formally, the buildability limit is defined as Equation 3.3:

$$BL = \rho g \dot{H} t / \sqrt{3} \quad \text{Equation 3.3}$$

Together, the limits defined above can be joined to form a 'print window'.

3.2.4 Defining the Print Window

Three material yield stress related printing limits have been presented. The combination of these limits can be used to form a print window. If the mortar yield stress falls outside this window at any time during the printing process, some type of failure will occur i.e. either filament deformation due to insufficient shape stability, loss of pumpability/extrudability or a gravity-induced strength-based failure. Figure 3.2 shows a schematic representation of the print window. Apart from the strength-based failure mechanism, another failure mode is a stability-induced failure, known as elastic buckling, principally impacted by the stiffness of the printing mortar and the loss of force and moment equilibrium during concrete printing, which is beyond the scope of this study.

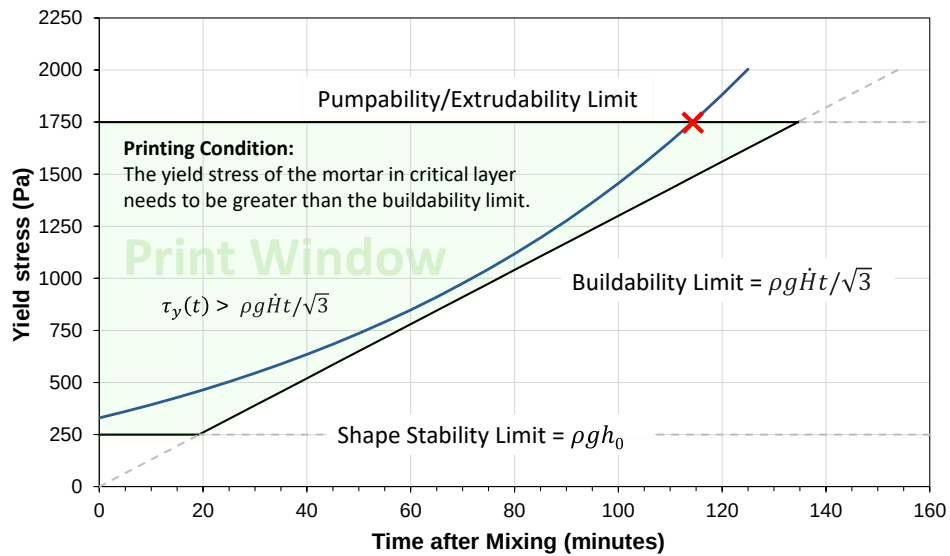


Figure 3.2. A print window can help define an optimal yield stress evolution based on the printing conditions.

3.2.5 Optimisation

Given the yield stress evolution needs to progress inside the print window for printing to take place, further attention can be given to the behaviour of the yield stress evolution curve inside the print window. Ideally, the yield stress development should display the following key features: it starts above the shape stability limit or starts below the shape stability limits but develops with a structuration rate greater than the buildability limit, it never intersects with the buildability limit, and it prolongs the time period until the pumpability/extrudability limit is reached. The first two points are necessary for continuous printing to take place but maximising the printing time of each mixture is also very important in case of mixing in batches instead of

instantaneous mixing and printing. Slower structuration will help avoid the formation of cold joints between layers and decrease the number of batches required to complete printing (in case of batch mixing preparation method and not the instantaneous mixing). The latter point results in a higher degree of automation, specifically when instantaneous mixing concrete preparation is not practicable, since the demand from operators to make and change new mixtures is reduced.

Figure 3.3 shows two examples of what may be considered non-optimised yield stress evolutions through the print window. While both Mortar 1 and 2 in this example do not have any issues with shape stability (sufficient initial yield stress), the yield stress development of Mortar 1 is considered too quick. Mortar 1 will not have any issues with buildability as well (never intersects with buildability limit). However, in this example, the mortar has reached the pumpability limit after about 55 minutes, which is much less than the theoretical maximum open time of around 110 minutes (where the pumpability/extrudability limit intersects with the buildability limit). On the other hand, Mortar 2 displays a yield stress development that is too slow. Using this mortar, printing could take place for approximately the first 45 minutes before it would have to be stopped. Otherwise, a strength-based failure would occur in the first printed layer.

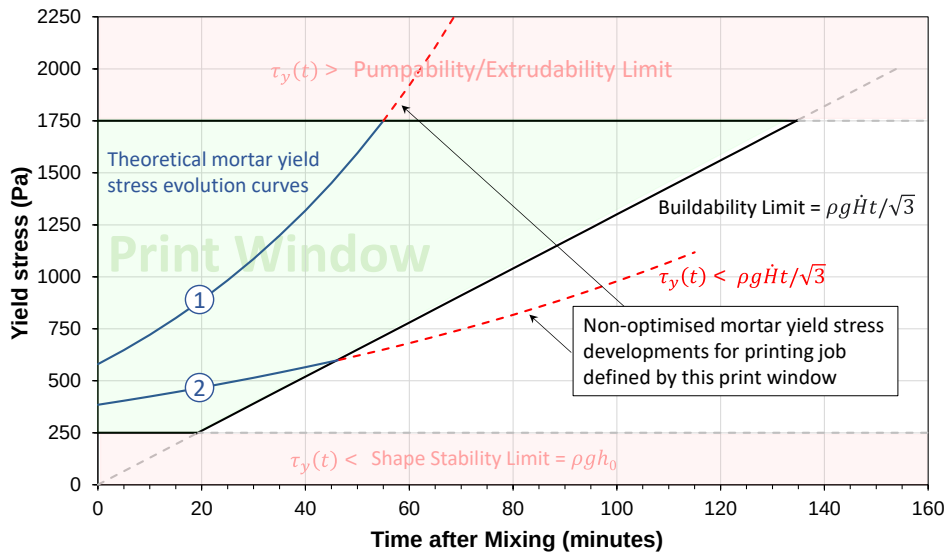


Figure 3.3. Theoretical yield stress evolution of two mortars (1 and 2) represents non-optimised material properties based on the printing requirements defined by the print window.

In some cases, the yield stress evolution of a mortar or concrete is linear over the time frames being discussed here. Figure 3.4 indicates two examples of how optimised mortar yield stress evolutions might progress through the predetermined print window.

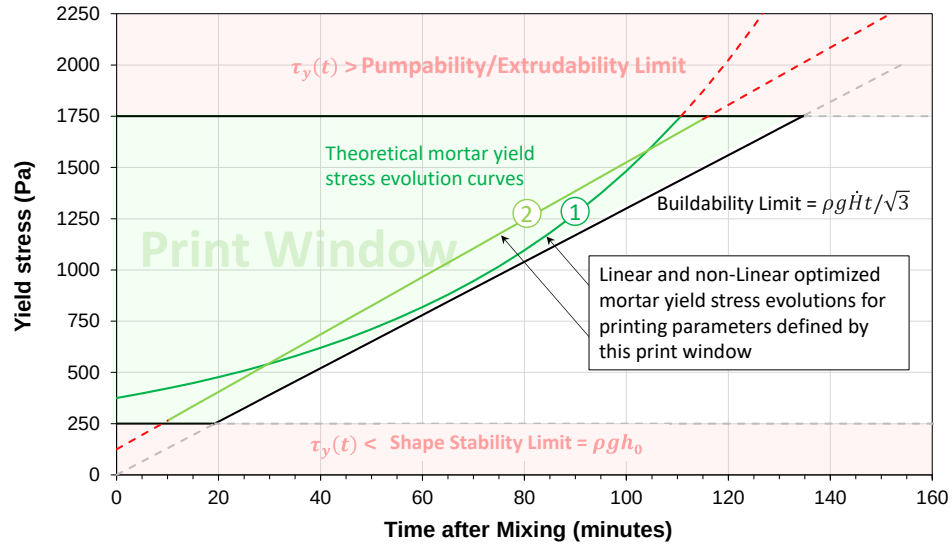


Figure 3.4. Examples of how linear and non-linear yield stress evolutions might ideally progress through the print window.

Two optimum yield stress evolutions are proposed in Figure 3.4. In this example, Mortar 1 and 2 display an exponential and a linear structuration rate, respectively. Mortar 1 displays good yield stress evolution behaviour for the given print job because it satisfies shape stability and buildability criteria but also progresses in such a way that the open time is extended as far as reasonably possible. As shown in Figure 3.4, Mortar 2 might not have an adequate initial yield stress for filament shape stability at time zero. However, after around 10 minutes of structuration, the yield stress has built up enough for shape stability and printing could begin. The progression of the yield evolution then tracks parallel to the buildability limit, resulting in a sufficiently long open time.

A main focal point of this research relates to how the yield stress evolution of mortars can be controlled for optimisation as outlined above, where only batch mixing (and no instantaneous mixing) concrete preparation can be utilised. However, it should be pointed out that this method is not the only tool to achieve this goal. For example, if a mortar had a shallow structuration development (e.g. Mortar 2 in Figure 3.3) instead of modifying the mixture to increase the rate of structuration, the slope of the buildability limit could be reduced (either by reducing the layer height or nozzle

velocity). While changing the print window limits is potentially simpler than modifying the mortar mixture, they do carry their own limitations. If the nozzle velocity is reduced, the overall print time is increased or cold joints between layers might form. Reducing the layer height would also have the same effect. Furthermore, changes to these parameters have other practical limitations, for example, how fast/slow the nozzle can move while keeping the volume of the extrusion consistent, whether inertia forces will deform the extruded filament and what print resolution is required [41,43]. Overall, having more tools for optimisation is preferable to obtain the best performance possible in any 3D printing job.

3.3 EXPERIMENTAL METHOD AND MATERIALS

The theory presented above relies on the ability to have control over the yield stress evolution of printing mortars. A key objective of this research is to demonstrate how this might be achieved. The experiments were conducted in two parts. First, the effect of water to cement ratio as well as the amount of superplasticiser, accelerator and retarder on early-age yield stress development were investigated. The second experimental part looked at how the results from the first set could be implemented to effectively optimise a mortar given predefined printing parameters. For this purpose, rheological measurements of fresh mortar samples were carried out to determine the yield stress evolution over the first two to three hours after mixing. Moreover, a small-scale 3D printing was conducted using a custom-made laboratory scale printer. The shape stability and buildability of the printed layers were measured for mixes with optimised ratios.

3.3.1 Materials

Ordinary Portland Cement (General Purpose cement, equivalent to CEM I-32.5N, OPC) and fine washed sand were supplied by Cement Australia and Boral, respectively. Figure 3.5 depicts cement and fine sand's particle size distribution (PSD). Calcium carbonate fine powder was supplied by Enfield Produce (Sydney), and a viscosity modifying admixture (VMA), and a superplasticiser (MasterGlenium SKY 8379) were supplied by Sika and BASF, respectively. Where indicated, an accelerator and a retarder (tartaric acid) were also used. The admixtures, when used, were added to the mixtures in the following order: tartaric acid crystals, superplasticiser, VMA and accelerator. The order of mixing was in accordance with the manufacturers'

recommendations in order to keep the compatibility of the admixtures with the general purpose cement used in this study.

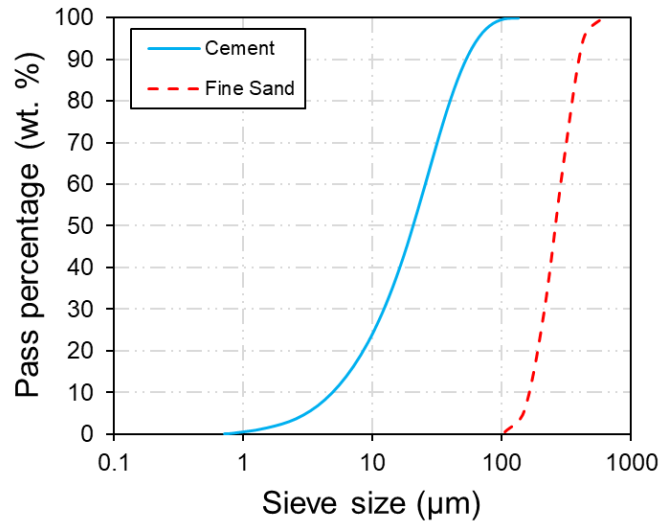


Figure 3.5. Particle size distribution (PSD) of cement and fine sand

3.3.2 Mix design

Table 3.1 listed the mix designs with their associated codes. The labels W, SP, A, and R represent the water to cement, superplasticiser to cement, accelerator to cement, and retarder to cement ratios, respectively. The subscript values indicate the ratio of their correspondent labels multiplied by 100. The values of label "W" represents the water to cement ratio by weight of cement, while the values of additives are expressed as a percentage by weight of cement. Moreover, the following ratios were kept constant in all the mixes: sand/cement (S/C): 1.49; calcium carbonate/cement (CC/C): 8.10%; and VMA/Cement (VMA/C): 0.30%.

Table 3.1. Mortars mix design. The S/C: 1.49, CC/C: 8.10%, and VMA/C: 0.30% were constant in all mixes.

Mix Code	Water/Cement Ratio	Percentage by weight of cement (%)		
		Superplasticiser	Accelerator	Retarder
W ₄₂ SP ₄₀	0.42	0.40	0	0
W ₄₀ SP ₄₀	0.40	0.40	0	0
W ₃₈ SP ₄₀	0.38	0.40	0	0
W ₃₆ SP ₄₀	0.36	0.40	0	0
W ₄₀ SP ₆₀	0.40	0.60	0	0
W ₄₀ SP ₅₀	0.40	0.50	0	0
W ₄₀ SP ₃₀	0.40	0.30	0	0
W ₄₀ SP ₂₀	0.40	0.20	0	0
W ₄₀ SP ₅₀ A ₁₅₀	0.40	0.50	1.5	0
W ₄₀ SP ₅₀ A ₇₅	0.40	0.50	0.75	0
W ₄₀ SP ₅₀ A ₅₀	0.40	0.50	0.50	0
W ₄₀ SP ₅₀ A ₂₅	0.40	0.50	0.25	0
W ₄₀ SP ₄₀ R ₃₀	0.40	0.40	0	0.30
W ₄₀ SP ₄₀ R ₂₅	0.40	0.40	0	0.25
W ₄₀ SP ₄₀ R ₂₀	0.40	0.40	0	0.20
W ₄₀ SP ₄₀ R ₁₅	0.40	0.40	0	0.15
W ₄₀ SP ₄₀ R ₂₇	0.40	0.40	0	0.27

3.3.3 Sample Preparation

Each mortar sample was made up of 1 kg of dry ingredients (cement, sand and calcium carbonate). The dry ingredients were mixed with a stand mixer at 675 rpm for 120 seconds, ensuring a homogenous distribution of particles was achieved. The tap water was separated into two containers containing 90% and 10%, respectively. The admixtures, when used, were added to the container containing 10% of the water in the following order: tartaric acid crystals, superplasticiser, VMA and accelerator. The order of mixing was suggested by suppliers. With the mixer turned on, the container

with 90% of the water was slowly poured into the dry ingredients and mixed for 30 seconds. Lastly, the remaining 10% of the water that also contained additional admixtures was added, and the mortar was mixed at 675 rpm for 150 seconds.

3.3.4 Rheological properties testing

Immediately after mixing, the mortars were transferred to a container $130 \times 130 \times 70 \text{ mm}^3$, and the time was recorded. At approximately 10 min intervals, a HAAKE Viscotester 550 Rheometer was used to measure the static yield stress of the mortars. A vane geometry with four rectangular blades with a height of 20.1 mm and a diameter of 10 mm was used. Each yield stress measurement was taken at different points in the container, which were sufficiently far away from each other so that the sample could be considered undisturbed. Figure 3.6 illustrates the container and vane dimensions as well as testing locations for mortar yield stress measurements. After being lowered into the mortar, the vane was rested for sixty seconds with no rotation in order to neutralize any residual stress from the disturbance caused by insertion. The vane was then programmed to rotate at 0.2 rpm, and a torque-time plot was produced. The maximum torque was recorded and converted to a yield stress by dividing the reading by the vane constant (i.e. 3.681×10^{-6}). By repeating this process over the first 100 to 180 mins, the yield stress evolution could be constructed for each mortar sample. The selected rotation rate of 0.2 rpm is sufficiently slow as not to cause any strain rate effect on the torque being measured [44].

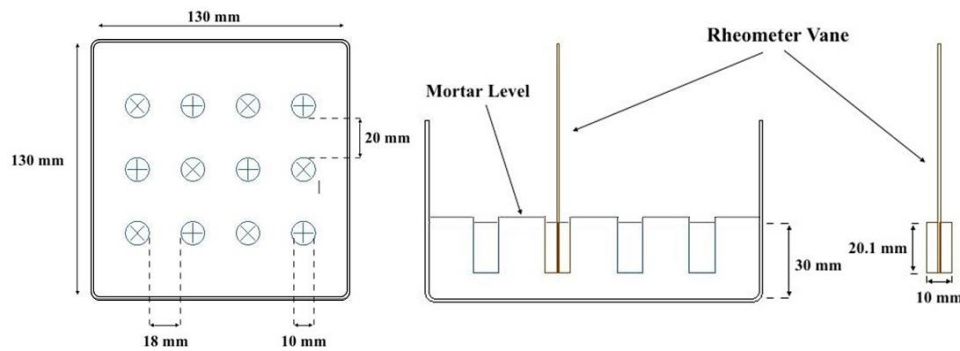


Figure 3.6. A schematic of the container, vane, and testing locations for yield stress measurements over time.

3.3.5 3D printing

To validate the theoretical framework proposed, concrete printed specimens have been prepared using a small 3D printer. The shape stability and buildability were investigated after printing consecutive layers. The laboratory-scale 3D printer consists

of three main parts: an extruder, an actuator, and a controller. The extruder was a commercial cordless electric cement mortar gun that provided 4500 Nm of force with a maximum extrusion speed of 2125 mm/min. The printer nozzle was designed with a square opening of 25 mm × 15 mm made of a 3D-printed Onyx material.

The actuator consists of an outer frame with a working area of 1000 mm × 1000 mm × 750 mm. The connection was carefully chosen to keep the robustness of the printer when the printer's extruder moves in various x, y or z axes. Supporting plates were accommodated on the actuator C-beams connection to damp the resonance induced by stepper motors and the inertia of the extruder due to the acceleration and deceleration. Two C-beams supported the z-axis of the machine to increase the height of the printing and increase the rigidity of the z-axis under the weight of the extruder.

The printer's primary component is a microcontroller unit (MCU). The high torque GRBL bundle, comprises a CNC Shield V3, four A4988 stepper drivers, and an Arduino UNO board, was selected as the microcontroller unit. This device has sufficient processing power and many input/output (I/O) pins for future expansion. Additionally, it supports GRBL firmware, which is rather simple to set up. Controlled by the integrated Arduino UNO compatible with GRBL, the GRBL controller, and universal G-Code sender makes it simple to use. A 12V power supply unit (PSU) with appropriate capacity is supplied for the MCU, as well as other electrical components such as fans and lights. Figure 3.7 shows the laboratory scale custom-made 3D printer, nozzle dimensions and the printing parameters. Printed samples were prepared by printing a minimum of three consecutive layers. Changes in filament dimension (filament height and width) at different rest times were measured. The shape stability and buildability properties of selected mixes were investigated considering the printing parameters which will be discussed in Section 3.4.

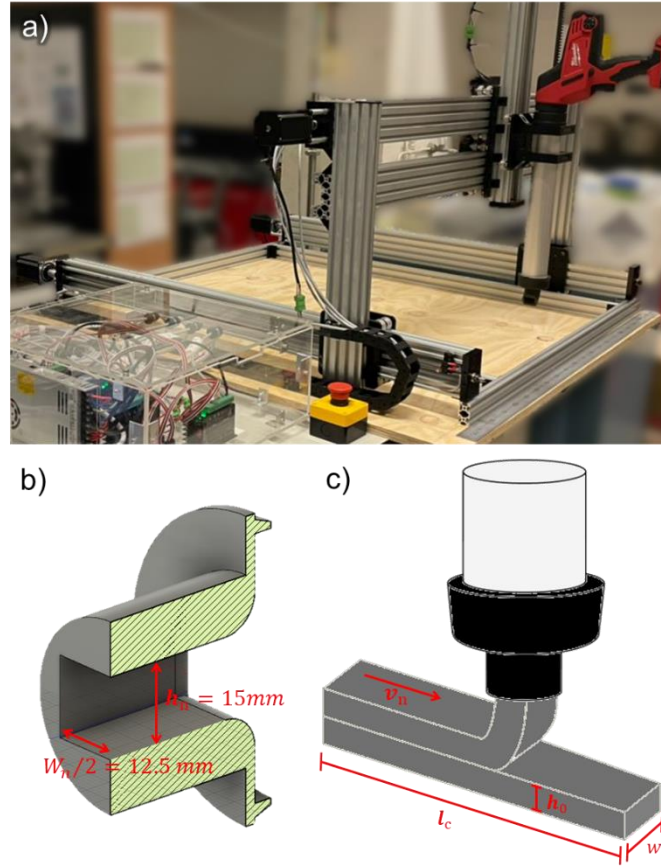


Figure 3.7. (a) Laboratory-scale 3D printer, (b) nozzle dimensions (W_n : nozzle width, h_n : nozzle height), (c) printing parameters and filament dimensions (v_n : printing speed, w : filament width, h_0 : filament height and l_c : filament length).

Shape stability evaluation

Extruded material must preserve its shape after printing. This can be assessed using a parameter termed the shape stability factor. As Tay et al. [45] mentioned in their research, the universal equation for shape stability ratio depends on the flow rate, printing speed and the nozzle dimensions variation. According to Tay et al. [45], this ratio is defined as:

$$SR = \frac{1000 \times Q}{S_n \times v_n} \text{ or } \frac{W \times h_0 \times l_c}{S_n \times v_n} \rightarrow SR = \frac{W \times h_0}{W_n \times h_n} \quad \text{Equation 3.4}$$

Where Q (ml/s), W (mm), h_0 (mm) and l_c (mm) are the printing mortar flow rate, width, height, and length of filament, respectively. The S_n (mm²) is the surface area of the nozzle's cross-section, and v_n (mm/s) is the printing speed. In this study, the surface area of the nozzle's cross-section was equal to $h_0 \times W = 375 \text{ mm}^2$, the flow rate and printing speed (800 mm/min) were considered constant, and a single layer with a length of 250 mm was printed to evaluate the shape stability of the printed specimen.

Therefore, Equation 3.4 is basically the simplified experimental measurement of the shape stability in this study. A filament was printed at different rest times, ranging from 7 minutes to 45 minutes. The filament's width and height were measured using an image processing software (ImageJ) to measure the printed specimen's average cross-section area. The average value obtained was divided by the ideal surface area (375 mm^2) of the filament (nozzle opening), resulting in the dimensionless parameter of shape stability.

The SR coefficient was used in previous studies to depict the shape stability of the printed filaments. However, changes in the height (W) and width (h_0) of the filament are inversely interconnected and such that (i.e. $W \geq W_n$ and $h_0 \leq h_n$) their multiplication in the SR equation might not completely reflect their influence on the shape stability. Therefore, another coefficient was also defined to determine the optimum shape stability besides the SR coefficient. Since the $0 \leq h_0 / h_n \leq 1.0$ and $0 \leq W_n / W \leq 1.0$ are correct equation, then the “Avg” coefficient which is defined as: Avg = average ($h_0 / h_n, W_n / W$) is also between 0 and 1.0. The lower “Avg” coefficient means inferior shape stability and the Avg = 1.0 is the perfect shape stability. To illustrate the shape stability of printed filament both coefficient values were plotted against resting time (t_{rest}).

Buildability evaluation

The average deformation in printed layers height was measured using an image processing software (ImageJ). Printing of three consecutive layers was conducted at three different time intervals based on chosen shape stability, buildability and extrudability limits: 1) immediately after crossing the shape stability limit, 2) in the middle of the open time, and 3) after exceeding the extrudability limits. It is illustrated that the optimised printing mixture with the shallowest buildability characteristics slope, which was designed to avoid crossing the buildability limit but to be as close as possible to the buildability limit's slope of predefined print job, follows its predicted trend of yield stress evolution. Moreover, it was shown that considering the interlayer printing gap time (20 minutes for the predefined print job in this study), the deformations in critical layers are negligible. It was shown that no deformation happens in critical layer when the yield stress evolution of a printing mixture stays within the print windows limits of the predefined print job.

3.4 RESULTS AND DISCUSSION

The first four test sequences investigated the effect of additives and water/cement ratio on the early age yield stress evolution. It was found that for the mortars that did not contain a retarder (i.e. tartaric acid), a linear to exponential yield stress evolution proposed by Perrot, et al. [19] fit the recorded data well. The equation that describes this evolution is shown below:

$$\tau_y(t) = A_{thix} \cdot t_c (e^{t_{rest}/t_c} - 1) + \tau_{y0} \quad \text{Equation 3.5}$$

In Equation 3.5, A_{thix} represents the initial linear structuration rate in Pa/min. After this initial period, the equation describes a transition to an exponential structuration rate where t_c is a characteristic time that should be chosen to obtain the best fit with experimental data [19]. The term t_{rest} is the time in minutes after the mortar has been mixed and the term τ_{y0} represents the initial yield stress (at $t_{rest} = 0$). For mortars containing tartaric acid, the yield stress evolution was best described with linear or bi-linear equations.

3.4.1 Effect of Water/Cement Ratio on Yield Stress Evolution

The density of fresh mortars varied between 2040 kg/m³ and 2100 kg/m³ for mixes with different W/C ratios. The effect of the water/cement ratio on yield stress evolution is presented in Figure 3.8. As might be expected, increasing the water content produces a mortar with higher initial fluidity, which results in lower initial yield stress values (taken as the intercept of the fitted curve with the y-axis). Increasing the water content also decreases the rate at which the yield stress increases. This effect can be observed in Figure 3.8, where mixtures with a higher water content are seen to have shallower yield stress evolution curves. Table 3.2 indicates the input parameters for Equation 3.5, which were used to fit curves to the experimental data. Decreasing W/C by approximately 20% resulted in a significant increase in the initial yield stress from 86.9 Pa for W₄₂SP₄₀ to 1300.3 Pa for W₃₆SP₄₀. Moreover, the initial linear structuration rate (A_{thix}) was tripled when the W/C increased by 20%.

Table 3.2. Parameters used to calculate best fit curves for water/cement ratio experimental data.

Mix Code	W/C	$\tau_{y,0}$ (Pa)	A^{thix} (Pa.min ⁻¹)	t_c (min)	R ²
W ₃₆ SP ₄₀	0.36	1300.3	17.5	74.4	0.998
W ₃₈ SP ₄₀	0.38	1095.3	7.9	54.3	0.994
W ₄₀ SP ₄₀	0.40	484.1	4.8	53.1	0.991
W ₄₂ SP ₄₀	0.42	86.9	5.4	63.8	0.991

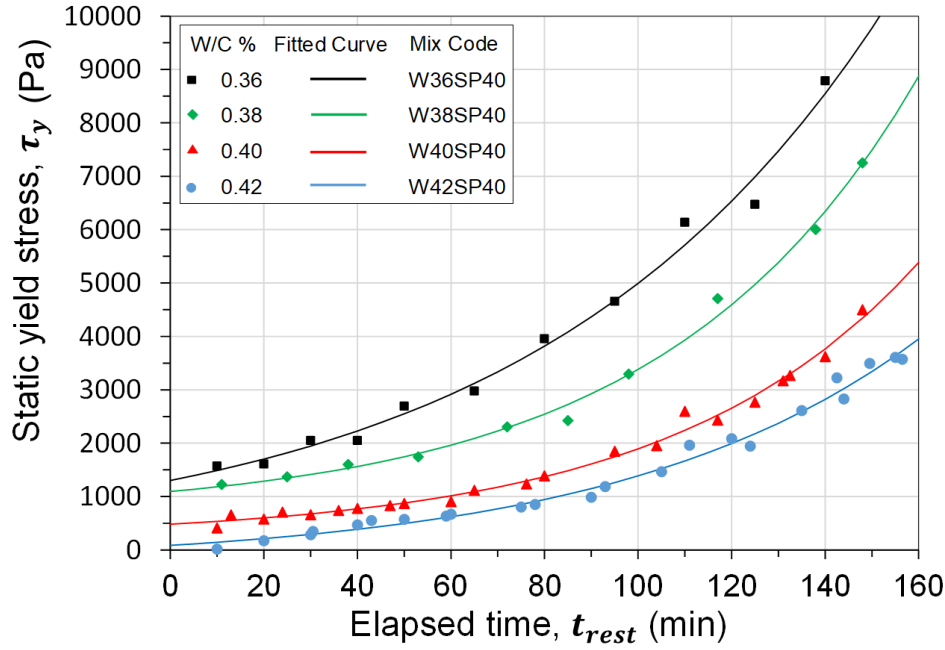


Figure 3.8. Effect of water/cement ratio on yield stress evolution.

Small changes to water/cement ratio can control yield stress evolution to improve mortar performance for 3D printing. For example, if the extruded filament layer height was 10 mm, then the mortar with a water/cement ratio of 0.42, W₄₂SP₄₀ in Figure 3.8, would not have sufficient initial yield stress for shape stability to be maintained since $(\tau_{y0} = 86.9 \text{ Pa}) < (\rho g h_0 = 203 \text{ Pa})$. However, decreasing the W/C ratio by 5.5% resulted in initial yield stress of 484.1 Pa for W₄₀SP₄₀, which can pass the shape stability limit for this specific print job. An average mortar density of 2070 kg/m³ is assumed for the calculations. If, for example, another printing job has a layer height of $h_0 = 20 \text{ mm}$ (considering that the other printing parameters are similar), then $\rho g h_0 = 406 \text{ Pa}$, and initial yield stress higher than this value would be sufficient for shape stability to be achieved. Therefore, W₄₂SP₄₀ would not be appropriate for the new printing job (unless a time gap of about 20 mins is allowed between mixing and print time), while W₄₀SP₄₀ with $\tau_{y,0} = 484.1 \text{ Pa}$ can be used to

start the printing immediately after the mixing. While making that adjustment would improve the mortar from a shape stability perspective, the effects on pumpability, buildability and open time must be taken into consideration. This will be discussed further in the upcoming sections. Also, it was found that a similar adjustment could be made by changing the superplasticiser amount.

3.4.2 Effect of Superplasticiser on Yield Stress Evolution

One of the main uses of superplasticiser is to increase the slump or fluidity of a mixture to make pumping or compaction easier without having to increase the water/binder ratio. As a result, it would be expected that the initial yield stress would be reduced if the superplasticiser proves to be effective [46]. The effect of the superplasticiser amount on yield stress evolution is presented in Figure 3.9. Similar to increasing the water/cement ratio, an increase in superplasticiser content also decreases the initial yield stress and the rate at which the yield stress evolves (structuration rate). Table 3.3 indicates the parameters used for the fitted curves.

The initial yield stress as a function of water/cement ratio showed a non-linear behaviour, while the initial yield stress as a function of the superplasticiser was linear over the tested range. Therefore, controlling the mixture yield stress development by changing the superplasticiser ratios can provide a more predictable outcome. A correlation was found between superplasticiser content and initial yield stress. The relationship is presented in Figure 3.10 and could potentially be used as a simple predictive model for adjusting the initial yield stress of a mortar in response to changes in printing parameters. In particular, it would be useful to use when changes to the layer height, h_0 , are required. It should be noted that the correlation found here is limited to the data gathered and further investigations are required to confirm that such a relationship holds when applied to different mortar mix designs.

Table 3.3. Parameters used to calculate best fit curves for superplasticiser experimental data.

Mix Code	SP/C (%)	$\tau_{y,0}$ (Pa)	A^{thix} (Pa.min ⁻¹)	t_c (min)	Δ_{cb} (Pa.min ⁻¹)	R ²
W ₄₀ SP ₂₀	0.20	1053.1	10.1	62.1	30.0	0.954
W ₄₀ SP ₃₀	0.30	674.7	8.8	71.3	24.5	0.988
W ₄₀ SP ₄₀	0.40	484.1	4.8	53.1	16.7	0.991
W ₄₀ SP ₅₀	0.50	235.4	2.4	45.8	8.9	0.985
W ₄₀ SP ₆₀	0.60	0.0	2.7	60.6	2.7	0.956

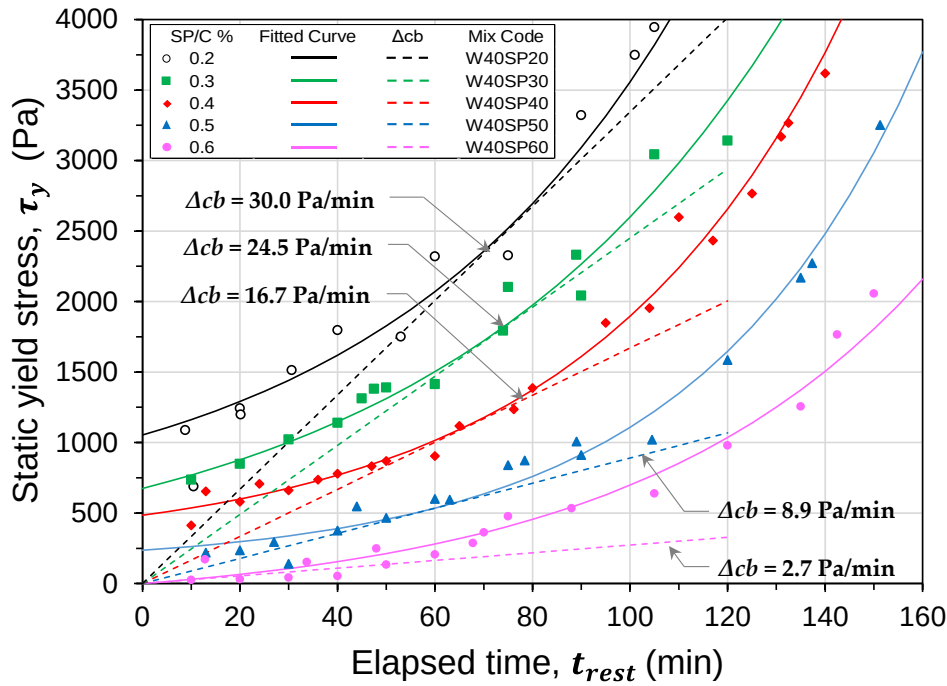


Figure 3.9. Effect of superplasticiser content on yield stress evolution.

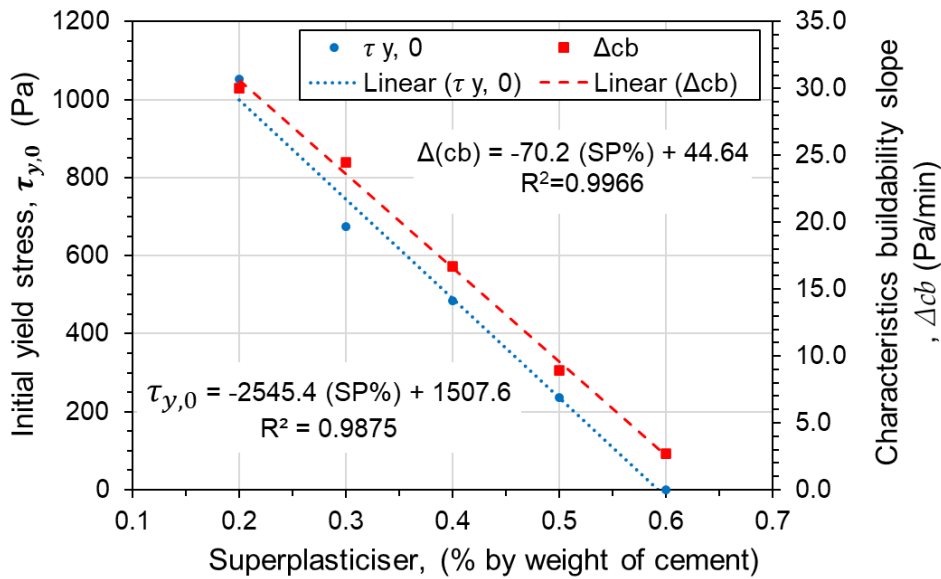


Figure 3.10. A linear correlation between initial yield stress and characteristic buildability slope (Δ_{cb}) with superplasticiser contents.

If the relationship shown in Figure 3.10 was used to adjust the initial yield stress of a mortar in response to a change in layer height, it would also affect the rate at which the yield stress evolves (see Figure 3.9). Furthermore, the new layer height would also mean that the vertical build rate changes (assuming the contour length and print head velocity remain the same). Changing the vertical build rate results in a change to the

buildability limit. As a result, it would be necessary to check whether the new structuration rate of the mortar is sufficient to avoid an intersection with the new buildability limit. To achieve this, it is convenient to have some way of measuring the structuration rate of the mortar. When the yield stress evolution of a mortar is linear, the rate of structuration can simply be taken from the slope of the yield stress development over time and is referred to as A_{thix} . However, quantifying the structuration rate of non-linear yield stress evolutions, as seen in Figures 3.8 and 3.9, is not straightforward.

In the context of the theory presented earlier, it is important that the condition in Equation 3.1 is satisfied for continuous printing to take place, which means that the yield stress evolution of a mortar should not intersect with the buildability limit. Therefore, one way to characterise the structuration of mortars with non-linear yield stress evolutions is to calculate the maximum slope of the buildability limit before it intersects with the line of yield stress evolution. This concept is presented in Figure 3.11 using W₄₀SP₄₀ as an example (and ignoring the time gap between mixing time and the start of the printing time). The maximum slope of the buildability limit that can be achieved is named '*characteristic buildability slope*' (Δ_{cb}). The slope of this line is also proportional to the maximum vertical build rate that can be achieved, $\dot{H}_{max}$, which still allows the condition in Equation 3.1 to be satisfied. The characteristic buildability slope can be defined by Equation 3.6. Since the characteristic buildability slope is proportional to the maximum vertical build rate that can be supported by a mortar, it is essentially a measure of its buildability.

$$\Delta_{cb} = \frac{\rho g \dot{H}_{max}}{\sqrt{3}} \quad (\text{Pa/min}) \quad \text{Equation 3.6}$$

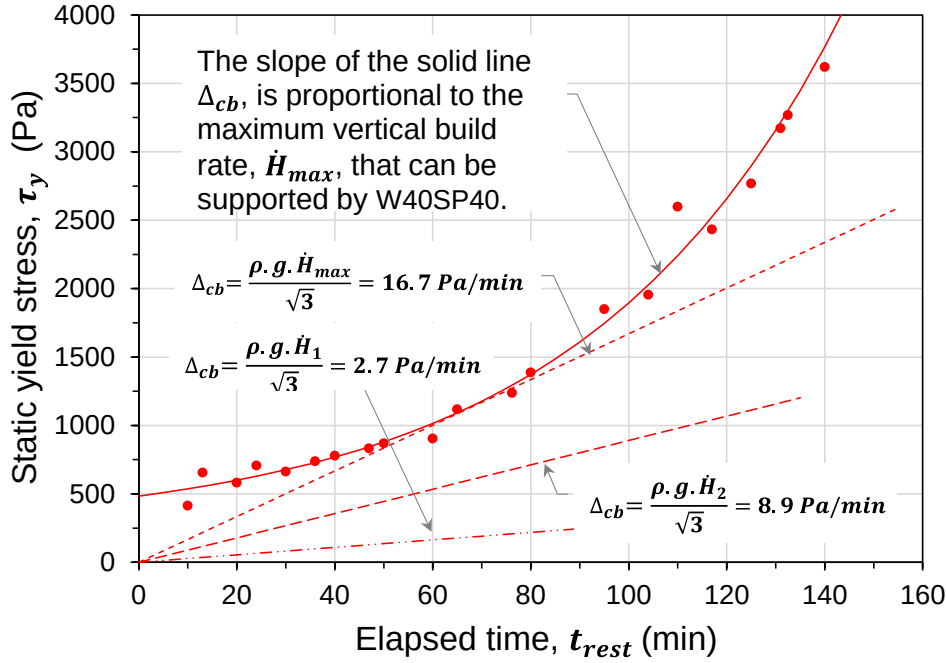


Figure 3.11. Illustration of the concept of characteristic buildability slope.

The characteristic buildability lines were constructed in Figure 3.9 such that the slope was increased until the line touched the best-fit curves of the experimental data. The slope of these lines has been plotted as a function of superplasticiser content and is shown in Figure 3.10, which can be sustained by a mortar (the buildability), is linearly related to the amount of superplasticiser in the mixture (assuming all other constituents are kept constant). Since there is a linear relationship between superplasticiser content and both initial yield stress and buildability, there should also be a linear relationship between initial yield stress and buildability.

Although changes in the initial yield stress and buildability occur simultaneously with changes in the amount of superplasticiser, it can be shown that their respective changes are generally supportive of each other in the context of the print window theory. For example, if a new print job requirement was simply an increase in layer height, then the relationship in Figure 3.10 could be used to calculate the required superplasticiser content for shape stability to be maintained (a decrease in superplasticiser will be expected). Since the layer height is now larger, the vertical build rate will also be increased, resulting in a steeper buildability limit. Therefore, the structuration rate, or Δ_{cb} , should also be increased. This requirement is supported by the initial decrease in superplasticiser, which was in response to the changed layer height (see Figure 3.10). While these changes generally support each other, gaining a

higher degree of control may be necessary for full optimisation. The next sections illustrate how this might be achieved.

3.4.3 Effect of Accelerator Content on Yield Stress Evolution

The effect of varying the accelerator contents from zero to 1.5% of cement weight on the yield stress development was investigated, and the results are shown in Figure 3.12. The mix without accelerator was W₄₀SP₅₀. Table 3.4 indicates the parameters used for the curves fitted to the measured data. The characteristic buildability slopes for each mixture are also presented in Figure 3.12.

Increased amounts of accelerator results in increased structuration rates which correspond to the increased buildability. This is not unexpected since the purpose of accelerating agents is to impart higher rate of early strength development. Unlike changes to the water/cement ratio and superplasticiser amount, the initial yield stress is not significantly impacted by changes in accelerator content. A small reduction was observed in mixes containing accelerator compared to the control up to 0.75 wt.% of cement. However, at 1.5 wt.% of accelerator, the yield stress dropped significantly which might be because of initial dilution effect due to additional water content of accelerator. Regardless, the yield stress development at this high percentage of the accelerator is very quick, offsetting the small initial yield stress. The characteristic buildability slopes also show a linear relationship with the accelerator contents, as shown in Figure 3.13.

Table 3.4. Parameters used to calculate best fit curves for accelerator experimental data.

Mix Code	Acc/C %	$\tau_{y,0}$ (Pa)	A^{thix} (Pa.min ⁻¹)	t_c (min)	Δ_{cb} (Pa.min ⁻¹)	R ²
W ₄₀ SP ₅₀	0.00	235.4	2.4	45.8	8.9	0.985
W ₄₀ SP ₅₀ A ₂₅	0.25	134.7	4.9	56.9	10.4	0.992
W ₄₀ SP ₅₀ A ₅₀	0.50	126.2	7.5	66.5	13.4	0.984
W ₄₀ SP ₅₀ A ₇₅	0.75	201.4	8.3	59.0	16.7	0.995
W ₄₀ SP ₅₀ A ₁₅₀	1.50	70.0	21.3	100.8	27.0	0.961

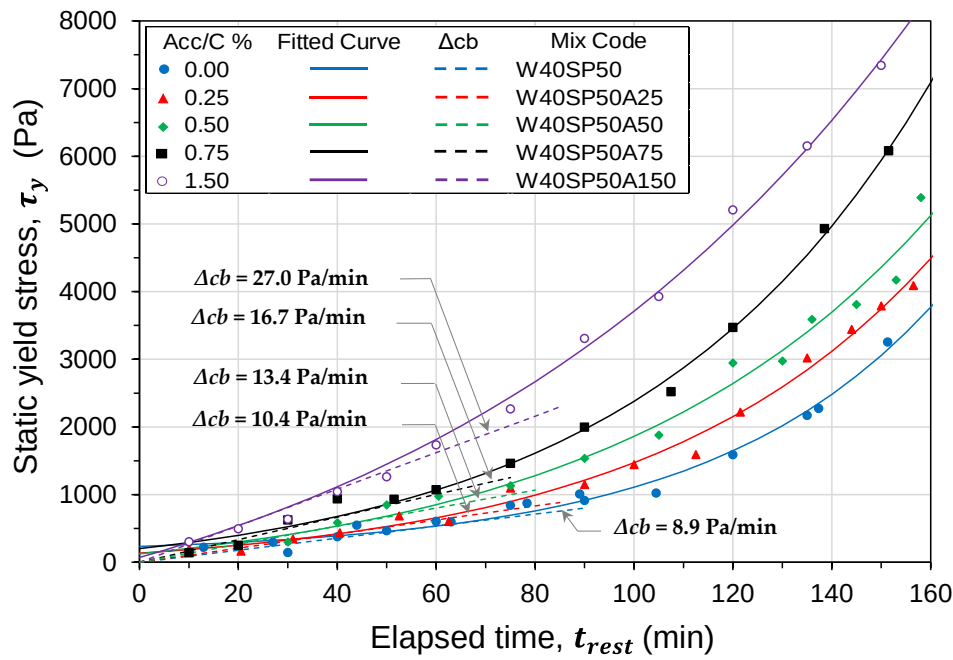


Figure 3.12. Effect of accelerator on yield stress evolution and corresponding characteristic buildability slopes.

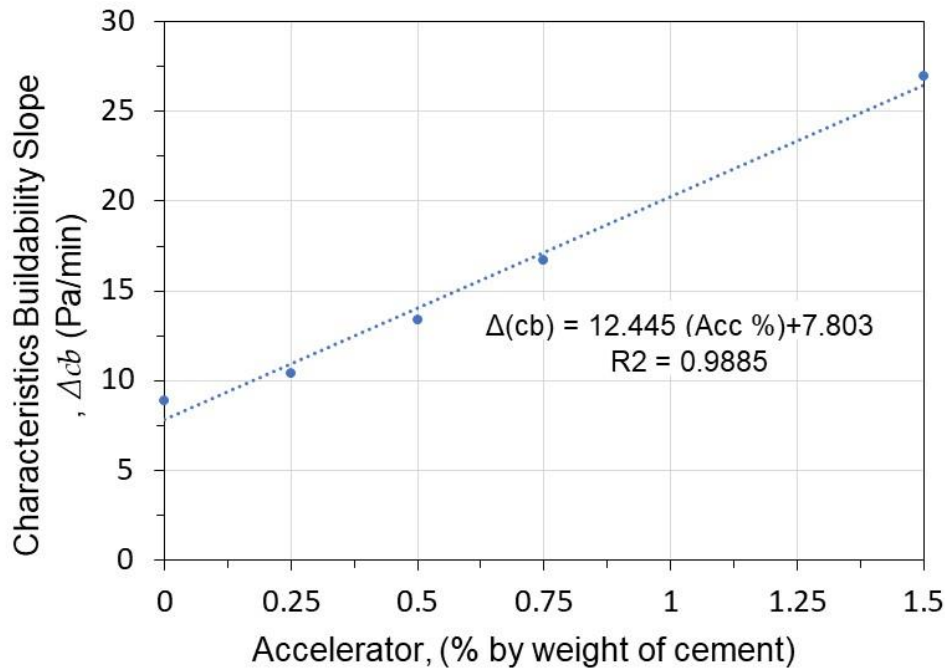


Figure 3.13. A linear correlation found between accelerator and characteristic buildability slope.

The results in Figure 3.12 and Figure 3.13 indicate that changes to accelerator content could be used to improve mortar performance where a change in the structuration rate is required. For instance, if the vertical build rate of a printing job is to be increased by either shortening the contour length or increasing the print head speed, the structuration rate (buildability) of the mortar should also be increased, otherwise a strength-based collapse may occur during printing. If the increased vertical

build rate was due to a shortening of the contour length, another option is to slow down the print speed and extrusion rate, allowing more time for the mortar to develop strength in relation to the vertical construction rate. However, a longer gap time between successive layers may cause cold joints (i.e. reduced adhesion between layers) [30,37,47], so changing the mortar structuration rate to match the new vertical build rate by using accelerators may be a better option in this situation. Because of this fact, in-line addition of accelerators at the print head has been utilised for most commercial 3D printers which work at relatively high speed. In this case, higher buildability can be achieved at higher percentage of accelerators without compromising pumpability and extrudability of the mix because the mixing and extrusion with the accelerator happen at a fraction of minute at the printhead.

3.4.4 Effect of Retarder Content (Tartaric Acid) on Yield Stress Evolution

The effect of tartaric acid varying between 0 % and 0.3%. of cement weight on yield stress evolution is presented in Figure 3.14. The control mix for these series was W₄₀SP₄₀. Mortars containing tartaric acid displayed different yield stress evolution behaviour. The results showed linear, and bi-linear approximated evolutions in these samples compared to the linear-exponential evolutions displayed by samples without tartaric acid and with other additives.

W₄₀SP₄₀R₃₀, which contains 0.30% tartaric acid, resulted in a significantly retarded structuration rate compared to the control sample, W₄₀SP₄₀, which contained no tartaric acid. At 120 minutes, W₄₀SP₄₀R₃₀ developed a yield stress of 582.6 Pa which is less than one-quarter of the yield stress of W₄₀SP₄₀. Adding tartaric acid amounts higher than 0.3 % had little effect in retarding the mix further, which suggests this may be the upper limit for effective tartaric acid addition (at least in this mortar system). As can be seen in Figure 3.14, W₄₀SP₄₀R₂₅ displays a similar buildability to the control mix (W₄₀SP₄₀) but has a linear evolution over the measured range. The buildability of W₄₀SP₄₀R₂₅ is measured by the characteristic buildability slope and the buildability of W₄₀SP₄₀ is taken as the slope of the linear evolution, A_{thix} . In this way, the tangent line of W₄₀SP₄₀ and linear line-of-best-fit for W₄₀SP₄₀R₂₅ would have similar slopes (and can thereby support similar maximum vertical build rates). After about 80 minutes, the structuration rate of W₄₀SP₄₀ and W₄₀SP₄₀R₂₅ diverge, with the former increasing exponentially and the latter continuing in a linear fashion over the

tested range. Therefore, a retardation effect on the mix containing tartaric acid is observed during that time frame.

Figure 3.14 also indicates that lower inclusion rates of tartaric acid result in accelerated structuration as opposed to a retarding effect. This is because tartaric acid acts as a chelating agent, which means it can bind to and remove certain ions from solution. At low concentrations, tartaric acid binds to the calcium ions in the cement, making them more available for hydration reactions. At higher concentrations, however, tartaric acid can inhibit the hydration reactions by binding to too many ions, reducing the availability of calcium ions for hydration. At 80 minutes after mixing, the sample containing 0.20% tartaric acid, W₄₀SP₄₀R₂₀, shows a yield stress of about 50% higher than the control (W₄₀SP₄₀). Similarly, W₄₀SP₄₀R₁₅, which contains 0.15% tartaric acid, displays a yield stress of more than 220% higher. These observations suggest that the mortar system is sensitive to small changes in the amount of tartaric acid used. From a material efficiency point of view, it is interesting to observe that a smaller amount of tartaric acid results in a more accelerated structuration over the time frame analysed.

The mixes containing tartaric acid presented in Figure 3.14 display an initial period of linear structuration, which are represented by the solid lines-of-best-fit. The equation of these lines and R² values are also presented in Figure 3.14. The slope of these lines (i.e. the rate of structuration or A_{thix}), was plotted as a function of the tartaric acid amount, and the results are shown in Figure 3.15.

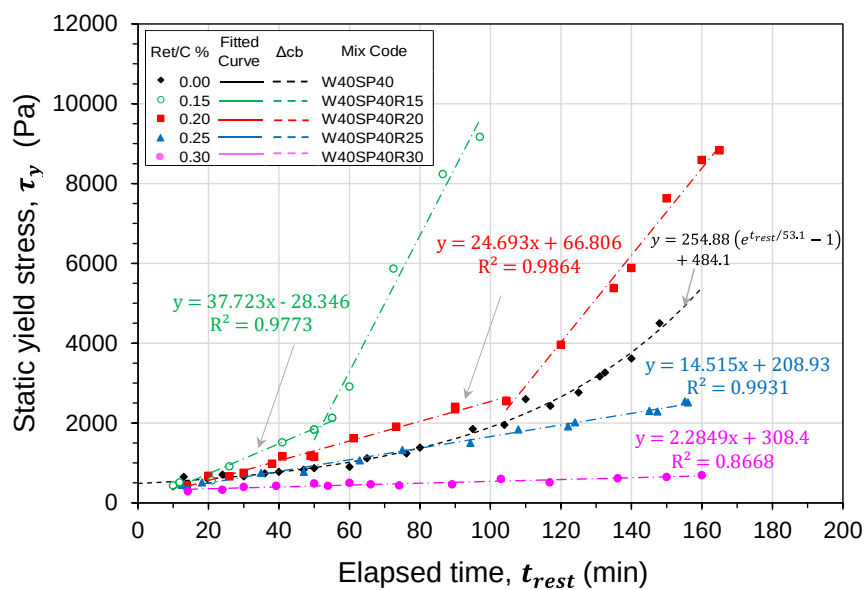


Figure 3.14. The effect of tartaric acid on mortar yield stress evolution.

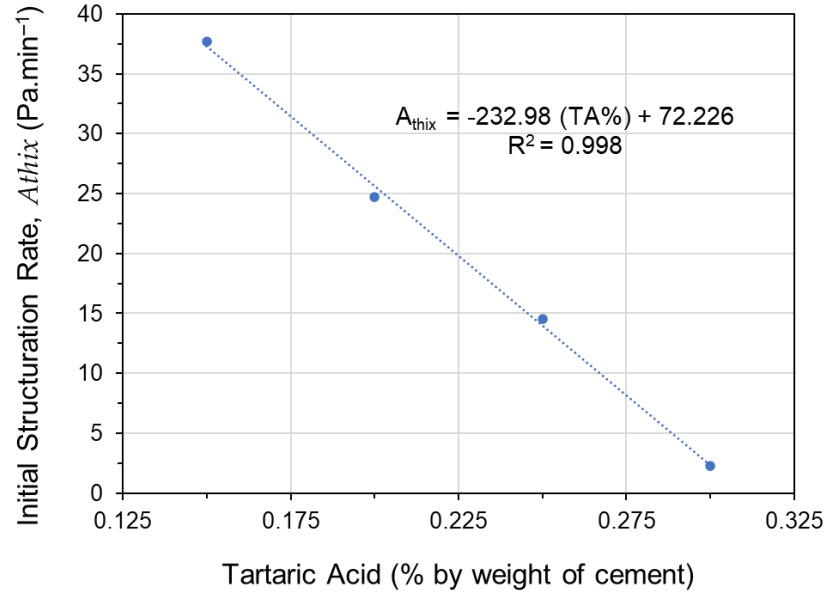


Figure 3.15. A linear correlation between tartaric acid contents and structuration rate over the observed range.

Although a linear correlation was observed between tartaric acid content and initial structuration rate over the presented range, this relationship did break down outside of these boundaries. Adding tartaric acid amounts higher than 0.3 % had little effect in retarding the mix further, which suggests this may be the upper limit for effective tartaric acid addition (at least in this mortar system). At the other end, a mixture containing 0.1 % tartaric acid was tested, and it displayed a very quick initial structuration, but soon after, it appeared to be stagnating. However, the range of structuration rates in which a linear correlation was found to tartaric acid content is quite broad (2.3 – 37.7 Pa/min). Therefore, this relationship could prove to be a useful tool when a specific rate of structuration is required i.e. responding to changes in vertical build rates in 3D printing applications.

3.4.5 Verification of the predictive model by small-scale 3D printing

A printing speed of 800 mm/min with a rectangular nozzle size of 25 mm × 15 mm, a printing contour length of 16 m (a room with 4 m × 4 m walls), and a gap time of 20 minutes between layers were assumed for the print job.

The main aim of this research was to understand whether modifying mixture design could be used for the 3D printing process optimisation of various printing jobs. This section adopted two approaches to verify the presented predictive model. Firstly, tartaric acid experimental results were used to determine how the predictive model could be implemented for mortar optimisation purposes. To achieve this, the proposed

predictive model using the experimental results was implemented on the base mortar W₄₀SP₄₀, which had an open time of 60 minutes (considering the predefined print job), and the mixture was modified (W₄₀SP₄₀R₂₇) to stay longer (70 min) within the print window limits of the predefined printing job.

In the second approach, the effect of mixture optimisation on shape stability and buildability properties of the printed specimens were evaluated against the concept of print window theory and characteristic buildability slope (Δ_{cb}). The 3D printer was used to print samples from superplasticiser experimental results (Figure 3.9) using the printing parameters defined above.

A predictive model for mortar optimisation using tartaric acid

As mentioned before, the vertical build rate of a print job can be calculated prior to the beginning of printing and this value determines the buildability limit (see Equations 3.2 and 3.3). In turn, the buildability limit determines some minimum structuration rate that the mortar must display in order for continuous printing to take place without structural collapse. One way of determining the optimal structuration rate is to simply match it to the buildability rate (or slope of the buildability limit). However, as will be shown later, some factors of safety may also need to be considered to ensure $\tau_c(t) > \rho g \dot{H} t / \sqrt{3}$ for the entire build time. Since samples with tartaric acid display a predictable, linear structuration rate (at least for some initial period), the process of optimising the yield stress evolution for printing purposes could potentially be more straightforward. An example of how optimisation of this type could be carried out is presented below.

From the filaments height and considering that the difference in the density of mixes with varying superplasticiser to cement ratios was negligible ($\rho_{avg} = 2070 \text{ kg/m}^3$) the shape stability limit was calculated.

$$SL = \rho g h_0 = 2070 \times 9.81 \times 0.015 = 304.6 \text{ Pa}$$

From the contour length and print speed, the time to print one layer of the structure is 20 minutes. From these results, it is possible to calculate the vertical build rate as follows:

$$\dot{H} = 0.015 / 20 = 0.00075 \text{ m/min}$$

From Equation 3.3, it is also possible to calculate the buildability limit as follows:

$$BL = \frac{2070 \times 9.81 \times 0.00075}{\sqrt{3}} t \approx 8.8 t$$

Therefore, the slope of the buildability limit will be 8.8 Pa/min. The 3D printing limits can now be plotted and are presented in Figure 3.16 and Figure 3.17. Table 3.5 summarises the calculations of the printing parameters and limits.

Table 3.5. Printing parameters and limits calculations for a defined printing job.

Printing parameters and constants			Printing limits calculations			
Average density of mixes with varying SP/C ratios*	ρ (kg/m ³)	2070	Shape stability limit	$\rho g h_0$	(Pa)	304.6
Filament height (Nozzle height)	h_0 (m)	0.015	Vertical build rate	Equation (3.2)	(m/min)	0.00075
Printing speed	v_n (m/min)	0.8	Buildability limit constant	Equation (3.3)	(Pa/min)	8.793
Contour length	l_c (m)	16	Extrudability Limit		(Pa)	1000
Gravitational acceleration	g (m/s ²)	9.81				

* The difference in the density of mixes with varying SP/C ratios was negligible.

Since the results from Figure 3.14 indicate that the structuration of a mortar with tartaric acid will be initially linear, the yield stress as a function of time will take the form $\tau_y(t) = A_{thix} \cdot t + \tau_{y0}$. It is also expected that there will be a non-zero initial yield stress τ_{y0} . This should provide some separation between the yield stress development and the buildability limit (factor of safety). Therefore, a desirable A_{thix} can simply be taken as 8.8 Pa/min, matching the slope of the buildability limit.

Using the equation of the line presented in Figure 3.15 (Equation 3.7) it is possible to calculate the required tartaric acid content to achieve the structuration rate of 8.8 Pa/min.

$$A_{thix} = -232.98 \cdot TA_{\%} + 72.226 \Rightarrow TA_{\%} = 0.272 \text{ \%wt.} \quad \text{Equation 3.7}$$

To demonstrate how the relationship in Figure 3.15 can be implemented, a mortar was mixed (W₄₀SP₄₀R₂₇ from Table 3.1) using the same formulation as others containing tartaric acid but with 0.27 % tartaric acid by weight of cement (as calculated above). According to Figure 3.15, this should result in the mortar having an initial structuration rate of $A_{thix} = 8.8 \text{ Pa/min}$. Figure 3.16 shows the yield stress evolution of W₄₀SP₄₀R₂₇ alongside the buildability limit and shape stability limit of the job. It will be further shown in Section 3.4.5.20 that after 120 min, disruptions and loss of extrudability occurred. Therefore, a pumpability limit of 1000 Pa was also included to illustrate a completed print window.

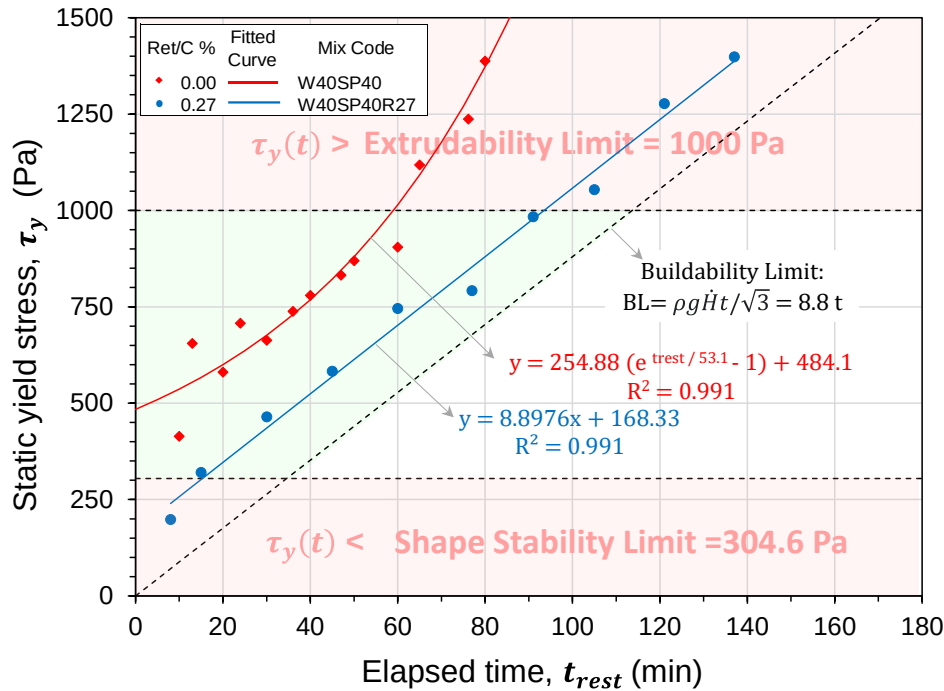


Figure 3.16. Yield stress evolution of W₄₀SP₄₀R₂₇ and 3D printing limits calculated based on parameters for the defined print job.

As shown in Figure 3.16, the line-of-best-fit for W₄₀SP₄₀R₂₇ yield stress measurements indicates a slope of 8.9 Pa/min, which is very close to the targeted 8.8 Pa/min. In this case, the relationship determined in Figure 3.15 and presented in Equation 3.6 was used accurately as a predictive model. Based on the “print window” theory, W₄₀SP₄₀R₂₇ would be quite suitable for the print project outlined in the example. As is required by the theory, the printing can start when the initial yield stress is just above the shape stability limit. Since the equation states an initial yield stress requirement of 304.6 Pa, for the optimised mix with tartaric acid the printing

technically need to be started after about 15 minutes. Also, since the slope of the linear rate of structuration of $W_{40}SP_{40}R_{27}$ is greater than that of the buildability limit, the lines are not expected to intersect, in which case strength-based failure in the lower layers should be avoided. Lastly, the open time is around 95 minutes, which is close to the theoretical maximum of approximately 115 minutes (based on a pumpability limit of 1000 Pa).

Shape stability and buildability evaluation

The appropriate structuration rate could well be estimated by simply comparing it to the buildability rate (i.e. slope of the buildability limit). In other words, the buildability limits determine the lowest structuration rate a mortar must obtain to avoid strength-based plastic collapse failure. The previous section showed that an optimised mixture could be obtained using its predictable structuration rate (linear behaviour for tartaric acid). A similar optimisation process can be applied to optimise the yield stress evolution of a printing mixture that displays non-linear structuration behaviour, e.g., mortars with superplasticisers. Based on this, $W_{40}SP_{30}$ and $W_{40}SP_{50}$ can be considered examples of mixes with adjusted superplasticiser with higher and lower structuration rates compared to $W_{40}SP_{40}$. Figure 3.17 shows that all three mixes displayed a greater structuration rate than the buildability limit based on the defined printing job here (i.e. 8.8 Pa/min). Therefore, these mixes theoretically comply with the requirement of buildability because their yield stress evolution curves are above the buildability limit. However, the initial yield stress of $W_{40}SP_{50}$ was predicted to be lower than the shape stability limit (for the first 22 minutes), meaning that the mortar would not be printable immediately after mixing. Moreover, since the $W_{40}SP_{50}$ had the shallowest buildability characteristics slope (8.9 Pa/min), which is almost equal to the slope of the buildability limit (8.8 Pa/min), the buildability of $W_{40}SP_{50}$ must be tested, specifically when its yield stress evolution curve became almost tangent to the buildability limits (at around 60 minutes). Considering that the characteristic buildability slopes of $W_{40}SP_{30}$ and $W_{40}SP_{40}$ are steeper than that of $W_{40}SP_{50}$, if $W_{40}SP_{50}$ shows appropriate buildability properties, then it can be concluded that the other mixes also meet the requirements for buildability within the limits of the defined print job.

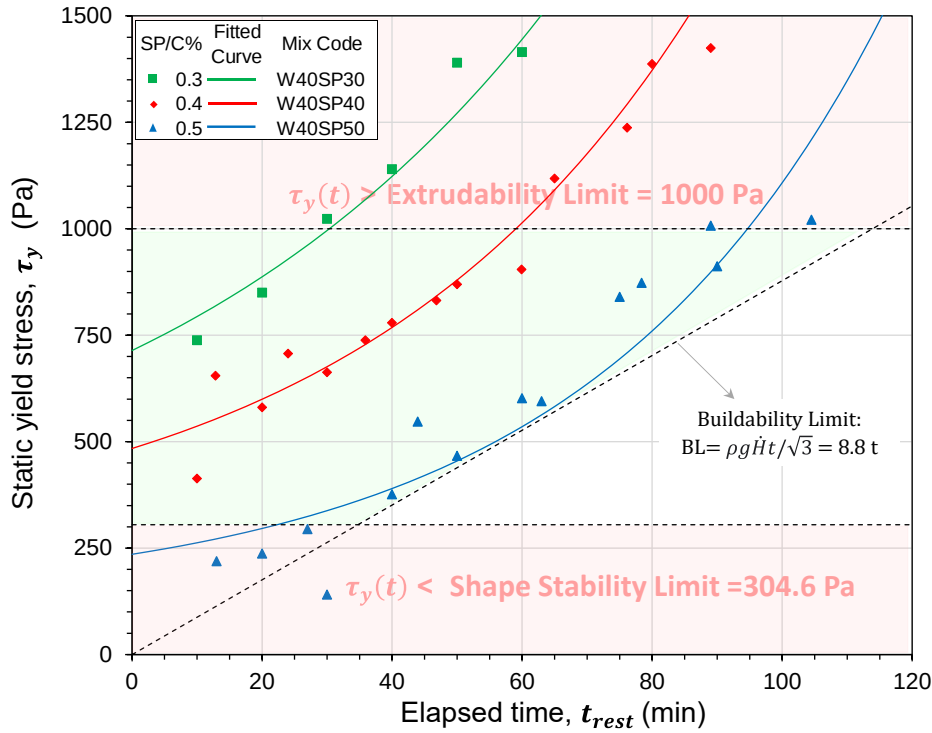


Figure 3.17. Yield stress evolution of W₄₀SP₃₀, W₄₀SP₄₀, W₄₀SP₅₀. 3D printing limits calculated based on parameters for the defined print job.

The capacity of a printing mortar at fresh state to withstand deformation induced by the extrusion pressure, the deposited layer's self-weight, and the weight of the subsequent layers to be deposited on top is a pivotal property for the 3D printing mortars, best described as its shape stability and buildability. By depositing a layer on top of another layer, the stress in underlying layers increases by an amount equal to ρgh_0 . While the stress level in the layers may remain below the yield stress and no flow occurs, the amount of strain in the layer may compromise control of the printed specimen's finished geometry. This demonstrates the critical significance of laboratory testing of printing concrete's shape stability and buildability at the mixture design stage.

A rectangular nozzle opening (compared to conical design) was selected as the printing nozzle. According to the Roussel research [41], this results in a laminar flow and avoids materials shearing in the nozzle. Therefore, printing mortar leave the nozzle as a rigid continuous filament that is almost unsheared. Due to the fact that the deposited material was not sheared in the nozzle, deposited layers are already flocculated and exhibiting a yield stress after deposition.

In this study, a shape stability parameter (SR) was defined as the ratio of the printed filament cross-section area to that of the nozzle to evaluate the shape retention

capacity of a printing mortar. Moreover, the average value of filament height and width divided by nozzle height and width, respectively, was another shape stability coefficient. For both values, the optimal shape stability is defined when this ratio becomes equal to 1.0. Figure 3.18 (a) shows the shape stability ratios and changes in the filament dimension of $W_{40}SP_{50}$. As can be seen, the SR gradually decreased (Avg increased) with the increase of rest time and reached its optimal value after about 30 minutes. Moreover, from Figure 3.18 (a), it is evident that as the resting time increases the changes in width of the printed filament is greater than its height.

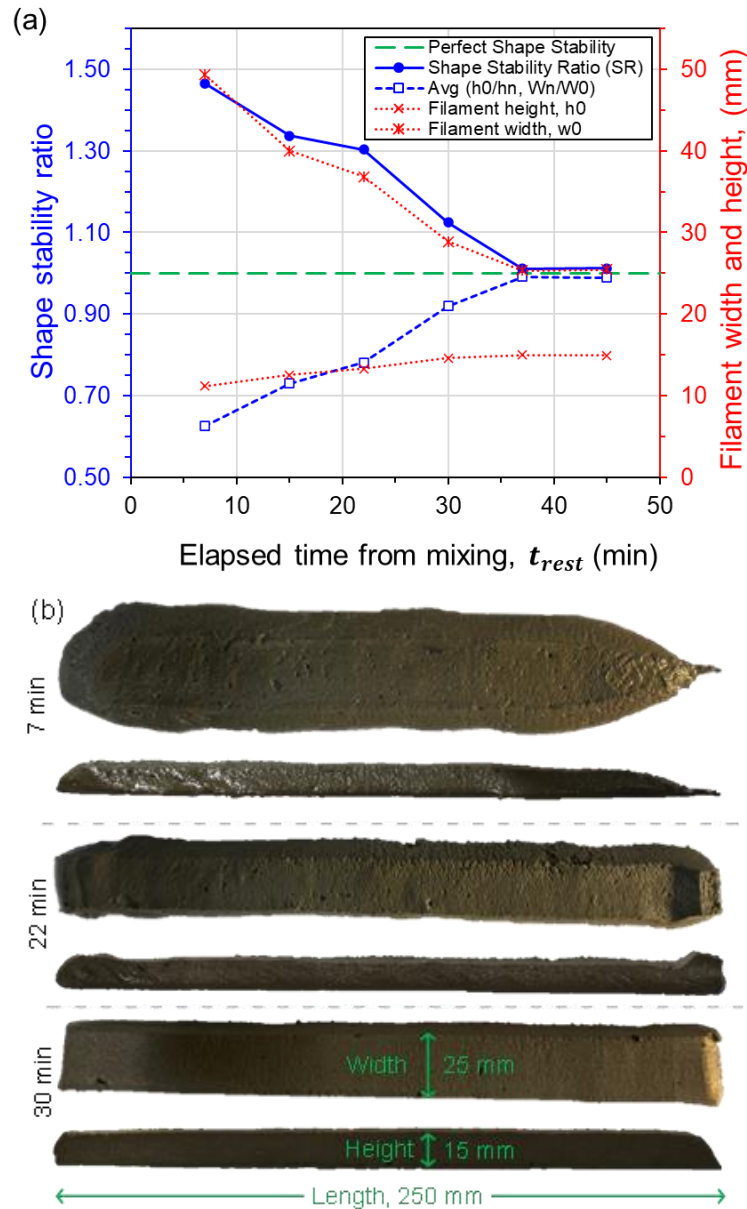


Figure 3.18. (a) Shape stability ratio and (b) changes in filament dimensions of $W_{40}SP_{50}$, at different rest times.

The highest SR value (the lowest shape stability) of 1.45 is associated with the time 7 minutes, which is equal to when the mixing is finished. This phenomenon is because immediately after mixing, sufficiently large inter-particle force and chemical connections (flocculating structure) are not formed to prevent deformation in the printed layer [39]. Moreover, a higher superplasticiser to binder ratio in the mix design increases the flocculating structure's collapse [48]. Therefore, the mortar did not have enough time to build up the strength to resist deformation caused by its self-weight and the shearing from the extrusion pressure. However, as the rest time increases, the coagulation of cement particles increases resulting in appropriate resistance to breakdown of internal structure and consequently better shape stability and buildability. As soon as the $W_{40}SP_{50}$ pass the shape stability limit of 304.6 Pa after about 22 min, it can be seen that the printed filament was able to maintain the nozzles' dimensions and the width and height tended to converge to the ideal values of 25 mm and 15 mm, respectively. Therefore, the SR started to decrease (Avg started to increase) rapidly and converged to the optimal value of 1.0 after 22 minutes from the start of the mixing process. As it is shown in Figure 3.18 (b), the ideal shape stability obtained after about 30 minutes when the SR became smaller than 1.1. In support of this, it has been shown in [45] that the SR of filaments with the best printing quality, in which the filaments have no breaks and cracks, was within the range of 1.0 to 1.4.

The average deformation in the thickness of printed layers was measured to show the buildability of $W_{40}SP_{50}$ for 3D printing. Three consecutive layers were printed at different rest times of 1) immediately after crossing the shape stability limit (30 minutes), 2) in the middle of the open time (60 minutes), and 3) after exceeding the extrusion limits (120 minutes). It is noteworthy that even though the interlayer printing gap time of the predefined print job was 20 minutes, to evaluate the buildability of $W_{40}SP_{50}$, no interlayer printing gap time was considered between $L_1 - L_2$ and $L_2 - L_3$ at each of the measurements rest time (30 min, 60 min and 120 min) mentioned above. Although this was more realistic to consider the interlayer printing gap time, this was done to make the changes in dimension of the printed layers more visible. Moreover, testing was conducted at different t_{rest} , which can cover this difference in the performance of the experiments. A batch of $W_{40}SP_{50}$ mortar was prepared and poured into three containers to spend their resting time. The first container was used to load

the extruder after 30 min of rest, and the second and third containers after 60 min and 120 min.

Figure 3.19 shows the buildability evaluation of $W_{40}SP_{50}$ at $t_{rest} = 30$ minutes from the start of mixing. As can be seen, the first deposited layer (L_1) maintained its dimensions after deposition (acceptable shape stability) and had an average height of 15 mm. Figure 3.19 (b), shows the printing of the second layer (L_2) immediately after the printing of L_1 (interlayer printing gap time = 0 minutes). As can be seen, the L_1 experienced a 20% reduction in its height, while no deformation was observed in L_2 . By printing the L_3 on top of L_1 and L_2 , height reduction in L_1 increased to 33% while L_2 squeezed by 20%. This was consistent with the results on the yield stress evolution of $W_{40}SP_{50}$ shown in Figure 3.17. At $t_{rest} = 30$ minutes, $W_{40}SP_{50}$ developed approximately 350 Pa yield strength and has just passed the shape stability limit. Therefore, the mortar only developed enough strength to resist deformation caused by its own weight and not the weight of subsequent layers. Thus, printing subsequent layers resulted in large deformation (strength-based failure) in the critical layer.

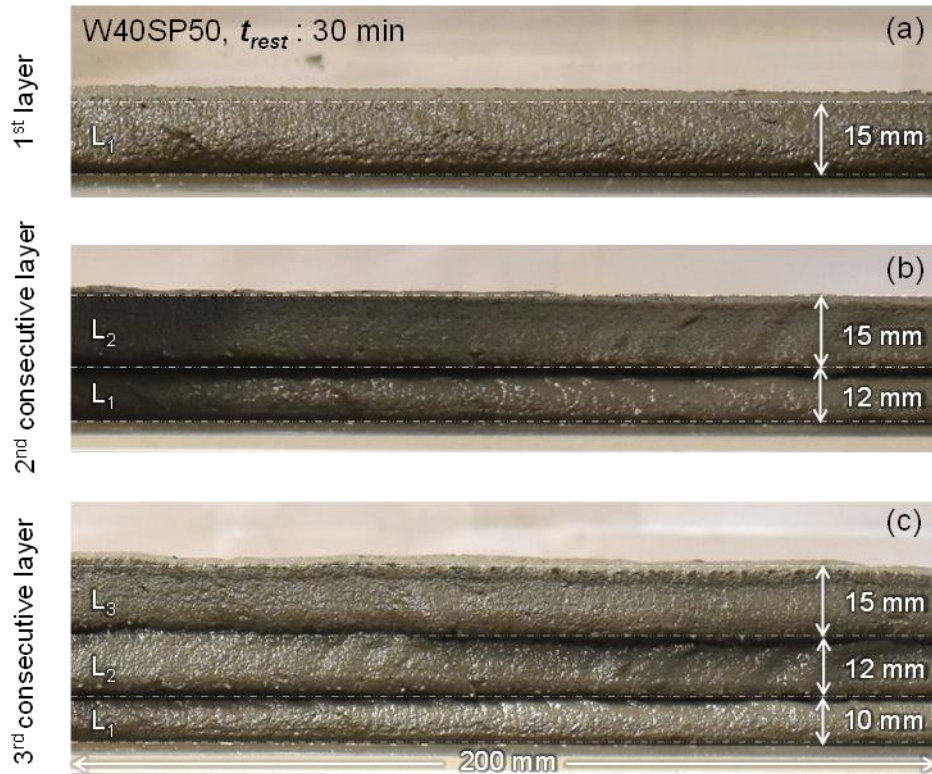


Figure 3.19. Buildability evaluation of $W_{40}SP_{50}$ at printing time of $t_{rest} = 30$ min, (a) appropriate shape stability of 1st layer, (b) deformation of 1st layer (no buildability) under the weight of 2nd layer (c) failure of 1st layer (no buildability) after printing of the three consecutive layer.

Figure 3.20 represent the deformation test results of printing layers at $t_{rest} = 60$ minutes. As can be seen, the filament's height increased to 15.1 mm. This is due to the fact that the material's flow through the nozzle is slightly greater than the printing speed resulting in a slight increase in the filament height. At $t_{rest} = 60$ minutes, the loading stress from L_2 acting on the bottom layer (L_1) resulted in a 0.6% reduction in the height. When L_3 was printed, no further deformation was observed in L_1 height while L_2 experienced similar amount of decrease in the height. These results illustrated that the optimised printing mixture with the shallowest buildability characteristics slope, designed to avoid crossing the buildability limit but to be almost tangent to the buildability limit's slope of the predefined print job, followed its predicted trend of yield stress evolution and showed acceptable buildability properties. This can also be derived that by simulating the predefined print job in which the printing interval time is 20 minutes, $W_{40}SP_{50}$ can gain large enough yield stress to resist deformation caused by subsequent layer deposition.

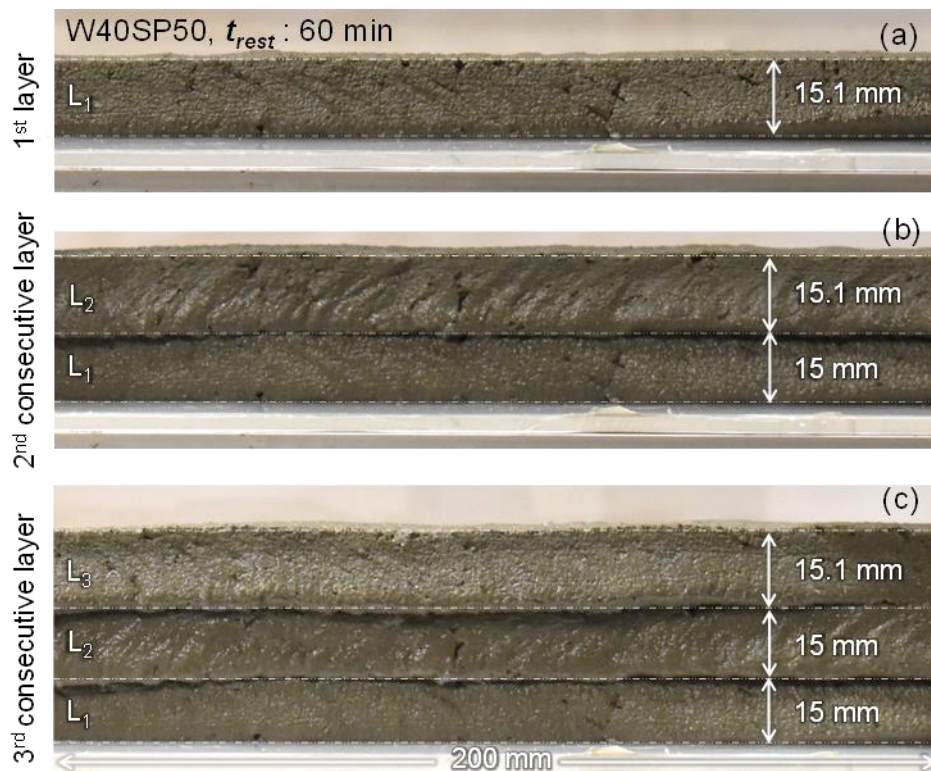


Figure 3.20. Appropriate shape stability and buildability of $W_{40}SP_{50}$ after printing three consecutive layers at $t_{rest} = 60$ min.

The yield stress value above which pumpability or extrudability begins to deteriorate is significantly relying on the pumping/extrusion technology utilised. As seen in Figure 3.21, extrusion of $W_{40}SP_{50}$ at an advanced stage, beyond the

extrudability limit, resulted in disrupted filament and loss of extrudability. Although excessive stiffness of mixture could result in discontinuities in the extruded filament, the loss of extrudability in this research is mostly associated with the limitation imposed by the pump type and its maximum capacity.

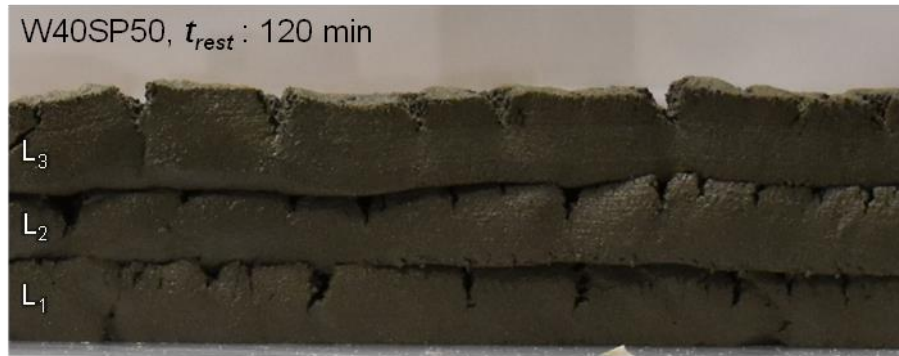


Figure 3.21. Disruption and loss of extrudability of W₄₀SP₅₀ at $t_{rest} = 120$ min.

3.5 CONCLUSIONS

The following conclusions have been drawn from the theoretical and experimental research carried out.

- A theoretical framework based on rheological limits was proposed to optimise mortar formulations for 3D printing applications. The theory suggested that controlling the yield stress evolution could be used as a tool for printing optimisation.
- The rheological limits are based on relating shape stability, pumpability and buildability to yield stress evolution. An optimal yield stress evolution must avoid the above limits while also maximising open time.
- A method of assessing the buildability of a mortar with an exponential structuration rate was proposed.
- The effect of the water to cement ratio and superplasticiser amount on early age yield stress development was similar, whereby the trend observed was a decrease in the initial yield stress and structuration rate with an increase in water or superplasticiser content. However, the initial yield stress was linearly correlated with superplasticiser amount, suggesting a predictive model could be developed to modify the initial yield stress values in response to changes in layer height. Since these changes also affected the

buildability, it was found that it may also be necessary to make use of the correlation between accelerator and buildability for optimisation.

- Increases in accelerator content resulted in faster structuration rates over the observed time frames. It was found that there was a linear correlation between the accelerator amount and buildability rates. As a result, a linear model could be implemented to modify the accelerator content in mortars in response to changes in vertical construction rates between print jobs for optimisation purposes.
- It was shown that tartaric acid could be used as an accelerator, or a retarding agent based on the dosage used. Mortars containing tartaric acid displayed initially linear structuration rates and there was a strong correlation between the amount of tartaric acid used and the slope of these structuration rates. Using these results, a simple optimisation method, based on the proposed theory, was tested with promising results.
- The shape stability and buildability properties of printed specimens were evaluated for a mix with a characteristic buildability slope approximately tangential to the slope of buildability limit. It has been illustrated that the proposed concept for mixture optimisation and buildability assessment works appropriately.
- The results showed that, for a predefined print job, the open time could be enhanced by up to 33% using the predictive model for optimisation of yield stress development.

Further investigations are recommended to determine the boundaries of the correlations found and their adaptability to different mortar/concrete systems.

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Chapter 4: Shrinkage Behaviour of Cementitious 3D Printing Materials: Effect of Temperature and Relative Humidity

Extrusion-based concrete 3D printing is at its infancy and many aspects of this new technology need to be thoroughly investigated to pave the way for its widespread use in construction. Since the inherent drying shrinkage of the hardened cement paste is the source of the drying shrinkage of 3D printed concrete, the shrinkage behaviour of cementitious 3D printing materials with very high cement to fine aggregate ratios is one of the major challenges for researchers working on this innovative technology. Besides, due to the absence of formwork in this technique, an outdoor 3D printing environment causes excessive moisture loss and drying shrinkage cracking. This chapter presents the first comprehensive investigation on the effects of different outdoor environmental conditions i.e. relative humidity (RH) and temperature on the moisture loss, drying and autogenous shrinkage of cementitious 3D printing materials, considering different sand to cement (S/C), and surface to volume (S/V) ratios of free-formed specimens. Mass loss and length change of mortars which were cured for up to 168 days under standard condition (24°C-50%RH with 24 hours of sealed initial curing) were compared with those at 24°C-50%RH, 35°C-85%RH and 35°C-45%RH (free-formed specimens without initial curing) to investigate the effect of outdoor printing environment and the absence of formworks on the deformations caused by shrinkage. The drying shrinkage results indicate that 28 days free-formed specimens under different non-standard curing conditions show a length change up to 30% lower than specimens in the standard environment. Moreover, increasing the sand to cement ratio from 0.8 to 1.0 results in a 10% decrease in the drying shrinkage strain. This study also discusses the higher susceptibility of free-formed specimens to carbonation shrinkage and demonstrates that printed specimens have higher shrinkage deformation in the longer term compared to conventional casting specimens. The results of nitrogen adsorption-desorption analysis also prove that the total porosity in free-formed

specimens in all environmental conditions reduces and reaches a finer pore structure after 112 days compared to conventional casting specimens. These results point to the importance of internal or external curing for reducing shrinkage in concrete 3D printing.

4.1 INTRODUCTION

In recent years, the use of additive manufacturing techniques, i.e. three-dimensional (3D) printing, in construction has received significant attention [1]. Compared to the conventional casting method of concrete, extrusion-based concrete/mortar 3D printing offers several advantages, such as architectural freedom for fabricating nonrectilinear structures, reducing production costs by removing formwork [2,3], and increasing the sustainability of the production process by using eco-friendly materials. Furthermore, decreasing formwork wastage, minimizing the construction time by automation [4], and increasing the safety level by using robots working remotely in a hazardous environment [5] are other benefits. However, durability-related challenges linked to the nature of 3D printing can adversely affect the mechanical performance, dimensional stability and structural integrity of the printed products. Higher evaporation rates and surface drying due to the higher surface to volume (S/V) ratio of printed elements without formwork results in a higher early-stage water loss and a higher rate of drying shrinkage [6,7]. Besides, since autogenous shrinkage is most noticeable in concrete with a water-to-cement (W/C) ratio under 0.42, higher cement content and lower W/C ratio (less than 0.3) in printing mixtures compared to conventional casting mixtures induces shrinkage cracking. This may increase the autogenous shrinkage rate of concrete [8,9]. Furthermore, the small aggregates (< 2 mm) in printing mortars and the restriction on the use of coarse aggregate in the mixture design, which is necessary to avoid clogging the delivery piping system and printing nozzle, can intensify the magnitude of drying shrinkage in 3D printing mixtures [10]. Therefore, it is crucial to investigate the shrinkage behaviour of 3D printed cementitious materials.

In concrete 3D printing, a higher likelihood of surface water evaporation exists as no formworks are used during the printing of structures [11] and the early-stage water loss results in a lower degree of hydration [12,13]. To decrease the level of water loss after deposition of the concrete layers, it is necessary to control the water transport properties within the fresh 3D printed concrete [4]. Also, plastic shrinkage cracking is

induced by the evaporation of surface water which can adversely affect the layer-to-layer interfacial adhesive properties, specifically the interlayer bonding in 3D printed specimens [4,6,14]. A few studies have been conducted on the influence of interlayer bonding on the structural integrity of printed concrete which consider the loss of moisture [4,6,15–17]. Sanjayan et al. [4] investigated the detrimental impacts of surface moisture loss (i.e. water evaporation and bleeding) on the interlayer bonding of 3D printed specimens. They highlighted that during the first 20 min after deposition of a $250 \times 25 \times 15 \text{ mm}^3$ filament, approximately 160 mg water was evaporated (at 24°C and 65% RH), which resulted in relatively 50% lower interlayer bonding in specimens with printing gap of 20 min between subsequent layers. Nerella et al. [6] carried out a study on the effect of layer-interface properties on the mechanical strength of 3D printed concrete produced by the extrusion technique. They concluded that entrapment of air between the layers during deposition, drying shrinkage and carbonation processes (in the case of extended gap time) result in weak bonding between the interfaces of printed layers [6].

Limited studies investigated the shrinkage behaviour of construction materials concerning the 3D printing environment [17–20]. Le et al. [17] investigated the drying shrinkage of printed concrete according to BS-EN 12617–4:2002 [21] in three curing conditions: i) water immersed; ii) covered in damp hessian under ambient temperature (100%RH and $15\text{--}25^\circ\text{C}$); and iii) climatic chamber with 60% RH and 20°C for six months. They found that the 184-day drying shrinkage of the printed concrete was about 180, 570 and 855 microstrain under the three curing conditions, respectively. Zhang et al. [18] cut $100 \times 100 \times 400 \text{ mm}^3$ specimens from a printed cement mortar block and measured their drying shrinkage under the curing condition of 20°C - 50% RH for three months. In their study, the drying shrinkage strain was in the range of 800 to 850 microstrain after 56 days [18]. Previous studies on the drying shrinkage of printed concrete [17–19] showed that 3D printed cementitious materials had a lower drying shrinkage in all temperature and relative humidity levels compared to sprayed mortars (at the same age) [22,23] cured at the standard condition of 20°C and 50%RH, which exhibited a drying shrinkage in the range of 750-1000 microstrain. Kim et al. [19] studied the mitigation of drying shrinkage in cementitious mixtures for use in 3D printing by adding styrene-butadiene rubber (SBR). They conducted drying shrinkage tests in accordance with ASTM C596-01 [24] and found that the 28-day drying

shrinkage of printing mixtures with SBR/cement ratio of 0 to 0.2, cured at 23°C - 60%RH, decreased from 331 to 144 microstrain. This demonstrated the potential of employing SBR to increase the dimensional stability of concrete. Federowicz et al. [20] investigated the shrinkage evolution of 3D printed concrete under three different curing regimes of atmospheric conditions, foil-sealed curing and internal curing by shrinkage-reducing agents (SRA) in a short term period of 7 days at 20°C and 50% RH. They demonstrated that the 7-day total shrinkage strain (autogenous and drying) of 3D printing mortar was significantly higher (385%) for free-formed specimens compared to the foil-sealed specimens, and incorporating 2% and 4% of SRA into the mixtures resulted in approximately 4% and 20% decrease in the shrinkage of the mixtures, respectively [20].

Previous studies on shrinkage of 3D printed concrete, measured the shrinkage according to international standards in which moist curing or at least 24 h initial curing inside a mold (initial sealed curing) at the standard condition was adopted. Based on the available literature, no study has been conducted to date on the effect of temperature and relative humidity resembling an outdoor free-from 3D printing environment, on the water loss from the surface and development of drying shrinkage strain in 3D printing concrete. One study by Federowicz et al. [20] evaluated the shrinkage development of concrete in open-to-atmosphere conditions under standard temperature and relative humidity. They only measured the short-term shrinkage strain (within 28 days) and disregarded measuring the relative contribution of autogenous shrinkage to the total shrinkage. Therefore, additional experimental studies are required to understand the effect of climatic parameters and free-form high surface exposure (no initial curing and large S/V ratio) on the long-term autogenous and drying shrinkage of printed cementitious materials. Such studies are important because in extrusion-based 3D printing, no initial curing (maturing) occurs and printed structures are exposed to the open atmosphere from the beginning.

To address the abovementioned research gaps this chapter presents the first study on the effect of both climatic parameters and no-initial-curing condition (a larger surface area exposure compared to conventional casting) on the evolution of shrinkage of 3D printing mortars, as well as their influence on degree of hydration and other mechanical properties. 3D printing mortars were designed by considering the general design principles for 3D printing of cementitious materials, such as adequate

flowability (easily extrudable), static yield stress (well-buildable), proper setting time and mechanical strength [17,25,26]. Flow table and static yield stress tests were conducted to adjust the sand-to-cement ratio (S/C) to obtain mixtures with the most suitable rheological behaviour for 3D printing. Compression and flexural strength tests were also carried out to ensure that the mechanical properties of the mixtures are acceptable. The 3D printing conditions without formwork and different climatic parameters (temperature and relative humidity) were simulated for the mixtures. The standard curing procedure for conventional casting (covering the concrete with plastic sheets following ASTM C171-07 [27]) was also adopted to investigate the effect of curing at different climate conditions on drying shrinkage and degree of hydration. The evolution of autogenous shrinkage in the 3D printing mixtures was also investigated under standard (24°C) and high (35°C) temperatures. Finally, the microstructure of 3D printing mortars was analyzed with nitrogen sorption techniques to study the effect of pore size distribution on the drying and autogenous shrinkage development.

4.2 BACKGROUND AND RESEARCH AIM

This study aims to evaluate whether the original dimensions of the cementitious mortars, which are designed for 3D printing, are maintained with no initial curing (standard for conventional casting) and when the temperature and humidity are modified to resemble different outdoor printing environments. Moreover, the dimensions of printing filaments are mostly limited up to 50 mm diameter [11], which can increase the variation in drying or carbonation shrinkage strains. Therefore, this study experimentally investigates the capacity of printing mortars in outdoor printing environments in terms of the autogenous and drying shrinkage strain, as well as pore structures over a long-term period (up to 168 days). Findings of this study will contribute towards addressing durability-related problems in extrusion-based concrete 3D printing and demonstrate the importance of internal or external curing for alleviating inherent shrinkage in the concrete 3D printing process. The results of this research will serve as a benchmark for future studies on the influence of non-uniform shrinkage on the structural integrity of printed products.

4.3 MATERIALS AND METHODS

4.3.1 Materials

Ordinary Portland cement (OPC) as a binder was supplied from Cement Australia and conformed to the requirements of General Purpose (Type GP, equivalent to CEM I- 32.5N) cement according to AS3972 standard [28].

Table 4.1. Chemical composition and properties of Ordinary Portland Cement, silica fume and silica sand.

Ordinary Portland Cement	Mass content (%)	Silica Fume	Mass content (%)	Silica Sand	Mass content (%)
Portland Clinker	<97%	SiO ₂	~93	SiO ₂	99.5
		Fe ₂ O ₃	~0.1	Fe ₂ O ₃	0.03
Gypsum (CaSO ₄ 2H ₂ O)	2-5%	Al ₂ O ₃	-	Al ₂ O ₃	0.1
		TiO ₂	-	TiO ₂	0.07
Limestone (CaCO ₃)	0-7.5%	Chloride	<0.06	Chloride	-
		Na ₂ O	<1.0	Na ₂ O	-
Calcium oxide (CaO)	0-1%	Water Content	<1.0	Water Content	<0.21
		Loss on Ignition	<6.0	Loss on Ignition	<0.15
Hexavalent Chromium Cr (VI)	<10 ppm	Max Particle Size (µm)	1.0	Max Particle Size (µm)	600
		Specific surface (m ² /g)	20-25		
		Bulk Density Undensified (kg/m ³)	120-180	D50 (µm)	260
Total respirable silica	Below detection limits	Bulk Density Densified (kg/m ³)	580-700	Apparent Density (kg/m ³)	1500

Table 4.1 presents the chemical composition of OPC used in this study. Silica fume composed of spherical glass particles with a particle size much smaller (less than 1.0 µm) than OPC particles and a specific surface area of 20–25 m²/g was supplied by Simcoa Microsilica in Western Australia, which adheres to the requirements of ASTM C1240 [29] and AS 3582.3 [30]. The chemical and physical properties of silica fume are given in Table 4.1. Washed high-purity silica sand with a maximum particle size of 600 µm and fineness modulus of 1.29 was used as a fine aggregate. The silica

sand was supplied from Sibelco Australia Ltd, sourced from Lang Lang river area in Victoria, and contained more than 99% crystalline silica as shown in Table 4.1. Figure 4.1 presents the particle size distribution of the OPC and silica sand used in this study, which was determined by a laser diffraction particle size analyzer Malvern Mastersizer 3000.

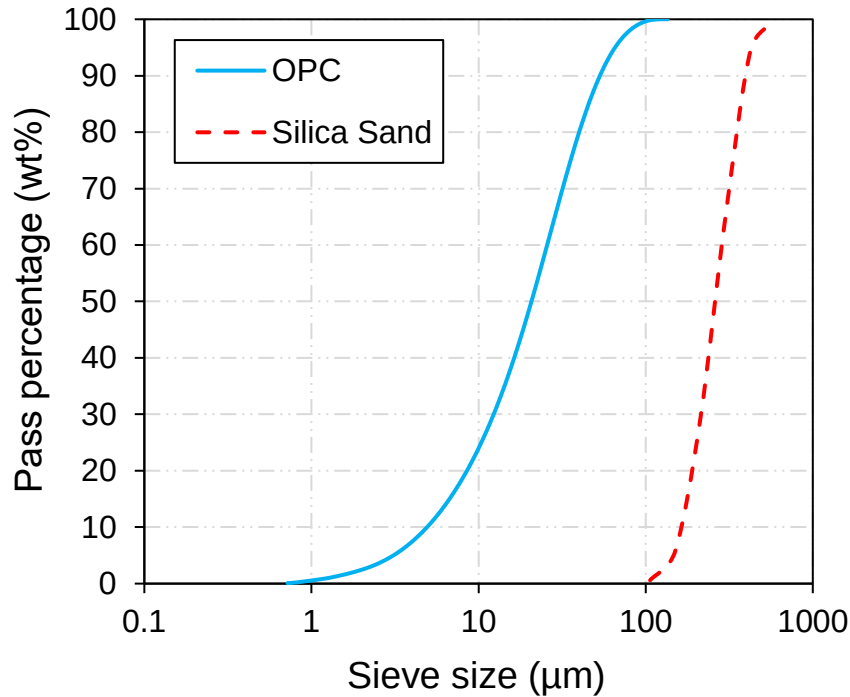


Figure 4.1. Particle size distribution (PSD) of OPC and silica sand

The chemical additives used in this study were a high range water reducer (HRWR), Viscocrete 20HE, and viscosity modifying admixture (VMA) both sourced from Sika. The HRWR was polycarboxylate-based with a density of 1.09 g/cm^3 as per the requirements of AS 1478.1 [31], which is suitable for a high binder content. VMA (density: 1.02 g/cm^3) was also used to avoid bleeding, control segregation and increase the mixture's homogeneity.

4.3.2 Mixture design and specimen production

To obtain a mortar suitable for 3D printing, the mixture proportion was designed based on a water-to-cement (W/C) ratio of 0.35 and different sand-to-cement (S/C) ratios ranging from 0.8 to 1.2. Based on the study of Zhang et al. [18] on the high-thixotropy 3D printing mortar, 2% silica fume, 0.26% HRWRA and 0.0125% VMA as weight proportions of cement were used. Table 4.2 shows the proportions of 3D printing mixtures used in this study.

Table 4.2. Mixture proportions of 3D printing concrete.

Cement	Sand	Silica Fume	High Range Water Reducer %	Viscosity Modifying Agent %	Water
1	0.8	0.02	0.26	0.0125	0.35
1	0.9	0.02	0.26	0.0125	0.35
1	1.0	0.02	0.26	0.0125	0.35
1	1.1	0.02	0.26	0.0125	0.35
1	1.2	0.02	0.26	0.0125	0.35

Dry and wet mixing processes were conducted using a 3 liter Hobart planetary mixer. First, a solution was prepared by mixing tap water, VMA and HRWR. The dry constituents were mixed separately for 2 min at low speed (136 rpm). The mixing process continued for 3 min at low speed (136 rpm) by gradually adding the solution to the dried mixture, which was followed by hand mixing for 2 min. Finally, the mortar was mixed at speed II (280 rpm) for about 1 min to obtain a homogenous mixture.

4.3.3 Curing process and simulating the free-form condition

To investigate the effect of different outdoor environments on mechanical performance and shrinkage strain development in 3D printing mortar, three different climate classes shown in Table 4.3 were considered as curing conditions for the mixtures.

Table 4.3. Curing temperature (T) and relative humidity (%RH) of different climate classes in this study.

RH _L T _H	Standard	RH _H T _H
45% - 35°C	50% - 24°C	85% - 35°C

The meteorological data of annual average daily mean temperature and relative humidity over 30 years from all around Australia were obtained from the Australian Government's Bureau of Meteorology [32]. The data was classified into four categories from low to high humidity and temperature, and combined to create 16 different climate classes covering the entire continent. The most habitable regions of the continent were covered by the average weather condition of 18-24°C and 43-55% RH, which was considered as the standard curing condition (24°C–50%RH) in this study. To investigate the different levels of drying, two other climate classes were selected to reflect the effect of higher/lower relative humidity and higher temperature

compared to the standard condition. It should be noted that the outdoor temperatures are not identical to the climatic classes. However, these curing conditions are attributed to the average environmental conditions in the temperate, tropical and arid regions (lower latitude, e.g. northern land) of the Australia continent.

To simulate the free-form condition of 3D printing and compare it with the cast condition, two methods of “control” and “free-form” initial curing were defined. Before starting the shrinkage measurement, control specimens were initially cured for 24 h inside the molds covered with a plastic sheet at the standard condition. The samples were then demolded and curing was initiated at the standard condition. Free-formed specimens, directly after molding, were placed inside the environmental chamber operating at different curing atmospheric conditions listed in Table 4.3 without plastic covering. Immediately after the initial setting (approximately 4 hours versus 24 hours in standard condition), the molds were removed and curing continued at the same condition inside the chambers.

4.3.4 Testing methods

The flowability and rheometry tests were conducted immediately after the mixing process was complete to identify mixtures with optimal printing qualities. Shrinkage and mechanical properties tests were conducted on two selected mixtures offering acceptable printing quality, which was determined by comparing their rheological data with that obtained from the literature [18,26]. The test procedures used in this study are listed in Table 4.4.

Table 4.4. Test procedures used in this study.

Target characterization	Test procedure	Ref.
Flowability	ASTM C1437-07	[33]
Setting time	ASTM C191-08	[37]
Compressive strength	ASTM C109-08	[38]
Flexural strength	BS EN 196-1:2005	[39]
Drying & autogenous shrinkage	BS EN 12617-4: 2002, ASTM C596-07	[21], [24]

Flowability and setting time

Spread diameter testing was carried out by following ASTM C1437-07 [33] to measure the fresh mortars' flowability. Rheological behaviour was tested by a

HAAKE Viscotester 550 rheometer and a vane geometry. The vane had four perpendicular rectangular blades with dimensions of 5 mm width and 20.1 mm height. The static yield stress developments were measured approximately every 10 min over a 90 min period after mixing. The measurements were taken at different points (with a 20 mm distance to avoid interruption) in the container such that the specimens were not agitated before testing. A constant shear rate of 0.2 s^{-1} was applied, and the maximum torque was recorded and converted to yield stress according to the method used in previous studies [34–36]. Initial yield stress at time zero τ_{y0} , was extrapolated using the following yield stress evolution equation by Perrot [26]:

$$\tau_y(t) = A_{Thix} \cdot t_c (e^{t_{rest}/t_c} - 1) + \tau_{y0} \quad \text{Equation 4.1}$$

Where: A_{Thix} is the constant rate of increase in yield stress over the dormant period (linear structuration rate) in Pa/min; t_c is a fitting characteristic time; and t_{rest} is the time since mixing was initiated [26]. A Vicat needle test was used to determine the initial setting time of the printing mortars according to ASTM C191-08 [37]. A periodic penetration of a Vicat needle with a tip area of 1 mm^2 into the fresh mixture was performed by an automatic Vicat machine. The depth of penetration was recorded every 15 min. The elapsed time from the start of mixing until a penetration depth of 25 mm was reported as the initial setting time.

Compressive and flexural strength

Specimens were cast into 50 mm cubic molds for compression testing according to ASTM C109-08 [38]. The test was conducted using a loading rate of 1 MPa/s. Flexural specimens were prepared with dimensions of $40 \text{ mm} \times 40 \text{ mm} \times 160 \text{ mm}$. The specimens were tested under three-point bending with a span of 100 mm and a displacement controlled rate of 0.5 mm/min in accordance with BS-EN 196-1:2005 [39]. Three nominally identical samples for each unique mixture-curing configuration were tested for compressive and flexural strength at 28 days of curing and average values were reported.

Evaluation of hydration degree

Thermogravimetric analysis (TGA) was performed on the samples after 28 days of curing. In each test, approximately 10 mg of the dried powder was heated from room temperature to $1000 \text{ }^\circ\text{C}$ under the flow of inert gas (N_2) with a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ using a Perkin Elmer TGA 8000 testing instrument. The degree of hydration was

calculated using the amount of non-evaporable water content of the samples using Equation 4.1 [40,41].

$$\% HD_{TGA}(t) = (W_n(t)/(M_c \cdot W_n(\infty)) \times 100 \quad \text{Equation 4.2}$$

M_c and $W_n(t)$ are the initial anhydrous paste mass of the sample and non-evaporable water content at time t , respectively. The non-evaporable water content is measured as the percentage of the weight loss from 145°C to 1000 °C minus the weight loss from 600 °C to 800 °C which is the result of CO₂ release due to the decomposition of calcium carbonate (CaCO₃) [41]. $W_n(\infty)$ is the non-evaporable water content (g/g of cement) as $t \rightarrow \infty$ ($t \rightarrow \infty$ refers to the time when 1 g of cement is fully hydrated), which is estimated as 0.2293 g [42].

Drying and autogenous shrinkage and weight loss measurement

Drying and autogenous shrinkage tests were performed on mixtures with S/C of 0.8 and 1.0. Specimens were cast in 25 mm × 25 mm × 285 mm and 40 mm × 40 mm × 160 mm steel molds complying with ASTM C596-07 [24] and BS-EN 12617-4: 2002 [21], respectively. Two different standards were used because different dimensions are stipulated in ASTM C596-07 [24] versus BS-EN 12617-4: 2002 [21]. Each specimen could resemble a small printing filament with S/V ratios of 1.67 cm⁻¹ and 1.125 cm⁻¹ in extrusion-based 3D printing, respectively. Drying shrinkage specimens were cured at different environmental conditions presented in Table 4.3, while autogenous shrinkage evolution was measured at two different temperatures of 24°C and 35°C under sealed curing condition (100% relative humidity). For both the drying and autogenous shrinkage measurements, the length and weight changes of the specimens were monitored using a length comparator and digital scale on alternate days during the first week, and after 14, 21 and 28 days of curing. The shrinkage strain was measured by averaging the readings of three identical specimens. The drying shrinkage measurement following ASTM C596-07 [24] continued up to 168 days. The drying shrinkage measurement for control specimens started after 24 h of initial curing in a sealed plastic bag at 24°C, while free-formed specimens were measured immediately after the initial setting time of concrete (i.e., demolding time). Table 4.5 presents a summary of the drying shrinkage test configuration. For the autogenous shrinkage tests, the molds' interior was brushed by sealing oil and covered with two layers of polyethylene (PE) films consecutively. After the initial setting time in a sealed plastic bag, the two ends and the two sides of the molds were disassembled.

Then, the specimens were wrapped tightly with PE film to prevent moisture loss during the measurements and placed inside the chambers. The moisture loss from the autogenous shrinkage specimens was negligible, i.e., less than 0.03%. The autogenous shrinkage measurements were started after the initial setting time.

Table 4.5. Drying shrinkage tests configuration.

Standard, Mold size (Surface/Volume)	Initial curing method	Temperature Relative Humidity%	S/C	Specimen code	
ASTM C596-07 [24] 25 mm × 25 mm × 285 mm S/V = 1.67 cm ⁻¹ (SV-A)	Control (Ctrl)*	24 °C 50%	0.8	Ctrl- 245008	
			1.0	Ctrl- 245010	
	BS-EN 12617-4:2002 [21] 40 mm × 40 mm × 160 mm S/V = 1.125 cm ⁻¹ (SV- B)	Free-formed (FF)**	24 °C 50%	0.8	FF-245008
				1.0	FF-245010
			35 °C 85%	0.8	FF-358508
				1.0	FF-358510
		35 °C 45%	0.8	FF-354508	
			1.0	FF-354510	

* Control samples cured for 24 h in 24°C and ~100% RH (sealed plastic bag) before the start of measurements.

** Free-formed samples cured in the environmental chamber immediately after placement and measurements were started after the initial setting time of 4.5 h.

The specimen codes are shown in Table 4.5. Ctrl and FF represent control and free-formed methods of initial curing, respectively. The second part includes a six digits code representing the drying temperature (first two digits), humidity (second two digits) and S/C ratio (last two digits), respectively. For example, Ctrl-245008 is a specimen with S/C of 0.8 which was initially cured under the control condition and dried at 25°C and 50% RH. Furthermore, for simplicity, the specimens with S/V of 1.67 cm⁻¹ (25 mm × 25 mm × 285 mm) and 1.125 cm⁻¹ (40 mm × 40 mm × 160 mm) are referred to as SV-A and SV-B specimens, respectively.

Micropore structure analysis: Nitrogen adsorption-desorption (NAD)

The specific surface area and pore volume were evaluated by physisorption (monolayer, multilayer and capillary condensation) data for gas-solid systems of nitrogen as an adsorptive gas on the adsorbent surface of the crushed mortar powders. The amounts of adsorbate nitrogen required to cover pores' internal surface were calculated at different low-pressure levels using the continuous flow method. Since the relatively weak van der Waals interaction between the adsorbate gas molecules and

the porous adsorbent medium is the reason behind the physical adsorption, the characterization is typically conducted at the boiling point of nitrogen to facilitate the adsorption of a sufficient amount of adsorbate nitrogen on the surface of porous materials [43]. In this study, the surface areas and the pore size distribution (in the mesopore range) were calculated by the Brunauer–Emmett–Teller (BET) and Barrett-Joyner-Halenda (BJH) method, respectively, from data acquired using a micromeritics 3Flex surface and micropore analyzer.

The control and free-formed drying shrinkage specimens were crushed after 112 days of the drying process. Then, particles with sizes within the range of 1.18 mm to 1.7 mm were sieved out using the corresponding sieves. After sieving, the hydration arresting process was carried out by solvent exchange method in acetone. 4 g of the crushed specimens was soaked into 20 mL of acetone for four days, and the solvent refreshed every once a day. Before testing, the crushed specimens were dried in an oven at 50 °C for 16 h and degassing was conducted for 24 h under vacuum. Finally, the nitrogen adsorption-desorption (NAD) test was carried out on the specimens.

4.4 RESULTS AND DISCUSSION

4.4.1 Properties of concrete in the fresh state: printing quality of mixtures

It is well known that the printing quality of cementitious printing materials depends on the extrudability, shape stability and buildability properties of the fresh mixtures. The printing quality can be considered acceptable when all the three requirements of extrudability, shape stability and buildability are met. The extrudability is controlled by the flowability of the mortar in through the hose and nozzle to lay down a defect-free filament. There must be no surface defects in the printed layer, including any discontinuities caused by excessive stiffness or insufficient cohesion. A higher flowability results in a better extrudability [44]. On the other hand, the printed filament must be stiff enough to maintain its shape after extrusion (shape stability) and support the weight of subsequently printed layers (buildability) [26,44,45]. As previously stated in the literature, cementitious mortars with the flowability within the favorable range of 75% – 110% and shear strength between 0.55 – 1.0 kPa are potentially suitable to pass all the requirements for smooth extrusion-based concrete 3D printing [10,44,46]. In this study, to find the optimal mixture design that is potentially suited for printing in terms of extrudability and

buildability, the rheological behaviour of mortars was studied using the flow table test and a rheometer.

Flowability

Figure 4.2 shows the average flow of mixtures with different S/C ratios within 60 min after mixing. The dormant period (open time) is defined as the rest time after preparing the fresh mixture. As shown in Figure 4.2, at a given dormant period, an increase in the S/C ratio resulted in a decrease in the flowability of the mixtures. Immediately after mixing, mixtures with S/C ratios of 1.2, 1.1, 1.0 and 0.9 exhibited 11.6%, 10.3%, 7% and 5.7% lower flowability compared to those with S/C ratios of 0.8, respectively. The number of nucleation sites and the total water consumption increased by a higher amount of sand, which resulted in increased yield stress and consequently decreased flowability [47]. Furthermore, the flowability of all the mixtures decreased between 4.5% to 22.6% when the dormant period was extended from 10 to 60 min. Extending the dormant period enhances the hydration degree of the mixture, resulting in the rapid development of stiffness in the freshly mixed cementitious mixtures [44].

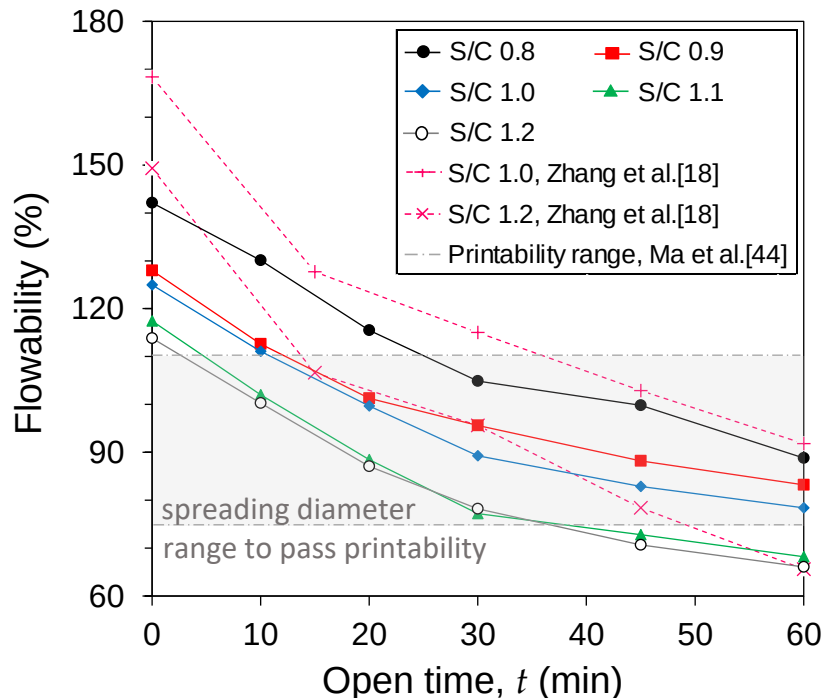


Figure 4.2. Variation of flowability of different mixes with time and comparison to the similar 3D printing concrete in Ref. [18, 44]

As shown in Figure 4.2, the flowability trend of the mixture with S/C ratio of 0.8 was within the range of the flowability trend of the printable mixtures suggested in the study by Zhang et al. [18] with S/C ratios of 1.0 and 1.2. In this study, using lower content of finer sand resulted in relatively similar flowability compared to the study by Zhang et al. [18]. This is attributed to the use of fine sand with smaller particle size, which results in the formation of thinner water layers around the sand particles and higher inter-particle friction, which increases the viscosity [44,48]. Therefore, a lower amount of finer sand is required in our study to achieve the desired flowability for extrusion-based printing. It can also be observed from Figure 4.2 that mixtures with S/C = 0.9 and 1.0 exhibited a relatively similar flowability reduction rate. After 10 min from mixing, the flowability of the mixtures dropped from nearly 130% to 110%, which is equal to the standard flow of hydraulic cement mortar as defined in ASTM C109/C109M-02 [38]. This flow rate is also equal to the upper threshold of the spreading diameter range (75% - 110%) to pass printability according to the study by Ma et al. [44]. In this study, mixtures with S/C ratios of 0.9 and 1.0 developed flowabilities of 113% - 78% from 10 to 60 min after mixing, which indicates appropriate mixtures for extrusion-based 3D printing. As can be observed in Figure 4.2, the flowability for mixtures with S/C ratios of 1.1 and 1.2 was in the range of 100% to 66% from 10 to 60 min after mixing, and lost their extrudability after about 30 min. To a certain extent, increasing the sand content reduced the extrudability open time and resulted in a lower flowability by promoting the flocculation structure. However, mixtures with S/C ratios of 0.8 to 1.0 were potentially appropriate for extrusion-based 3D printing.

Rheological behaviour: evolution of yield stress

To investigate the buildability and flowability characteristics of 3D printing mixtures, the development of yield stress was evaluated over 90 min after mixing. Figure 4.3 shows the variation of static yield stress evolution with time. The results followed the rheological model (Equation 4.1) by Perrot et al. [26] for thixotropic cementitious materials as shown in Table 4.6. It was observed that for the mixture with a S/C ratio of 0.8, the yield stress evolution versus time was relatively linear, but an increase in S/C above 0.8 resulted in an exponential development of yield stress.

The fine aggregate content in the mixture and its fineness modulus significantly influence its rheological behaviour. The fine aggregate's smaller particle sizes result

in a higher surface area per volume and higher water absorption, thereby reducing the fluidity [49].

Table 4.6. The fitting parameters of static yield stress evolution equation of Perrot's [26] rheological model of thixotropy under various S/C ratios.

S/C	$\tau_{0,0}$ (Pa)	A_{Thix} (Pa.min ⁻¹)	t_c (min)	R ²
0.8	206.6	16.75	120.6	0.987
0.9	805.8	14.08	63.6	0.996
1.0	739.6	23.47	81.8	0.937
1.1	1471.2	29.09	53.0	0.988
1.2	1900.3	46.98	76.0	0.993

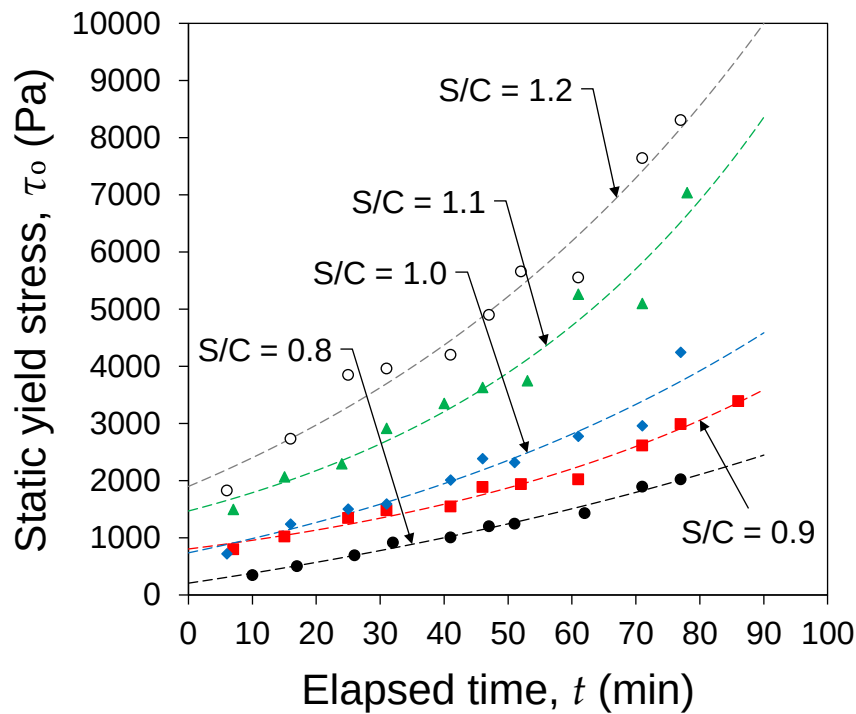


Figure 4.3. Variation of static yield stress evolution with time compared with the curves fit of Perrot's [26] rheological model of thixotropy.

Figure 4.4 shows the results of the initial yield stress ($\tau_{0,0}$) and structuration rate (A_{thix}) obtained from Perrot et al. [26] model with varying S/C ratio. As shown in the figure, an increase in S/C ratio from 0.8 to 1.2 led to a significant increase in initial yield stress ($\tau_{0,0}$) and the structuration rate (A_{thix}) by approximately 819% and 180%, respectively. Mixtures with S/C of 0.8 and 1.0 developed 0.55 kPa and 1.1 kPa yield stress after 15 min of the dormant period, respectively. This indicates that these

mixtures are appropriate for printing purposes in terms of extrudability and buildability according to previous studies [10,17,46]. A higher ratio of S/C (i.e. 1.1, 1.2) with a larger $\tau_{0,0}$ (> 0.9 kPa) may limit extrudability, as was reported previously [25,46]. In this study, mixtures with S/C of 0.8 and 1.0 had appropriate $\tau_{0,0}$ and A_{thix} for printing purposes and were selected for further investigations on drying shrinkage. Fig. S1 and S2 in the Supporting Information (Appendix A) show the printing quality of mixture with S/C of 1.0. Two- and three-layer specimens were printed using a custom-made concrete 3D printer with a nozzle opening of 15 mm $\times$ 25 mm to show the acceptable printing quality of the mixture.

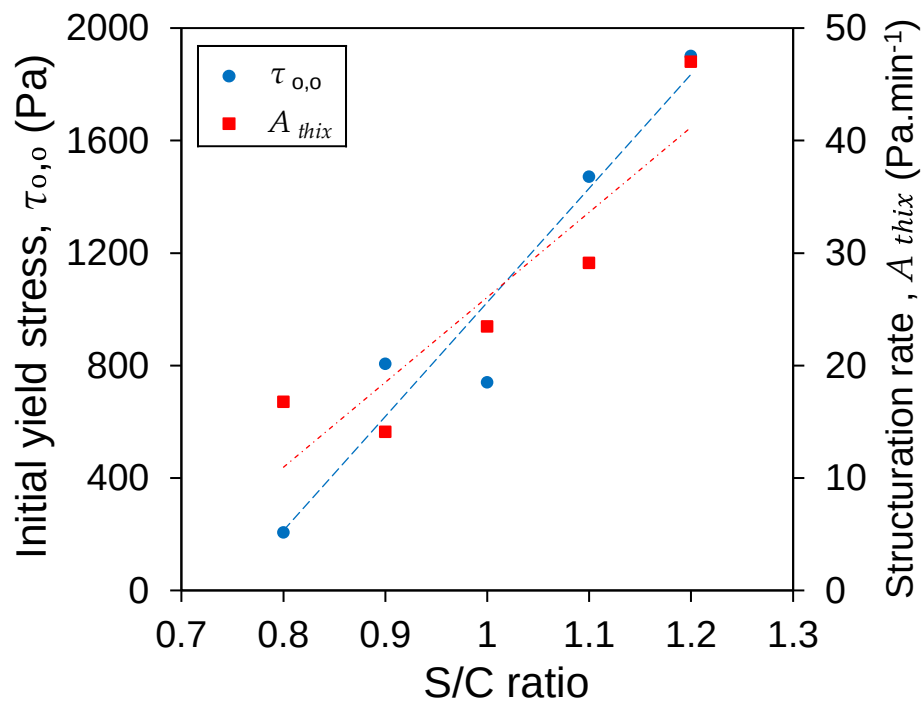


Figure 4.4. The effect of S/C on initial static yield stress and A_{thix} of mortar specimens.

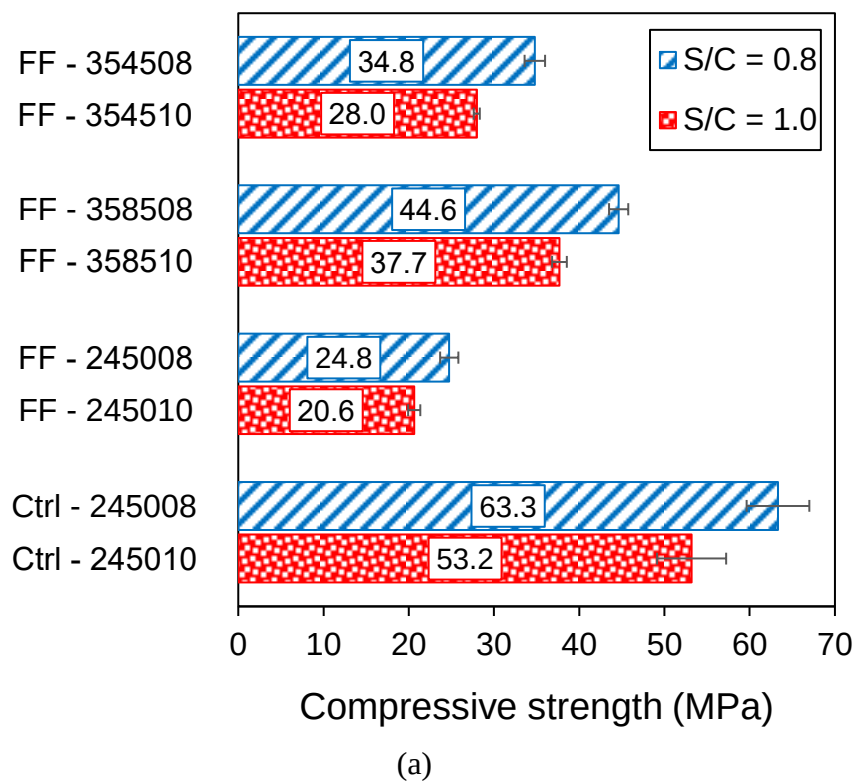
Initial setting time

The average initial setting times for the mixture with S/C ratios of 0.8 and 1.0, used for shrinkage measurements, were 263 and 246 min, respectively. Therefore, a demolding time of 4.5h (start time for drying shrinkage measurement) for free-formed specimens was considered after mixing was initiated.

4.4.2 Compressive and flexural strengths

Figure 4.5 shows the 28-day compressive and flexural strengths of mixtures with S/C ratios of 0.8 and 1.0 under different environmental conditions presented in Table 4.3. It can be seen in Figure 4.5 (a) that the control mixture with S/C ratios of 0.8 and

1.0 exhibited a compressive strength of 63.3 MPa and 53.2 MPa, respectively. The mixtures' compressive strength decreased with an increase in the S/C ratio from 0.8 to 1.0 for a given curing condition. The free-formed mixtures with a S/C ratio of 1.0 at the standard environmental condition, 35 °C–85% RH, and 35 °C–45% RH exhibited 20%, 18% and 24% lower compressive strength compared to those with a S/C ratio of 0.8, respectively. The lower compressive strength of the specimens with a higher S/C ratio than those with a lower S/C ratio is consistent with of previous studies ([50] [51]). This observation can be because the added fine sand introduces interface transition zone (ITZ) into the printing mortar. The ITZ between the aggregate and the surrounding cement paste is a weak zone due to the higher porosity of ITZ in comparison to that of bulk cement paste, and thus the strength of the cement paste of ITZ is lower. Since the volume and surface area of the sand increases, the volume fraction of ITZ also increases. The composite effect induced by the added fine sand, strengthens the printing mortar. The cement paste matrix, on the other hand, is weakened due to the large amount of interface area created by the added sand. These two contradictory effects offset each other, and the combination of them leads to the reduced strength [52].



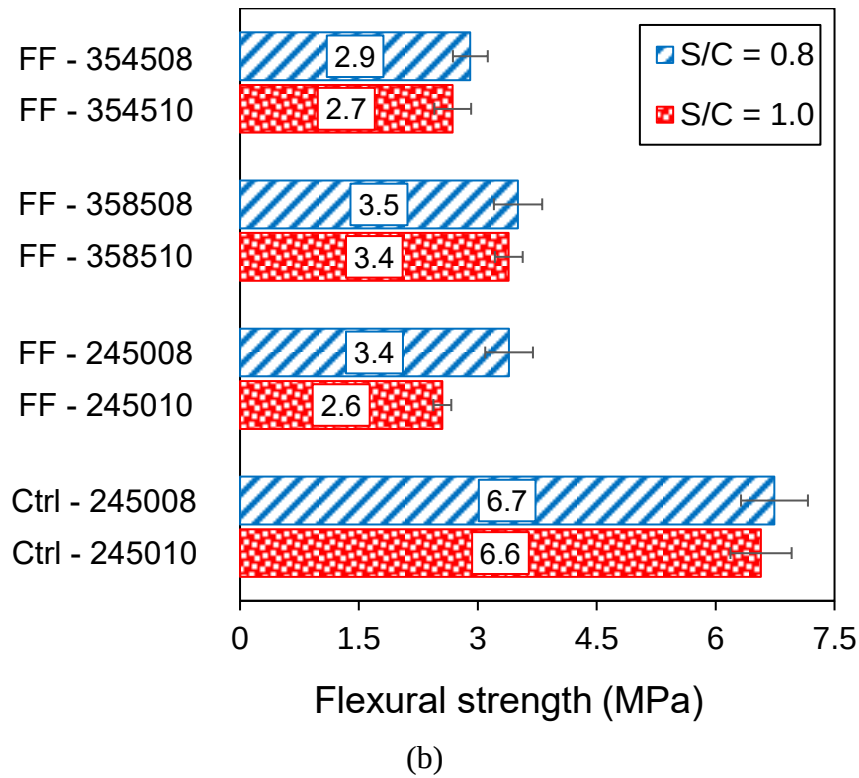


Figure 4.5. (a) compressive and (b) flexural strength of mixtures with S/C ratio of 0.8 and 1.0 at 28 days.

By comparing the specimens under free-form curing condition with those under the conventional casting (control), it can be seen that the compressive strength of the free-formed specimens was considerably lower than the control specimens for a given S/C ratio. The largest strength reduction (61%) was observed for the specimens with the curing condition of 24 °C and 50% RH. In contrast, the smallest strength reduction (29%) was observed for the specimens with the curing condition of 35 °C and 85% RH. The lower compressive strength of the free-formed specimens compared to the control specimens is attributed to the higher surface exposure of free-formed specimens and water evaporation rate, which results in a lower amount of available water for hydration. This leads to a lower compressive strength compared to the control specimens which were sealed for the first 24 hours [53]. It can also be seen in Figure 4.5 (a) that the compressive strength of the free-formed specimens at a higher temperature but similar relative humidity (35 °C–45% RH), and higher temperature and higher relative humidity (35 °C–85% RH), increased by approximately 26% and 81%, respectively, compared to the standard curing condition (24 °C–50% RH). At the same temperature of 35 °C, an increase in the relative humidity from 45% to 85% caused strength increases of 28% and 35% at S/C ratios of 0.8 and 1.0, respectively. The loss of strength in free-formed specimens (at elevated temperature and low/high relative

humidity) compared to control ones is attributed to the chemical and physical effects. The chemical effect is due to changes in the hydration degree level (Figure 4.6) and hydration products' structure. The lower compressive strength of the printing mortars cured in free-form condition compared to the standard condition can be associated with a lower hydration degree. On the other hand, the physical effects include an increase in the macroporosity and a higher chance of microcracking in cement paste due to the moisture loss difference of aggregates and hardened cement paste [54,55].

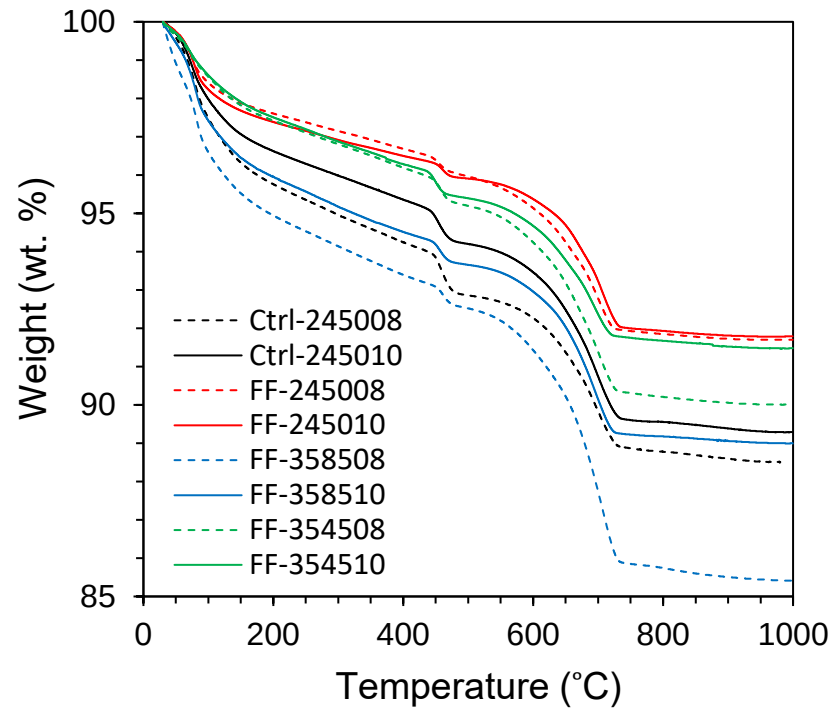
Figure 4.5 (b) shows that the flexural strength of free-formed specimens cured at 24 °C–50%RH, 35 °C–85%RH, and 35 °C–45%RH was approximately 55%, 48% and 58% lower compared to that of the control specimen, respectively. Increasing the S/C ratio from 0.8 to 1.0 in free-formed specimens resulted in 24%, 3% and 7% decrease in the flexural strength at standard environmental condition, 35 °C–85%RH, and 35 °C–45%RH, respectively. These trends are in agreement with the compressive strength test results at 28 days and indicate that irrespective of the applied curing conditions, removing the initial sealed curing (≤ 24 h which regularly occurs in 3D printing) can cause a significant reduction (up to 60%) in the compressive and flexural strength of 3D printing mixtures due to the loss of moisture, evaporation and dissipated hydration [54–56].

4.4.3 Hydration degree

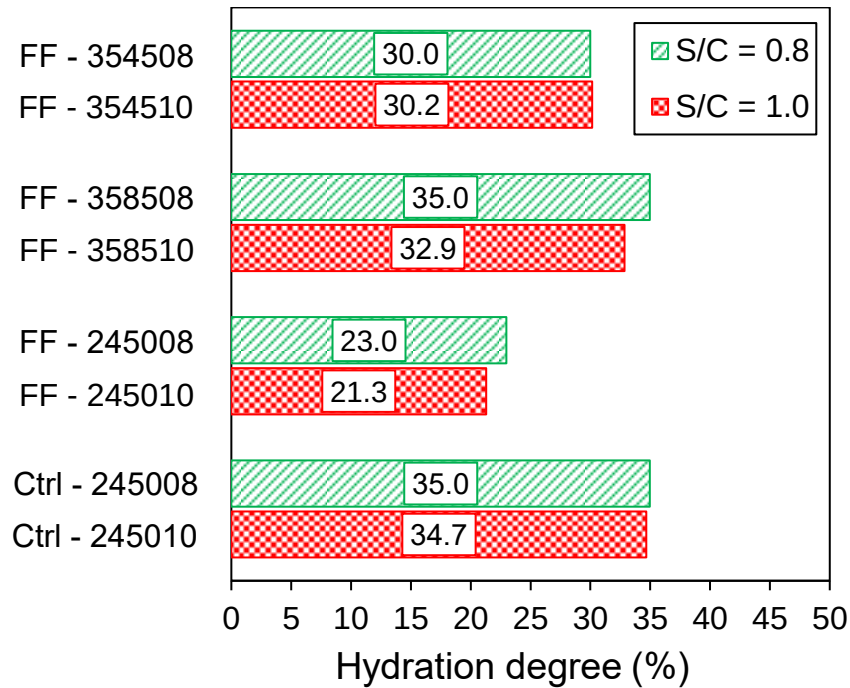
Figure 4.6 shows the influence of different environmental conditions on the hydration degree of the specimens after 28 days of curing. The hydration degree values were calculated using Equation 4.1 and each term of the equation was derived from the TGA weight loss plots in Figure 4.6 (a). From the results presented in Figure 4.6 (b) it is apparent that the higher evaporation rate and W/C ratio of 0.35 (which is in the lower range compared to the literature [57,58]) caused a relatively lower degree of hydration at all temperatures and relative humidities.

By comparing the hydration degree of specimens under free-form curing condition with those under the conventional casting (control) condition, it can be seen that by curing at 24 °C–50% RH, the specimens experienced the lowest degree of hydration (12-13% lower compared to the control sample). On the other hand, curing at 35 °C and 45% RH resulted in 4-5% decrease in hydration degree compared to the control sample. However, an increase in the relative humidity from 45% to 85% at the same temperature of 35 °C resulted in a similar hydration degree of free-formed

specimens to that of the control specimens. The results can be explained by the early-stage water loss under the free-formed curing condition, specifically in an environment with lower humidity, which limits the formation of hydration products [58].



(a)



(b)

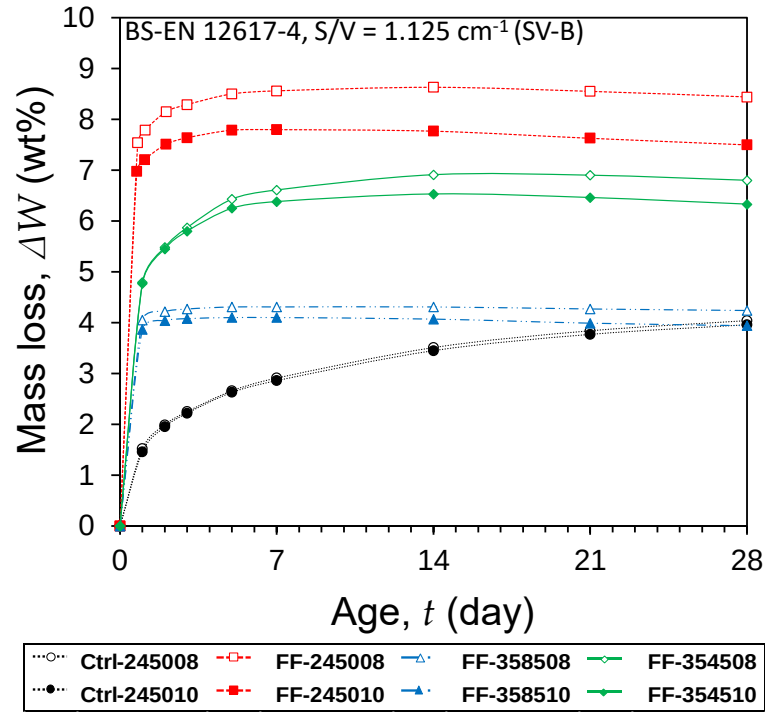
Figure 4.6. Variation of (a) weight loss and (b) hydration degree (%) of mixtures with S/C ratios of 0.8 and 1.0 after 28 days of curing at different temperature and humidity

As shown in Figure 4.5 and Figure 4.6, the hydration degree of the specimens cured at 35°C–85% RH was relatively equal to that of control specimens but their compressive and flexural strengths were lower than those under the standard curing condition. This can be attributed to the macroporosity and higher incidence of microcracking as discussed in Section 4.4.2, as well as increased plastic shrinkage cracking at free-formed curing condition. These results suggest that high temperatures generally accelerate the early-age strength development of concrete while reducing long-term strength development. The loss of strength at elevated temperature is caused by a decrease in the hydration degree and an increase in the total porosity (macro and mesoporosity) [53,54].

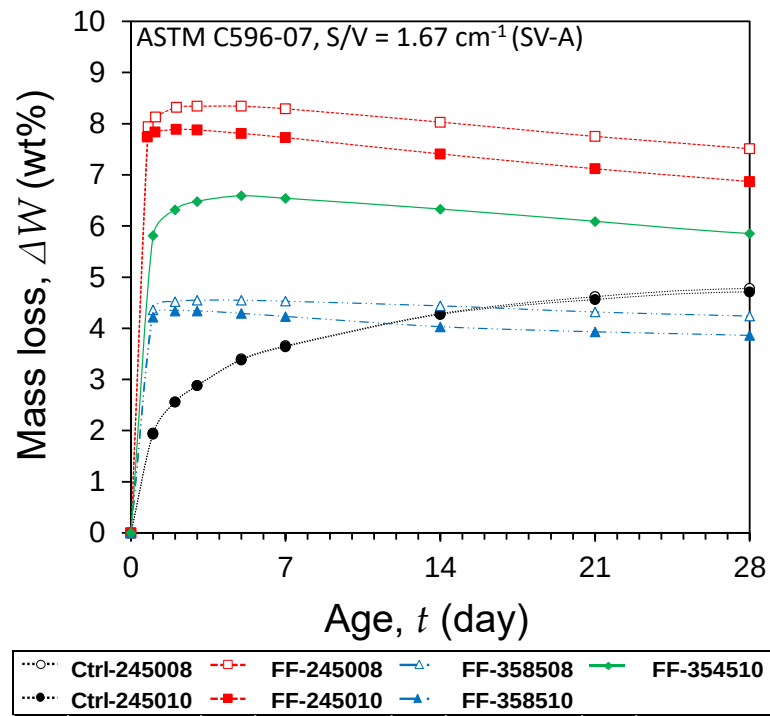
4.4.4 Drying shrinkage

The mass loss and drying shrinkage evolution of control and free-formed specimens cured at different environmental curing conditions are presented in Figure 4.7, Figure 4.8 and Figure 4.9. Shrinkage testing specimens with surface per volume ratios of 1.125 cm^{-1} (SV-B) and 1.67 cm^{-1} (SV-A) were prepared according to BS-EN 12617-4: 2002 (40 mm × 40 mm × 160 mm) [21] and ASTM C596-07 (25 mm × 25 mm × 285 mm) [24] standards, respectively. In this section, the drying shrinkage strain measurements of SV-B and SV-A specimens were carried out over durations of 28 and 168 days, respectively. The first measurement was performed after removing the mold. This time was when simulating the 3D printing surface exposure started for free-formed specimens (initial setting time of base mixes = 4.5 h) and when the initial curing (24 h sealed curing inside the mold) of control specimens has finished. It should be noted that for S/C ratio of 0.8 at 35 °C and 45% RH, the drying shrinkage measurement was not performed since the specimens were broken during the demolding.

The specimens can be indicative of printing filament with a diameter of 25 mm (for SV-A) and 40 mm (for SV-B) in extrusion-based 3D printing. As shown in Figure 4.7, SV-A specimens with higher S/V ratio than the SV-B specimens exhibited greater mass loss (because of water evaporation), which increased their shrinkage and adversely affected their shrinkage development in the longer term. However, SV-B specimens with a lower S/V ratio showed higher water retention capacity that significantly increased the self-desiccation process.



(a)

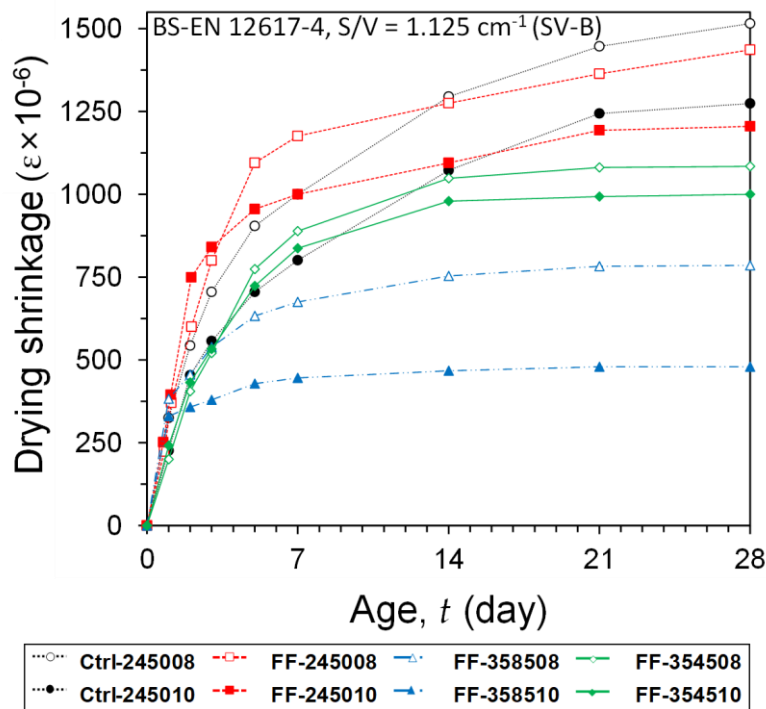


(b)

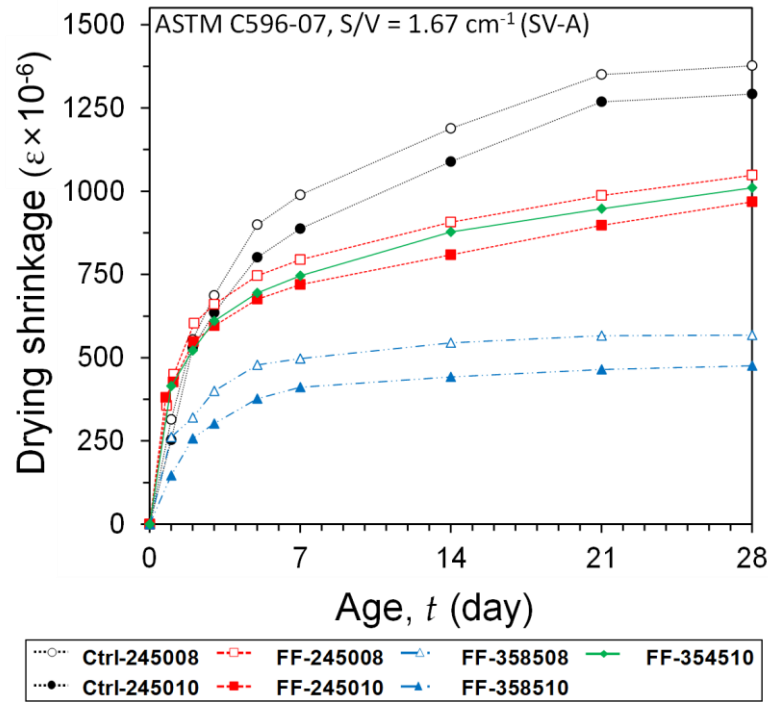
Figure 4.7. Variation of 28-days weight loss of control (ctrl) and free-formed (FF) specimens with S/C of 0.8 and 1.0 in three different curing conditions conforming with BS EN 12617-4: 2002 [21] (a) and ASTM C596-07 [24] (b) standards.

Effect of Sand/Cement (S/C) and Surface/Volume (S/V) ratio

As can be seen in Figure 4.8 (a) and (b), in both S/V ratio of 1.125 cm^{-1} and 1.67 cm^{-1} , the first three days shrinkages were more than 50% of the ultimate shrinkage at 28 days. Within the first 28 days, the increasing rate of shrinkage strain for the control specimen with S/V ratio of 1.125 cm^{-1} was relatively similar to that of their companion specimens with S/V of 1.67 cm^{-1} for a given S/C ratio. Shrinkage strain values of control specimens with S/C of 1.0 in both S/V ratios were approximately $1300 \mu\epsilon$ at 28 days of standard curing. The control specimens with S/C of 0.8 had approximately 10% higher drying shrinkage than those with S/C of 1.0, for a given S/V ratio. This was attributed to the fact that the restraining effect of fine aggregates decreased by reducing the S/C ratio, resulting in larger shrinkage deformation in specimens with a smaller S/C [59,60]. These results are different from those provided by Zhang et al. [18], who indicated that changes in the S/C ratio in 3D printing mortar do not have a noticeable effect on the drying shrinkage before 56 days.



(a)



(b)

Figure 4.8. Variation of 28-days drying shrinkage of control (ctrl) and free-formed (FF) specimens with S/C of 0.8 and 1.0 in three different curing conditions conforming with BS EN 12617-4: 2002 [21] (a) and ASTM C596-07 [24] (b) standards.

Under the drying condition, the shrinkage strain of hardened mortar is caused by capillary water evaporation, i.e. drying shrinkage, and capillary water consumption within the specimens, i.e. autogenous shrinkage. As shown in Figure 4.8 (a) and (b), at both SV-A and SV-B ratios, the 28-day shrinkage deformations in free-formed specimens with S/C of 1.0 at different environmental curing conditions of 24 °C–50% RH, 35 °C–45% RH and 35 °C–85% RH were about 1300, 1000 and 500 $\mu\epsilon$, respectively. As the drying continued within the first 28 days, the internal relative humidity of specimens (both SV-A and SV-B) was reduced continuously and the moisture in capillary pores began to evaporate which induced capillary tension, finally resulted in high drying shrinkage strain at 28 days [61].

Under the curing condition of 24 °C–50% RH, for the SV-A specimens (S/V of 1.67 cm^{-1}), the difference between the drying shrinkage of specimens with S/C of 0.8 and 1.0 at 28 days was 86 $\mu\epsilon$ for control and 80 $\mu\epsilon$ for free-formed conditions. When the dimension of the specimens changed to SV-B (S/V of 1.125 cm^{-1}), the drying shrinkage approximately tripled to 241 $\mu\epsilon$ and 231 $\mu\epsilon$ for control and free-formed condition, respectively. This discrepancy in the shrinkage strain development of

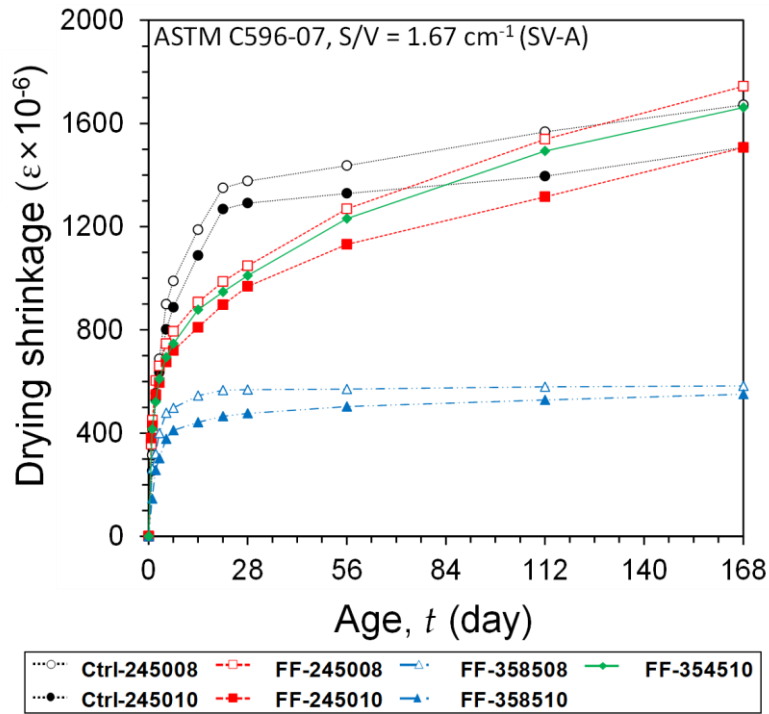
specimens with different S/V ratios (but similar curing condition of 24 °C–50% RH in free-formed and control conditions) can be attributed to the both capillary water evaporation and capillary water consumption within the specimens with smaller S/V (SV-B) ratio that has higher water retention capacity [62,63]. The SV-A and SV-B specimens (with similar S/C ratios) were from a same batch and the drying surface areas of both were relatively equal ($S_{SV-A} = 1.03 S_{SV-B}$), while the volume of SV-B specimens was 30% larger than that of the SV-A specimens. Moreover, as shown in Figure 4.7 (a) and (b), SV-B specimens lost less water through evaporation than the SV-A specimens. Therefore, SV-B specimens (with a smaller surface to volume ratio) exhibited higher water retention capacity. The higher water retention capacity of SV-B specimens resulted in more significant self-desiccation (i.e. prolonged hydration reaction with anhydrous cement), and water evaporation leading to higher total shrinkage (drying and autogenous shrinkage) strain compared to SV-A specimens. As shown in Figure 4.6, since a lower hydration degree was observed in free-form condition, unreacted cement particles were remained available for further hydration reaction [64]. Therefore, the higher water retention capacity of SV-B specimens contributed to a larger amount of water consumption by unreacted (or partially reacted) Portland cement particles and resulted in the formation of smaller pores (see Section 4.4.5). This phenomenon induces a higher level of tension in the capillary water inside the pore resulting in a slightly larger deformation in SV-B specimens at 28-days [61,65].

The above explanation can be supported by comparing the mass loss graphs of SV-B and SV-A control specimens, i.e. Ctrl245008 and Ctrl245010, presented in Figure 4.7 (a) and (b). It can be observed that SV-B specimens exhibited higher water retention capacity by gradually losing water during the 28 days and finally reaching a lower constant amount of water loss at nearly 4%. However, the SV-A control specimens' mass loss values showed a faster water loss rate and finally reached higher water losses of 5% at 28 days of standard curing. Furthermore, as discussed in Section 4.4.3, the free-formed specimens showed a sudden loss of moisture during the first day compared to the control specimens. This higher amount of mass loss not only impeded further hydration as discussed previously but also resulted in a decreasing trend in the mass loss. Therefore, the shrinkage strain data acquisition for SV-A specimens

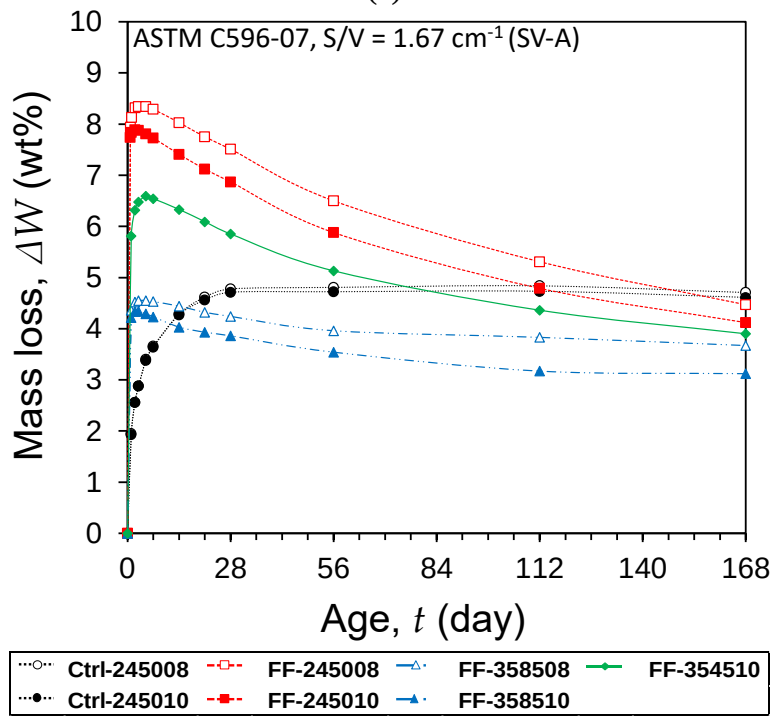
extended to 168 days to investigate the effect of age on long-term shrinkage strain and mass loss behaviour of the specimens.

Long term shrinkage strain development of free-formed specimens (SV-A)

The long-term shrinkage strain development of free-formed and control conditions was investigated for SV-A specimens until 168 days of curing. It can be seen in Figure 4.9 (a) that the control mixture with S/C of 1.0 reached a 28-day shrinkage strain of 1300 $\mu\epsilon$, which is about 5% lower than what was reported previously by Benoît et al. [66] for cement mortar with S/C of 1.0, W/C of 0.35, and compressive strength of 63 MPa, under the same curing condition. The free-formed specimens with S/C of 1.0 exhibited 25% lower 28-day drying shrinkage at 24 °C and 50% RH compared to the control specimens. The lower 28-day drying shrinkage of the free-formed specimens may be explained by the fact that by mimicking an open-to-atmosphere curing condition the water-saturated cement paste lost a considerable amount of water (about 8% based on Figure 4.9 (b)) at the early stage of hydration reaction which caused the reduction in shrinkage strain development at an early age [66]. However, as shown in Figure 4.9 (a), from 28 days until 168 days, the shrinkage strain of free-formed specimens, which were cured at 24 °C and 50% RH with both S/C ratios of 0.8 and 1.0 increased linearly, and their rates of increase (i.e., 4.9 and 3.7 $\mu\epsilon$ /day, respectively) were about 2.5 times higher than those of the control specimens. The 168-day shrinkage strain of free-formed specimens was higher than that of the control specimens. Due to the high evaporation rate from the surface of free-formed specimens at early ages, the capillary spaces initially occupied by free water were dried. Lack of sufficient water for hydration at early ages hindered the progressive growth of hydration products within the capillary spaces, resulted in greater amount of air voids and unhydrated cement residue close to the surface of free-formed specimens. The presence of this porous structure close to the surface of specimens may facilitate the potential water absorption from the ambient relative humidity of atmosphere at later ages [67]. Therefore, the hydration of unreacted/partially reacted cement can continue by the water absorption and moisture transfer into cement porous structure at later ages, which can contribute to the higher shrinkage strains at 168 days.



(a)



(b)

Figure 4.9. Variation of 168-days drying shrinkage and weight loss of control (ctrl) and free-formed (FF) specimens with S/C of 0.8 and 1.0 in three different curing conditions conforming with ASTM C596-07 [24] standards.

Comparing the results of the mass loss of free-formed specimens with those of the control specimens in Figure 4.9 (b), it is observed that free-formed specimens cured in all environmental conditions experienced a sudden weight loss between 4.5% to 8.5% during the first three days from demolding, which was accompanied with a

weight gain trend (i.e, descending mass loss trend) later on. This phenomenon is more noticeable in the long-term period for specimens with larger S/V ratio [68]. At 168 days, the descending mass loss curves of free-formed specimens in all three environmental conditions converged to mass loss values within the narrow range from 3% to 4.5%, which is up to 1.5% lower than that of control specimens after the same period. In contrary, the control specimens showed a gradual ascending mass loss curve which leveled out at nearly 4.5% after 28 days until 168 days.

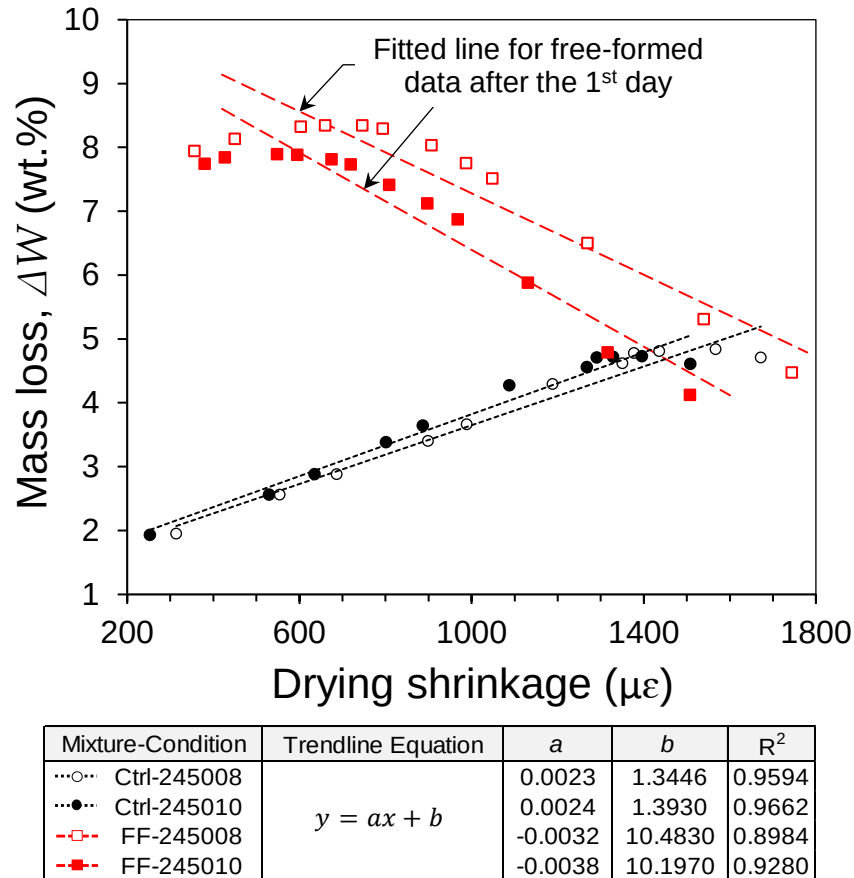


Figure 4.10. Drying shrinkage versus mass loss for free-formed and control samples cured at the standard condition for 168 days.

Figure 4.10 shows a plot of the mass loss against the shrinkage strain of free-formed and control specimens under the standard curing condition. The moisture loss behaviour of control specimens is attributed to the drying of initially well-cured specimens. However, a weight gaining behaviour (i.e, descending mass loss trend) was observed for free-formed specimens. This behaviour was observed previously for cement-based mortars similar to 3D printable mortar mixtures and attributed to carbonation shrinkage [69]. Two possible mechanisms may explain the weight gain trend in this study. Firstly, an active pozzolanic reaction could occur between cement

particles and silica fume [70,71]. Secondly, the carbonation and further hydration could occur due to the high porosity of the samples and a significant amount of anhydrous cement content due to inadequate initial curing [69,72]. Based on the study by Persson [73], owing to the low internal relative humidity and consequently slow hydration in concrete with low W/C, the pozzolanic reaction between cement particles and remained silica fume is possible at least until 15 months of age. This will cause cracking in concrete materials containing silica fume when autogenous shrinkage exceeds the tensile strain of the cement paste [73]. Moreover, several studies (e.g. [74–76]) conducted on the carbonation consequences in mature concrete concluded that carbonation leads to increases in weight and shrinkage. Moreover, the carbonation reaction can release water by decomposition of $\text{Ca}(\text{OH})_2$ and contribute to the hydration of remaining anhydrous cement and CaCO_3 deposition in the empty voids of the cement paste, which can induce higher capillary tension and subsequently higher shrinkage strain. To further support this assumption and explain the carbonation development in free-formed specimens in the long term, TGA tests were conducted on free-formed specimens (FF-245010) at different ages (after 28, 160 and 565 days). The quantity of calcium carbonates formed in 3D printing mortar were calculated from TGA analysis data based on the CO_2 weight loss caused by the decomposition of calcium carbonate [77]. As further discussed in Supporting Information (Appendix A, Section S2) and considering the weight gaining behaviour of printed specimens, carbonation has occurred in free-formed condition. This also supports the assumption that 3D printed mortars are susceptible to carbonation shrinkage. In the current study, the shrinkage strain measured for free-formed and control specimens at 168 days of curing at 24 °C and 50% RH ($\sim 1600 \mu\epsilon$) was about 6% lower than that ($\sim 1700 \mu\epsilon$) of previously reported total shrinkage (simultaneous drying and carbonation) of mortars stored at the same condition [69].

Effect of environmental condition on free-formed specimens

The shrinkage strain gradually increased in free-formed specimens at standard curing condition to more than $1300 \mu\epsilon$ after 112 days. This is equivalent to the maximum shrinkage of sprayed concrete after 210 days at 20 °C and 50% RH which shows 3D printable mixtures' limitations to resist drying shrinkage [22,23]. As previously discussed, the limited shrinkage resistance capacity can be related to the incompleting initial curing of specimens because of the free-form condition or

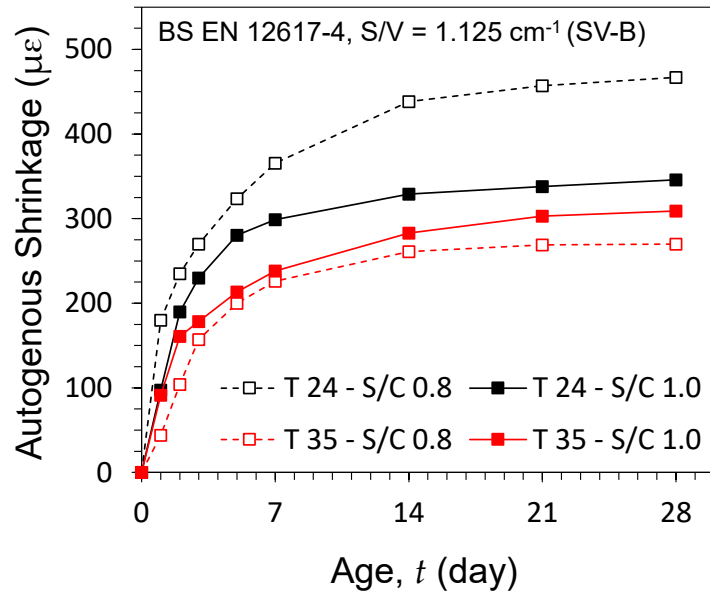
carbonation of hydrated products. It can also be seen in Figure 4.9 (a) and (b) that compared to the control condition, the drying shrinkage of free-formed specimens decreased when temperature increased from 24 °C to 35 °C at a relatively constant humidity between 45% and 50%. However, in the free-formed condition, specimens cured at 35 °C–45% RH, exhibited a similar 28-day shrinkage compared to those at 24 °C–50% RH. The shrinkage decreased by approximately 2.5 times when the relative humidity nearly doubled at the constant temperature of 35 °C. These results are consistent with those reported previously by Le et al. [17], which investigated the effect of different humidity levels on the drying shrinkage of 3D printing mixtures. It is also noteworthy that about 55% of the total shrinkage strain in free-formed specimens cured at 35 °C–85% RH was related to the autogenous shrinkage (because of higher relative humidity). The amount of drying shrinkage in this environmental condition was insignificant compared to the drying shrinkage of free-formed specimens in other environmental conditions.

Although the shrinkage under 3D-printing-simulated environmental conditions was lower than the standard condition, the hydration reaction and ultimate strength were adversely affected (Figure 4.6). In other words, the evaporation of water at early ages also decreases the moisture loss at later age and thus diminishes the measured drying shrinkage strain. However, this reduction is due to the lack of enough water which hinders hydration, induces plastic shrinkage cracking, and decreases the strength and durability of the final printed structure [78].

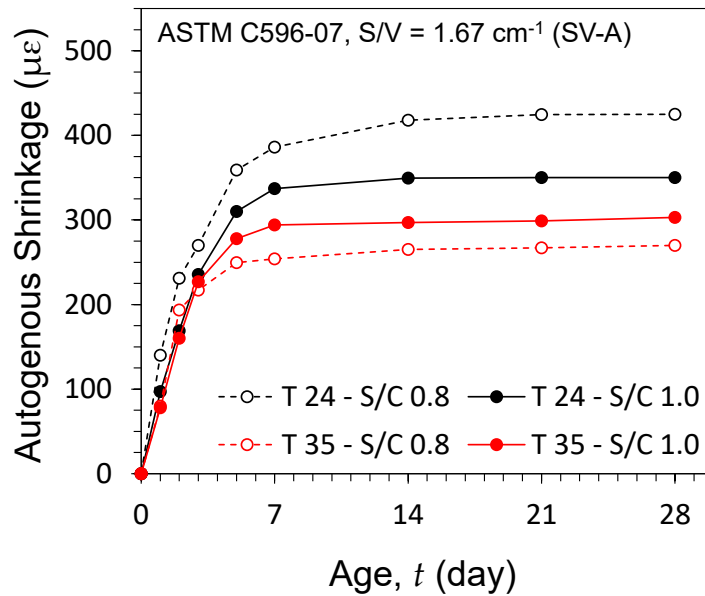
4.4.5 Autogenous shrinkage

The main aim of this section was to measure the ultimate autogenous shrinkage of 3D printing mortar at 28 days. Figure 4.11 (a) and (b) presents the development of autogenous shrinkage strain of 3D printing mixtures with S/C of 0.8 and 1.0 cured at two different temperatures of 24 °C and 35 °C and two different S/V ratios of 1.67 cm⁻¹ (SV-A) and 1.125 cm⁻¹ (SV-B) following ASTM C596-07 and BS-EN 12617-4: 2002, respectively. Generally, autogenous shrinkage tests are carried out in semi-adiabatic conditions at a constant atmospheric temperature which means that the temperature of the concrete increases due to cement hydration, allowing thermal deformation and autogenous shrinkage to occur at the same time. However, using small specimens (i.e., 25 mm and 40 mm width for SV-A and SV-B specimens, respectively) ensured that the heat evolution of cement hydration dissipates rapidly and the conditions can be

assumed truly isothermal rather than semi-adiabatic [79]. For this reason, the effect of temperature variation during the first day was neglected in the autogenous shrinkage test. As shown in Figure 4.11 (a) and (b), the autogenous shrinkage of 3D printing mortars cured at low and high temperatures were within the range of 270 $\mu\epsilon$ to 475 $\mu\epsilon$. The effects of S/V, S/C, and environmental conditions were investigated on the ultimate autogenous shrinkage strain.



(a)



(b)

Figure 4.11. Effect of S/C ratio and temperature on autogenous shrinkage development of specimens prepared in accordance with (a) BS EN 12617-4: 2002 [21] and (b) ASTM C596-07 [24] standard.

Effect of Surface/Volume (S/V) ratio

Autogenous shrinkage is an intrinsic characteristic of cementitious materials and its ultimate value is independent of the shape and size of the specimen [80]. However, as shown in Figure 4.11, the SV-B specimens had a slower rate of autogenous shrinkage evolution than those SV-A specimens for a given S/C ratio and temperature. SV-B specimens leveled out to their ultimate autogenous deformation values in all curing conditions after 14 days compared to those SV-A specimens that took only 7 days. The slower rate of autogenous shrinkage evolution in SV-B specimens may be attributed to the prolonged self-desiccation process originating from slower moisture diffusion rate and longer diffusion length within the samples with smaller S/V ratios. In fact, as the self-desiccation proceeds with the formation of hydrated products, the remaining moisture can be reduced with increasing difficulty, such that diffusivity diminishes with decreasing moisture content. Therefore, increasing the moisture ingress distance (larger size or thickness of samples) leads to a slower rate of autogenous shrinkage development [69]. It should be noted that the slight difference in the ultimate autogenous shrinkage values observed in this study may be attributed to the challenging nature of measuring autogenous shrinkage alone, and further modifications to test methods may be needed for enhanced accuracy in future studies.

Effect of Sand/Cement (S/C) ratio

As shown in Figure 4.11, at a standard curing temperature of 24 °C, free-formed specimens with S/C of 0.8 exhibited the highest autogenous shrinkage strain values of about 465 $\mu\epsilon$ and 425 $\mu\epsilon$ at 28 days for S/V of 1.125 cm⁻¹ (SV-B) and 1.67 cm⁻¹ (SV-A), respectively. Increasing the S/C ratio from 0.8 to 1.0 (at 24 °C) resulted in a 20-25% decrease in the autogenous shrinkage for a given S/V ratio. This can be explained by the fact that the self-desiccation process is more dominant in mixtures containing higher cement content, resulting in larger autogenous shrinkage strain [81]. S/C ratio has a significant effect on the dimensional stability of cement-based concrete, and the deformation originated from shrinkage strain decreases with increasing the fine sand content [82]. Another important factor that can reduce the autogenous shrinkage is the large particle size of aggregates. To avoid clogging of the delivery piping system, the maximum diameter of aggregate in extrusion-based 3D printing is limited and it is often set for relatively 0.1 of the diameter of the printing nozzle [7]. Aggregates of a maximum size of 2-3 mm are typically chosen to be used in concrete 3D printing

technique [11,46]. The particle size distribution of fine aggregates in this study was analogous to that of other studies for mortar 3D printing [4,17,44] with a median (d_{50}) and maximum (d_{max}) diameter of 260 μm and 600 μm , respectively. These results are in agreement with the study by Shen et al. [81], which showed that increasing the particle size of aggregate from 212 μm to 2 mm can reduce the autogenous shrinkage by 31%. This is attributed to the rise in the restraining effect of sand on autogenous shrinkage [83].

Effect of temperature

The autogenous shrinkage test results with respect to the curing temperatures are illustrated in Figure 4.11. Generally, it is accepted that the driving force of autogenous shrinkage is the change in capillary pore pressure caused by progressive capillary pores refinement induced by cement hydration [84]. Some of previous studies have shown that the curing temperature highly influences both the development rate and magnitude of autogenous shrinkage, which increases proportionally to the curing temperature [85,86]. In contrast with the findings of these studies, some studies reported that specimens exposed to high curing temperature at early ages experienced lower ultimate autogenous shrinkage compared to that of their companion specimens exposed to relatively lower curing temperature [87–90].

As shown in Figure 4.11, by increasing the curing temperature from 24 °C to 35 °C, irrespective of S/V ratios, the 28-day autogenous shrinkage strain of specimens with S/C of 0.8 and 1.0 decreased by about 40% and 12%, respectively. This is in agreement with the findings reported by Maruyama [91], which had samples exposed to constant temperatures of 10 °C, 20 °C and 30 °C (to imitate various weather conditions). They reported that the autogenous shrinkage strain of silica fume cement pastes with a very low water-to-binder ratio decreased as the curing temperature after mixing was increased. The results shown in Figure 4.11 were in agreement with the findings of studies in Refs. [88–90], suggesting that higher temperatures at early age do not necessarily lead to higher deformations. Various chemical and microstructural changes were probably responsible for this decrease in the magnitude of autogenous shrinkage as the curing temperature increased [89,90]. An increase in the curing temperature at early ages changes the chemical composition and structure of the calcium silicate hydrates (C-S-H) during their formation. It is broadly accepted that high curing temperature promotes the formation of inner C-S-H and increases the

polymerisation (length of the chains) of the C-S-H gel [92,93]. Previous studies have shown that changes in the C-S-H gel structure are linked to the deformations of cement pastes and pointed out that an increase in the curing temperature pre-shrinks the low-density C-S-H gel, resulting in a reduced early-stage autogenous shrinkage of low W/C ratio concretes [93,94]. Moreover, it was reported previously that curing at a high temperature can modify the gel microstructure by changing the distribution of hydration clusters and densification of C-S-H, resulting in an increase in the proportion of larger pores in cement paste (coarsening of the mesopores caused by the formation of a more porous and continuous pore structure) [89,95]. The results of the NAD analysis presented in Section 4.4.6, (Figure 4.12, Figure 4.13 and Figure 4.14) can support this hypothesis. As can be seen in Figure 4.14 (b), which presents the pore size distribution of free-formed and control specimens with S/C = 1.0, with regard to different environmental curing conditions, curing at elevated temperature resulted in a more porous structure (mesopore in the range of 4.5-50 nm) for FF-354510 compared to FF-245010 and Ctrl-245010.

The importance of the curing temperature in 3D printing is because concrete 3D printing is conducted without formwork in which the printed parts are exposed to different environmental temperatures during printing and curing. Furthermore, mortars for 3D printing are often designed with low water and high cement content, supplementary cementitious materials (e.g., silica fume), and fine sand, that makes them potentially prone to high autogenous deformation [81]. The results showed that autogenous shrinkage formed up to 30% of the total shrinkage deformation of 3D printing mortars at different curing environments. However, further research and experimental data is still required to fully investigate the effect of curing environment in general and high temperature in particular on the autogenous shrinkage development of 3D printing mortars.

4.4.6 Micro-porosity analysis

Figure 4.12 presents the NAD isotherms of control and free-formed specimens with S/C of 0.8 and 1.0 cured at 24 °C – 50% RH, and free-formed specimens with S/C of 1.0 cured at 35 °C – 45% RH and 35 °C – 85% RH at the age of 112 days.

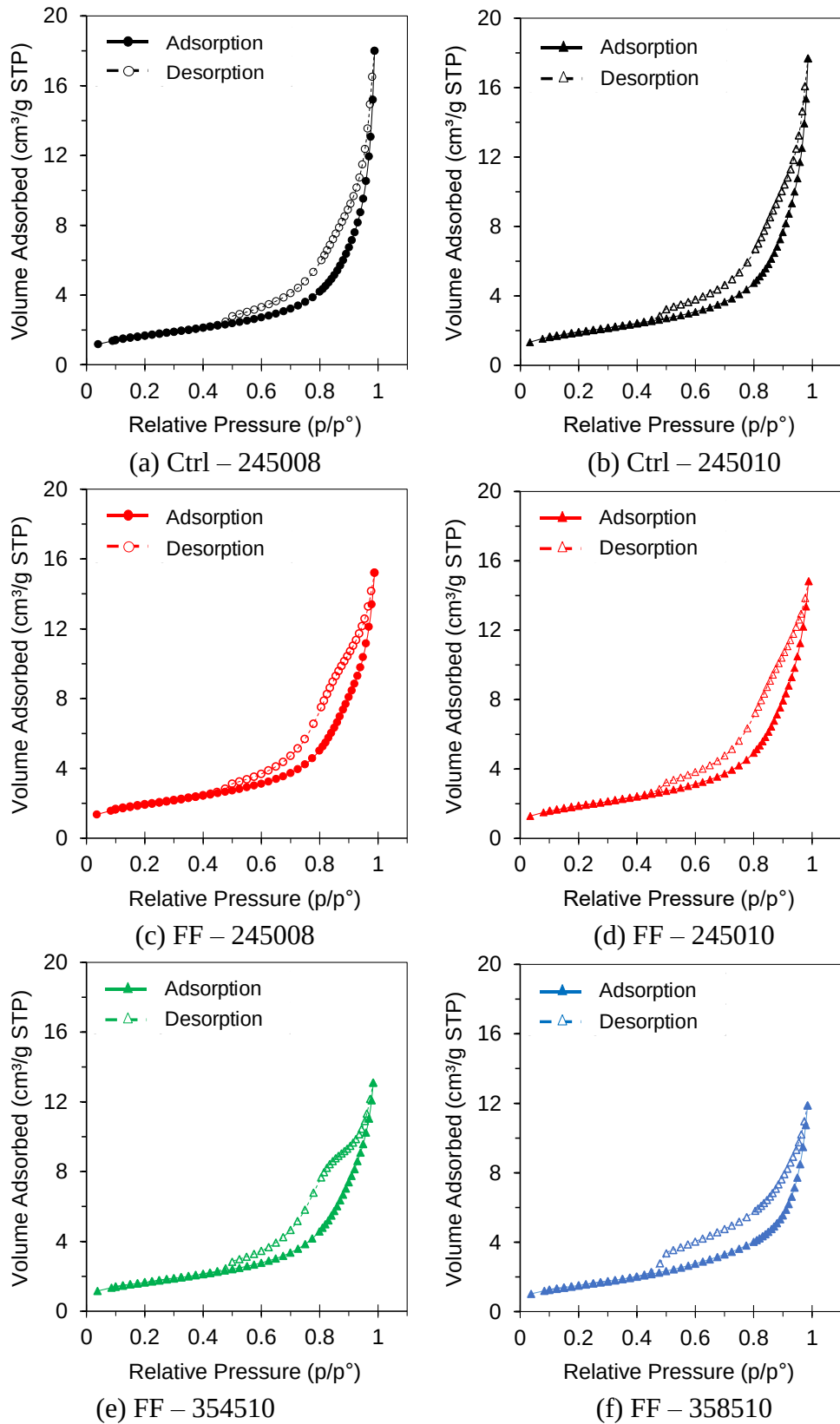


Figure 4.12. N₂-adsorption and desorption isotherms of control specimens compared to free-formed specimens with S/C ratio of 0.8 and 1.0 at different curing temperature and relative humidity after 112 days.

The BET and BJH data analysis were carried out on the NAD isotherms to calculate the specific surface area and pore volume of the specimens, respectively (Table 4.7). Figure 4.12 shows that for a given S/C ratio, the adsorption-desorption isotherms at all curing conditions had a mesoporous adsorbent behaviour with the isotherm of Type IV denoting monolayer-multilayer adsorption at low relative pressure ($p/p^0 < 0.4$) and denotes an H3 type hysteresis loop between adsorption and desorption curves [96]. The shape of the hysteresis loop shows the characteristic features of the adsorbent i.e. 3D printing mortar specimen. The shape of the hysteresis loop at $p/p^0 > 0.4$ is related to the capillary condensation in mesopore (5-50 nm) and middle capillary pore (50-100 nm) structure and the start of the loop also indicates the start of capillary condensation process [43,96]. This type of hysteresis loop (type H3 loop) is observed since the plate-like particles of C-S-H are non-rigidly aggregated, giving rise to slit-shaped pores within C-S-H gel structure [43,97]. Based on Table 4.7, for the mixtures with S/C of 1.0 which were cured at 24 °C and 50% RH for 112 days, free-formed and control specimens exhibited nearly similar specific surface area of 6.67 m²/g (BJH: 8.34 m²/g) and 6.74 m²/g (BJH: 8.17 m²/g), respectively.

Table 4.7. Specific surface area and pore volume of control and free-formed specimens at 112 days which were cured at different temperatures and relative humidities.

Evaluation method	Specific Surface Area (m ² /g)					
	Ctrl- 245008	Ctrl- 24501	FF- 245008	FF- 24501	FF- 35851	FF- 35451
BET surface area	5.91	6.74	6.76	6.67	5.50	5.89
BJH desorption cumulative surface area of pores between 1.7 nm and 100 nm width	7.27	8.17	8.15	8.34	8.29	8.09
	Pore Volume (cm ³ /g) - [%]					
	Ctrl- 245008	Ctrl- 24501	FF- 245008	FF- 24501	FF- 35851	FF- 35451
Total pore volume of pores less than 20 nm width - [% participation to the total volume]	0.0128 - [45.7]	0.0149 - [54]	0.0159 - [67.1]	0.0159 - [68.8]	0.0116 - [62.4]	0.0141 - [69.1]
Total pore volume of pores less than 50 nm width - [% participation to the total volume]	0.0184 - [65.7]	0.02 - [72.5]	0.0191 - [80.6]	0.0192 - [83.1]	0.0148 - [79.6]	0.0165 - [80.9]
BJH desorption cumulative volume of pores between 1.7 nm and 100 nm width	0.0276	0.0270	0.0232	0.0227	0.0184	0.0201

In general, the surface area of hydrated cement particles increases with an increase in the degree of hydration for the same curing time [98]. The degree of hydration is also correlated with the W/C ratio. Considering the lower hydration degree of free-formed (21.3 %) compared with control (34.7 %) specimens, the similar surface area in these specimens after a long-term period of 112 days can be attributed to the pore structure refinement due to the precipitation of carbonated products in capillary pores [99]. However, increasing the curing temperature in the free-formed specimen with S/C of 1.0 at a relatively constant humidity (between 45% and 50%) decreased the BET surface area to 5.89 m²/g. It appears that the air curing at an early-age and drying at higher temperature resulted in the formation of a densely packed gel structure with a high coordination number, which reduced the specific surface area and resulted in a smaller textural pore size[53]. At 35°C, increasing the relative humidity by approximately twofold to 85% decreased the specific surface area to 5.50 m²/g and resulted in the lowest total pore volume.

The total pore volume and pore size distribution were measured with the BJH theory using the desorption curve. Since the Kelvin equation, which is the basis for BJH theory, considers the formation of a meniscus (which does not exist during the adsorption), it is more accurate to use the desorption data to calculate the pore size distribution [100]. Figure 4.13 and Figure 4.14 represent the cumulative pore volumes and the pore size distribution graphs of different specimens, respectively. The nitrogen sorption analysis indicated the pore structure characteristics with a diameter between 3 nm and 100 nm. As can be seen in Table 4.7 and Figure 4.13, in the range of pore sizes measured, the control specimens with S/C ratios of 0.8 and 1.0 had the largest total pore volume of 0.0276 and 0.0270 cm³/g, respectively. The total pore volume of free-formed specimens cured at 24°C and 50% RH with both S/C ratios of 0.8 (0.0232 cm³/g) and 1.0 (0.0227 cm³/g) decreased by approximately 16% compared to the companion control specimens. The free-formed specimens with S/C of 1.0 cured at a higher temperature compared to the standard condition (but relatively similar humidity) exhibited approximately 11% lower total pore volume than those cured at the standard curing condition.

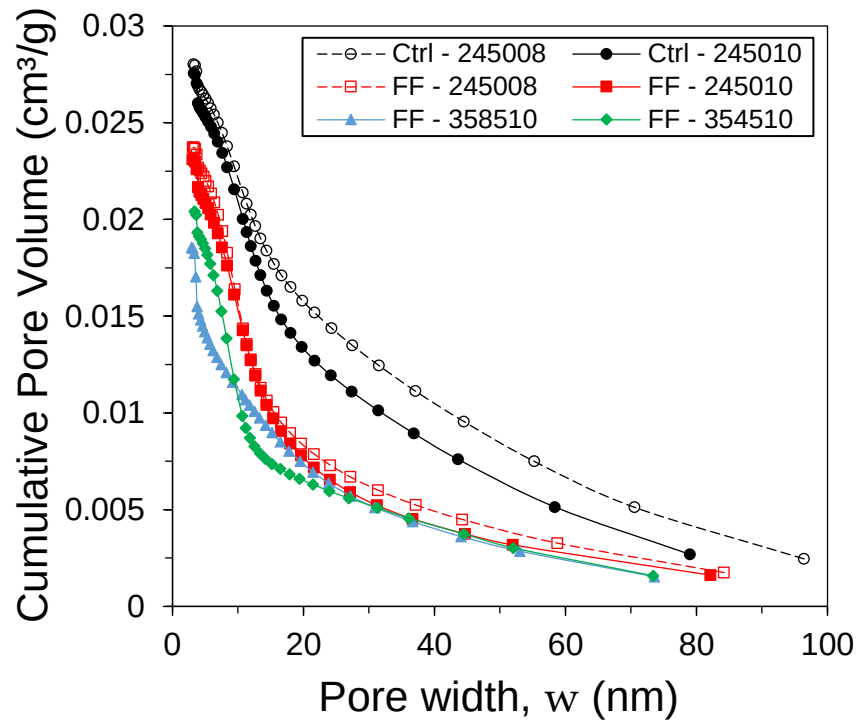


Figure 4.13. BJH desorption cumulative pore volume vs. pore width after 112 days for control and free-formed specimens with S/C of 0.8 and 1.0, cured at different temperature and relative humidity.

Figure 4.13 also shows that the free-formed specimens with a higher curing temperature and relative humidity (85% RH) exhibited the highest reduction (19%) in total pore volume compared to the free-formed specimens at the standard curing condition. This can be explained by the relatively rapid densification of the pore structure under a higher curing temperature of 35 °C and relative humidities (85% RH), leading to lower mesoporosity; the most likely hypothesis is a densification of the C-S-H gel phase [95]. According to MA et al. [61], the capillary stress is the predominant mechanism in shrinkage development of hardened cement mortars cured at the range of 45%-90% relative humidity. Therefore, the porosity results are consistent with the shrinkage strain results presented in Figure 4.9 (a) and (b) at 112 days. The higher surface exposure of free-formed specimens compared to conventional casting specimens results in excessive moisture evaporation at an early age. This significant moisture loss at an early age causes a lower total porosity at later ages in the free-formed hardened mortar which ultimately increases the shrinkage strain [61].

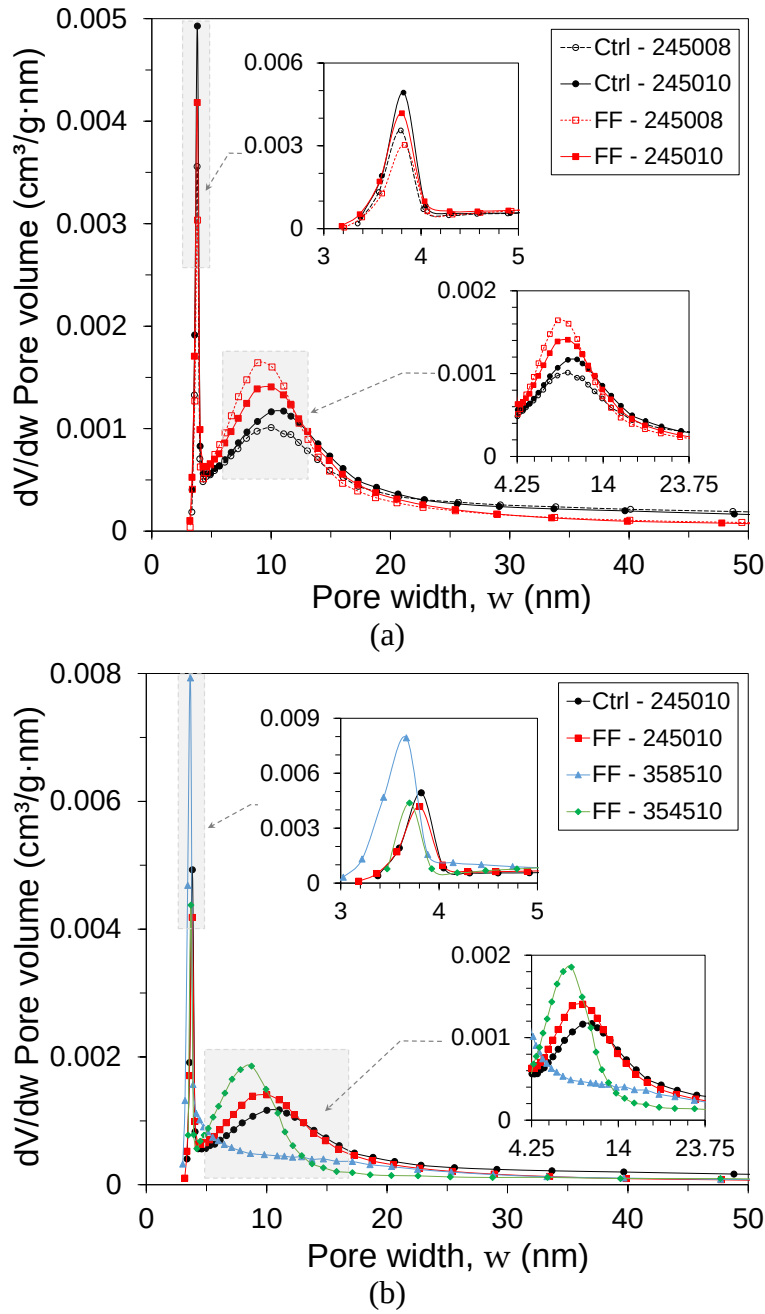


Figure 4.14. BJH desorption dV/dw pore volume vs. pore width at 112th days of drying for: (a) control and free-formed specimens with S/C ratio of 0.8 and 1.0, cured at standard condition and (b) control and free-formed specimens with S/C of 1.0, at different environmental temperature and relative humidity.

Figure 4.14 (a) and (b) present a comparison between pore size distribution of free-formed and control specimens, as well as a comparison of the effect of environmental curing condition on the pore structure of mixtures with S/C = 1.0. The pore size distribution graphs can be divided into three main regions. First, in all mixture-curing configurations, nitrogen sorption graphs showed a strong pore size peak between 3 and 4 nm. The second region is the capillary pores with the size in the range of $4.5 \text{ nm} < w < 20 \text{ nm}$, in which all the mix-curing configurations showed

another peak, except the free-formed specimen at 35 °C – 85% RH. The third region is middle capillary pores with a size range larger than 20 nm in which no peak was observed. The strong peak in the first region can be attributed to the nitrogen condensation in the interglobule pores of the C-S-H microstructure, signifying that the low-density C-S-H was formed [97]. The peaks in the second and third regions are also attributed to the densification in the microstructure with an increase in temperature and time of curing, which leads to a reduction in the volume of larger pores (10 - 1000 nm) and an increase in the volume of smaller pores (<50 nm) [54,101].

The participation percentage of mesopores with a size less than 50 nm to the total volume of capillary pores in free-formed specimens with S/C of 0.8 and 1.0 were 80.6% and 83.1% compared to those in control specimens, which were 65.7% and 72.5%, respectively. Therefore, free-formed specimens had a finer pore structure than the casting samples at 112 days. A comparison between the shrinkage results of free-formed specimens in 35 °C-45% RH and 35 °C-85% RH shown in Figure 4.9 (a) and (b) and the pore structure shown in Figure 4.14 (b) indicates the significant impact of environmental condition on the development of shrinkage in the mortar 3D printing technique. The total volume of pores with a size smaller than 50 nm was very similar in both conditions of 35 °C-45% RH and 35 °C-85% RH at 112 days (79.6% and 80.9%, respectively). However, the fineness of the pore structure in FF-358510 specimens (43% of total pore volume was attributed to the size of 3.5 nm) which were exposed to a high temperature and relative humidity for a long time, can be attributed to the formation of hydrated products inside the capillary pores. The pore size of 3.5 nm agrees well with the interglobule pore size of high-density C-S-H, and this peak is likely to indicate the nitrogen condensation in the interglobule pores of the C-S-H microstructure [101]. At about half the relative humidity for FF-354510 specimens, only about 21.5% of the pores were with the size 3.5 nm and about 47.5% of pores were between 3.5 nm and 20 nm with a 10% at about 9 nm. This appears to be related to precipitation of carbonated products and formation of low-density C-S-H inside the capillary pores which induced higher shrinkage strains (by nearly 500 $\mu\epsilon$) in the long-term period.

4.5 Conclusions

The influence of three different environmental conditions (i.e. relative humidity and temperature) on the evolution of shrinkage and associated mechanical and physical

properties of 3D printing mortars were investigated. Free-formed and conventionally cast mixtures with S/C of 0.8 and 1.0 were selected. The shrinkage strain measurement following BS-EN 12617-4: 2002 and ASTM C596-07 were carried out for the specimens with surface to volume (S/V) ratios of 1.67 cm^{-1} and 1.125 cm^{-1} , respectively. The following conclusions were drawn:

- For a given S/V ratio and at any curing age, increasing the S/C ratio of a printable mortar from 0.8 to 1.0 resulted in a decrease in the drying shrinkage strain of control and free-formed specimens ($\sim 10\%$) which were cured at different environmental curing conditions with different temperatures and relative humidity.
- Compared to conventional casting (control) specimens, the drying shrinkage strain of printable mortars at 28 days decreased (by 25 – 30 %) when free-form condition (3D printing environment) was simulated for both S/C ratios of 0.8 and 1.0 at standard curing condition (24°C – 50% RH). This reduction can be associated with excessive moisture loss at an early age due to higher surface exposure in free-formed specimens compared to the control specimens.
- In free-form curing conditions, an increase in mass with an increase of drying shrinkage was observed, confirming that 3D printing mortars are susceptible to carbonation shrinkage. A small printing filament size, higher surface exposure and higher water evaporation rate are the important factors contributing to the possibility of carbonation shrinkage in a free-formed mortar compared to the conventional cast specimen. Also, the long-term shrinkage strain of free-formed mortars was higher than that of the conventional casting concrete after 168 days of standard curing.
- For the free-formed specimens cured at a relatively constant humidity between 45% and 50%, an increase in temperature from 24°C to 35°C had a small influence on the drying shrinkage development of free-formed specimens. However, the shrinkage deformation of free-formed specimens decreased approximately 2.5 times when the tropical weather curing condition (35°C and 85% RH) was simulated.

- This research highlighted that in printing mixtures with high cement content, the autogenous shrinkage can form a great proportion (up to 30%) of total shrinkage deformation. Further experimentation is needed to elucidate the effect of high temperature curing environment on the development of the autogenous shrinkage.
- The results indicated that irrespective of the selected S/C ratio, the total porosity of free-formed specimens in all 3D printing-simulated environmental conditions was smaller (at 112 days) than that of conventional cast specimens. Furthermore, the free-formed specimens reached a finer pore structure during the same period. These results were consistent with the shrinkage strain of specimens in free-formed conditions and showed that higher shrinkage strain at later ages was attributed to excessive water loss and lower total pore volume of free-formed specimens.
- The lower compressive strength of the free-formed specimens compared to the control ones can be associated with a lower hydration degree, an increase in the macroporosity and a higher chance of microcracking in cement paste caused by excessive moisture loss.

The outcome of this study indicates the significant effect of environmental conditions, mix design optimization (e.g. maximizing the S/C ratio), and size effect of printing filaments on the shrinkage development of 3D printing cementitious materials. The findings can serve as a benchmark for future studies on the shrinkage strain development and the structural integrity of printed products under the influence of different curing methods (internal or external curing) and the use of shrinkage compensating admixtures in 3D printing mixes.

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Chapter 5: Drying shrinkage behaviour of geopolymer mortars for use in extrusion-based construction 3D printing: Effect of LSS aggregates, graphene oxide and nanoclay at different environmental conditions

The environmental effect of C3DP has become a contentious issue regarding its large OPC consumption and over-exploitation of abiotic resources such as natural aggregate. Therefore, the viability of developing optimised geopolymer printable mixtures using FA and GGBS as a substitution for OPC and use of underutilised aggregate in C3DP mixtures have been investigated to some extent. Such a binder might be explored not only for rapid vertical building rates of slender and more shape-stable parts, but also as a method of possibly decreasing the environmental impact of C3DP. However, using geopolymer mortar and underutilised aggregate in C3DP needs further care as otherwise cold joints may form and increased shrinkage deformation may occur. This chapter discusses the rheological, mechanical and shrinkage properties of waste-based geopolymer mortar prepared with natural sand (NS) and lead smelter slag (LSS) as fine aggregates to be used in extrusion-based 3D printing. The hardened state properties of the optimal printable geopolymer mixture were tested under free-formed and conventional casting conditions at different curing temperatures and humidities. Firstly, the effect of different mixture-design parameters, including binder composition (fly ash (FA) to ground granulated blast furnace slag (GGBS) ratio), alkaline activator modulus, activator to binder ratio and aggregate type, on the yield stress development was evaluated to find the optimal ratios for the potentially printable mixture. Then, to further improve the printability properties of the optimal mixture by inducing colloidal interaction (thixotropy effect) into the geopolymer binder system, the effect of adding nano clay (NC) and graphene oxide (GO) on the yield stress development and viscosity recovery properties of the mixtures was examined. The modification performance of GO and NC in geopolymer mixtures was

compared based on the results of rheometry, isothermal calorimetry, compressive strength, drying shrinkage strain evolution, scanning electron microscopy (SEM), x-ray diffractometry (XRD) and porosimetry analyses. Finally, the effect of various outdoor environmental conditions, i.e., temperature and relative humidity, on the pore water evaporation and 28-day drying shrinkage of 3D printable geopolymers was studied, considering the effect of NS, LSS, NC and GO in free-formed condition. Moisture loss and drying shrinkage evolution of free-formed nanomodified LSS-based geopolymers, which were cured under different environments of 24 °C – 50%RH, 35 °C – 90%RH and 35 °C – 50%RH, were compared to those cured under control condition. The findings of this chapter are expected to serve as a benchmark for further studies on the effect of different curing techniques (internal or external) on the hardened state dimensional stability of 3D printed products using alkali-activated binder systems with the aim of enhancing the structural integrity of the printed products by controlling the water evaporation and drying shrinkage development.

5.1 INTRODUCTION

Concrete is the most used construction material globally due to its appropriate physical, chemical, mechanical and durability properties [1]. A core component of cement-based concrete (generally cementitious materials) is ordinary Portland cement (OPC). OPC production is the most energy-consuming and pollutant-emitting aspect of cement-based concrete manufacturing, with a ~7% contribution to the global greenhouse gas emissions owing to its carbon dioxide (CO₂) emission annually [2–4]. Due to the significant energy consumption in OPC production, it is estimated that the cement industry is responsible for approximately 2.8 billion tonnes of CO₂ emissions per year, which is equivalent to around 5-6% of global CO₂ emissions [5,6]. The specific emissions per ton of cement produced vary depending on the manufacturing process and the fuel used, but on average it is around 0.8 -1 tonne of CO₂ per tonne of cement [7]. Initiatives have been undertaken recently to address these sustainability challenges of the construction industry and improve the built environment sustainability by minimising CO₂ emissions related to OPC manufacturing and enhancing the eco-friendliness of concrete manufacturing processes [8].

Some efforts that are underway to achieve abovementioned sustainability goals are as follows. Firstly, reducing high energy demand and CO₂ emissions of OPC production by enhancing cement plant efficiency [3]. Secondly, improving the

environmental performance of concrete production by substituting or increasing the proportion of raw materials that attain a higher level of sustainability (such as supplementary cementitious materials and underutilised aggregate) with the OPC and non-renewable natural aggregate in the concrete mixture [3,9–11]. Finally, upgrading the environmental performance of concrete production by developing novel automated construction technology that guarantees superior concrete properties whereas minimising its avoidable negative environmental consequences [12]. Because of its widespread usage, even a minor enhancement in the environmental performance of concrete might result in a substantial improvement in the eco-sustainability of the built environment.

Construction 3D printing (C3DP) technology and alkali-activated binder (typically known as geopolymer) system are two ecologically conscious advancements in the production of concrete that can be considered solutions to improve sustainability in the construction industry [8]. It has been shown that employing C3DP technology offers lower waste generation and higher resource efficiency as opposed to conventional construction technology [13,14]. Besides, alkali-activated concrete was developed as an alternative for traditional OPC-based concrete to reduce the structures' embodied carbon and decrease the OPC binder carbon footprint in the construction industry [15–18].

Even though C3DP technology offers substantial advantages in terms of labour cost-efficiency, formwork costs reduction, waste generation reduction, faster production speed, and application diversity for manufacturing low-cost non-rectilinear structures [19,20]. According to previous studies [20–22], cement-based C3DP mixtures require at least approximately 40% higher OPC content in their mixture compared to conventional casting concrete. Moreover, in C3DP mixtures, the fine aggregate content is generally about 2 times higher than that in conventional casting concrete [21]. This is because using coarse aggregate is limited due to the specific rheological and printability properties required for extrusion-based 3D printing, final surface finish and avoiding the blockage in the pumping and delivery system due to the small size of printing nozzles [23,24].

Consequently, the environmental effect of using C3DP in the construction industry has become a contentious issue regarding its large OPC consumption and over-exploitation of abiotic resources such as natural sand (NS) [22]. Alhumayani et

al. [25] carried out a life cycle assessment study on large-scale C3DP technology and determined that the most significant environmental effect of C3DP is associated with its vast OPC consumption, which necessitates the use of greener raw material [25]. Han et al. [20] studied the environmental and economic assessment of a building constructed with C3DP technology using underutilised raw materials. They outlined that although employing C3DP technology may substantially reduce construction costs, the significantly higher binder content used in C3DP mixtures as opposed to that in casting concrete mixtures increases CO₂ emissions in construction.

In order to minimise CO₂ emissions related to OPC usage in C3DP technology, several studies (e.g., [16,18,26–30]) have examined the viability of developing optimised 3D printable mixtures with supplementary cementitious materials (e.g. fly ash (FA), ground granulated blast furnace slag (GGBS)). The alkali-activated binders designed based on various ratios of FA and GGBS have been the most widely used alternative for OPC in C3DP mixtures [22]. Studies were conducted focusing on yield stress development, structural rebuilding and buildability of alkali-activated mortars for C3DP. For instance, Zhang et al. [26] investigated the influence of the Si/Na ratio in alkaline activators on the structural rebuilding and yield stress development of 3D printing geopolymer pastes prepared with GGBS. According to their findings, a lower Si/Na ratio in alkaline activator enhanced the structural rebuilding of geopolymer paste. Alghamdi et al. [16] examined the extrudability and buildability of FA-based 3D printable geopolymer incorporated with a minor proportion of limestone, OPC and GGBS. They found lower and upper bound of yield stress for printable mixtures at 150 Pa and 700 Pa, respectively [16].

It has been demonstrated that the optimal C3DP mixtures need to possess appropriate thixotropic characteristics, high yield stress, and low viscosity [18,31]. However, previous studies on the rheological properties of geopolymers reported that, as opposed to the OPC [32], alkali-activated binders do not have thixotropy properties due to the lack of colloidal interaction, which provides initial yield stress [28,33]. The yield stress development in geopolymer concrete is controlled by the percolation of aluminosilicate gel formed in the geopolymer system [33]. Therefore, some studies also were conducted to address this limitation by incorporating thixotropic agents such as nanoclay (NC). These studies showed that geopolymer mixtures could be tailored to obtain suitable buildability and mechanical properties for C3DP [34]. Panda et al.

[28] investigated the FA/GGBS-based mortar for extrusion-based 3D printing by examining the extrudability, shape stability, and buildability properties. Various S/B ratios of 1.0, 1.2, 1.4, 1.6 and 1.8 were considered with a FA:GGBS:SF binder composition of 0.78:0.14:0.08, AB of 0.42 and W/B ratio of 0.5. They reported that the optimum mixtures (S/B = 1.4) with yield stress within the range of 600 and 1000 Pa exhibited acceptable extrudability, while the acceptable shape stability coefficient was found between 0.85 and 0.90. A further modification was done by incorporating 1.2% NC to enhance the buildability performance due to the induction of thixotropic behaviour in the mixture. In another research by Panda et al. [35], the suitability of geopolymer mortars for use in C3DP was investigated by considering various mixing parameters such as MR, AB, WS ratios and NC modification. According to their findings, the optimum mixtures had FA:GGBS composition of 0.85:0.15 activated by AB and WS ratios of 0.35 and 0.30, respectively [35]. They reported that incorporating 0.5% (by weight of binder) NC improved the thixotropy and yield stress development of geopolymer mortar. However, NC incorporation reduced the mechanical strength of the mortar by approximately 17% [35]. Alkali-activated 3D printable mortars were developed by Chougan et al. [36]. The fresh state properties, including yield stress, shape retention and buildability properties, as well as the mechanical performance, were investigated for NC modified and control mixtures. According to their findings, the mixture modified with 1.0 wt% NC exhibited the optimum printing properties with 20% higher flexural and compressive strength compared to the control mixture [36].

The preceding studies revealed that incorporating NC into geopolymer-based 3D printable mixtures was effective for optimising materials printing requirements, especially by providing preferential nucleation sites [37] for hydration products precipitation and growth [38], inducing the shear-thinning behaviour and increasing the early structural build-up properties [36]. However, as discussed above there is still a lack of consensus on the results of the mechanical strength of NC-modified 3D printing mixtures. Moreover, based on the available literature, there is still no research on the drying shrinkage evolution of NC-modified 3D printable mixtures. It has been reported that NC-modification in cement-based concrete increased the shrinkage deformation due to the dispersion issues and probable increase of hydration degree [39]. Therefore, it is of great significance to investigate the effect of NC-modification

on the shrinkage evolution of 3D printing mixtures, especially under the formwork-free condition of C3DP and in an alkali-activated binder system.

Using Graphene-based nanomaterials (GBNs), i.e., graphene oxide (GO) and reduced graphene oxide (rGO), in alkali-activated mortars can be considered as a feasible solution to address the deficiencies that using NC additives may have for nanomodification of 3D printable alkali-activated mortars. GBNs have recently gained significant research interest in cement-based and alkali-activated concretes as relatively novel and advanced additives [40,41]. Rather than the enhancement of rheological and mechanical properties [42], it has been recently established that the incorporation of GBNs improved the resistance of alkali-activated materials to drying shrinkage evolution [43,44]. Ho et al. [43] investigated the effect of GO-modification on the fresh-state properties, mechanical strength and durability properties of FA/GGBS-based geopolymer mortar. According to their findings, adding 0.05% and 0.1% GO (wt%), improved the compressive and tensile strengths of the mortars. Moreover, the 28-day drying shrinkage deformation of 0.5% and 0.1% GO-modified mortars prepared with LSS reduced by 22% and 28%, respectively. The observed shrinkage-reducing behaviour was attributed to the microstructure densification and the crack propagation control with GO-modification. Liu et al. [45] investigated the effect of adding GO and rGO on the mechanical strength, microstructure and hydration degree of FA-based geopolymer mortars. They reported that GO-modification increased the dissolution rate of amorphous phases of FA particles and accelerated the geopolymerisation reactions. Moreover, they reported that the inclusion of GO and rGO reduced the porosity of the mortars and increased their flexural strength by up to 25% compared to that of the plain mortar. Recently, some studies have been conducted on the development of GBN-modified geopolymer ink and FA/GGBS alkali-activated mortars. Zhong et al. [46] reported that by incorporating 4% GO the yield stress of printing geopolymer ink increased from 4 Pa to 2000 Pa. They also reported that the compressive strength and elastic modulus of the printed GO-modified geopolymer ink increased with the increase of GO dosage from 4 to 10%. Zhou et al. [47] conducted similar research on 3D printing geopolymer ink modified with GO and outlined that GO-modification enhanced the fresh-state properties and mechanical strength of the 3D printing geopolymer ink.

Implementing GBNs modification into 3D printable mixtures has been rarely studied due to the relatively modern nature of C3DP technology. Rather than the studies on the use of GO in geopolymer ink, only one study has been carried out on developing FA/GGBS-based geopolymer mortar for C3DP using nano graphite platelet. Therefore, this chapter tried to further investigate the influence of using GO-modification on the rheological properties (i.e., yield stress evolution and viscosity recovery capacity), mechanical performance, microstructure modification and drying shrinkage development of FA/GGBS-based 3D printing geopolymer mortar, considering the formwork-free condition of 3D printing and various curing temperatures and humidities. The results of GO-modification were also compared to those of NC-modification. It is believed that using geopolymer binders in C3DP mixtures not only reduce the environmental effect of C3DP associated with its binder but also obtain a higher sustainability level as opposed to conventional casting via mixture optimisation and reduction of its dependence on the binder materials [22]. Yao et al. [8] conducted a life cycle assessment study on using geopolymer in C3DP and concluded that using alkali-activated binders can reduce the total carbon emission of concrete elements produced by the C3DP technique. However, over-exploitation of abiotic resources was still an environmental impact category where C3DP ranks low, and further improvements are necessary. Han et al. [20] used a life cycle assessment method and compared the environmental impact and economic benefits of conventional concrete manufacturing with C3DP when using recycled concrete aggregates in the mixtures. According to their research, substituting natural aggregate with recycled aggregate in C3DP can reduce its total global warming potential by approximately 2%. Moreover, it can significantly reduce the cost of building materials.

Several studies were conducted on the development of C3DP mixtures by substituting natural aggregate with underutilised aggregate, including mine tailing (waste aggregate) [48,49], recycled sand [50–53], and glass sand [54,55]. The studies on underutilised aggregate incorporation into C3DP mixtures exhibited that, at specific substituting ratios, the inclusion of recycled aggregate in the mixtures can increase the yield stress and structural build-up performance of the 3D printable mixtures while reducing their flowability and print open-time [50,51,53]. According to the results of the mechanical strength tests for C3DP mixtures with underutilised aggregate, it is generally expected that partial or full replacement of natural aggregate with

underutilised aggregate reduces the mechanical performance of the concrete [52,54,56]. Moreover, due to the higher water absorption characteristics and presence of capillary porosity, incorporating recycled aggregate in the C3DP mixtures might result in an increased drying shrinkage, adversely affecting the durability-related properties of the concrete [53]. Therefore, further research is required to find the most appropriate underutilised replacement material for natural aggregate that can improve the sustainability level of C3DP mixtures, while not sacrificing the mechanical performance and dimensional stability of the printed element.

Lead smelter slag (LSS), also known as black sand, is an industrial by-product from the metallurgical industry produced during pyrometallurgical processing of lead concentrates (wastes). LSS exhibited excellent mechanical strength and shrinkage performance when used as a substitution material for natural aggregate in cement-based and geopolymer concrete and mortar [57]. The similarity between LSS and natural aggregate physical and mechanical properties made it a suitable substitution for natural aggregates [57,58]. Atzeni et al. [59] performed the first study to establish that LSS can be used as sand in cement-based concrete. Additional investigations by Alwaeli [60] and Saikia et al. [61,62] revealed that the mechanical performance of cement-based concrete and mortar prepared using LSS was superior to that prepared with NS. Since LSS is enriched by silica, aluminium, calcium and iron oxide [63], it may be a suitable alternative material for binder or filler to be used in geopolymer concrete. Albitar et al. [58] studied using LSS as binder and filler in alkali-activated concrete. They showed that both approaches of full substitution of NS with LSS and 75% replacement of FA with LSS in the binder improved the mechanical strength of the alkali-activated concrete. The drying shrinkage of the concrete with high volume LSS as a binder was lower than that with FA [58]. Gholampour et al. [2] studied the complete substitution of NS with LSS in FA/GGBS-based mortars. Using LSS instead of NS reportedly increased the compressive and tensile strength of mixtures with binder proportions FA : GGBS of 1.0 : 0.0, 0.8 : 0.2, and 0.5 : 0.5 by up to 8%. Moreover, LSS-based geopolymer mortars showed a lower drying shrinkage at all ages for a given binder ratio [2].

Given that using LSS enhanced the strength and the resistance to drying shrinkage of geopolymer mortar, substituting NS with LSS in alkali-activated mixtures designed for C3DP might be a sustainable solution to address the concerns of higher

environmental impact, weak mechanical characteristics and excessive drying shrinkage of printable waste-based alkali-activated mortars, especially in C3DP. Therefore, understanding how LSS-based alkali-activated mortar would perform in terms of rheological behaviour, mechanical strength, and drying shrinkage is significantly critical for facilitating their use in extrusion-based C3DP technology.

5.2 RESEARCH SIGNIFICANCE AND NOVELTY

This chapter presents the first experimental study to evaluate the rheological and mechanical properties as well as the resistance to drying shrinkage of geopolymer mortars prepared with industrial by-product fine aggregate known as LSS for extrusion-based 3D printing. The performance of NS and LSS geopolymer mortars was investigated when the outdoor 3D printing environments were simulated by eliminating the initial curing (immediately removing the moulds/formworks) under three different outdoor printing environments with various temperature-relative humidity conditions. Moreover, this is the first experimental investigation of the thixotropy properties of printing geopolymer mortars containing GO as a rheological properties modifier. Furthermore, nano-modified geopolymer mortars that were modified with GO and NC (which is known as a conventional thixotropy modifier to enhance geopolymer rheological properties for extrusion-based 3D printing) were compared on their drying shrinkage development, moisture loss, mechanical properties and microstructure when cured under conventional casting and free-formed curing.

This study provides a baseline for future research on the influence of different curing processes (internal/external curing) on the shrinkage reduction (uniform/nonuniform) in geopolymer-based mortars intended for extrusion-based concrete 3D printing. Moreover, the outcomes of this research highlight the promising performance of GO modifications in comparison to NC in geopolymer mortars designed for extrusion-based 3D printing. This study presents a potential approach for developing environmentally-friendly 3D printing concrete based on industrial by-products, which can offer similar or better performance when compared to conventional construction materials such as cement-based concrete.

5.3 MATERIALS AND METHODOLOGY

5.3.1 Materials

Fly ash (FA) and ground granulated blast furnace slag (GGBS)

In this research, the fly ash (FA) was supplied by Boral, Australia. Figure 5.1 shows the particle size distribution of FA, measured by a laser diffraction particle size analyser Malvern Mastersizer 3000. Figure 5.2 (a) shows a scanning electron microscopy (SEM) image of the FA particle with spherical morphology [64]. The x-ray diffraction (XRD) pattern, including the constituents phase characteristic peaks of FA is shown in Figure 5.3. The XRD plot of FA showed crystalline peak pattern quartz (SiO_2 - COD# 1011159) and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ - COD# 9001567), which was consistent with what has been found in previous research [65]. The reactive chemical components of FA were determined by x-ray fluorescence (XRF) analysis and are shown in Table 5.1.

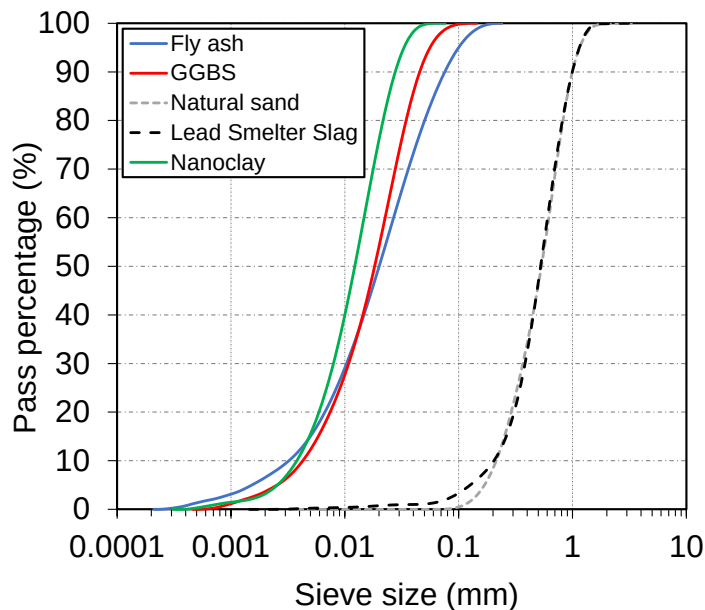


Figure 5.1. Particle size distribution of raw materials

The ground granulated blast-furnace slag (GGBS) was supplied by Cement Australia Pty Ltd. Maximum particle size of GGBS was 100 μm (Figure 5.1), and their microparticles had an angular morphology, as shown in Figure 5.2 (b) [66]. GGBS had an amorphous nature, as noticed by its XRD pattern shown in Figure 5.3, exhibiting broad humps at around $2\text{-}\theta = 18^\circ$ to 30° [29]. According to the supplier's datasheet, the GGBS consisted of more than 90% amorphous GGBS and less than 5% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The XRD plot of GGBS showed crystalline peak pattern $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

(COD# 1010981), Gehlenite ($\text{Ca}_2\text{Al}[\text{AlSiO}_7]$ - COD# 9006113) and Carnegieite (AlNaSiO_4 - COD# 1010953) [29,67]. The chemical composition of GGBS was measured by XRF analysis and listed in Table 5.1.

Table 5.1. Chemical composition of raw materials.

Compounds	FA (%)	GGBS (%)	NS (%)	LSS (%)	NC (%)
SiO_2	60.16	16.79	99.67	23.79	65.72
CaO	2.24	76.41	-	25.71	2.16
Al_2O_3	29.36	1.08	-	3.96	14.52
Fe_2O_3	4.48	0.32	0.13	20.13	4.42
SO_3	0.13	4.32	0.11	-	0.04
K_2O	1.18	0.82	-	0.29	0.95
Na_2O	0.03	-	-	0.30	0.75
TiO_2	1.29	0.1	0.05	0.28	1.37
MgO	0.55	-	-	6.05	9.35
MnO	0.12	0.03	-	-	0.15
SrO	0.14	0.03	-	-	-
ZnO	-	-	-	8.31	-
P_2O_5	0.19	-	0.01	-	0.44
Cr_2O_3	0.02	0.1	-	-	0.07
ZrO_2	0.08	0.01	-	-	0.05
Cl	-	-	0.03	-	-
V_2O_5	0.03	-	-	-	-
Pb_3O_4	0.01	-	-	11.19	-

Natural sand (NS) and lead smelter slag (LSS)

Black sand, or granulated lead (lead-zinc) smelter slag (LSS) from Port Pirie, South Australia, was used as fine aggregate in 3D printing geopolymer mortar in this study. Due to the high iron oxide concentration, LSS ranged in colour from black to red (mostly dark black). LSS was a granular substance with a specific gravity ranging from 2.65 to 3.79 and had a unit weight that ranged from less than 2.5 g/cm^3 to as high as 3.6 g/cm^3 [68]. As can be seen in Figure 5.2 (d), LSS was characterised as glasslike, angular, and sharp-cornered (cubical) particles, which is consistent with the literature [69]. LSS is porous by nature, and its water absorptions can be slightly higher than the natural river sand (NS) [68]. The water absorption of LSS in this study was about

1.4%. The LSS chemical composition by XRF analysis, particle size distribution, and XRD diffraction spectra are presented in Table 5.1, Figure 5.1 and Figure 5.2, respectively. The XRD plot of LSS showed crystalline peak pattern minium (Pb_3O_4 - COD# 9003043) and wustite (FeO - COD# 1011164), which was consistent with what has been found in previous research [2,70].

Washed high-purity NS was supplied by Sibelco Australia Ltd, sourced from the Lang Lang River area in Victoria. To exactly replicate the particle size distribution of LSS, three different classes of G16/30, G45 and G55 with different particle size gradings of 330 μm - 2544 μm , 105 μm – 1183 μm , and 71 μm - 806 μm , respectively, were mixed with specific proportion. The density and water absorption of NS were 2600 kg/m^3 and 0.4%, respectively. The maximum particle size of the modified NS and LSS was 2.1 mm, as shown in Figure 5.1. Figure 5.2 (c) shows the NS particles shape. The NS consisted of more than 99% crystalline silica, as shown in Table 5.1 and Figure 5.3.

Activator solution

12 Molar sodium hydroxide (NaOH) and grade D sodium silicate (Na_2SiO_3) solutions (supplied by PQ Australia Pty Ltd, Australia) with alkaline modulus ratio ($\text{MR} = \text{SiO}_2/\text{Na}_2\text{O}$ molar ratio) of 2.1 and density of 1.52 g/ml were used to prepare the alkaline activator solution for geopolymer mixes. The Na_2SiO_3 solution consisted of 14.6 wt% Na_2O , 29.6 wt% SiO_2 and 55.8 wt% water. As stated in Table 5.2 and Table 5.3, the proper quantity of NaOH was added to Na_2SiO_3 solution to reach the required activator MR for geopolymer mix design. The premixed alkaline activator solution was kept at ambient temperature to rest for 24 h before the start of mixing.

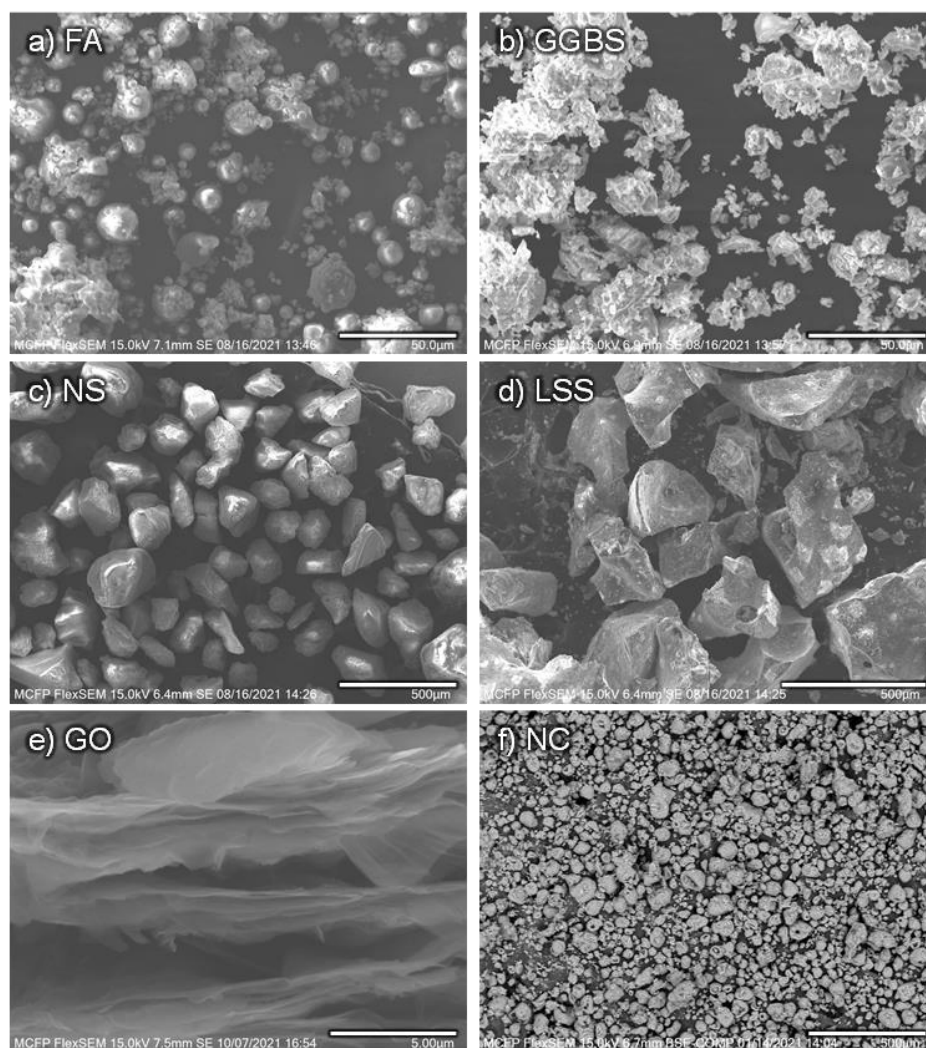


Figure 5.2. SEM images of raw materials shape and size, (a) FA, (b) GGBS, (c) NS, (d) LSS (e) GO layers, (f) NC.

Graphene oxide (GO)

25 mg/cm³ aqueous dispersion of graphene oxide (GO), a densely packed single layer of carbon atoms that are bound in a hexagonal lattice structure, was supplied by Graphenea, Spain. The GO can be available in powder, paperlike film and solution forms [71]. In this study, to improve the dispersibility of GO in the geopolymer mixes, an aqueous solution of GO was used. The maximum particle size of GO (D_{90}) in the slurry form was 30 µm. However, as per the supplier's recommendation, diluting the solution to 0.05 wt% can result in monolayer GO content, and sonication treatment also reduces the GO particle size. Figure 5.2 (e) shows the SEM image of a paperlike GO membrane prepared by water evaporation from aqueous GO dispersion. As shown in Figure 5.3, the XRD spectra of GO reveal a sharp peak at the 2-theta angle of 11.1°,

which corresponds to the (0,0,1) crystal plane of GO, with an intersheet spacing of 8.33 Å [72].

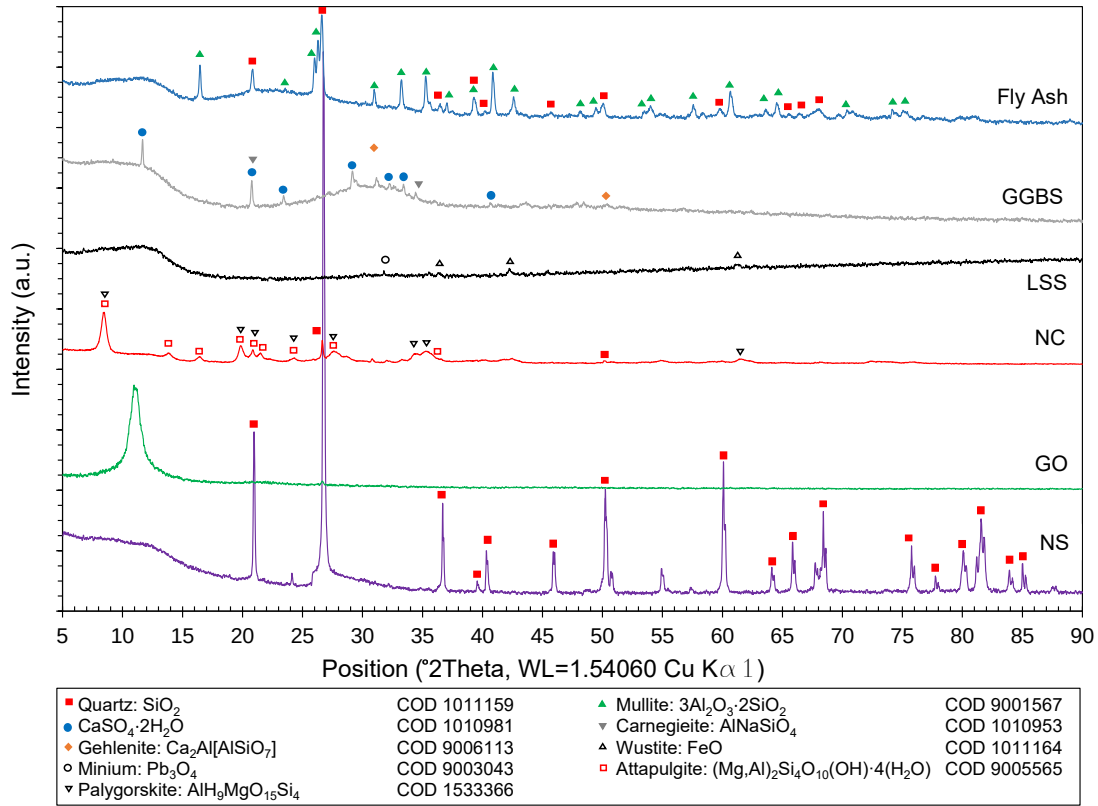


Figure 5.3. X-ray diffraction spectra of raw materials, including the characteristic peaks of the constituents phases.

Nanoclay (NC)

In this study, magnesium-aluminosilicate clay (attapulgite) was used as a low-dose rheology modifier and anti-settling agent to stabilise mixtures, provide better fine aggregate suspension, and improve the performance and paste quality of mixtures by enhancing flow characteristics (pumpability and workability) of 3D printing geopolymers under the shearing condition of 3D printing [28,73]. Attapulgite is a member of the palygorskite group of fibrous clay minerals. However, commercially it is most often known as nanoclay (NC). The theoretical formulation of NC is (Mg, Al)₂Si₄O₁₀(OH)·4(H₂O). Active Minerals International (Actigel), USA, supplied a highly purified form of the NC in this study. The NC consisted of spheroidal agglomerates (Figure 5.2 (f)) when supplied in a powder form. However, the liquid suspension of NC consists of uniformly sized, rod-shaped mineral particles [35]. The particle size distribution of NC was determined by laser diffraction analysis and is shown in Figure 5.1. The chemical composition of the NC determined by XRF analysis is displayed in

Table 5.1. The XRD pattern of NC (shown in Figure 5.3) showed a peak pattern of palygorskite with monoclinic (COD# 9005565) and orthorhombic (COD# 1533366) crystal systems.

5.3.2 Mixture design and sample preparation

The first step in designing waste-based geopolymer mortars with LSS for concrete 3D printing applications was to find an appropriate binder (FA:GGBS) ratio and adjust the alkaline activator parameters. To achieve this, the yield stress evolution of mixes presented in Table 5.2 was investigated to select the best rheological behaviour for the base mix design. In the next step, the effect of GO and NC on the yield stress development, structural rebuilding and durability properties of printable waste-based geopolymer mortar was investigated. Mixes in Table 5.2 were designed considering different parameters of FA:GGBS ratio, activator to binder ratio (AB) and activator modulus ratio ($MR = \text{SiO}_2/\text{Na}_2\text{O}$ molar ratio). Considering the mixture design of previous experimental studies on 3D printable geopolymer mortar [35] and waste-based nano-modified geopolymer composites [2,74] as benchmark studies, geopolymer mortar containing LSS as fine aggregate was designed with three FA:GGBS ratios of 1.0:0.0, 0.8:0.2 and 0.5:0.5. Additional water was added to keep the water to solid ratio (WS) constant at 0.35 for all mixes, while the fine aggregate to binder ratio was kept constant at 1.5. As discussed in Section 5.3.1.3, the alkaline activator with $MR = 2.1$ and 1.5 was used to compare the effect of MR on the yield stress development in the mixes. In addition, AB ratios of 0.35 and 0.40 were evaluated in terms of flowability to determine the optimal AB ratio. To prepare the mortar mixes, dry mixing was conducted for 3 min by the addition of FA and GGBS with saturated surface dry (SSD) fine aggregate (LSS/NS) and NC (where needed). Then, the alkali liquid was gradually added to the mixes, and wet mixing was continued for 5 min. To increase the flowability of the geopolymer mixes and avoid their immediate setting, the alkaline activator premix was pre-heated to $35\text{ }^{\circ}\text{C}$ to reduce the liquid viscosity to less than one poise ($1\text{ P} \sim 100\text{ mPa.s}$) before the start of mixing [75].

The mixtures presented in Table 5.2 and Table 5.3 were coded for the rheological properties experiments. Mixtures codes consist of two sections divided by a dash “-” mark. The first section before the dash includes information about the dry components, including the FA:GGBS (GGBS is shown by the letter “G” in the mix codes) ratios followed by the type of fine aggregate (LSS or NS). The FA and GGBS percentages in the binder are shown as subscript numbers. The second section after the dash exhibits the alkali solution parameters in the mixtures, including AB ratios (35 for AB = 0.35 and 40 for AB = 0.40) and MR (1.5 and 2.1). For example, FA₈₀G₂₀LSS-AB₃₅MR_{2.1} is a geopolymer mortar mixture with an FA:GGBS ratio of 0.8:0.2 made by lead smelter slag as fine aggregate activated by an AB ratio of 0.35 and activator modulus of 2.1.

Table 5.2. Mix design for the yield stress measurements of geopolymer mortars. The water to solid ratio (WS) for all the mixes was constant at 0.35.

Mix Code	Binder		Fine Aggregate		Activator		Activator ratios		
	FA (kg/m ³)	GGBS (kg/m ³)	NS (kg/m ³)	LSS (kg/m ³)	Na ₂ SiO ₃ (l)	NaOH (l)	Extra Water (l)	Activator to Binder ratio (AB)	SiO ₂ /NaO ₂ (MR)
FA ₁₀₀ G ₀ LSS-AB ₃₅ MR _{1.5}	980	0	0	1470	280	63	192	0.35	1.5
FA ₈₀ G ₂₀ LSS-AB ₃₅ MR _{1.5}	784	196	0	1470	280	63	192		
FA ₅₀ G ₅₀ LSS-AB ₃₅ MR _{1.5}	490	490	0	1470	280	63	192		
FA ₈₀ G ₂₀ NS-AB ₃₅ MR _{1.5}	784	196	1470	0	280	63	192	0.35	2.1
FA ₈₀ G ₂₀ LSS-AB ₄₀ MR _{1.5}	686	171.5	0	1286.3	280	63	150		
FA ₁₀₀ G ₀ LSS-AB ₃₅ MR _{2.1}	950	0	0	1425	333.3	0	201.7		
FA ₈₀ G ₂₀ LSS-AB ₃₅ MR _{2.1}	760	190	0	1425	333.3	0	201.7	0.35	2.1
FA ₅₀ G ₅₀ LSS-AB ₃₅ MR _{2.1}	475	475	0	1425	333.3	0	201.7		
FA ₈₀ G ₂₀ NS-AB ₃₅ MR _{2.1}	760	190	1425	0	333.3	0	201.7		
FA ₈₀ G ₂₀ LSS-AB ₄₀ MR _{2.1}	666.7	166.7	0	1250	333.3	0	160	0.4	

As will be discussed in Sections 5.4.1.1 and 5.4.1.2, the FA₈₀G₂₀LSS(or NS)-AB₃₅MR_{1.5} mixture was selected as a base mix in terms of proper FA:GGBS, AB and MR ratios for further nano modification in order to develop a waste-based 3D printable geopolymer mortar. To enhance the rheological properties (yield stress, thixotropy) of the base mixes and compare the effect of incorporating GO and NC on the fresh and

hardened state properties of 3D printable waste-based geopolymer mixes, four different dosages (by weight of binder) of 0, 0.03, 0.05 and 0.07 wt% for GO and 0, 0.17, 0.33 and 0.50 wt% for NC were considered. The NC dosages were selected according to the supplier's recommendation and by considering the previous research on the yield stress and thixotropy properties of 3D printing geopolymer concrete [28,76]. However, GO dosages were chosen based on trial mixing to replicate similar yield stress development behaviour to their counterpart NC-modified mixes. Table 5.3 represents the proportion of materials in the nano-modified mixtures. Mix codes shown in Table 5.3 are generated by removing the constant parameters from the code name of FA₈₀G₂₀LSS(or NS)-AB₃₅MR_{1.5}, followed by the type of nano materials (GO/NC) added to the mix, including the dosage values as a subscript. For instance, NS, LSS and LSS-GO_{0.07} in Table 5.3 represent unmodified (plain) FA₈₀G₂₀NS-AB₃₅MR_{1.5}, unmodified FA₈₀G₂₀LSS-AB₃₅MR_{1.5}, and nano-modified FA₈₀G₂₀LSS-AB₃₅MR_{1.5} with 0.07 wt% GO geopolymer mortars, respectively.

Where NC was added, it was blended with the dry mix. For GO, their exact quantity was calculated using the GO concentration (25 mg/ml) in the aqueous solution. To maintain the amount of mixing water constant across all GO-modified geopolymer mortars, the water fraction in GO aqueous solution was deducted from the extra water added to the mixes. To develop GO-modified mixes, GO solution was mixed with the extra water in a separate container, and then mechanical stirring was conducted for 2 min, continued by 30 min of sonication. The diluted GO solution was gradually added to the mixes after adding the alkaline activator, and the mixing was continued for 8 min. Then, the fresh mixtures were poured for the mechanical and durability tests or used for the fresh properties measurement.

Table 5.3. Mix design for investigating the effect of GO and NC incorporation on the properties of 3D printable geopolymer. MR, WS, AB and FA:GGBS was kept constant at 1.5, 0.35, 0.35 and 0.80:0.20, respectively.

Mix Code	Binder (Kg/m ³)		Alkaline Activator (Kg/m ³)			Fine Aggregate (Kg/m ³)		Additives (Kg/m ³)	
	FA	GGBS	Na ₂ SiO ₃ (29.6% SiO ₂ + 14.6% Na ₂ O)	NaOH 12M (36.1% NaOH)	Extra water to reach WS = 0.35	LSS	NC	GO (l) (25 mg/ml)	
	0.80B	0.20B	0.285B	0.065B	Added Water	Water GO	1.5 B	0.17 %- 0.50 % B	0.03%- 0.07% B

NS	784	196	280	63	192	-	1470	-	-
LSS	784	196	280	63	192	-	1470	-	-
LSS-GO _{0.03}	784	196	280	63	180.5	11.5	1470	-	11.8
LSS-GO _{0.05}	784	196	280	63	172.9	19.1	1470	-	19.6
LSS-GO _{0.07}	784	196	280	63	165.2	26.8	1470	-	27.4
LSS-NC _{0.17}	784	196	280	63	192	0.0	1470	1.6	-
LSS-NC _{0.33}	784	196	280	63	192	0.0	1470	3.2	-
LSS-NC _{0.50}	784	196	280	63	192	0.0	1470	4.9	-

5.3.3 Control and free-formed curing conditions

To explore the effect of diverse outdoor environment on mechanical performance and shrinkage strain growth of geopolymer-based 3D printing mortar, three different climatic classes of standard condition (T_s RH_s), high temperature-standard relative humidity (T_H RH_s), and high temperature-high relative humidity (T_H RH_H) given in Table 5.4 were used in this study as curing conditions for the mixtures of Table 5.3.

Table 5.4. Environmental temperature and relative humidity of distinct climate classes for geopolymer-based 3D printing mortar.

T_s RH _s	T_H RH _s	T_H RH _H
24 °C - 50%	35 °C -50%	35 °C - 90%

The curing weathers of Table 5.4 are not precisely the same as the actual outdoor environmental conditions. However, they are representative of the average temperature and relative humidity of the continent of Australia's temperate, tropical and dry regions. The discussion on how these classifications were obtained was explained in Section 4.3.3 of the thesis. Moreover, two initial curing procedures of “control” and “free-formed” were followed to replicate the initial curing of form-worked (conventional casting concrete) and free-formed (3D printing) concrete, enabling us to compare the effect of diverse temperature-relative humidity on geopolymer-based printing mortar, as well as the performance of nano-enabled (GO and NC) printing mixtures at simulated 3D printing curing environment.

The initial reading for shrinkage measurement was done after the initial curing process. The “Control” initial curing process was 24 h mould curing in plastic sealed condition continued by demoulding and 28 days of curing in T_s RH_s in the open-to-atmosphere state. The “free-formed” initial curing process was done by putting the samples in the environmental chambers immediately after moulding without any plastic sealing. Then demoulding of the samples was carried out at their initial setting

time (approximately 1 h for FA₈₀G₂₀LSS(or NS)-AB₃₅MR_{1.5}), and the initial readings were recorded. Finally, samples returned to their corresponding curing conditions in Table 5.4.

5.3.4 Testing procedure

Rheological measurement and setting time

Yield stress development

In this research, a HAAKE Viscotester 550 rheometer was used to measure yield stress development of the geopolymer-based 3D printing mortar during the first 60 min (before initial setting time) from the start of mixing (activator addition). The static yield stress was measured at different rest times after the start of mixing with an interval of approximately 6 min. The first measurement was recorded immediately after mixing was finished (10 min), and a four-blade vane geometry with a blade dimension of 5 mm × 20.1 mm (rectangular shape) was used to apply deformation at a constant shear rate of 0.2 s⁻¹. In this test, the shearing torque versus time was recorded. The shearing torque gradually increased to the maximum value before stabilising at an equilibrium value. The static yield stress was calculated by converting the maximum torque to yield stress using the vane geometrical parameter.

Viscosity recovery test

Viscosity recovery of the mixtures was measured with Anton Paar - MCR 702 TwinDrive rheometer to investigate the capability of the designed mixtures in recovering their initial viscosity after deposition of a filament. This test can imitate the extrusion-based concrete 3D printing process, resulting in deflocculation (during extrusion) and re-flocculation (after deposition) of the microstructure of the geopolymer mortars and changes in their fresh state properties after the filament deposition. The test simulates the materials states in extrusion-based concrete 3D printing by applying deformation at different shear rates in a three-step process of 0.01 s⁻¹ for 1 min, 300 s⁻¹ for 30 sec and 0.01 s⁻¹ for 1 min. These three steps represent (1) the resting period: when the mortar is not extruded, (2) the high shearing condition of mortar extrusion: when the mortar is pumped through the delivery system, and (3) the resting period after deposition: when the filament is printed. This method has been previously used in Ref. [29]. In this test, the apparent viscosity of the mix FA₈₀G₂₀LSS-AB₃₅MR_{1.5} as a control mix was considered, and the effect of GO and NC incorporation at different ratios on the control mix was investigated.

Isothermal calorimetry

The heat dissipation rate and the total heat generated during the geopolymerisation and polycondensation reactions were measured for all the paste mixtures in Table 5.3, in accordance with ASTM C1702-17 [77] using a TAM AIR Isothermal microcalorimeter for 48 h under a constant temperature of 23 °C. 100 g of samples were initially prepared outside of the calorimeter using temperature equilibrated materials, then 25 g of the samples were put into the sample vial and moved to the measurement chamber of the calorimeter within less than 2 min.

Axial compression test

The uniaxial compression test was done according to ASTM C109-08 [78] for three identical 50 mm cubic specimens at each composition-curing configuration, and the results were obtained by taking the average of the three test measurements. The loading rate for the tests was set at 0.5 N/mm².s. Free-formed specimens of the selected mortar compositions were tested after 28 days of curing in their corresponding environment shown in Table 5.4. The results were compared to conventional casting of 28-day cured specimens at T_s RH_s.

Drying shrinkage and weight loss measurement

The drying shrinkage strain was measured according to ASTM C596-07 [79] for the nano-enabled geopolymer mortar specimens of Table 5.3, except for the mixes with the minimum NC (0.17 wt%) and GO (0.03 wt%) content. Three nominally identical beam specimens for each geopolymer mix were cast with the dimension of 25 mm × 25 mm × 285 mm, and the drying shrinkage test results were reported by averaging the reading of the three specimens. The initial curing methods for the synthesised specimens were divided into two categories of free-formed (FF) and control (conventional casting, CC) conditions. In the free-formed method, to imitate the open-to-atmosphere curing environment of extrusion-based concrete 3D printing, specimens were exempted from the initial sealed curing in plastic pouches by immediately putting them inside the environmental chamber at different temperature-relative humidity conditions of Table 5.4. However, the control specimens were initially cured for 24 h at 100% relative humidity in sealed plastic pouches at 24 °C. To simulate the open-to-atmosphere curing environment, free-formed specimens were demoulded after 60 min (the initial setting time of the base mix). This was done to prevent any cracking during the demoulding process. The first length measurement

(initial reading) was recorded following ASTM C157-08 [80] after 24 h and 1 h for control and free-formed specimens, respectively. After the initial reading, samples returned to their corresponding drying temperature and relative humidity. The length changes and mass loss measurements were recorded at four different time intervals at the first day (generally 3, 6, 18 and 24 h), continued once a day during the first week and at 14, 21 and 28 days after the initial reading. Length changes and mass loss measurements were recorded using a high precision digital length comparator (0.001 mm) and a weighing machine (0.01 g), respectively. Table 5.5 summarises the drying shrinkage experiment setup. Drying shrinkage specimen codes consist of “Drying condition code” presented in Table 5.5 followed by the “Mix code” from Table 5.3. For example, FF-3590-LSS-GO0.05 is a geopolymer mortar mix with lead smelter slag as fine aggregate incorporated with 0.05 wt% GO, which was initially cured under the free-formed adjustment and was stored at 35 °C - 90% RH for the drying shrinkage test.

Table 5.5. Drying shrinkage experiment setup and initial curing adjustment.

Standard, Mould size	Initial curing method	Drying chamber temperature Relative Humidity (RH)	Drying condition code
ASTM C596-07 [79] & ASTM C157-08 [80] Mould size 25 mm × 25 mm × 285 mm	Control (CC): Initial curing was done for 24 h at 24 °C and ~100% RH in an airtight plastic pouch. Then, the specimens were demoulded, and measurements started. Specimens were stored in drying chambers afterwards until 28 days.	24 °C 50%	CC-2450
	Free-formed (FF): Without initial curing, specimens were stored in a drying chamber immediately after the placement. Specimens were demoulded, and measurements started after 1 h. Specimens were stored in their corresponding drying chambers afterwards until 28 days.	24 °C 50%	FF-2450
		35 °C 90%	FF-3590
		35 °C 50%	FF-3550

Microstructural analysis

X-ray diffraction (XRD)

In order to characterise the nano-enabled geopolymer mortars and raw materials mineralogical composition, x-ray diffraction (XRD) analysis was carried out using a Bruker D8 Advance X-Ray diffractometer with Cu-K α -radiation ($\lambda = 1.54060 \text{ \AA}$), operated at 40.0 kV and 40.0 mA. With a step size of 0.02 ° and 192 sec/step measuring

time, the scan pattern in the 2-theta range of 5° to 90° was recorded to determine the change in the crystalline microstructure of 3D printable geopolymer-based mortars because of the NC and GO incorporation as well as different drying environment temperatures and relative humidities.

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was conducted for surface imaging and morphology using a Hitachi FlexSEM 1000 scanning electron microscope, equipped with secondary electron (SE) and back-scattered electron (BSE) detectors as well as energy-dispersive x-ray spectroscopy (EDX) for elemental identification and mapping. Samples were taken from selected mixtures after 28 days of curing to examine the microstructure of the geopolymers mortars at different drying configurations.

Nitrogen adsorption - desorption (NAD)

A micromeritics 3Flex surface and micropore analyser was used to perform the N₂ gas sorption (pore size distribution) analysis in the relative pressure (P/P^0) ranging from 0.001 to 0.99 at the temperature of 77.3 K. Test samples were obtained from the free-formed and control nano-enabled and plain geopolymer mortars after drying shrinkage test in different drying environment at their 28 days of the drying process. The specimens were crushed and screened through a 500 µm mesh sieve to obtain powder samples. In addition, vacuum drying and degassing was conducted 24 h prior to the test. The pore size distribution analysis includes the cumulative and differential pore volume measurements calculated from the transformation of relative pressure using the Density Functional Theory (DFT) model. This model is based on the principles of statistical thermodynamics that considers the entire spectrum of adsorption-desorption isotherms to calculate the pore size distributions as opposed to the classical theories such as Brunauer–Emmett–Teller (BET) and Barrett-Joyner Halenda (BJH) which is bound to a specific region of the adsorption-desorption isotherm (for BJH theory, only desorption curves are used) rather than the entire curve [81]. Therefore, in this study, the microstructure porosity of the potentially 3D printable LSS geopolymer mortars was studied using the pore size distribution and total pore volume of the mortars extracted by using the DFT model.

5.4 RESULTS AND DISCUSSION

5.4.1 Yield stress development

Measurement of rheological behaviour, including yield stress and viscosity, is an indirect technique for evaluating concrete extrusion and pumpability properties. The ease of extrusion and the capacity of geopolymer mortar to flow easily under pumping pressure while maintaining and recovering the precededented fresh properties after the deposition can be designed and controlled by measuring these rheological parameters [82]. Static yield stress is the minimum required shear stress to be applied before the mix initiates flowing in the delivery system, while the viscosity is the resistance of the material against the flow when the flow is initiated [83]. According to the previous research, different parameters including binder types and ratios [28], the volume of the paste (fine aggregate to paste ratio), the morphology of the constituent particles [84], the liquid content in the mix (AB and WS ratios) and the $\text{SiO}_2/\text{Na}_2\text{O}$ MR of the activator [26] are important factors in the development of the yield stress and the viscosity of the geopolymer mortars appropriate for concrete 3D printing. In this section, the results of static yield stress development in the waste-based geopolymer mortars are presented and discussed by considering different ratios of FA:GGBS ranging from 1:0, 0.8:0.2, and 0.5:0.5 with the complete replacement of NS with LSS, different AB ratios of 0.35 and 0.4 and different MR of 2.1 and 1.5. The fine aggregate to binder and WS ratios were kept constant at 1.5 and 0.35, respectively. Trials tests for WS ratios of 0.3 was conducted. Since the workability of the mixes was very limited at $\text{WS} = 0.3$, this parameter was fixed at 0.35 in all mixes.

Effect of binder composition and activator molarity ratio

Figure 5.4 plots the static yield stress development results of the LSS geopolymer mortars with different FA:GGBS and activator modulus during the first 120 min after mixing. $\text{Na}_2\text{SiO}_3\text{-NaOH}$ solution with $\text{MR} = 1.5$ and 2.1 was used as an activator solution. Since one of the aims of this study was to develop a potentially printable waste-based geopolymer mortar, considering that the angular morphology of LSS aggregate can increase the yield stress development rate of the geopolymer mortars (compared to NS), the FA:GGBS ratio and activator modulus were adjusted on LSS rather than NS geopolymer mortars.

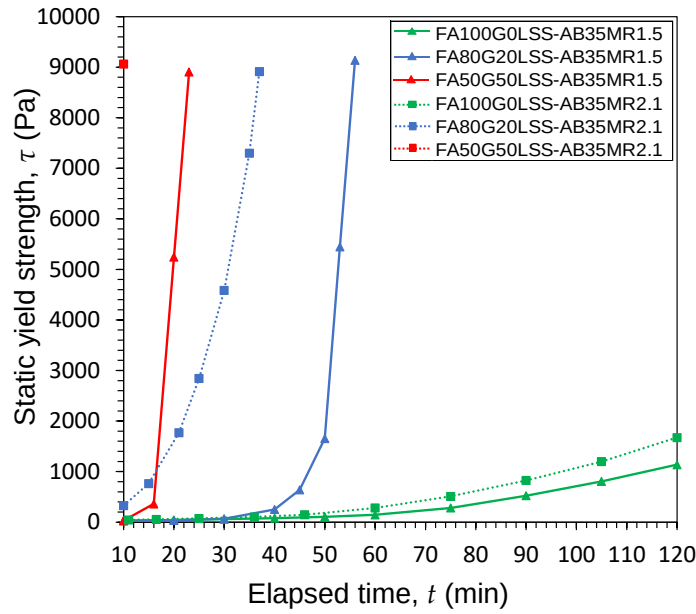


Figure 5.4. Effect of FA:GGBS and MR ($\text{SiO}_2/\text{NaO}_2$) ratio of activator on yield stress development of LSS geopolymer mortar.

According to previous studies in the literature, mortars that develop initial (minimum) yield stress within the range of 550 and 1000 Pa are potentially suitable for printing in terms of printing layers stability (strength-based) and extrudability [28,85,86]. Except for the FA₁₀₀G₀LSS-AB₃₅MR_{1.5} and FA₁₀₀G₀LSS-AB₃₅MR_{2.1} which had yield stress of 1000 Pa after 120 min, all the other mixes attained this yield stress limit in less than 45 min. The reason for the higher fluidity of FA₁₀₀G₀LSS series mixtures compared to other series mixtures can be the slower reactivity of FA than that of GGBS, which results in slower dissolution and gel restructuring rate in FA₁₀₀G₀LSS mixes [29]. Moreover, the FA particles are spherical in shape, providing a ball-bearing effect that enhances LSS particles movement in the flow and reduces the interparticle friction and interlocking effect in the geopolymer mortar [87]. As can be seen in Figure 5.4, the yield stress development accelerated by increasing the GGBS content. At AB = 0.35 and MR = 1.5, by increasing the GGBS from 0 to 20% and 50%, the time when the mix developed 1000 Pa shear stress decreased from 120 min to 45 min and 15 min, respectively. This is because the GGBS reactivity with alkaline activator solution is more rapid than that of FA, as well as the fact that GGBS has angular particle morphology compared to the spherical shape of FA [88]. By increasing the activator MR value from 1.5 to 2.1 at a constant AB ratio of 0.35, the yield stress development rate of all the mixes increased irrespective of the FA:GGBS

ratio. However, the rate of increase was significantly higher for the mixes with 20% and 50% GGBS in the binder.

As can also be seen in Figure 5.4, the FA₅₀G₅₀LSS-AB₃₅MR_{2.1} passed 9000 Pa immediately after mixing (10 min), while the FA₈₀G₂₀LSS-AB₃₅MR_{2.1} reached this stress after 35 min. The observed enhancement in the yield stress can be partially interpreted as being a result of an increase in the viscosity of the activator solution with an increase of MR [35]. The rate of yield stress evolution in FA₁₀₀G₀LSS was trivial within the first 60 min, while that of the FA₅₀G₅₀LSS mixes was extremely steep. Therefore, geopolymer mortar with FA₈₀G₂₀LSS solid fraction configuration was selected as a base mix of a printable waste-based geopolymer mortar for the rest of the study. Before investigating the effect of NC and GO on the fresh and hardened state properties of LSS geopolymer mortar, the effect of AB and LSS was studied and the results are presented in the following section.

Effect of activator to binder (AB) ratio and fine aggregate morphology

Figure 5.5 demonstrates the effect of changing the activator to binder ratio (AB = 0.35 and 0.40) and complete replacement of NS with LSS on the yield stress development of the geopolymer mortars with FA:GGBS = 0.8:0.2 at a constant WS ratio of 0.35. Increasing AB ratio reduces the concentration of solid particles in the geopolymer. Therefore, it is generally expected that increasing the AB results in the reduction of the yield stress [35]. Figure 5.5 represents the results for LSS- and NS-based geopolymers activated by MR = 1.5 and 2.1. It is shown that, at MR = 1.5, the yield stress of FA₈₀G₂₀LSS geopolymer mortars reduced significantly when the AB increased from 0.35 to 0.40. This reduction was observed by the delay made in the yield stress evolution. By increasing the AB from 0.35 to 0.40, the time when FA₈₀G₂₀LSS (activated by MR = 1.5) exceeded the 1000 Pa limit was delayed by 33%. The delay in the yield stress evolution was even higher (60%) for FA₈₀G₂₀LSS when the MR = 2.1 was used. This is because increasing the AB ratio causes an increase in the volume of the liquid in the mix, which results in a larger average interparticle distance and increased width of the liquid film around particles, thereby reducing the yield stress development [35].

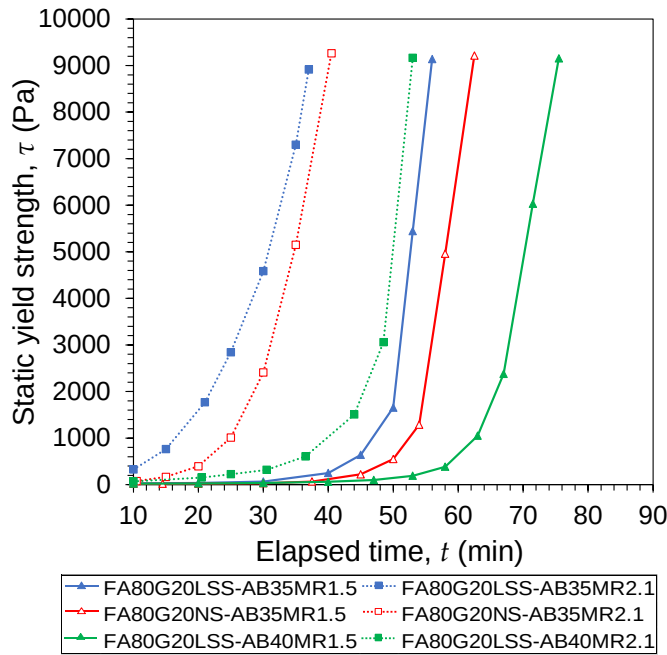


Figure 5.5. Effect of activator to binder ratio (AB) and replacement of NS with LSS on yield stress development of FA₈₀G₂₀-based geopolymer mortar.

It is also shown in Figure 5.5 that geopolymer mortar produced with NS experienced a delayed yield stress development compared with LSS. At constant AB of 0.35 and MR of 1.5, FA₈₀G₂₀NS exhibited approximately 67% lower yield stress than FA₈₀G₂₀LSS, while this reduction was approximately 49% when the MR increased to 2.1. This is because LSS particles have a higher degree of irregularity than NS; thus the interparticle friction in LSS mixes was higher, resulting in a higher yield stress in LSS mixes [2,43]. These findings suggest that the activator viscosity (Na₂SiO₃-NaOH) significantly impacts the geopolymer yield stress development. However, the yield stress is more controlled by interparticle contacts and the fluid film thickness. The values of the regulating factors in this study, including FA:GGBS, AB, and MR ratios, as well as the range of the yield stress development, are comparable to those of prior studies on the characteristics of different 3D printable geopolymers [28,35,89]. Because FA₈₀G₂₀LSS-AB₃₅MR_{1.5} exhibited a yield stress development behaviour that was reasonably comparable to those seen in prior studies on 3D printable geopolymers, this mixture was selected as a base mixture for further improvements with nanomaterials. Further improvement of the yield stress development and adjustment of thixotropy behaviours to enhance shape stability properties of the base mix will be investigated in Section 5.4.2.

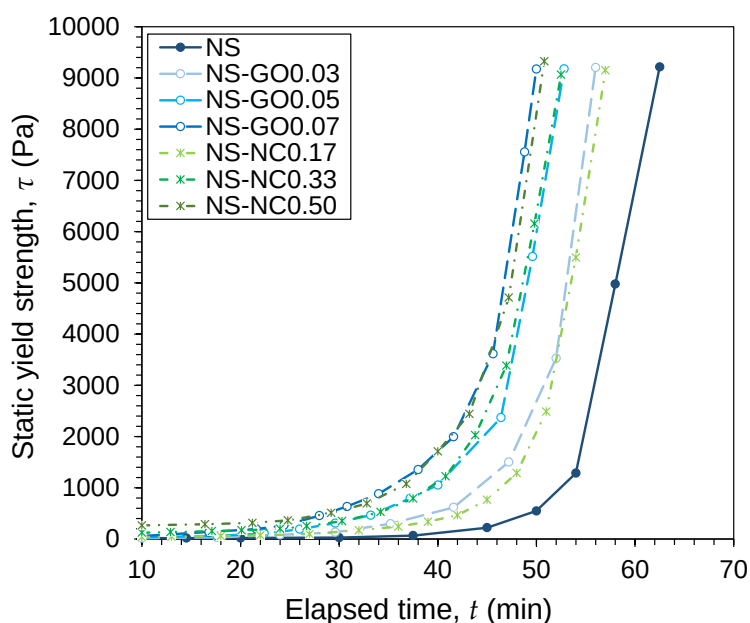
Effect of nanoclay (NC) and graphene oxide (GO)

As reported in previous studies [37,76,90], NC inclusion in the geopolymer mortars improves the structural rebuilding properties of fresh mixes by increasing their yield stress evolution at rest and reducing their viscosity when a shearing force is applied. One of the objectives of this study was to evaluate the effectiveness of GO inclusion as a thixotropy agent in printable geopolymer mortars and compare it with that of NC, which has been commonly used as a thixotropic agent in geopolymer mortars. Because GO has a sizeable hydrophilic surface area, their addition into geopolymer mortar can result in a high level of water absorption on the surface of GO nanosheets; thereby, the free water content required for hydrodynamic interaction in the mix is reduced. Thus, it is generally expected that by incorporating GO into the mixes, the yield stress increases and the flowability decreases [42].

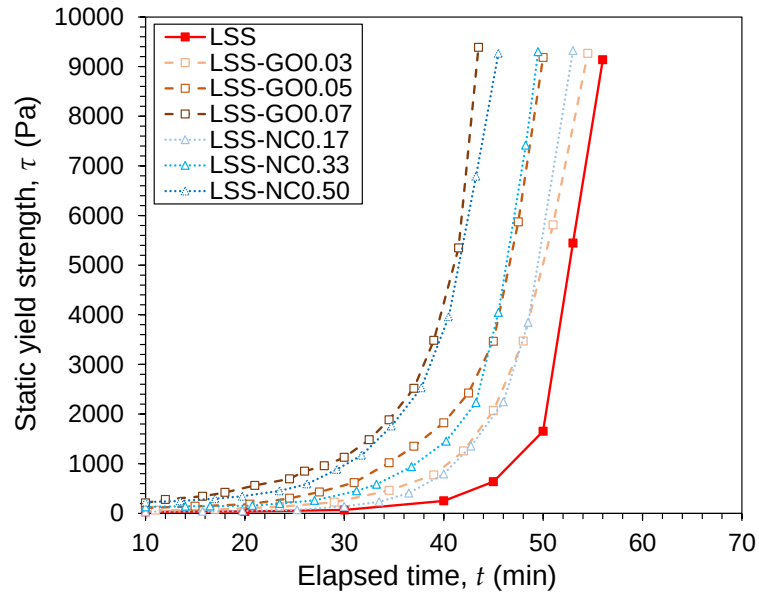
To examine this, FA₈₀G₂₀NS-AB₃₅MR_{1.5} and FA₈₀G₂₀LSS-AB₃₅MR_{1.5} were selected as base mixtures, and different NC and GO dosages were added as thixotropy modifiers. According to Ref. [35], since the 0.5 wt% NC inclusion in geopolymer mixture with a similar mix-design resulted in the highest yield stress, this ratio was selected as an upper limit for NC in this study and two smaller dosages of 0.17 and 0.33 wt% were also tested to investigate the effect of NC ratios in geopolymer mortars. Three thixotropy modification levels of 0.03, 0.05 and 0.07 wt% were also selected for GO in this study. Although previous studies on GO-enabled cement- and geopolymer-based materials [91] used GO dosage of up to 1% wt, it was illustrated that GO addition in even lower dosages than 0.1% can effectively enhance the rheological [42] and mechanical properties [92] of GO-enabled mortars. Preliminary tests carried out in this study revealed that a higher GO dosage (> 0.1% wt) significantly reduces workability. Therefore, the maximum GO incorporation dosage in this study was restricted to 0.07 wt%.

Figure 5.6 shows the results of yield stress development of geopolymer mortars activated by sodium silicate solution with MR = 1.5 at AB and WS of 0.35 containing NC and GO. A critical observation from Figure 5.5 and Figure 5.6 is that at MR = 1.5 for both LSS and NS geopolymer mortars, the initial yield stress was very small (50 Pa immediately after the mixing at 10 min). Moreover, the yield stress increase rate, known as A_{thix} in cement-based systems (discussed in Chapters 3 and 4 of the thesis) and defined as the linear slope of the yield stress-rest time diagram at early ages

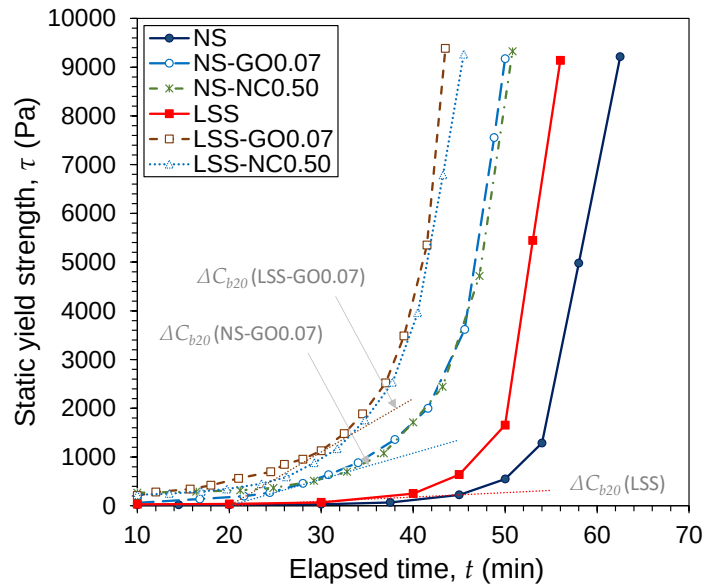
[32,93], was very small during the early ages lasting almost for the first 30 min. After this period, a sudden increase in yield stress growth rate was observed. Based on Figure 5.5, even using activator solutions with higher MR and decreasing the AB values did not significantly increase the growth rate at early ages. This can be attributed to the fact that unlike ordinary Portland cement systems in which colloidal reaction (due to the van der-Waals forces) contributes to the development of yield stress by the formation of a percolated rigid network between cement particles, the yield stress evolution in geopolymer paste at early ages is exclusively governed by percolation of an aluminosilicate gel between the precursors and there is no colloidal interaction between the geopolymer precursors particles [28,33]. This means that alkali-activated geopolymer binders lack thixotropy property; instead, the hydrodynamic interaction observed in geopolymer mortars is correspondent to the viscous nature of the alkali activating solution. Therefore, to adjust this and improve the thixotropy of the mixes, different inclusion rates for NC and GO were considered to be tested.



(a)



(b)



(c)

Figure 5.6. Effect of NC and GO on the yield stress development of FA₈₀G₂₀ with (a) NS and (b) LSS as fine aggregate; (c) Effect of NS and LSS on the yield stress development of FA₈₀G₂₀ geopolymer mortar containing 0.07% GO and 0.50% NC.

It can be observed from Figure 5.6 (a) and (b) that the inclusion of a small fraction of NC and GO significantly increased the yield stress growth rate (A_{thix}) in both NS and LSS geopolymer mortars at early ages. However, the initial yield stress (yield stress at $t = 10$ min) was not significantly increased. This is due to the poor cohesiveness of the early aluminosilicate gel formed during the first stages of the geopolymerisation reaction [33]. The modified geopolymer mortars (FA₈₀G₂₀LSS(or NS)-AB₃₅MR_{1.5}) started to gain strength after 20 min of adding alkaline activators.

Therefore, to quantitatively compare the effect of NC and GO inclusion on the yield stress growth rate after 20 min, the characteristic buildability slopes (ΔC_{b20} , discussed in Chapter 3 of the thesis) of the nano-enabled geopolymer mixes were obtained such that the slope of the line passing through the point [t = 20, yield stress = 0] touches the curve of the experimental data. Table 5.6 represents the results of the ΔC_{b20} for the modified geopolymer mortars.

Table 5.6. Characteristic buildability slopes (ΔC_{b20}) of nano-modified geopolymer mixes after 20 min of rest.

		NS Mix code	ΔC_{b20} Pa.min ⁻¹	LSS Mix code	ΔC_{b20} Pa.min ⁻¹
Nano modification	GO	NS	3	LSS	9
		NS - GO _{0.03}	14	LSS - GO _{0.03}	25
		NS - GO _{0.05}	34	LSS - GO _{0.05}	55
		NS - GO _{0.07}	54	LSS - GO _{0.07}	110
	NC	NS - NC _{0.17}	13	LSS - NC _{0.17}	13
		NS - NC _{0.33}	32	LSS - NC _{0.33}	37
		NS - NC _{0.50}	50	LSS - NC _{0.50}	93

As shown in Table 5.6 and Figure 5.6 (a) to (c), regardless of the type of fine aggregate, nano modification of base mixtures designed for extrusion-based 3D printing with NC and GO increased the ΔC_{b20} . Incorporating 0.17, 0.33 and 0.50 wt% NC into the LSS base mixture resulted in the multiplication of ΔC_{b20} by approximately 1.4, 4.1 and 10.1 times compared to the base LSS geopolymer mixture with no NC, respectively. This indicates that NC induced colloidal interaction in the system. Similar outcomes with higher increasing factors were achieved by GO-modification of LSS geopolymer mortars. Adding 0.03, 0.05 and 0.07 wt% GO increased the ΔC_{b20} of the LSS base mixture by approximately 2.7-, 6.1-, and 12.2-fold, respectively.

According to Figure 5.6 (c), LSS-GO_{0.07} and LSS-NC_{0.5} developed 0.55 kPa yield stress after 25 min of a dormant period, indicating that mixtures are potentially suitable for extrusion-based 3D printing in terms of extrudability and strength-based shape stability (buildability) according to previous studies [28,85,86]. This signifies that after about 25 min of resting period, these nano-modified geopolymer mixtures entered the printability window. Therefore, these mixes were selected for further

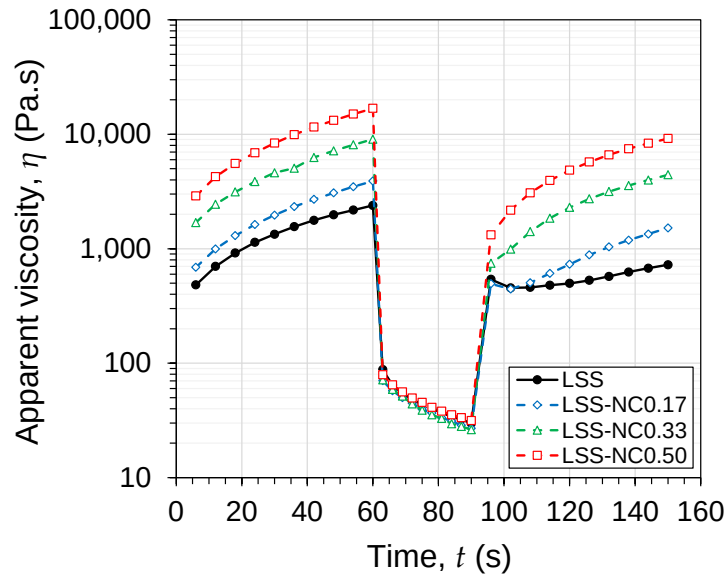
investigation on drying shrinkage. Further investigation on the effect of GO on thixotropy properties is presented in the following section.

5.4.2 Effect of graphene oxide (GO) and nanoclay (NC) on structural rebuilding

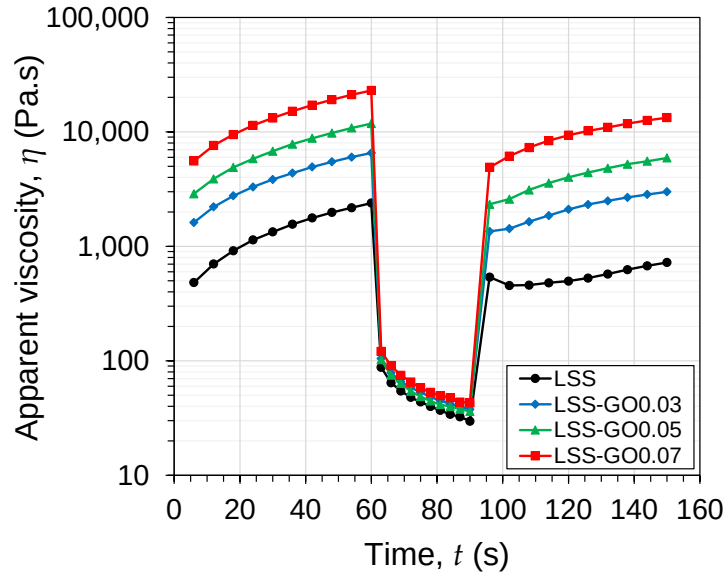
Besides the yield stress development, the buildability and shape stability of the geopolymers need to be modified to develop well-suited mortars for extrusion-based 3D printing. The viscosity recovery test evaluates the geopolymer mortar capacity to restore its fresh state characteristics (e.g., viscosity) immediately after deposition. The changes in the viscosity of LSS geopolymer mortar mixes were measured at rest, during the printing (by simulating the high shearing condition of pumping), and after the deposition for different inclusion ratios of NC and GO. It was reported previously [28] that a higher viscosity recovery capacity correlates directly to better shape stability and buildability.

Figure 5.7 (a) and (b) illustrate the recovery curves of base LSS and nano-modified geopolymer mixes with different dosages of NC and GO, respectively. It is visible that the viscosity of all mixes significantly increased with the incorporation of NC and GO. However, none of the mixes restored their viscosity to 100% after simulating the shearing condition of 3D printing. As shown in Figure 5.7 (a), the viscosity recovery of the LSS base mix (FA₈₀G₂₀LSS-AB₃₅MR_{1.5}) was 38.5% within 60 sec after simulating the extrusion shearing, while the inclusion of 0.17, 0.33 and 0.50 wt% NC increased the viscosity recovery to 39.7%, 49%, and 55.8%, respectively. As illustrated in Figure 5.7 (b), replacing the NC with GO (which resulted in relatively identical yield stress development to that of NC counterparts specimens) at dosages of 0.03, 0.05, and 0.07 wt% enhanced the viscosity recovery to 52.9%, 56.7% and 66.5%, respectively. This shows that the increase in the viscosity of GO-modified mixes was more prominent than their companion NC-modified mixes. From the comparison of the results in Figure 5.7 (c), it is found that the inclusion of 0.17% NC (LSS-NC_{0.17}) resulted in a 50% increase in the viscosity (both before and after the high shearing) compared to the base mix. However, LSS-NC_{0.17} showed nearly similar restoring behaviour (39.7%) to the control mix (38.5%). This can be due to the fact that the NC was used in the form of dry agglomerated powder in this study, which results in a lower level of dispersion (in comparison to the water pre-dispersed solution) in the geopolymer mortar at very low dosages [90]. The higher viscosity recovery of NC-modified mixes compared to that of the base mix can be associated

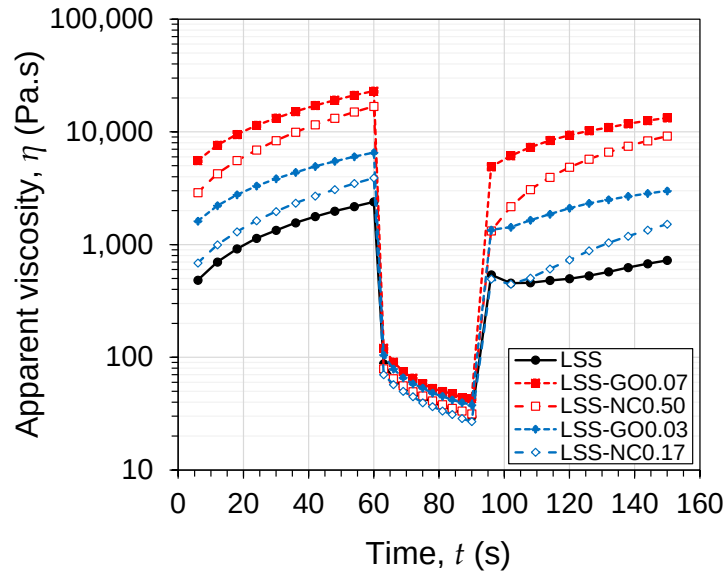
with a high level of van der Waals attraction forces induced by NC inclusion, resulting in rapid reflocculation after the extrusion [74]. These findings are consistent with those of previous studies, which reported that the face and edges of NC particles had opposite electric charges in an aqueous system, attracting each other and forming a “House-of-Card” microstructure when the suspension is at rest, providing a higher yield stress and viscosity [73,74,94]. Moreover, it was reported [95] that under extreme alkaline conditions ($\text{pH} > 11$), due to the increase in ionic strength of the suspension, the repulsion forces between the negatively charged face of NC particles are reduced, which causes reflocculation and a denser microstructure, providing higher viscosity. Given the extreme alkalinity in geopolymer systems, the observed increase in viscosity and thixotropy after the inclusion of NC can be interpreted as relevant outcomes.



(a)



(b)



(c)

Figure 5.7. Effect of (a) NC and (b) GO dosage on viscosity recovery (structural buildability) properties of FA₈₀G₂₀LSS-AB₃₅MR_{1.5} geopolymer mortar. (c) viscosity recovery comparison of counterparts nano-modified mixes with minimum and maximum nanomaterial dosage.

The viscosity recovery capacity of the GO-modified mixes, which exhibited comparable yield stress evolution to their NC-modified counterparts, was significantly better than that of the NC-modified mixes. As shown in Figure 5.7 (c), compared to the base mix, the inclusion of 0.03% of GO (LSS-GO_{0.03}) resulted in a 184% and 291% increase in the viscosity before and after the high shearing, respectively. However, the increase for LSS-NC_{0.50} were 53% (before high shearing) and 57% (after high shearing), respectively. Apart from the better dispersibility of the GO sheets in geopolymer mortars, this could be due to the fact that the GO sheets have a

functionalised negatively charged surface (hydrophilic) with a large specific surface area, absorbing free water content in the mix, which results in an increase in the interparticle friction and thereby increasing viscosity and yield stress of the mix. These findings were in line with the finding of Ref. [43] on the reduction of flowability of alkali-activated FA/GGBS mortars after adding 0.05 and 0.1 wt% GO. Moreover, previous research on GO incorporation into cement pastes suggested that the inclusion of GO in small dosages resulted in the creation of a flocculated structure that entraps free water content and increases the frictions between cement particles and GO sheets, enhancing the value of rheological properties [42].

As shown in Figure 5.7 (c), the apparent viscosity of LSS-GO_{0.07} and LSS-NC_{0.50} mixtures were 23000 and 17000 mPa.s, respectively, prior to applying the high-shearing (extrusion simulation). The mixtures were able to recover to approximately 15000 and 10000 mPa.s after extrusion simulation, respectively. The recovered apparent viscosity values of the abovementioned mixes (10000 to 15000 mPa.s) after the extrusion simulation were identical to that of the optimum geopolymer mix found by Biranchi et al. [28] (13000 to 15000 mPa.s), implying that the LSS-GO_{0.07} and LSS-NC_{0.05} mixtures were potentially printable mixes.

5.4.3 Reaction kinetic: Total heat and heat flow

In order to draw an experimental comparison between the effects of GO and NC on the geopolymerisation process of potentially printable geopolymer mortars, the isothermal calorimetry analyses were carried out on the mortars paste of Table 5.3 (FA₈₀G₂₀-AB₃₅MR_{2.1}) at 0.35 WS for different GO and NC dosages at a constant temperature of 20 °C for two days. Figure 5.8 (a) and (b) represent the effect of GO and NC incorporation on the heat of hydration rate and total hydration heat release of the pastes, respectively.

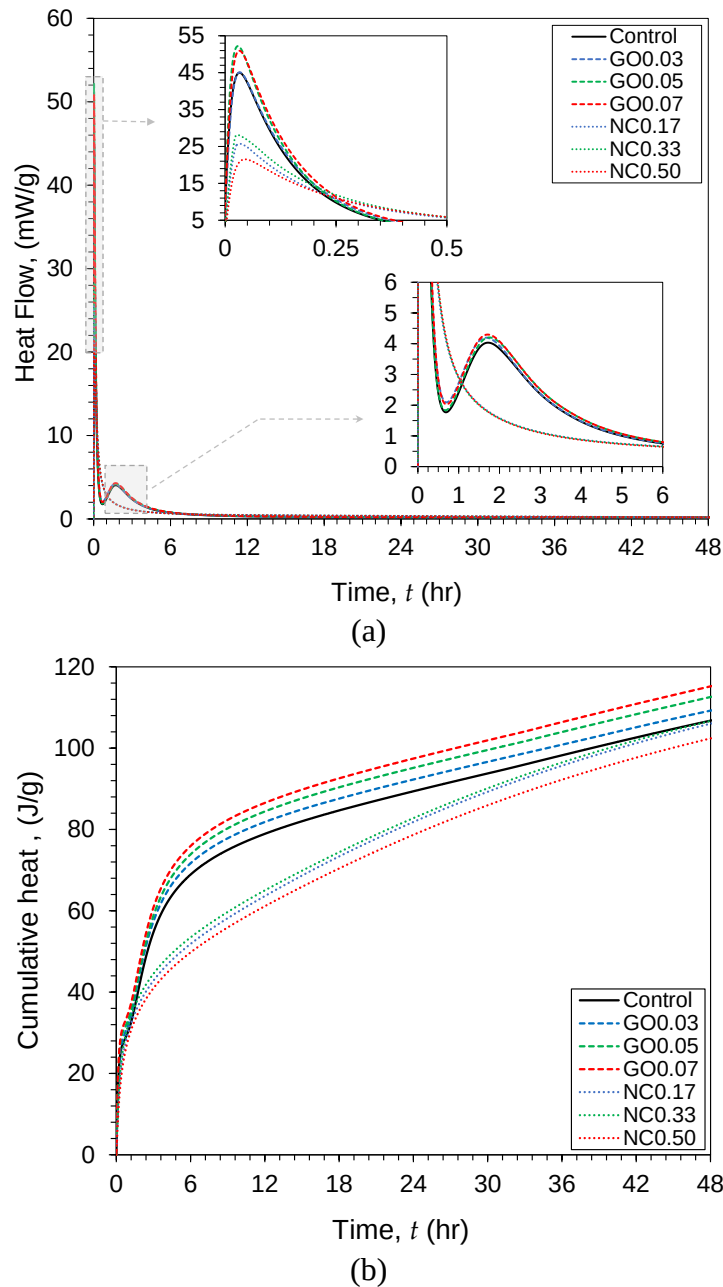


Figure 5.8. Effect of GO and NC incorporation with different dosages on (a) heat flow and (b) total heat evolution of FA₈₀G₂₀LSS printing geopolymer.

The heat flow response plot can typically be divided into four phases known as: the heat of wetting (initial dissolution), dormant period (induction), acceleration/deceleration and steady-state period [96]. As clearly shown in the enlarged part of Figure 5.8 (a), unlike base mix and GO-modified mixes, which displayed both primary and secondary calorimetric peaks, NC-modified mixes only showed primary single wide-ranging exothermic heat peak, which is attributed to the wetting stage. No additional notable heat characteristic peaks were recorded for NC-modified mixes even when the higher NC dosage was used or the response time was

extended. Moreover, increasing the NC dosage decreased the intensity of initial dissolution by approximately 50%. Even though the NC inclusion reduced the intensity of the first peak, as well as the fact that the heat flow of NC-modified mixes after the first peak was not significant, as shown in Figure 5.8 (b), the effect of NC on cumulative heat curves was negligible for NC of 0.17 and 0.33 wt% after 48 h and the total heat generated by NC-modified mixes were relatively equal to that of the base mix. This attenuation (disappearance) behaviour observed for NC geopolymer pastes can be attributed to the hydrophilicity of NC particles and a mechanism caused by the water-absorbing characteristics of NC during the geopolymerisation reaction [74,97]. A previous study [35] also observed a similar reduction behaviour in heat flow intensity and cumulative heat response for NC mixes. They reported that NC incorporation into the FA/GGBS geopolymer mixes designed for extrusion-based 3D printing did not affect the reaction mechanism significantly. Moreover, these results are consistent with the findings of Ref. [74] on the effect of NC dosage on alkali-activated slag/fly ash pastes, in which the addition of 3% NC resulted in the disappearance of the second calorimetric peaks for the mixture containing 30% GGBS.

The first heat response shown in Figure 5.8 (a) can be related to the heat generation immediately after contact between the binder precursors and alkaline activator caused by the dissolution of binder particles and partially caused by the formation of dissolved silicate species and their interaction with sodium and calcium ions [98,99]. It is worth noting that the heat evolution in the first stage can only be recorded partially in the measurement since the paste was prepared externally and the sample loading and reaching equilibrium in the instrument needed some time. It can also be noted from Figure 5.8 (a) that GO inclusion increased the magnitude of both the induction period peak and main hydration peak compared to the control geopolymer paste. The interpretation proposed for the hydration of GO-modified cement may also be adopted to assess the effect of GO in geopolymer pastes [100]. Results showed that the first peak for GO_{0.05} (52.2 mW/g at 103 sec) was the maximum, which was followed by GO_{0.07} (50.9 mW/g at 112 sec), GO_{0.03} (45.1 mW/g at 117 sec) and control mix (44.9 mW/g at 113 sec), denoting that the GO incorporation into geopolymer paste improves the dissolution of binder particles. This behaviour can be attributed to the fact that GO has a high specific surface area for absorbing water molecules, providing a higher concentration of OH⁻ ions formed during the breakdown

of alkaline activators, thereby accelerating the dissolving process of GGBS [99,101]. Furthermore, it was reported in Ref. [100] that the negatively charged surface of GO interacts with calcium ions, contributing to the dissolution of GGBS by the consumption of Ca^{2+} , which results in a higher polymerisation of hydration products. Moreover, as the results of the viscosity recovery tests presented in Section 5.4.2 suggested, the inclusion of GO can provide more nucleation sites for the formation of gel products, thereby accelerating the onset of the second peak by reducing the duration of the dormant period. A previous study [102] on the effect of graphene nanoplatelet (Gnp) reported a similar trend at a Gnp ratio of 0.1 vol%, and attributed that to the large specific surface area of the Gnp. Considering that the reduced graphene oxide (rGO) and GO exhibit comparable properties [103] in terms of water-sorptivity, the abovementioned findings are also consistent with the results of Ref. [101] on the effect of rGO on the intensity of the first and second calorimetric peaks and the total heat released for rGO admixed geopolymer pastes.

As it is shown in the enlarged part of Figure 5.8 (a) of the acceleration/deceleration stage, the maximum heat flow response attained for $\text{GO}_{0.07}$ (4.297 mW/g at 1.70 h), followed by $\text{GO}_{0.05}$ (4.203 mW/g at 1.74 h), $\text{GO}_{0.03}$ (4.196 mW/g at 1.67 h), and control mix (4.034 mW/g at 1.72 h). Additionally, the results showed that after 48 h, the cumulative heat evolution of $\text{GO}_{0.03}$, $\text{GO}_{0.05}$ and $\text{GO}_{0.07}$ was 2.3, 5.6 and 8% higher when compared to the control mix, respectively. These results are in line with the findings of Ref. [44] on the effect of Gnp and GO-modified alkali-activated slag/cement composites and Ref. [101] on the reinforcing mechanism of rGO on geopolymers.

5.4.4 Compressive strength in different curing conditions

To investigate the effect of GO and NC additives on the mechanical properties of geopolymer-based printable mortar in a simulated 3D printing environment, free-formed specimens dried at various curing environments were tested under axial compression at 28 days of curing. $\text{FA}_{80}\text{G}_{20}\text{LSS}$ mortar was selected as the base mortar. GO-modified mortars were prepared at the GO dosages of 0.05 and 0.07 wt%, and their NC-modified counterpart mortars (in terms of printability) were tested with NC dosages of 0.33 and 0.50 wt%. The results were compared to that of fully plastic-sealed specimens cured at 25 °C (standard curing) for 28 days to evaluate the performance of

nano-enabled mortars in simulated 3D printing environments. Geopolymer mortars with NS were tested to compare the effect of replacing NS with LSS as fine aggregate.

Figure 5.9 shows the variations of 28-day compressive strength of printing geopolymer mortar with different GO and NC dosages under different curing conditions. It is shown in Figure 5.9 that sealed cured NS geopolymer mortars (NS-FS-2450) attained 54.5 MPa compressive strength after 28 days. Replacing NS with LSS increased the strength by 9%. This is in line with the findings of the previous study on the compressive strength of ambient cured geopolymer mortars prepared with LSS [2]. The observed improvement in the strength can be attributed to the fact that LSS can partially react with the alkaline activator solution [2]. As was shown in Figure 5.1, the LSS had a broader particle size distribution under 200 μm , which may partially define the LSS higher reactivity with the alkaline activator, as well as the fact that a higher proportion of the LSS could act as a filler and reduce the voids, resulting in an increased mechanical properties. Previous studies also reported a smaller amount of voids for LSS geopolymer mortars, specifically at the binder-fine aggregate interfacial transition zone (ITZ), compared to NS geopolymer mortars [2].

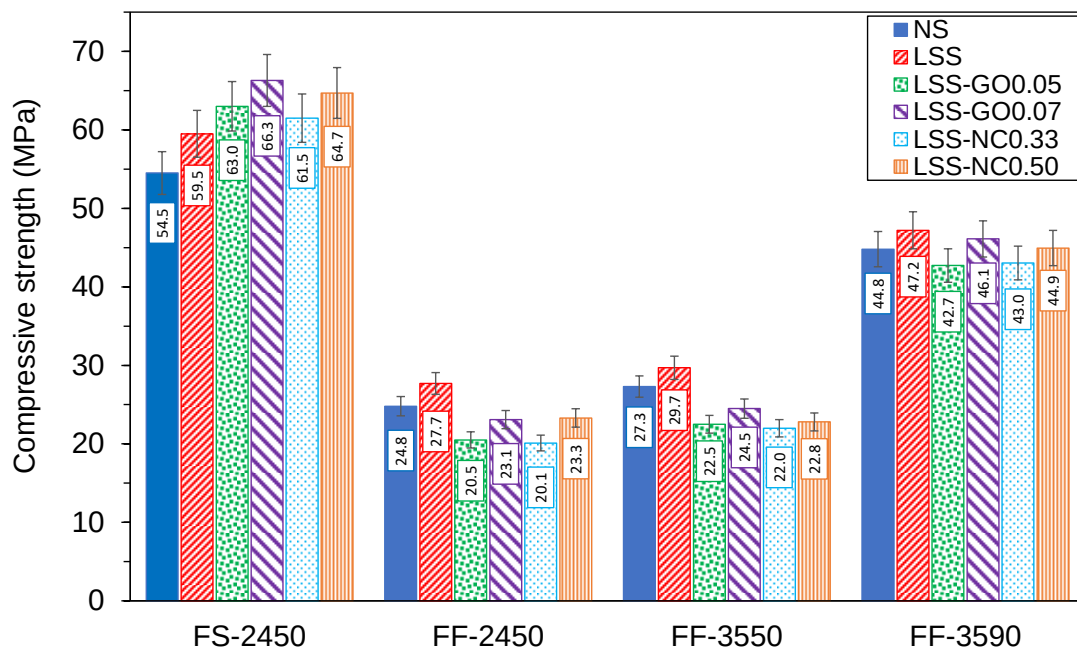


Figure 5.9. Variation of 28-day compressive strength of printing geopolymer mortar with different GO and NC dosages under different curing conditions.

As can be seen in Figure 5.9, the strength of LSS mortars modified with 0.05 and 0.07 wt% GO increased by 6% and 11.5%, respectively. This is in line with

previous research findings on the effect of incorporating GO into FA/GGBS and FA geopolymer mixes [43,45,101,104,105]. Primary glass network-forming alkalis in geopolymerisation are Al^{3+} and Si^{4+} ; divalent calcium and magnesium ions (Ca^{2+} and Mg^{2+}) operate as network modifiers together with any alkalis in the presence of these elements [106]. According to the previous experimental studies, the observed increase in the strength can be attributed to the fact that GO enhances the polymerisation of FA-based geopolymer by promoting the formation of FA hydrates with more network formers element (Si) and less network modifier disturbance (Ca). Negatively charged functionalised surface of GO increases the absorption of Ca, thereby selectively affecting the distribution of Si and Al and modifying the geopolymer network-forming ability, which causes the formation of hydration products with higher stiffness and mechanical strength [104]. In the fully sealed cured series, the inclusion of 0.33 and 0.50 wt% NC improved the strength by 3.4% and 8.7%, respectively. The observed enhancement in the strength can be attributed to the densification of the geopolymer paste caused by the pore filling feature of NC [107]. However, the previous research [35] reported a decreased compressive strength in NC-modified geopolymer mortars. This behaviour could be associated with the significant water absorption capacity of dry NC powder, which could slow down the gel formation, as well as the fact that the pore-filling mechanism may not be achieved due to the small NC content and high level of water absorption by NC particles [35,97].

It is shown in Figure 5.9 that, regardless of the curing condition parameters (temperature and relative humidity) and fine aggregate type used in the mixes, the geopolymer mortars strengths were substantially reduced when the initial curing was eliminated. The compressive strength of the NS series decreased to a similar extent as that of the LSS series. The free-formed plain LSS (and NS) geopolymer mortars under curing condition of 25 °C – 50% RH (FF-2450), 35 °C – 50% RH (FF-3550) and 35 °C – 90% RH (FF-3590) exhibited 53% (55% for NS), 50% (50% for NS) and 21% (17% for NS) decrease in the compressive strength compared to their counterpart specimens cured at conventional plastic sealed (FS-2450) condition, respectively. The lower compressive strength of free-formed geopolymer specimens can be associated with the rapid water evaporation at the early stage of the geopolymerisation reaction after eliminating the initial curing stage. This phenomenon might be explained by the fact that rapid evaporation of water at an early stage results in a higher amount of

porosity in the microstructure of the mix. Moreover, the high evaporation rate decreased WS and AB ratios, thereby adversely affecting the silica and alumina leaching from the binder materials, which leads to a lower rate of polymerisation reactions and more unreacted binder particles in the microstructure [58]. These results will be supported by the SEM images of plain LSS and NS geopolymers, which will be discussed later in Section 5.4.6.3.

Based on Figure 5.9, the compressive strength of NC and GO-modified specimens considerably decreased compared to the plain free-formed specimens at their corresponding T-RH% when the free-formed curing state for different T-RH% was simulated, whereas the nanomodification of LSS geopolymer mortar in the FF-2450 condition resulted in superior mechanical properties compared with the plain mortars. However, the GO-modified mortars outperformed the NC-modified counterparts in all various curing environments of FF-2450, FF-3550 and FF-3590. For the series of FF-2450, the LSS mixes comprising 0.07 wt% GO and 0.50 wt% NC showed about 16% lower 28-day strength than the plain LSS mortars, followed by 0.05 wt% GO and 0.33 wt% NC mixes, which exhibited approximately 26% and 27.4% decrease in 28-day strength, respectively. As shown in the results of the FF-3550 series, curing at a higher temperature (35 °C) and a similar relative humidity (50% RH) compared to that of FF-2450 resulted in a slightly higher mechanical strength for the free-formed geopolymer mortars. LSS-GO_{0.07} and LSS-GO_{0.05} in the FF-3550 condition showed a 6% and 9.8 % increase in their strength compared with their counterpart specimens in FF-2450. In the series of FF-3550, when comparing the results of the nano-modified mixes with those of plain free-formed LSS mixes, the strength reduction trend is relatively similar to that of FF-2450. The results showed that under the FF-3550 curing environment, the mixes containing 0.07 % GO, 0.50 % NC, 0.05 % GO and 0.33 wt% NC had 17.5, 23, 24 and 26% lower 28-day compressive strength than the plain LSS mixes, respectively.

In contrast to the FF-2450 and FF-3550 series, free-formed curing of nano-modified specimens at 35 °C – 90% RH resulted in the highest strength (minimum strength reduction) in free-formed specimens. Comparing the results of nano-modified mixes strength in the series of FF-3590 with their counterpart in the series of FF-2450 revealed that LSS-GO_{0.07}, LSS-NC_{0.50}, LSS-GO_{0.05} and LSS-NC_{0.33}, displayed 100, 93, 108 and 114% higher strength, respectively. Moreover, in the series of FF-3590,

when comparing the results of nano-modified specimens with those of the plain free-formed LSS mixes, the lowest strength reduction trend was observed. The results showed that under the FF-3590 curing environment, the mixes containing 0.07 % GO, 0.50 % NC, 0.05 % GO and 0.33 wt% NC only had 2.3, 4.8, 9.5 and 8.9% lower 28-day compressive strength than the plain LSS mixes, respectively. The reason behind the lower strength of the nano-modified specimens can be because of the fact that the water evaporation rate at the early stage was high. This assumption can be supported by the findings of the mass loss plots of the drying shrinkage specimens, which show a higher level of macroporosity in the nano-modified mixes. The inclusion of GO and NC enhanced the polymerisation reaction and reduced the mesoporosity (pore size < 50 nm) of the geopolymer matrix. However, the enhancement obtained by the densification of the geopolymer paste due to the inclusion of the nanomaterials, as well as a higher temperature (FF-3550) or relative humidity, was not enough to offset the reduction caused by the higher level of macroporosity. These findings suggest that adding GO to the geopolymer printing mortars as a rheological properties modifier can outperform NC in terms of mechanical properties.

5.4.5 Drying shrinkage development and moisture loss

Moisture loss and effect of LSS

Figure 5.10 shows the effect of GO and NC incorporation on drying shrinkage and mass loss evolution of printing geopolymer mortar under the control condition and standard curing environment (CC-2450). In this figure, the drying shrinkage and mass loss of printable mixes modified with GO and NC as well as the plain mixes (NS and LSS) under the conventional casting condition (CC) were measured for 28 days. Throughout the curing process, the sample weight loss was mostly due to moisture evaporation [108,109]. As shown in Figure 5.10, the evaporation rates were extremely high on the first day, to such an extent that all mixtures lost approximately 50% of their ultimate moisture loss (at 28 days) during the first day only. In the CC-2450 series (in Figure 5.10 (b)), the first-day weight losses of NS and LSS mixes were relatively similar at 4.5%. Adding 0.05 and 0.07 wt% GO to the LSS base mix reduced the first-day water losses to 4.4% and 4.1%, respectively. However, 0.33 and 0.50 wt% NC inclusion in the LSS mixes increased the weight loss on the first day to 4.6% and 4.8%, respectively. The 28-day mass loss of plain LSS mix was 0.25% lower than that of NS mix. This can be attributed to the fact that the LSS has a higher moisture retaining

capacity than the NS due to their unique physical properties and honeycomb structure. Thereby, using LSS instead of NS reduces moisture loss and drying shrinkage [43]. The addition of 0.05% and 0.07% GO reduced the 28-day ultimate water loss of LSS mixes from 7.1% (for CC-2450-LSS) to 7% (for CC-2450-LSS-GO_{0.05}) and 6.8% (for CC-2450-LSS-GO_{0.07}). 0.33% and 0.50% NC inclusion increased the water loss to 7.4% (for CC-2450-LSS-NC_{0.33}) and 7.2% (for CC-2450-LSS-NC_{0.50}), respectively.

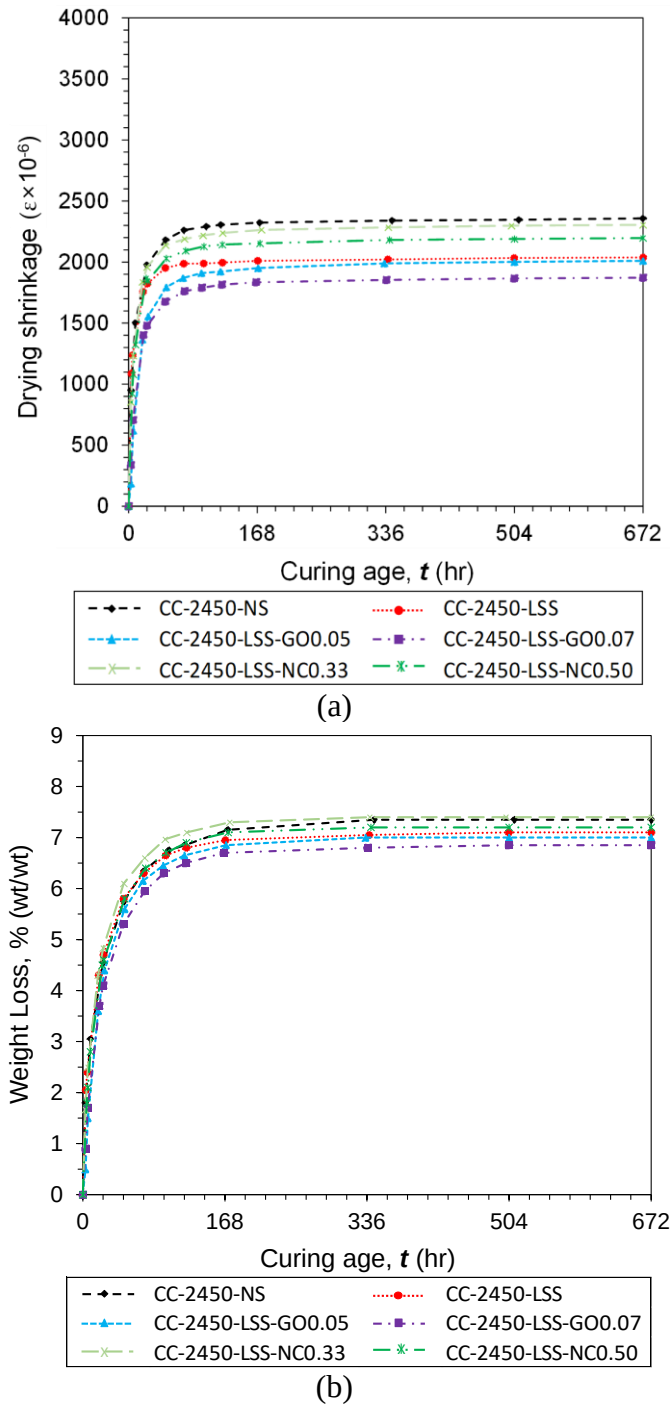


Figure 5.10. Effect of GO and NC incorporation on (a) drying shrinkage and (b) mass loss evolution of printing geopolymers at control condition: standard curing environment.

Based on Figure 5.10 (a) and (b), the drying shrinkage results of the CC-2450 series were consistent with the mass loss results. The drying shrinkage of both CC-2450-NS and CC-2450-LSS mixes during the first day was approximately equal at 1750 $\mu\epsilon$. However, the rate of drying shrinkage evolution reduced for CC-2450-LSS afterwards, and the ultimate drying shrinkage strain remained constant at approximately 2000 $\mu\epsilon$ throughout the measurement period of 28 days. At 28 days of curing, CC-2450-NS showed approximately 15.8% higher drying shrinkage compared to CC-2450-LSS, which had the highest value among all other mixes.

Effect of graphene oxide (GO) and nanoclay (NC) addition

As was shown in Figure 5.10, the nanomodification of CC-2450-LSS with GO reduced the drying shrinkage significantly. As suggested by previous research [43,45,105], this behaviour can be attributed to the fact that GO nanosheet can be converted to rGO when it is exposed to the strong alkaline environment of geopolymer. The in-situ rGO interacts with the FA particles chemically and physically, establishing mechanical interlocking effects between the geopolymer paste and rGO [43,45,110]. Moreover, GO/rGO bridges across the nano and microcracks in the geopolymer paste, thereby increasing the geopolymer paste microstructure strength [43,45,110]. Based on Figure 5.10, incorporating 0.05% GO into the LSS mix decreased the 1-, 3-, 7- and 28-day drying shrinkage by 14, 6, 3 and 2% compared to the CC-2450-LSS, respectively. Increasing the GO content in the mix resulted in a higher reduction in the drying shrinkage at all ages. CC-2450-LSS-GO_{0.07} showed approximately 19, 11.4, 9 and 8% reduction in 1-, 3-, 7- and 28-day drying shrinkage compared to CC-2450-LSS, respectively.

In contrast to the positive effect of GO inclusion on reducing the drying shrinkage of geopolymer mixes, it is shown in Figure 5.10 that incorporating NC in the mixes resulted in an increased drying shrinkage. This phenomenon can be described by the shrinkage behaviour of bulk wet clay pastes [38,111], which is most likely related to the NC's high water absorption capacity and their probable agglomeration in the mix [38]. As described by Ref. [56], water evaporation from clay pastes occurs in a three-stage process. First, the paste volume shrinks and the clay particles move closer with the evaporation of water. In this stage, the shrinkage is linearly correlated with the volume of evaporated water. The second stage is when the particles get in contact, and the water in between the clay particles evaporates,

resulting in pore network formation and nonlinear shrinkage development in the clay paste. Finally, the paste reaches a minimum volume known as the shrinkage limit. As suggested by previous studies [57,58], similar behaviour can occur in cementitious materials, leading to the generation of coarse porosity. Therefore, it can be inferred from these studies that inadequate initial curing (i.e., 1 day for CC specimens) and a high rate of evaporation caused by the open-to-atmosphere curing environment, which eliminates initial curing for FF specimens, resulted in the desorption of physically bonded water around NC particles in the mixes. This led to the generation of more porosities and changed the pore structure and the surface tension of the pores in the mortar, which caused an increased drying shrinkage strain. Incorporating 0.33% NC into the CC-2450-LSS increased the 1-, 3-, 7- and 28-day drying shrinkage by 6.6, 10, 12.6 and 13.1%, respectively. Increasing the NC content to 0.50% resulted in a decreased drying shrinkage, which can be attributed to the pore filling effect of NC and the higher compressive strength of CC-2450-LSS-NC_{0.50} compared to that of CC-2450-LSS-NC_{0.33}. However, CC-2450-LSS-NC_{0.50} had approximately 2, 5.3, 7 and 7.9% higher 1-, 3-, 7- and 28-day drying shrinkage compared to CC-2450-LSS, respectively. These results are consistent with those of a previous study [39], in which the effect of adding NC to cement mortars at various dosages ranging from 1 to 2 wt% (by weight of binder) was investigated. Gao et al. [39] reported that increasing NC dosage increased the mortars drying shrinkage and mass loss.

Effect of free-formed condition

Figure 5.11 shows the drying shrinkage and mass loss development of free-formed geopolymer mortars under the standard curing temperature and relative humidity (24 °C – 50% RH). Based on the figure, simulating the free-formed condition (FF-2450) for 3D printing geopolymer mortars increased the moisture loss of all mixes compared to conventional casting condition (CC-2450). This can be attributed to the higher evaporation rate, specifically from larger pores at early ages, due to the elimination of the initial curing stage in free-formed condition [108]. When geopolymer mixes in the FF-2450 condition were compared with their counterparts in the CC-2450 condition, the magnitude of the mass loss increase in plain free-formed LSS and NS (FF-2450-LSS and FF-2450-NS) mixes was lower than that of the nano-modified mixes. FF-2450-NS and FF-2450-LSS exhibited 0.25% and 0.3% higher mass loss compared to CC-2450-NS and CC-2450-LSS, respectively. However,

simulating the free-formed condition for GO- and NC-modified geopolymer mixes resulted in a significant increase in the mass loss and drying shrinkage compared to their CC-2450 counterparts. This behaviour can be because the high specific surface area of GO nanosheets and NC particles changed the micropore structure and the surface tension of the voids, resulting in a higher mass loss and drying shrinkage of the mix [38,44].

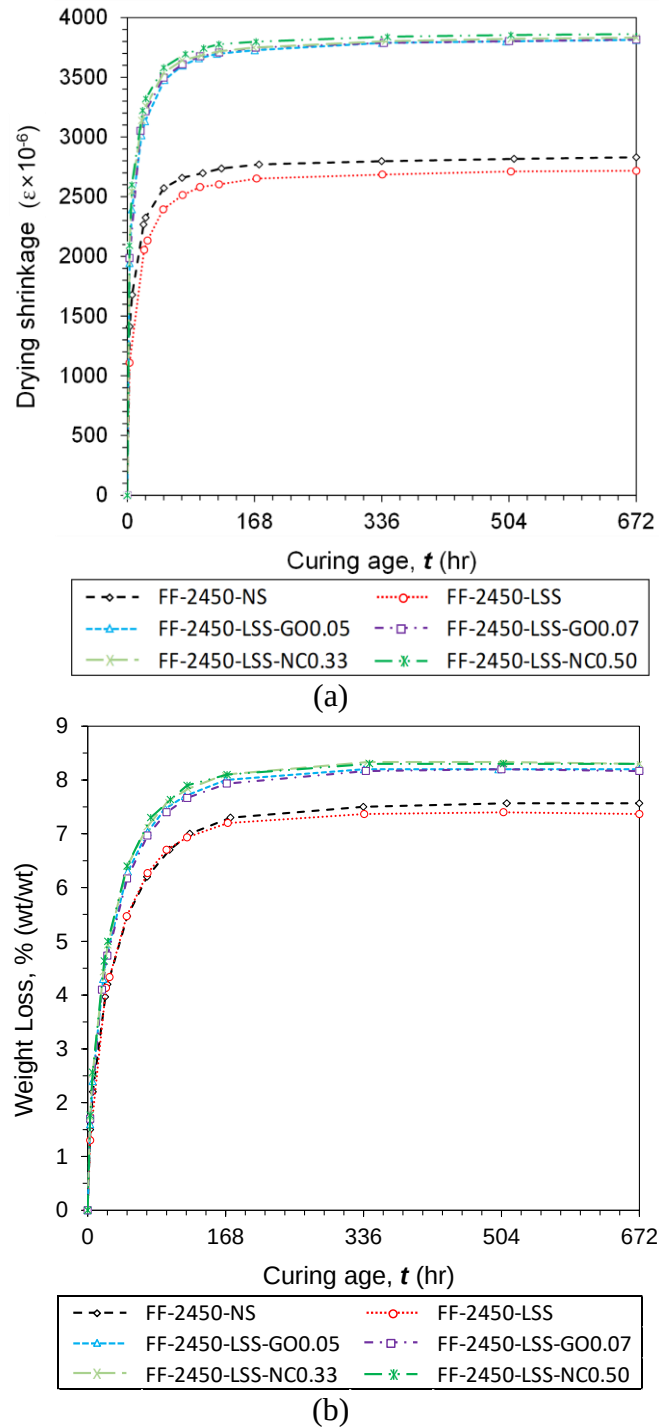


Figure 5.11. Effect of GO and NC incorporation on (a) drying shrinkage and (b) mass loss evolution of printing geopolymer mortar at the free-formed condition: standard curing environment.

In contrast to the positive effect of GO on mass loss and shrinkage strain development of 3D printable geopolymers under the CC-2450 condition, incorporating GO into the mixes adversely affected those characteristics under the FF-2450 condition. As shown in Figure 5.11 (b), compared to the CC-2450 condition, simulating the free-formed condition for LSS mixes incorporated with 0.05% GO resulted in a 0.4, 0.85, 1.15 and 1.2% increase in 1-, 3-, 7- and 28-day moisture loss, respectively. Increasing the GO dosage to 0.07% at the free-formed condition resulted in a similar moisture loss trend to that of 0.05% GO. Both FF-2450-GO_{0.05} and FF-2450-GO_{0.07} lost approximately 8.2% of their moisture after 28 days. However, FF-2450-LSS-GO_{0.07} showed a 0.6, 1.05, 1.2 and 1.35% increase in moisture loss at 1-, 3-, 7- and 28-day compared to CC-2450-LSS-GO_{0.07}, respectively. In the free-formed condition at the standard curing environment, the moisture loss behaviour of the NC-modified mixes was similar to that of the GO-modified mixes. Both FF-2450-NC_{0.33} and FF-2450-GO_{0.50} lost approximately 8.3% of their moisture after 28 days. In the FF-2450 condition, incorporating 0.33% and 0.50% NC to the mixes increased the 28-day moisture loss by 0.9% and 1.1% compared to their counterparts specimens in the CC-2450 condition, respectively.

As shown in Figure 5.11, the drying shrinkage development behaviour of free-formed mixes was correlated with the moisture loss evolution trend. In FF-2450, plain NS and LSS mixes developed 2830 $\mu\epsilon$ and 2717 $\mu\epsilon$ drying shrinkage at 28 days, respectively. By comparing Figure 5.10 (a) and Figure 5.11 (a), when NS was replaced with LSS in the mortar, the magnitude of the drying shrinkage development reduced by approximately 14% and 4% in CC-2450 and FF-2450 curing conditions, respectively. Apart from the higher strength of LSS mixes compared to that of NS (as previously discussed in Section 5.4.4), which contributed to reducing the drying shrinkage, this phenomenon can be attributed to the partial reactivity of the fine LSS with the binder. Similar behaviour was previously reported in Ref. [108] for the use of waste glass sand as fine aggregate in metakaolin-based geopolymer mortars. Therefore, using LSS instead of NS in geopolymer mortars designed for 3D printing can enhance the volume stability of the mortars under the free-formed condition.

As shown in Figure 5.11 (a) and (b), in FF-2450 condition, the drying shrinkage and mass loss of nano-modified mixes were not significantly dependent on the type or dosage of the nanomaterials. The results indicated that irrespective of the dosage, the

28-day drying shrinkage of all NC- and GO-modified mixes reached approximately 3750 $\mu\epsilon$ in FF-2450 condition, which was at least 70% higher compared to their CC-2450 counterparts. The shrinkage of the geopolymer in the free-formed condition was principally linked to the water evaporation due to the insufficient compactness of the water-saturated unreacted/partially reacted binder (FA and GGBS) particles in the early ages of the geopolymer slurry system [97,108]. Zhang et al. [97] investigated the effects of water in different curing conditions on the drying shrinkage of geopolymer composed of metakaolin and FA. They discovered that when the water evaporates from the geopolymer mix, the fine binder particle with a large specific surface area generates a significant shrinkage strain under the air-drying condition. Under the air curing condition this substantial shrinkage of geopolymers occurred because of the presence of voids that were not filled with hydrated products. Therefore, pore water evaporation at early ages resulted in the compaction of the inadequately compacted binder particles. This mechanism can explain the higher drying shrinkage of free-formed geopolymer mortars than conventional casting mortars of this study. Considering the fact that FA particles have slow reactivity with the alkaline activator [112], by simulating the extrusion-based 3D printing free-formed environment, the water was removed rapidly from the macropores of the mix during the early ages due to the higher exposure surface of the geopolymer mixes in free-formed condition. Therefore, a significant quantity of unreacted or under-reacted FA and GGBS components that were still present in the mixture became more compact and increased the drying shrinkage. The SEM images also supported this, which will be discussed later in Section 5.4.6.3.

Effect of temperature and relative humidity

Figure 5.12 and Figure 5.13 illustrate the mass loss and drying shrinkage development of free-formed mixes under the drying condition of 35 °C – 50% RH (FF-3550) and 35 °C – 90% RH (FF-3590). As shown in Figure 5.12, increasing the temperature to 35 °C in 50% RH resulted in a reduction of the drying shrinkage of GO- and NC-modified free-formed mixes. This can be attributed to the fact that by increasing the temperature, the geopolymerisation reaction is accelerated at early ages, thereby reducing the amount of unreacted binder particles in the system [108]. Therefore, the drying shrinkage driven by the water evaporation from the macropores and the compaction of the unreacted particles in the system is reduced. Comparing

Figure 5.11 (a) and Figure 5.12 (a), it is shown that FF-3550-LSS-GO_{0.07} and FF-3550-LSS-NC_{0.50} had approximately 16% and 12% lower drying shrinkage than their companion FF-2450 mixes, respectively. The reduction of the drying shrinkage of nano-modified mixes in the FF-3550 condition with respect to those in the FF-2450 condition can be supported by the results of NAD analysis, which will be discussed in Section 5.4.6.1. By comparing Figure 5.11 (b) and Figure 5.12 (b), the mass loss evolution of all the mixes under the FF-3550 condition was relatively similar (only increased by 0.2% compared to their counterpart mixes in FF-2450) to those under the FF-2450 condition. This behaviour can be due to the higher volume of the macropores in the FF-3550 mixes than that in the FF-2450 mixes, which led to more water loss from the macropores of the FF-3550 mixes by evaporation during the drying process [108].

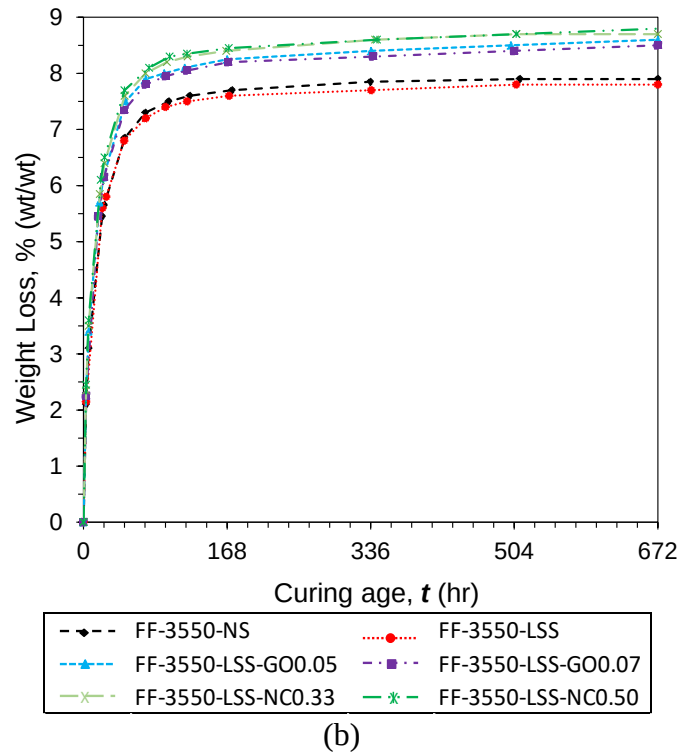
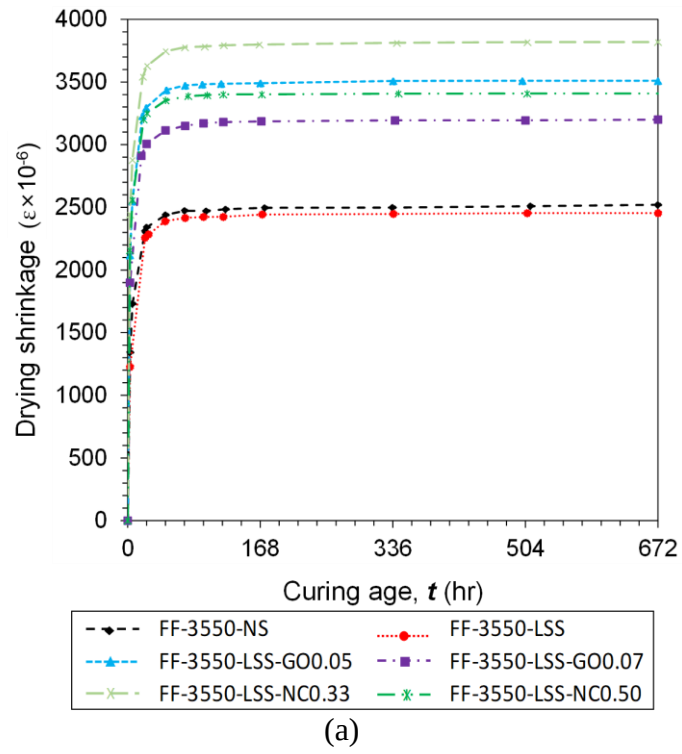


Figure 5.12. Effect of GO and NC incorporation on (a) drying shrinkage and (b) mass loss evolution of printing geopolymer mortar at free-formed condition: high temperature and standard relative humidity environment.

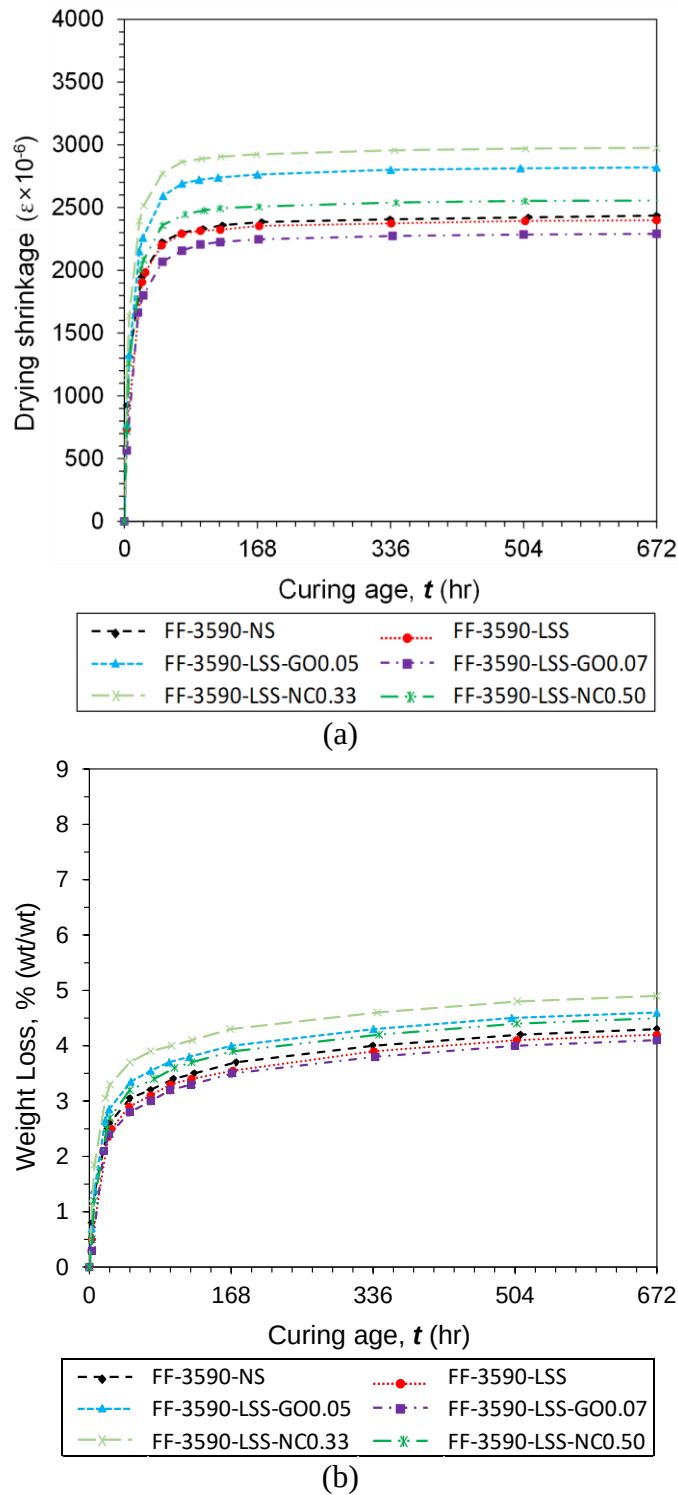


Figure 5.13. Effect of GO and NC incorporation on (a) drying shrinkage and (b) mass loss evolution of printing geopolymer mortar at free-formed condition: high temperature and relative humidity environment.

Although increasing the relative humidity of the high-temperature curing environment (FF-3550) by approximately twofold to 90% (FF-3590) resulted in more reduction in the drying shrinkage of the free-formed nano-modified geopolymer mixes, the 28-day drying shrinkage of plain LSS mixes was still higher by 17% than

that of their CC-2450 counterparts. This can be attributed to the fact that interruption in the geopolymerisation process caused by the early age evaporation of water in the geopolymer system by eliminating the initial curing could not be completely compensated even at high temperature and relative humidity. These findings can be supported by the NAD analysis, which will be discussed under Section 5.4.6.1.

As shown in Figure 5.13 (a), the 28-day drying shrinkage of FF-3590-LSS-GO_{0.07} and FF-3590-LSS-GO_{0.05} decreased by approximately 40% and 26% compared to those of FF-2450 counterparts, respectively. However, this shrinkage reduction was lower for the NC-modified mixes, which were approximately 34% and 22% for FF-3590-LSS-NC_{0.50} and FF-3590-LSS-NC_{0.33}, respectively. The lower drying shrinkage of FF-3590 mixes than that of FF-2450 mixes can be attributed to the fact that in high temperature and relative humidity (FF-3590), in which the mass loss of mixes was reduced by approximately twofold from about 8% in FF-2450 to 4-5% in FF-3590, the rapid formation of the geopolymer gel during high-temperature curing in the presence of higher relative humidity resulted in a less dense binder structure (the volume of pore size around 20 nm increased) compared with those in ambient-temperature cured mixes under the standard curing temperature and relative humidity [108,109]. Thus, the mean pore size of FF-3590 mixes was larger than that of FF-2450 counterparts, resulting in the reduction of the capillary pressure and the drying shrinkage of the FF-3590 mixes. The shrinkage reduction as a result of the nanomaterials incorporation can be because the GO and NC addition to the geopolymer mixes accelerate the geopolymerisation reaction with different mechanisms. As discussed previously under Section 5.4.3, GO enhances the dissolution of the precursors and accelerates the gel formation process by increasing the cohesiveness of the geopolymer microstructure. In comparison, the addition of NC accelerates the strength-gaining behaviour by increasing the number of nucleation sites for gel formation. The mechanical and drying shrinkage test results of this study indicate that the GO addition could be more effective than NC addition in terms of the compressive strength and the drying shrinkage behaviour improvement of geopolymer mortars.

5.4.6 Microstructure analysis

Nitrogen adsorption – desorption (NAD) analysis

The NAD technique was used to investigate the effect of the free-formed curing method and various curing environments on the pore structure and pore size

distribution of potentially printable geopolymer mortars modified with GO and NC additives. In this study, the NAD analysis was conducted on the drying shrinkage specimens. Samples were taken from the NS and LSS plain mixes as well as the 0.07% GO- and 0.50% NC-modified mixes cured under the various curing conditions of Table 5.5 at their 28 days of the drying shrinkage development. Figure 5.14 shows N_2 -adsorption (Ad) and desorption (De) isotherms of plain NS, plain LSS, 0.07% GO- and 0.50% NC-modified geopolymer mixes under the CC-2450 condition compared to those of free-formed LSS mixes at different curing temperature and relative humidity of FF-2450, FF-3550 and FF-3590 after 28 days of curing. In Figure 5.14, the output of the N_2 -sorption analysis is the sorption isotherm curves that show the quantity of the adsorbed N_2 against the relative pressure (P/P^0 , in which P and P^0 are the absolute saturated vapour pressure of the adsorbate N_2 , respectively).

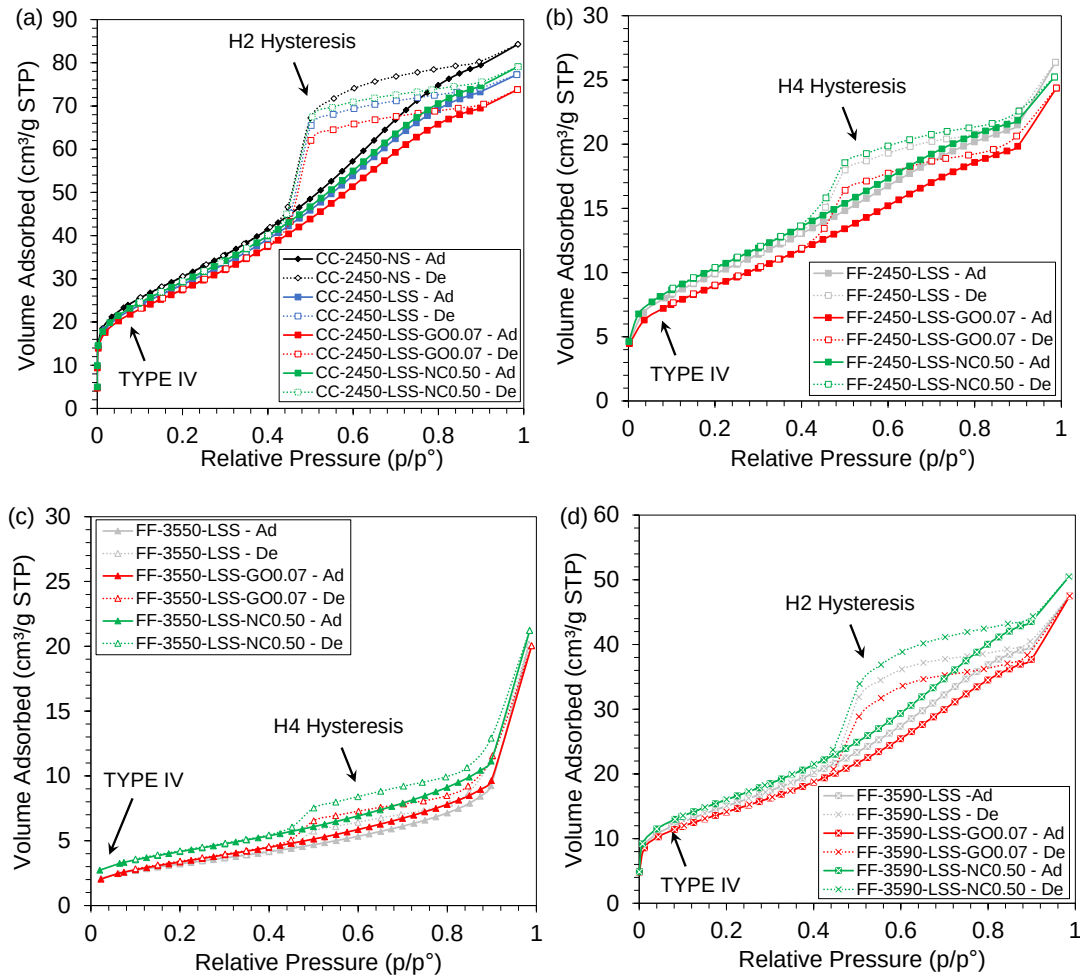


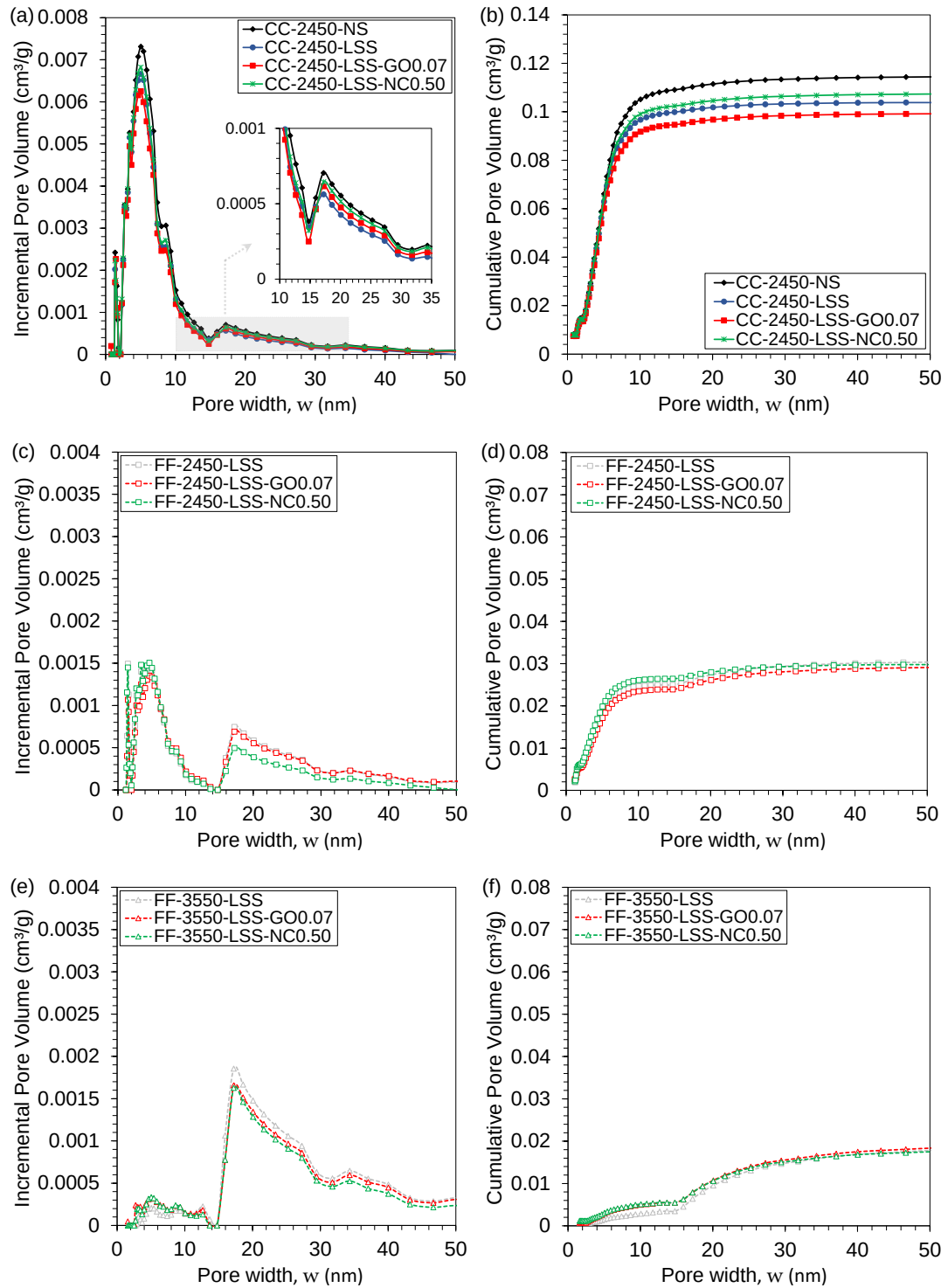
Figure 5.14. (a) N_2 -adsorption (Ad) and desorption (De) isotherms of plain NS, plain LSS, 0.07% GO- and 0.50% NC-modified geopolymer mortars under the CC-2450 condition compared to free-formed LSS mortars at different curing temperature and relative humidity of (b) FF-2450, (c) FF-3550 and (d) FF-3590 after 28 days.

According to the International Union of Pure and Applied Chemistry (IUPAC) standard classification [113], NAD analysis results for all mixes at various curing conditions of CC-2450, FF-2450, FF-3550 and FF-3590 exhibited that the adsorption curves proceed via monolayer-multilayer adsorption at a low relative pressure ($P/P^0 < 0.4$), followed by capillary condensation, resulting in type IV isotherm. These results are in line with the findings of previous studies [44,114,115]. Type IV or V isotherms were discovered as typical isotherms of mesoporous materials like geopolymer mortars. As can be seen in Figure 5.14(a) and (d), the hysteresis loop type of CC-2450 and FF-3590 mixes can be classified as H2 according to the IUPAC standard classification. However, free-formed mixes in FF-2450 and FF-3550 conditions exhibited H4 capillary condensation hysteresis loops, as illustrated in Figure 5.14 (b) and (c). The classification of the hysteresis loop is commonly linked to the thermodynamic effect and the connectivity of the pore network, providing information on pore shape, distribution and network connection [116]. Type H2 hysteresis loop denotes that relatively uniform channel-like pores with narrow openings (ink-bottle pores) were present in the mortar microstructure [44]. The H4 type hysteresis loop can be representative of a microstructure with narrow slit-like pores [117], particles with internal porosity with complex geometries and a wide range of sizes between 5 and 30 nm [118] and hollow spheres with mesoporous walls [119]. The findings of the NAD analysis are further supported by SEM images of the microstructures, which will be discussed in Section 5.4.6.3.

The pore network characterisation, including the surface area, pore size distribution and cumulative pore volume, can be calculated from the isotherm curves using the classical adsorption-desorption theories such as Brunauer–Emmett–Teller (BET) and Barrett-Joyner Halenda (BJH). However, in this study, for the calculation of the pore volume and size distribution, the Density Functional Theory (DFT) was used [120]. This is because the results obtained from the DFT analysis can cover a wider range of the pore size distribution (< 50 nm) and provide more information on the pore characteristics compared to the BJH analysis, which only provides information for the pore size in the range below 25 nm. The classical theories only gather the data from a specific region of the adsorption-desorption isotherm (for BJH theory, only desorption curves are used) rather than the entire curve. However, the DFT method is based on the principles of statistical thermodynamics that considers the

entire spectrum of adsorption-desorption isotherms and is not bound to a narrow range of relative pressures (pore sizes) [81]. In this study, the DFT analysis approach for slit-shaped porosity was carried out to extract further information on the pore size distribution and total volume of potentially 3D printable LSS geopolymer mortars modified with GO and NC. The results were also used to better understand the impact of free-formed conditions under varying environmental temperatures and relative humidities on the micropore structure of the synthesised geopolymer mortars. Nonetheless, to avoid incorrect interpretation from the conversion of the relative pressure to pore size distribution with DFT model, the SEM analysis was also conducted on some mixes to support the findings of NAD analysis.

Figure 5.15 shows incremental and cumulative pore volumes of plain NS, plain LSS, 0.07% GO- and 0.50% NC-modified geopolymer mixes under the CC-2450 condition compared to those of free-formed LSS mixes at FF-2450, FF-3550 and FF-3590 curing conditions after 28 days. As shown in Figure 5.15, the NAD analysis identified the porosity within 1 nm to 50 nm. The pore size distribution curves of all synthesised geopolymer mixes had two peaks located at around 5 nm and 17 nm, regardless of the nanomaterial type (GO or NC), the initial curing condition (CC or FF) and the environmental parameters ($T - RH\%$). According to the previous studies [108,109], geopolymer materials generally display two sharp peaks with the size around the abovementioned values in the mesoporous range (< 50 nm).



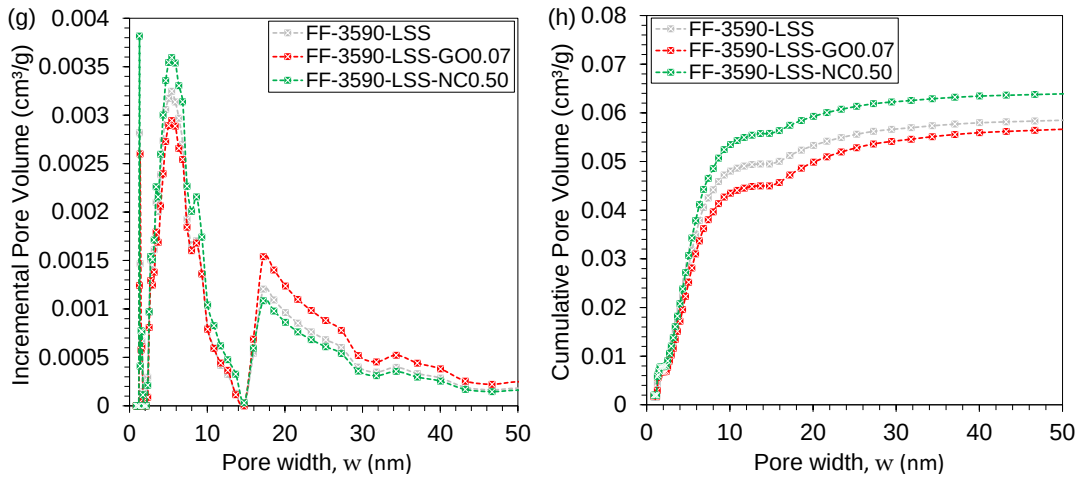


Figure 5.15. (a) & (b) Incremental and cumulative pore volumes of plain NS, plain LSS, 0.07% GO- and 0.50% NC-modified geopolymer mortars under the CC-2450 condition compared to free-formed LSS mortars at different curing temperature and relative humidity of (c) & (d) FF-2450, (e) & (f) FF-3550 and (g) & (h) FF-3590 after 28 days.

Based on Figure 5.15 (a), at the CC-2450 curing condition, all the geopolymer mixes exhibited a strong peak in the first region with size within the range of 1 nm to 10 nm (centred at approximately 5 nm). This is in line with the findings of the previous studies, in which peaks within this range were observed in FA-based geopolymer composites [117,121]. Moreover, the results are also consistent with previous research findings on the nanopore structure of metakaolin-based geopolymers [108,109,122]. The strongest peak in the first and second region (enlarged part of Figure 5.15 (a)) was observed for the NS geopolymer mix, indicating that the CC-2450-NS mixes contained a higher level of mesoporosity in their microstructure. By replacing NS with LSS, the incremental pore volume of the voids band with a peak centred at 5 nm was reduced from $0.00731 \text{ cm}^3/\text{g}$ to $0.00665 \text{ cm}^3/\text{g}$. Moreover, the volume of pores band with the peak centred at 17 nm in CC-2450-LSS was the minimum (at $0.00056 \text{ cm}^3/\text{g}$) among all other mixes, as shown in the enlarged part of Figure 5.15 (a). Considering the higher strength of LSS mixes compared to that of NS mixes, this observation may be attributed to the fact that the partial reaction of the LSS with the binders reduced the porosity, which resulted in a more densified microstructure in LSS mixes due to the reduction of the ITZ area [43]. The SEM images also depicted the strong bonding of LSS particles and geopolymer paste, which will be further discussed in Section 5.4.6.3. As it is shown in Figure 5.15 (b), when NS was replaced with LSS in the mortar, the total volume of pores smaller than 50 nm in CC-2450 condition decreased by approximately 6% from $0.1143 \text{ cm}^3/\text{g}$ (for CC-2450-NS) to $0.1072 \text{ cm}^3/\text{g}$ (for CC-2450-LSS). These results are consistent with the drying shrinkage development

behaviour, in which the higher volume of mesoporous structure in CC-2450-NS resulted in the higher 28-day drying shrinkage when compared to LSS and nano-modified LSS geopolymer mixes. This observation suggests that using LSS as a fine aggregate in printable geopolymer mortar can improve the mechanical properties and durability of the printed products.

Incorporating 0.50% NC into the LSS geopolymer mix (CC-2450-LSS-NC_{0.50}) increased the incremental pore volume of the pores band with the peak centred at 5 nm (first region) and 17 nm by 2.5% and 14.6% compared to that of the plain mixes, respectively. This alteration in CC-2450-LSS-NC_{0.50} microstructure was reflected in the cumulative pore volume curves in Figure 5.15 (b), where the NC-modified mixes exhibited a 3.3% increase in the total pore volume of pores smaller than 50 nm compared to the unmodified LSS mixes. These findings also justify the higher drying shrinkage of NC-modified geopolymer mixes compared to the plain LSS geopolymer mixes discussed earlier in Section 5.4.5.2. As it is illustrated in Figure 5.15 (a) and (b), incorporating 0.07% GO into the LSS geopolymer mix (CC-2450-LSS-GO_{0.07}) resulted in the densification of the microstructure. In CC-2450-LSS-GO_{0.07}, the pore volume with the size around 5 nm tended to reduce by approximately 6%, whereas the pores around the size of 17 nm exhibited a 9.5% increase in their volume compared to those of unmodified mixes. These changes in the microstructure resulted in a 4.5% reduction in the cumulative pore volume of pores smaller than 50 nm compared to the unmodified LSS mixes. These findings are consistent with the results reported by Liu et al. [45], in which the total porosity and average pore diameter of GO-modified FA-based geopolymer composite decreased by approximately 25% at a GO dosage of 0.1%. The result showed that the refinement and densification of the microstructure obtained by GO inclusion resulted in the development of a lower drying shrinkage and a higher strength of the geopolymers compared to those containing NC.

For the free-formed mixes, as shown in Figure 5.15 (c) to (h), the cumulative pore volume in the geopolymer mixes reduced when the initial curing was eliminated. This phenomenon can be attributed to the reduction of the amount of hydration products due to the water evaporation from the mixes, interrupting the reaction between the alkaline activator solution and binder precursors. Compared to the CC-2450-LSS mix, the total pore volume of the pores smaller than 50 nm in FF-2450-LSS, FF-3550-LSS and FF-3590-LSS mixes decreased by approximately 70, 83 and 44%,

respectively. However, the pore size distribution varied significantly when the temperature and humidity changed. In the FF-2450 series, as shown in Figure 5.15 (c), incorporating NC into the geopolymer mix resulted in a more microstructure refinement by increasing the intensity of the first peak at around 5 nm and decreasing the intensity of the second peak at 17 nm. In contrast to the NC effect, GO inclusion increased the volume of the pores at around 17 nm, while slightly decreased that of the pores at around 5 nm. These results are consistent with the drying shrinkage results, where the addition of NC resulted in a higher level of drying shrinkage development in the geopolymer mixes than the addition of GO.

As the results of FF-3550 series reveal (Figure 5.15 (e) and (f)), curing at higher temperature in free-formed condition make the microstructure of the geopolymer coarser. Figure 5.15 (f) illustrates that the total porosity of the mesoporous structure (< 50 nm) was relatively equal for FF-3550-LSS, FF-3550-LSS-NC_{0.50} and FF-3550-LSS-GO_{0.07} at approximately $0.0174 \text{ cm}^3/\text{g}$. However, compared to the FF-2450 series, increasing the temperature at a constant relative humidity in the free-formed condition resulted in a pore-widening effect. As also shown in Figure 5.15 (f), pores ranging in size from 15 to 50 nm accounted for more than 80% of the total volume of pores smaller than 50 nm in the FF-3550 series, while this value was about 17% for FF-2450 series. Rovnaník et al. [109] also reported the pore-widening effect in metakaolin-based geopolymer when the mixes were cured at an elevated temperature at the early-stage of hardening. The lower level of microstructure densification in metakaolin-based geopolymer compared to those mixes cured under the ambient condition was attributed to the immediate formation of the geopolymer gel caused by the acceleration in the reaction rate under a high-temperature curing environment [108,109].

According to previous studies [108,123] proposed for micromechanical modelling of drying shrinkage development based on the pore size distribution, the capillary tensile force as a driving force for drying shrinkage is inversely correlated with the radius of the capillary pores where the meniscus forms. Therefore, it can be deduced from the results of the NAD analysis that the pore-widening effect occurred at higher drying temperature in FF-3550 compared to that in FF-2450 contributed to the reduction of the drying shrinkage development of the geopolymer mortars. These results are in line with the findings of Collins et al. [124], who investigated the interrelationship between pore size distribution and drying shrinkage in alkali-

activated slag concrete, and reported that the pores with a size smaller than 16 nm play an important role in accelerating the drying shrinkage development rate in the concrete.

Compared to the FF-2450-LSS mixes, increasing the temperature and relative humidity of the drying environment to 35 °C and 90% increased the volume of the fine pores around the size 5 nm and 17 nm by 129% and 61%, respectively. These alterations in the microstructure of FF-3590 series can be attributed to the fact that the level of gel formation interruption caused by the evaporation of water from the mixes at early-stage of hardening decreased in FF-3590 (according to Figure 5.13 (b), the moisture loss from the FF-3590 series mixes reduced by approximately 50%) resulted in the formation of more gel products compared to that of FF-2450 series mixes by prolonging the reaction between the alkaline activator solution and binder precursors. These results also indicate that incorporating GO as a thixotropy modifier in geopolymer mortars designed for extrusion-based 3D printing can densify the microstructure of the mixes more effectively than incorporating NC. These findings were also reflected in the total porosity of the mixes, where the cumulative volume of the pores smaller than 50 nm for FF-3590-LSS, FF-3590-LSS-GO_{0.07} and FF-3590-LSS-NC_{0.50} increased by 92, 94 and 114% compared to those of their counterparts mixes in FF-2450 series, respectively.

The results of the NAD analysis for the FF-3590 series were consistent with those of the drying shrinkage, confirming that replacing GO with NC as a thixotropic modifier in geopolymer mortars resulted in the densification of the microstructure and decreased total volume of the mesoporous structure. Moreover, as can be seen in Figure 5.15 (h), the pores with the size between 15 to 50 nm in the FF-3590-NC_{0.50}, FF-3590-LSS and FF-3590-GO_{0.07} comprised approximately 13, 15 and 21% of the total porosity with the size smaller than 50 nm, respectively. This observation suggests that the capillary tensile force, which is directly linked to the drying shrinkage development, was minimum in GO-modified mixes compared to that of the plain and NC-modified mixes. As the results of this study showed, GO-modification of geopolymer mortars not only enhanced the strength, but also improved the durability of the mixes in free-formed condition.

XRD spectra analysis

The XRD spectra of potentially printable geopolymer mortars in conventional casting and free-formed curing methods under various curing environments are presented in this section. Powder samples were taken from the plain and nano-modified LSS geopolymer mixes compositions in the drying shrinkage experiment after 28 days of curing. The crystalline peaks alteration and the amorphous humps formation were examined.

Figure 5.16 illustrates a comparison between the XRD spectra of plain LSS mixes cured under different curing conditions of 28-day sealed curing (FS-2450-LSS), conventional casting (CC-2450-LSS) and free-formed conditions (FF-2450-LSS, FF-3550-LSS and FF-3590-LSS), where the influence of the initial curing elimination and various temperatures and relative humidities can be observed on geopolymerisation. A comparison of XRD spectra of powdered precursors (FA and GGBS) and the FA/GGBS-based geopolymers in Figure 5.16 demonstrates that some of the primary peaks in the GGBS and FA spectra vanished or their intensity diminished. Regardless of the curing (drying) conditions, the crystalline peaks of unreacted GGBS located at 2-Theta (2θ) of 11.6° and 23.4° disappeared. Moreover, the intensity of crystalline peaks in raw FA located at 2-Theta (2θ) of 16.4° , 20.8° , 30.9° , 33.2° , 35.2° , 39.3° , 40.9° , and 60.7° reduced compared to the synthesised geopolymer materials such as FS-2450-LSS and CC-2450-LSS series. This phenomenon indicates that the geopolymerisation reaction occurred, which resulted in the dissolution of raw materials and the formation of amorphous aluminosilicate gel [83,125]. Another important feature of the geopolymerisation reaction is the presence of a broad hump within the range of 16° to 38° [65]. It should be noted that the humps also were present in the XRD spectra of unreacted FA and GGBS. However, when the reaction happened, the location of the hump slightly changed to a higher 2-Theta centred at around 29° .

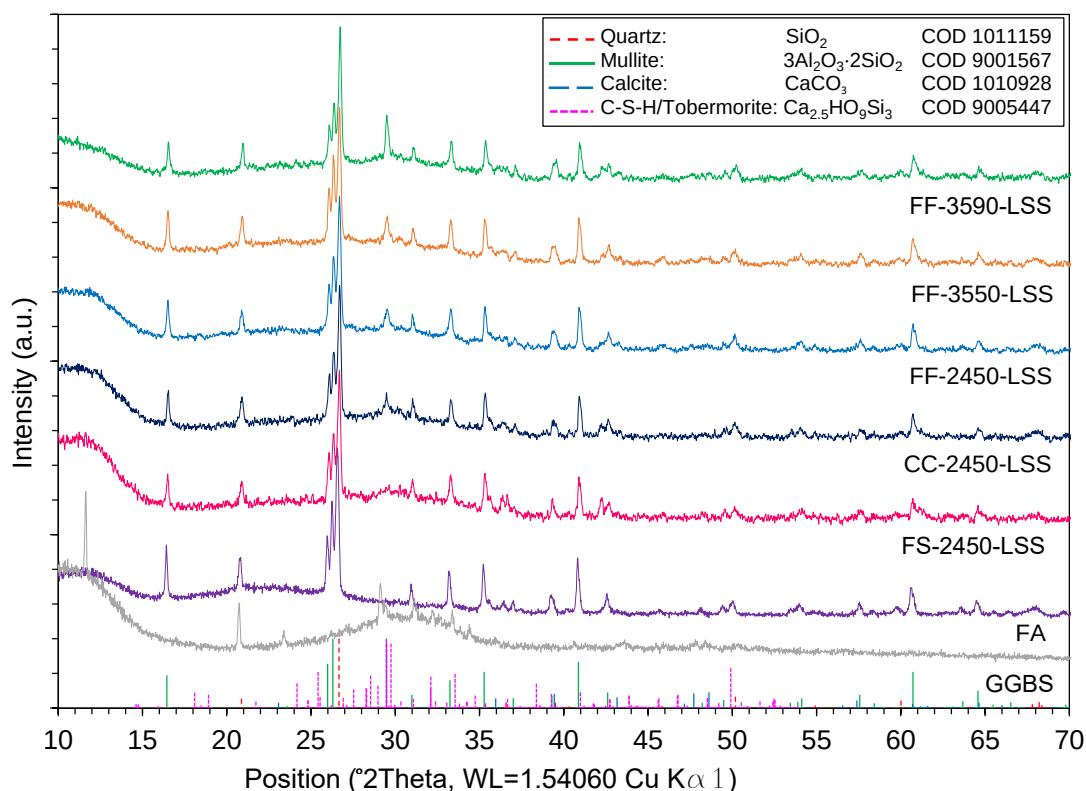


Figure 5.16. XRD spectra of 28-day cured (dried) 3D printing geopolymer mixes under fully sealed (FS), conventional casting (CC) and free-formed (FF) conditions at various environmental curing temperatures and relative humidities.

Based on Figure 5.16, the intensity of the XRD peaks of the plain LSS geopolymer cured at free-formed conditions of FF-2450 and FF-3550 associated with mullite was slightly higher compared to those of CC-2450 and FS-2450-LSS conditions. This indicates that the partial dissolutions of crystalline mullite of FA particles were interrupted by eliminating the initial curing under the free-formed conditions. Moreover, in FF-2450-LSS and FF-3550-LSS, the broad hump of amorphous aluminosilicate gel tended to be at a lower 2-Theta angle with slightly lower intensity compared to those of CC-2450-LSS and FS-2450-LSS. This is because of the presence of more unreacted FA glassy content in the mixes and the fact that the hump related to the FA unreacted amorphous content is centred on lower 2-Theta in the range between 15° and 30° [29]. As the previous study suggested [65], the quantity of the amorphous aluminosilicate gel is directly linked to the mechanical strength of the synthesised geopolymer mixes. These results are in line with the previous findings that showed the strength of free-formed mixes decreased, indicating that the rapid evaporation of water in mixes under free-formed conditions interrupted the dissolution of precursors by alkaline activator and gel formation process, resulting in the presence

of more unreacted or partially reacted glassy and crystalline residue of FA particles. Simulating the free-formed condition at high temperature and relative humidity for LSS geopolymers (FF-3590-LSS) resulted in a relatively similar XRD pattern to those of CC-2450 and FS-2450-LSS in terms of peaks intensity and the location of amorphous gel hump. This indicates that an outdoor printing environment with a higher relative humidity (lower evaporation rate) and temperature (i.e., FF-3590) compared to the FF-2450 can compensate for the lack of amorphous gel formation at early ages associated with eliminating the initial curing.

As shown in Figure 5.16, calcium carbonate (calcite) was formed in the microstructure of all free-formed mixes regardless of the temperature and relative humidity. The main peaks associated with the calcite phase were located at 29.4° and 39.4° . The highest intensity of calcite peaks was detected in LSS mixes cured under FF-3590, followed by those under FF-3550, FF-2450 and CC-2450. The calcite main peaks intensity was minimum for FS-2450. According to the previous studies [112,125,126], the presence of calcium carbonate is linked to the superficial carbonation reaction of GGBS particles as well as the carbonation reaction of dissolved Ca (sourced from GGBS) with CO_2 at a higher relative humidity, resulting in the formation of dense CaCO_3 layers reducing the microstructure porosity. These findings are in line with the results of NAD analysis, in which FF-3590 mixes showed a higher volume of pores with a size smaller than 10 nm compared to their FF-2450 and FF-3550 counterparts mixes. Removing the initial curing facilitated the carbonation reaction due to the higher exposure of the mixes to atmospheric CO_2 . Therefore, it was expected that the fully sealed cured mixes contained low content of calcium carbonates since the presence of CO_2 was limited in a fully sealed curing condition. Besides the above-mentioned findings, it is worth noting that the characteristic peaks of C-S-H and calcite are overlapping, as shown in Figure 5.16. According to previous studies [127,128], the C-S-H phase present in NaOH-activated geopolymer pastes is more crystalline in their nature, especially in low-calcium systems (e.g., 20% GGBS), and contains a lower amount of water, thereby they may be more detectable in XRD analysis of FA/GGBS-based geopolymers. Therefore, besides the presence of calcite phase in the microstructure, higher intensity of peaks located at 29.4° , 25.5° , 29.4° , and 49.9° in free-formed mixes at different curing temperatures and relative humidities

can also be attributed to the possibility of a slight presence of disordered C-S-H gel, which may contribute to the microstructure through bridging its components [125].

Figure 5.17 illustrate the XRD spectra of 28-day cured geopolymer mixes modified by 0.07% GO and 0.50% NC under free-formed conditions at various environmental curing temperatures and relative humidities. A slight broad amorphous hump associated with C-A-S-H and N-A-S-H aluminosilicate gel was detected in the range between 16° and 35° . As previously discussed, the broad hump of amorphous silica gel in free-formed mixes tends to be at a lower 2-Theta angle due to the presence of a higher amount of unreacted or partially reacted glassy content of FA in the system. This broad diffraction pattern also remained unchanged in nano-modified geopolymer mixes under FF-2450 and FF-3550 conditions compared to the that of plain LSS geopolymer mix at FF-2450. This observation indicates that the effect of incorporating a slight dosage of GO and NC into the mixes on the amorphous silica gel formation was not detectable via XRD analysis when the initial curing was eliminated. This also indicates that the interruption occurred in the dissolution of precursors and polymerisation reaction due to the evaporation of water (when initial curing elimination was simulated) was the dominant mechanism, and the GO addition could not compensate for its adverse effect on the gel formation process significantly.

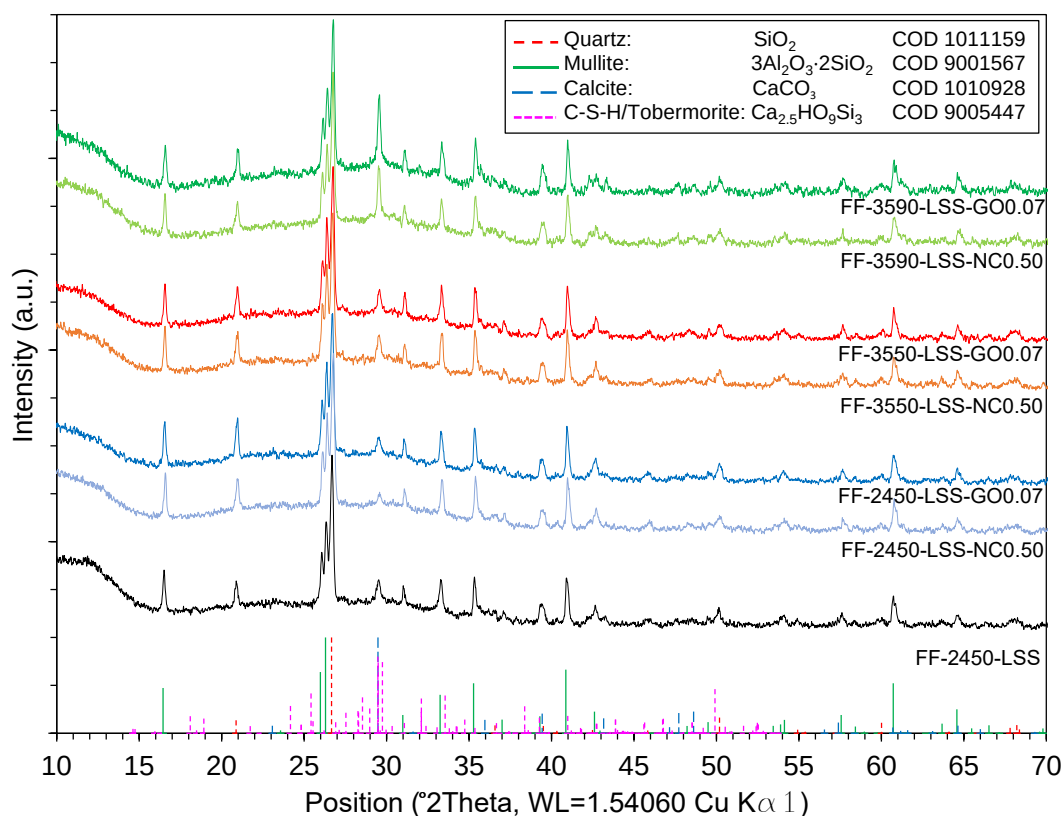


Figure 5.17. XRD spectra of 28-day cured (dried) 3D printing geopolymer mixes modified by 0.07% GO and 0.50% NC under free-formed (FF) condition at various environmental curing temperatures and relative humidities.

As it is shown in Figure 5.17, in the FF-3590 series, when the rate of evaporation (moisture loss) was significantly lower (approximately 50%), the location of the amorphous silica gel hump moved to a higher 2-Theta angle (centred at $\sim 29^\circ$). This indicates that a lower rate of moisture loss in FF-3590 decelerated the rate of interruption in the dissolution reaction of the glassy content in FA, resulting in a lower amount of amorphous silica gel in the microstructure [45]. Besides, in FF-3590-LSS-GO_{0.07}, the intensity of the peaks was higher than that of FF-3590-LSS-NC_{0.50}. Although the higher intensity of the main peaks of primary crystalline phases can be attributed to the lower degree of dissolution of FA particles, a previous study [45] reported that by incorporating GO into FA-based geopolymer mixes, the primary spectra peaks of quartz and mullite increased slightly. It is well known that the crystalline phases in precursors do not participate in geopolymerisation reactions [129]. However, Liu et al. [45] reported that since the main characteristic peaks of quartz and zeolite located at 2-Theta of 20.8° and 26.6° are overlapping, the higher peaks intensity in GO-modified mixes can also be attributed to the formation of zeolite-like phases in the microstructure that was facilitated by the interaction between

GO sheets and crystal nucleus [130]. According to previous studies [45,131], the zeolite-like crystals growth is an energy-consuming reaction and depends on different parameters such as activation energy and mass transfer rate. Therefore, only a small fraction of geopolymer gel can attain the required energy level to form the zeolite monocrystalline layer. Liu et al. [45] suggested that GO incorporation into the geopolymer mix facilitates the zeolite crystal growth due to its inherent high electron-activity and ions absorption nature, contributing to the zeolite phase formation. Therefore, the higher intensity of the peaks associated with the limited formation of crystalline structure in the geopolymer gel demonstrates the effectiveness of GO in improving the dissolution and polymerisation reaction even in free-formed conditions when GO is used as an additive in geopolymer mortars.

SEM analysis

The typical SEM images of LSS geopolymer mixes cured for 28 days in various outdoor environments under conventional casting (control: CC), and free-formed curing conditions are shown in Figure 5.18 and Figure 5.19, respectively. Samples were taken from the drying shrinkage specimens to review the effect of NS replacement, initial curing elimination (free-forming), and various curing temperatures-relative humidities on the microstructure and the pore networks of the synthesised specimens.

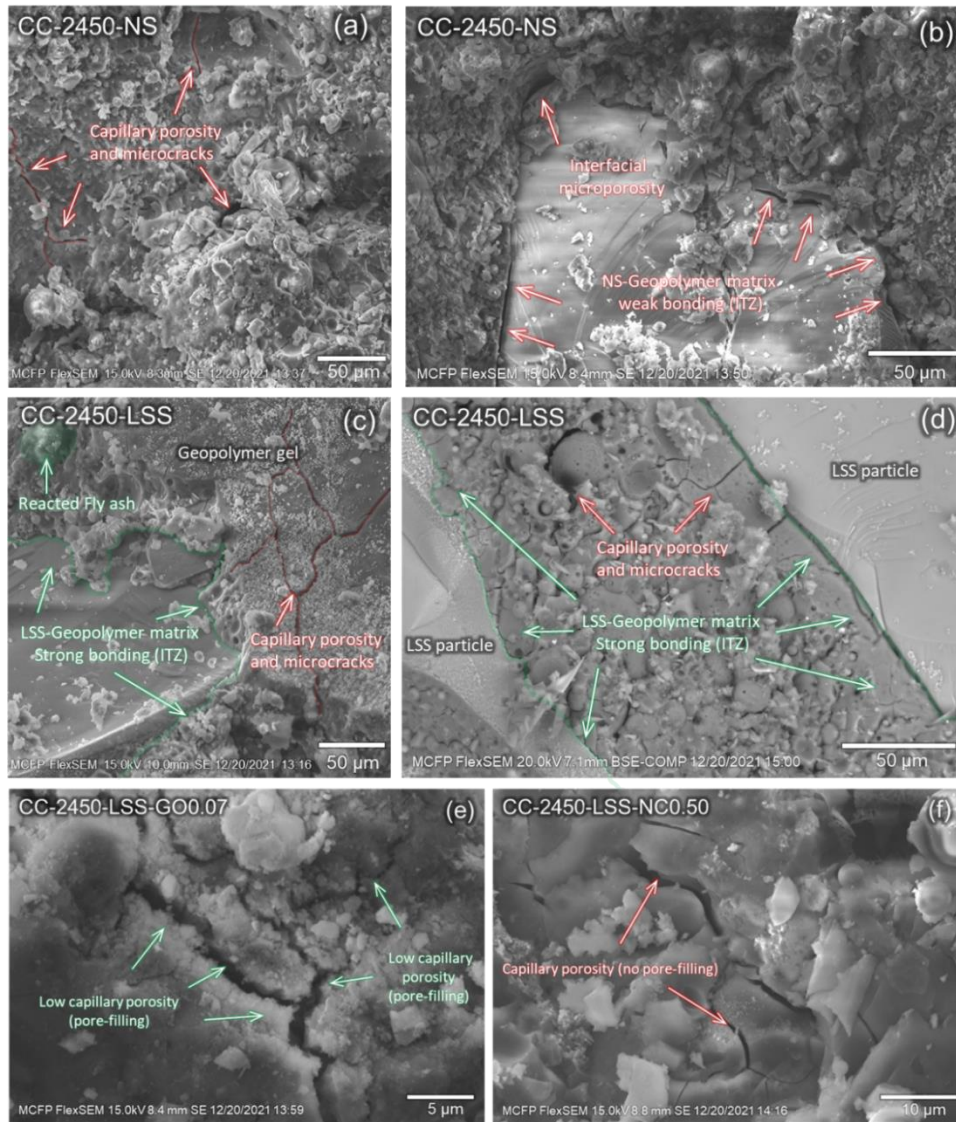


Figure 5.18. SEM images of plain and nano-modified geopolymer mortars designed for extrusion-based 3D printing cured under control conditions at 24 °C-50% RH (CC-2450): (a) & (b) plain NS, (c) & (d) plain LSS, (e) GO-modified, (f) NC-modified.

As can be seen in Figure 5.18 (a) to (d), the geopolymer matrix in the microstructure of CC-2450-NS and CC-2450-LSS were almost similar in terms of the size and width of the micropores and microcracks. This observation can be attributed to the fact that the geopolymer matrix was made of a similar FA:GGBS ratio and the molarity ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ was constant in both mixtures binder. However, as clearly can be seen in Figure 5.18 (c) and (d), strong bonding between LSS and geopolymer matrix was present in CC-2450-LSS when compared to the CC-2450-NS mixes where wider interfacial microporosities were detected. As it was previously suggested by Ho et al. [43] and also shown in Figure 5.2 (c) and (d), the LSS particles exhibit a higher moisture retaining capacity due to their specific surface morphology (porous nature)

compared to the NS particles [68], which might have contributed to a stronger bonding between the LSS and geopolymer matrix. Moreover, as previously stated in Section 5.4.6.1 and found by Ho et al. [43], the LSS might partially react with the geopolymer matrix to offer a strong bonding, which results in the reduction of ITZ porosity.

Figure 5.18 (e) and (f) show the microstructure of GO- and NC-modified geopolymer mixes, respectively. Detecting the GO/rGO in the microstructure of the mixes of this study was very challenging because of the low dosages of GO sheets. However, as can be seen, incorporating 0.07% GO into the geopolymer base mix in the control condition at 24 °C - 50% RH resulted in the formation of a more compact microstructure compared to the plain mixes. The pore-filling effect is clearly observed in CC-2450-LSS-GO_{0.07}, where the reaction products of C-S-H and N-A-S-H filled the microcracks and micropores of the gel matrix. This observation is in line with that of the previous research on the effect of GO on hydration and microstructure of the FA-cement system [132], where the GO incorporation into the mix improved the subsequent hydration of FA and filled the micropores with the reaction products. Although the inclusion of NC into the geopolymer mix (CC-2450-NC_{0.50}) resulted in a more refined microstructure compared to the plain mixes, as previously discussed in Section 5.4.6.1, a similar pore-filling effect was not observed for NC-modified mixes shown in Figure 5.18 (f).

The SEM images of Figure 5.19 (a) to (f) illustrate the effect of curing in outdoor 3D printing environments at different temperatures and relative humidities on the microstructure of the geopolymer mortars designed for extrusion-based 3D printing. By comparing Figure 5.19 (a) and (b) for FF-2450-LSS with Figure 5.18 (c) and (d) for CC-2450-LSS, it can be seen that compared to the control mixes in the free-formed condition, the microstructure of FF-2450-LSS was less dense and the compactness was reduced due to the interruption in dissolution and geopolymerisation reaction caused by rapid water evaporation at early-age. As previously discussed in Section 5.4.4, this resulted in an increased amount of unreacted or partially reacted FA in the geopolymer matrix. In addition, a higher macro and microporosity can be observed in the microstructure, which explains the lower compressive strength of the free-formed mixes compared to that of the mixes under the control condition.

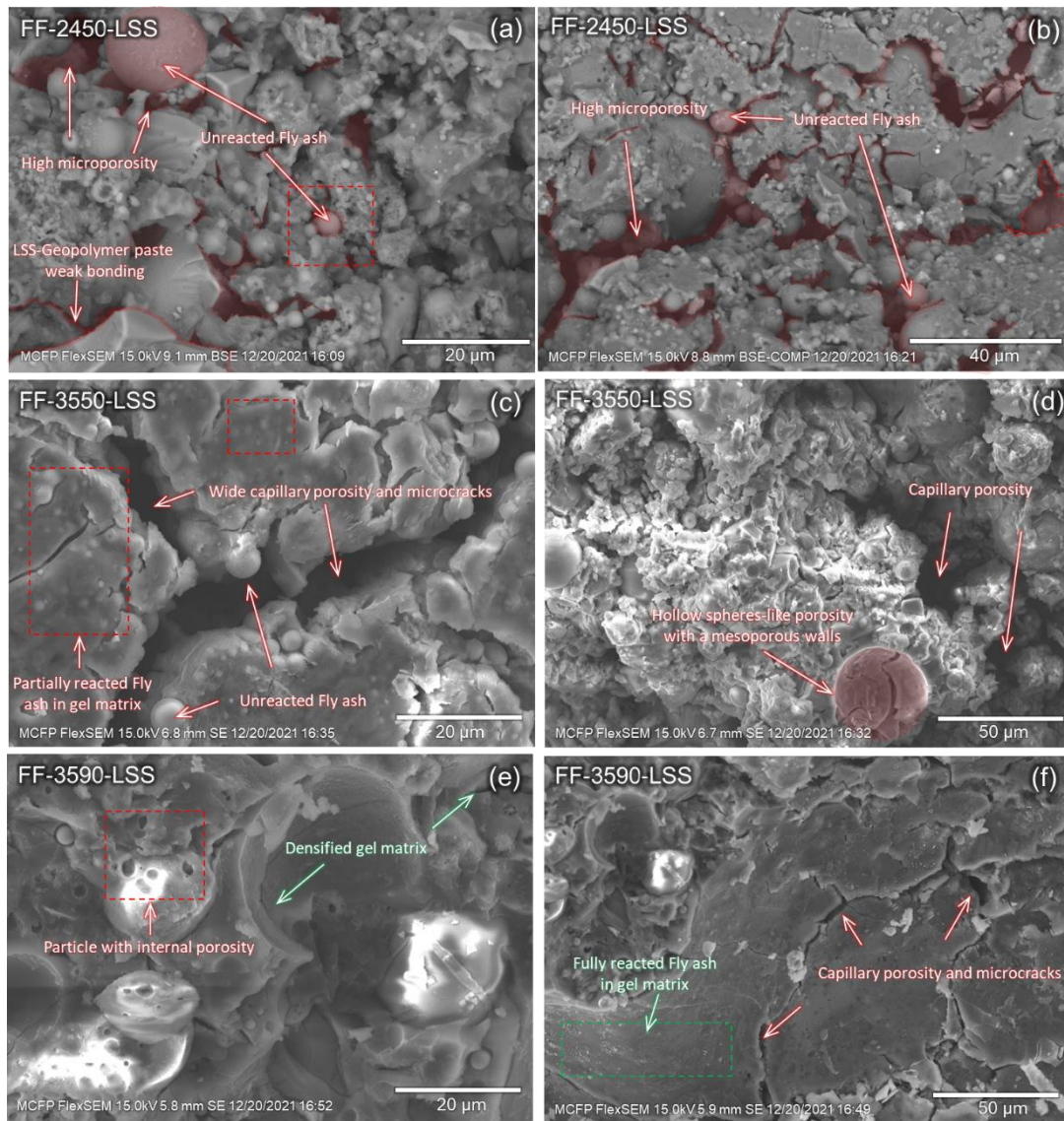


Figure 5.19. SEM images of plain LSS geopolymer mortars designed for extrusion-based 3D printing cured under free-formed condition at 24 °C - 50% RH (FF-2450): (a) & (b) plain NS, (c) & (d) plain LSS, (e) GO-modified, (f) NC-modified.

As previously stated in Section 5.4.6.1 and is shown in Figure 5.19 (c) and (d), increasing the curing temperature at a constant relative humidity (50% RH) for free-formed mixes resulted in the reduction of the volume of fine pores below 10 nm and coarsening of the microstructure. By comparing the SEM image for FF-2450-LSS and FF-3550-LSS mixes in Figure 5.19 (a) to (d), it can be seen that the size of microcracks (in the range of micrometre) and porosities in the microstructure were relatively similar. These findings also support the results of the compressive strength reduction of the free-formed mixes and are in line with the pore network analysis by NAD discussed in Section 5.4.6.1. As previously stated, besides the slit-like pores, particles with internal porosity and hollow spheres with the mesoporous surface (footprint of

unreacted or partially reacted FA in geopolymer matrix) can be detected in Figure 5.19 (a) to (f).

The microstructure of FF-3590-LSS mixes shown in Figure 5.19 (e) and (d) represents that curing at a high temperature and relative humidity resulted in the formation of a more densified geopolymer matrix. In addition, the number of partially reacted FA particles inside the geopolymer matrix was reduced. However, large microcracks caused by rapid water evaporation at early ages were still detectable in the microstructure of free-formed mixes, explaining the reduction of the strength compared to the mixes cured in the control condition. These results are in line with the results of NAD analysis in which by increasing the relative humidity at 35 °C, the volume of porosity below 10 nm increased, representing that more reaction products were formed.

5.5 CONCLUSIONS

This chapter has presented the results of the effect of mixture nanomodification with NC and GO on rheological properties of a potentially printable geopolymer mortar and the first study on the effect of nanomodification and outdoor 3D printing environments with different temperatures and relative humidities (i.e., 24 °C – 50%, 35 °C – 50%, and 35 °C – 90%) on the compressive strength, drying shrinkage, and microstructure of 3D printing (extrusion-based) FA/GGBS-based geopolymer mortars prepared with NS and LSS. The following conclusions can be drawn based on the presented results:

- The LSS (NS) mortar with an alkaline activator's AB ratio of 0.35 and MR ratio of 1.5 containing a binder composition of 80% FA and 20% GGBS (FA₈₀G₂₀LSS(NS)-AB₃₅MR_{1.5}) was chosen as a base mortar that exhibited appropriate rheological properties comparable to 3D printable geopolymer mortars.
- The yield stress evolution at rest for the LSS base mortars was improved by incorporating NC into the base mixture at three dosages of 0.17, 0.33 and 0.5 wt%. Then the LSS base mortars were modified with GO to obtain relatively identical yield stress development behaviour to NC-modified mixtures. Incorporating 0.03, 0.05 and 0.07% wt% GO resulted in similar

behaviour to LSS mixtures modified with 0.17, 0.33 and 0.5% NC, respectively.

- The results of yield stress evolution versus age at rest showed that LSS mortars modified by 0.03, 0.05 and 0.07% GO exhibited increased characteristics buildability rate (ΔC_{b20} , which is proportionate to the maximum vertical building rate achievable for the mixture) by 2.7, 6.1, and 12.2 times compared to the base LSS mortar, respectively.
- The viscosity recovery capacity of the LSS-GO-modified mortars (e.g. 67% for LSS-GO_{0.07}), which exhibited comparable yield stress evolution to their NC-modified counterparts, was higher than that of the NC-modified mixtures (e.g. 56% for LSS-NC_{0.5}).
- Increasing the NC dosage in 3D printing geopolymer paste reduced the intensity of the initial dissolution peak in the heat flow curve of calorimetry analysis by approximately 50%. In contrast, GO modification improved the dissolution of the binder particles resulting in a higher peak intensity of up to 15%. The 48-h cumulative heat generated by NC-modified pastes was relatively equal to that of the base paste. However, the GO incorporation into geopolymer paste increased the total heat of the reaction by 2.3, 5.6 and 8% for the GO dosage of 0.03, 0.05, and 0.07%, respectively,
- Approximately 10% increase in the 28-day compressive strength was observed for using LSS fine aggregate instead of NS in 3D printing geopolymer mortars that were prepared under both fully sealed (FS) and outdoor 3D printing environment (free-formed, FF) methods at 24 °C – 50%.
- Free-formed 3D printing geopolymer mortars cured at 24 °C – 50% (FF-2450) showed up to a 55% reduction in compressive strength compared to their counterpart mortars cured in conventional plastic sealed (FS-2450) condition. The GO-modified mortars outperformed their NC-modified counterparts in all three outdoor 3D printing environments (FF-2450, FF-3550, and FF-3590).

- Irrespective of the curing temperature and relative humidity, the LSS mortars exhibited a lower drying shrinkage (up to 16% in CC-2450) than the NS mortars in both conventional casting and free-formed conditions.
- GO-modification of 3D printing LSS geopolymer mortar reduced the 28-day drying shrinkage under CC-2450 condition (with a maximum reduction of 8% for 0.07 wt% GO dosage) compared to plain LSS mortars. This is due to the improvement of the geopolymer matrix in GO-modified mortars (pore-filling effect, GO/rGO bridging), resulting in a more compact microstructure compared to those of plain or NC-modified LSS mortars. In contrast, incorporating NC into the base mortars resulted in a higher drying shrinkage at all dosages.
- Simulating the free-formed condition increased the 28-day drying shrinkage of GO- and NC-modified (irrespective of dosage) LSS geopolymer mortars by approximately 70% compared to their CC-2450 counterparts. This indicates that formwork-free conditions can adversely affect the resistance to drying shrinkage of 3D printing geopolymer mortars modified by NC and GO.
- Increasing the temperature to 35 °C in 50% RH reduced the drying shrinkage in GO- and NC-modified free-formed mortars due to the reaction rate acceleration. When the relative humidity increased to 90% (at 35 °C) to simulate the high temperature-high humid condition, the drying shrinkage of free-formed mortars was reduced up to 42% (for FF-3590-LSS-GO_{0.07}) compared to that of FF-2450 counterpart mortars.
- SEM and NAD analyses revealed that the mechanical and durability properties of 3D printing geopolymer mortars are interconnected with their physicochemical and microstructural properties. The incorporation of GO in geopolymer mortars resulted in the refinement of the porosity and reduced the cumulative porosity of the GO-modified free-formed and conventional casting mortars.

The results of this study indicate the potential of using an industrial by-product of steel industry as natural fine aggregate alternatives to increase sustainability in the concrete 3D printing. This study depicted promising results for using GO as yield stress and

thixotropy modifier instead of NC in 3D printable geopolymer mortars. Moreover, these findings illustrated that replacing GO with NC can enhance the mechanical and durability properties of the geopolymer designed for extrusion-based 3D printing under different outdoor printing environments. In addition, these findings are expected to serve as a benchmark for further studies on the effect of different curing techniques (internal or external) on the hardened state dimensional stability of 3D printed products using geopolymer binders systems.

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Chapter 6: Conclusions and suggestions for future work

6.1 CONCLUSIONS

The overall aims of this research were divided into two primary goals. Firstly, research was conducted to understand the material-process interaction and realise how to control the yield stress evolution and optimise cement-based printable mixtures across different 3D printing jobs to avoid strength-based failure during 3D printing. Secondly, experimental work was done to gain a comprehensive understanding of one of the primary concerns in construction 3D printing, i.e. the shrinkage behaviour of printable materials, by considering the effect of mixture design, formwork-free conditions and different outdoor printing environments on the dimensional stability of cement-based and geopolymer concrete. To achieve these objectives, the effect of mixture design modification on rheological parameters was investigated first. Then, the effect of formwork-free curing conditions and different curing environments (temperatures and relative humidities) on the mechanical performance, shrinkage behaviour and microstructure of printable mortars (cement-based and geopolymer-based) were studied. The following sections elaborate on the most important findings from the research conducted:

6.1.1 Optimising cement-based mortar's mixture design for C3DP by considering rheological limits

- Based on experimental findings reported in Chapter 3, controlling the yield stress evolution could be used as a tool for printing optimisation in cement-based mortars. Experiments were conducted to find relationships between water to cement ratio (W/C), superplasticiser, accelerator, and retarder dosage with the initial yield stress and structuration rate (A_{thix}) to be used as controlling factors for optimising the yield stress evolution. As a result, a theoretical framework based on rheological constraints was presented to optimise mortar compositions for 3D printing. Shape stability, extrudability/pumpability, and buildability were linked to the development of yield stress, which is the basis of the rheological constraints to avoid strength-based failure during printing. A yield stress evolution that

maximises open time while avoiding the aforementioned constraints was considered optimum.

- A method of assessing the buildability of a mortar with an exponential structuration rate was proposed. The maximum slope of the buildability limit that can be achieved for a mixture before it intersects with the fitted exponential curve of yield stress evolution was named as '*characteristic buildability slope*' (Δ_{cb}). Since the characteristic buildability slope is proportional to the maximum vertical build rate ($\dot{H}_{max}$) that can be supported by a mortar, it is essentially a measure of the mortar's buildability.
- W/C ratio and superplasticiser dosage both had an identical effect on early age yield stress development, with the observed trend being a reduction in initial yield stress and structuration rate with increasing W/C or superplasticiser dosage. A linear correlation was found between the initial yield stress and superplasticiser dosage, implying that the initial yield stress values might be modified to account for variations in filament height using the predictive model.
- It was revealed that since variation in filament size and its corresponding mixture modification with superplasticiser affected the buildability characteristics of the mixture and the print job, it might be required to optimise the buildability of the modified mixture (with superplasticiser) considering the correlation between accelerator dosage and structuration rate. Accelerator dosages were shown to have a linearly positive correlation with buildability rates. Therefore, in response to variation in vertical building rates originating from the scale or complexity across different print jobs, a linear model might be used to modify the accelerator dosage in the mixture.
- It was shown that tartaric acid, depending on the content, may be utilised as either an accelerator or a retarding agent. The initial structuration rates of mortars containing tartaric acid were linear, and the slope of these rates correlated with the concentration of tartaric acid. Using these findings, a straightforward optimisation approach was tried and shown to be effective based on the suggested theory.

- In order to demonstrate that the proposed theoretical model for mixture optimisation works appropriately, small-scale printing of a mixture with a characteristic buildability slope almost equal to the buildability limit of a defined print job was carried out. The results of shape stability and buildability measurements showed that the concept of mixture optimisation works appropriately.

6.1.2 Shrinkage behaviour of cement-based 3D printing mortars: effect of temperature and relative humidity

- Two printable cement-based mixtures with sand to cement (S/C) ratios of 0.8 and 1.0 were developed based on the findings in Chapter 3 to be further studied for the autogenous shrinkage and long-term drying shrinkage under the free-formed condition at three different environmental conditions simulating the standard, arid and tropical weather.
- Mechanical strength was found to be lower in the free-formed compared to the control specimens because of a combination of factors, including lower hydration degree, increased macroporosity, and a greater likelihood of microcracking in the cement paste.
- For a given S/C ratio, under a curing environment of 24 °C – 50% RH, free-formed specimens exhibited 28-day drying shrinkage deformation approximately 30% lower than conventional casting specimens. However, the rate of drying shrinkage development for free-formed specimens was higher, and their long-term drying shrinkage (6 months) exceeded that of conventional casting specimens.
- It was found that the reduction in shrinkage at an early age was linked to higher water evaporation from free-formed specimens with higher surface area to volume ratio (S/V) and disruption in the hydration process, while the higher shrinkage at a later age was associated with carbonation of free-formed specimens.
- The free-formed specimens exhibited a weight-gaining behaviour with increased shrinkage deformation, indicating that 3D printable mortars were prone to carbonation shrinkage compared to the conventional casting specimens.

- The drying shrinkage development of free-formed specimens at 45-50% relative humidity was not very sensitive to the increase in the temperature. However, increasing the curing environment's humidity to 85% at 35 °C (representing tropical weather) resulted in almost 2.5 times lower drying shrinkage.
- Based on the findings in chapter 4, autogenous shrinkage may account for up to 30 % of the overall shrinkage deformation in printing mixes due to the presence of high cement content in the printable mixture.
- This research highlighted that in printing mixtures with high cement content, the autogenous shrinkage can form a significant proportion (up to 30%) of total shrinkage deformation.
- Based on the findings in Chapter 4, the free-formed specimens achieved a more refined pore structure after 4 months of curing compared to conventional casting. Additionally, the total volume of porosities below 100 nm of free-formed specimens in all 3D printing-simulated environments was lower than that of traditional cast specimens. It was shown that the higher shrinkage in free-formed specimens was linked to this phenomenon.

6.1.3 Shrinkage behaviour of geopolymers 3D printing mortars: Effect of mixture nanomodification and environmental conditions

- The findings of Chapter 5 exhibited that to address the concerns with the higher environmental impact of cement-based 3D printing mortars due to the higher volume of OPC and fine aggregate (natural sand, NS) content in the printable mortars compared to conventional concrete, it is possible to develop a fly ash/slag (FA/GGBS) based printable geopolymer mortar using complete substitution of the natural aggregate with lead smelter slag aggregate (LSS) and a novel thixotropy modifier, graphene oxide (GO). The base mixture designed for 3D printing was obtained by adjusting different mixture-design parameters, including the binder composition (FA:GGBS), activator to binder ratio (AB), and alkaline activator modulus ($MR = \text{SiO}_2/\text{Na}_2\text{O}$ molar ratio). The base mixture was further modified with graphene oxide to pass the printability requirements.

- It was found that the geopolymer mortar with FA:GGBS ratio of 0.8:0.2, AB of 0.35 and MR of 1.5 prepared with LSS or NS is potentially printable. It was shown that the yield stress development and viscosity recovery capacity of geopolymer mortars, which have a direct relationship with shape stability, can be further improved by incorporating a very small dosage of nanoclay (NC < 0.5 wt% of binder) and graphene oxide (GO < 0.1 wt% of binder) into the base geopolymer mortar. However, GO incorporation resulted in a higher characteristics buildability rate and viscosity recovery capacity.
- GO modification increased the rate of the dissolution of the raw binder particles, resulting in higher cumulative heat of reaction after 48 h compared to the plain mixture. However, the NC modification reduced the dissolution rate and led to approximately equal heat of hydration compared to the plain mixture after 48 h. These behaviours indicated that GO modification outperformed NC modification in terms of forming higher amounts of reacted products.
- Compared to mortars prepared with NS, printable geopolymer mortars prepared with LSS aggregate exhibited higher mechanical performance in conventional casting and free-formed conditions when cured at 24 °C – 50% RH.
- Under the standard curing environment of 24 °C – 50% RH, formwork-free printable geopolymer mortars (FF-2450) exhibited lower mechanical strength compared to their conventional casting counterparts. Moreover, irrespective of being free-formed or conventional casting, for a given curing environment, the mechanical strength of geopolymer mortars modified with GO was higher than those modified with NC.
- When LSS was fully substituted for NS, geopolymer mortar showed higher resistance to drying shrinkage at both free-formed and conventional casting conditions.
- Compared to plain mortars, GO-modified geopolymer mortars exhibited higher resistance to drying shrinkage in conventional casting under 24 °C – 50% RH. This was associated with improved geopolymer gel formation,

reduced capillary porosity, and crack bridging properties induced by adding GO to the mixtures. However, NC-modification geopolymer mortar under a similar curing configuration resulted in lower resistance to drying shrinkage.

- The findings of Chapter 5 revealed that the absence of proper initial curing at an early age (1st day) in free-formed specimens under the standard curing environment (24 °C – 50% RH) resulted in increased 28-day drying shrinkage deformation of all nanomodified (GO or NC) geopolymer mortars compared to that of their counterpart plain mortar. This can be associated with the interruption in the dissolution due to higher surface water evaporation and an increase in the surface tension of the pore structure due to the presence of nanomaterials.
- Simulating the Arid (35 °C – 50% RH) and Tropical (35 °C – 90% RH) curing environment for free-formed GO- and NC- modified mortars resulted in lower 28-day drying shrinkage compared to that of their counterpart in the standard curing environment (24 °C – 50% RH). However, the drying shrinkage reduction for the Tropical was more noticeable than in the Arid curing environment.
- The microstructural analysis (porosimetry and scanning electron microscopy) exhibited that adding nanomaterials refined the pore structure of the free-formed and conventional casting geopolymer mortars. However, it was found that GO-modification of printable geopolymer mortar was more efficient in gel densification and in reducing the total porosity of the microstructure than the NC-modification. Moreover, as shown by SEM analysis, printable geopolymer mortars' physiochemical and microstructure characteristics were interconnected to the nanomodification and the curing environment parameters (including temperature and relative humidity). It was found that these characteristics significantly affected the durability properties and mechanical strength of the free-formed specimens.

In addition, the findings of this research are expected to serve as a benchmark for further studies on the effect of different curing techniques (internal or external) on the hardened state dimensional stability of 3D printed products using cement-based or alkali-activated binders systems to enhance the structural integrity of printed products

by controlling the water evaporation and drying (and autogenous) shrinkage development.

6.2 RECOMMENDATION FOR FUTURE RESEARCH

Many material science-related challenges remain for construction-scale additive manufacturing. The following future research is recommended:

- More research is needed to establish the limits of the identified correlations in Chapter 3 and the extent to which they may be applied to various mortar/concrete systems. Moreover, further research is recommended to identify the active mechanisms for tartaric acid accelerating and retarding behaviour.
- More research is needed to determine the effect of shrinkage in individual layers (non-uniform shrinkage) on the structural integrity of printed products by exploring the shrinkage development of 3D printed parts in relation to the changes in the internal relative humidity inside or between the printing filaments.
- A comprehensive study of the carbonation shrinkage of 3D printed concrete is highly recommended, which examines the impact of filament size, the composition of concrete mixtures, and environmental factors such as temperature, humidity, and exposure time on the carbonation shrinkage of 3D printed concrete.
- A thorough investigation into the impact of chemical shrinkage, hydration rate and high-temperature curing environment on the autogenous shrinkage of 3D printing mixes is recommended. Furthermore, an improved measurement technique is suggested for further study to accurately measure and analyze the effect of temperature on the autogenous shrinkage development within the first 24 hours after 3D printing. This could involve modifying current methods or exploring new techniques specifically designed for the unique characteristics of 3D printed concrete, with a focus on continuous data collection at very short time intervals, to capture the dynamic nature of shrinkage development in 3D printed concrete.

- More in-depth research is needed to investigate the effect of GO and NC incorporation on the chemical and autogenous shrinkage development in 3D printing geopolymers, as well as the effect of different outdoor 3D printing environments on the non-uniform shrinkage development of 3D printed products prepared with alkali-activated binders.
- Lastly, in future work, the hybrid use of GO and NC could plausibly lead to a higher rate of reaction and mechanical strength performance together with more efficient thixotropy properties. The effect of a higher dosage of graphene oxide on rheological properties and hardened state properties should be explored for free-formed geopolymer mortars.

Appendices

Appendix A

Supporting Information for Chapter 4

S 1. Printing quality of the mix with S/C of 1.0 and mixture proportion shown in Table 4.2.

Fig. S1 and S2 show printing quality of two-layer and three-layer specimen with S/C of 1.0, respectively.

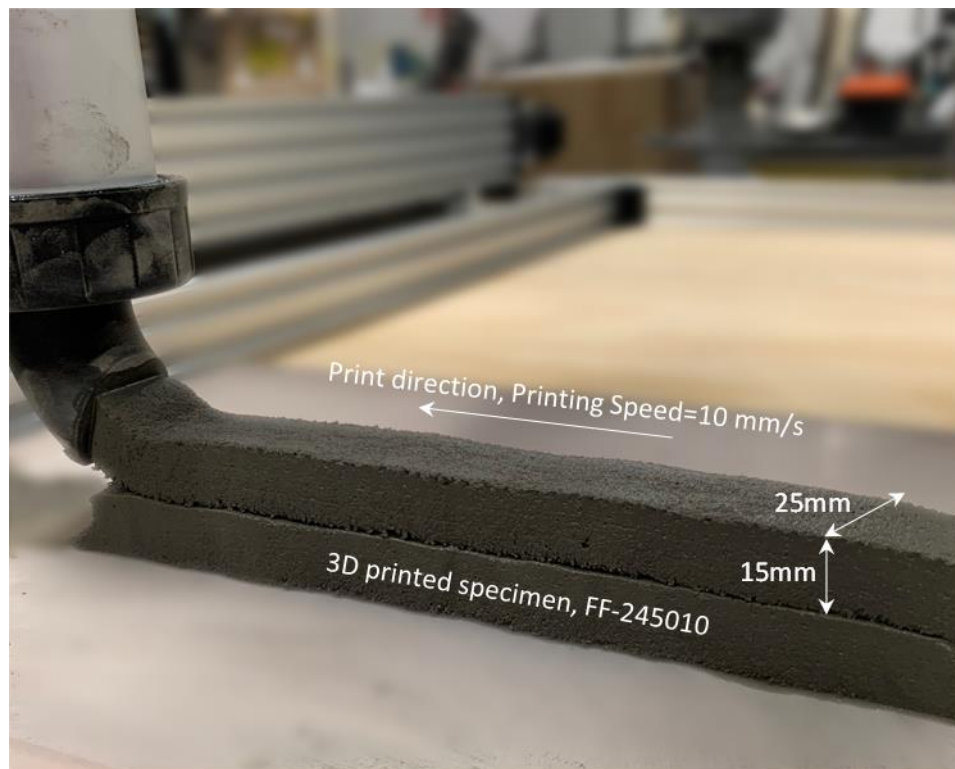


Figure S 1. Printing quality of two-layer specimen with S/C of 1.0.



Figure S 2. Printing quality of three-layer specimen with S/C of 1.0.

S 2. Carbonation of free-formed specimens in 24 °C and 50% RH

To further investigate the carbonation development in free-formed specimens in long term, TGA tests were conducted on the free-formed specimen (FF-245010) at different ages (after 28, 160 and 565 days) and the results were compared to that of control specimen (Ctrl-245010) at 28 days. This analysis can provide information on the quantity of calcium carbonates formed in 3D printing mortar based on the CO_2 weight loss caused by the decomposition of calcium carbonate. Fig. S3 shows the thermogravimetry analysis (TGA) results of printing mortar with S/C ratio of 1.0 under different initial curing of 28 days sealed curing, 1 day sealed curing (control) and no initial curing (free-formed) conditions. It is well-known that portlandite ($\text{Ca}(\text{OH})_2$) dehydroxylates and calcite (CaCO_3) decomposes at around 460 °C and between 600 and 800 °C, respectively [77]. Moreover, the weight loss in the range of 600 °C – 650 °C and at around 720 °C is related to the presence of mono- or hemi-carbonates, and coarse carbonated products (CaCO_3) in the uhydrated cement, respectively [77].

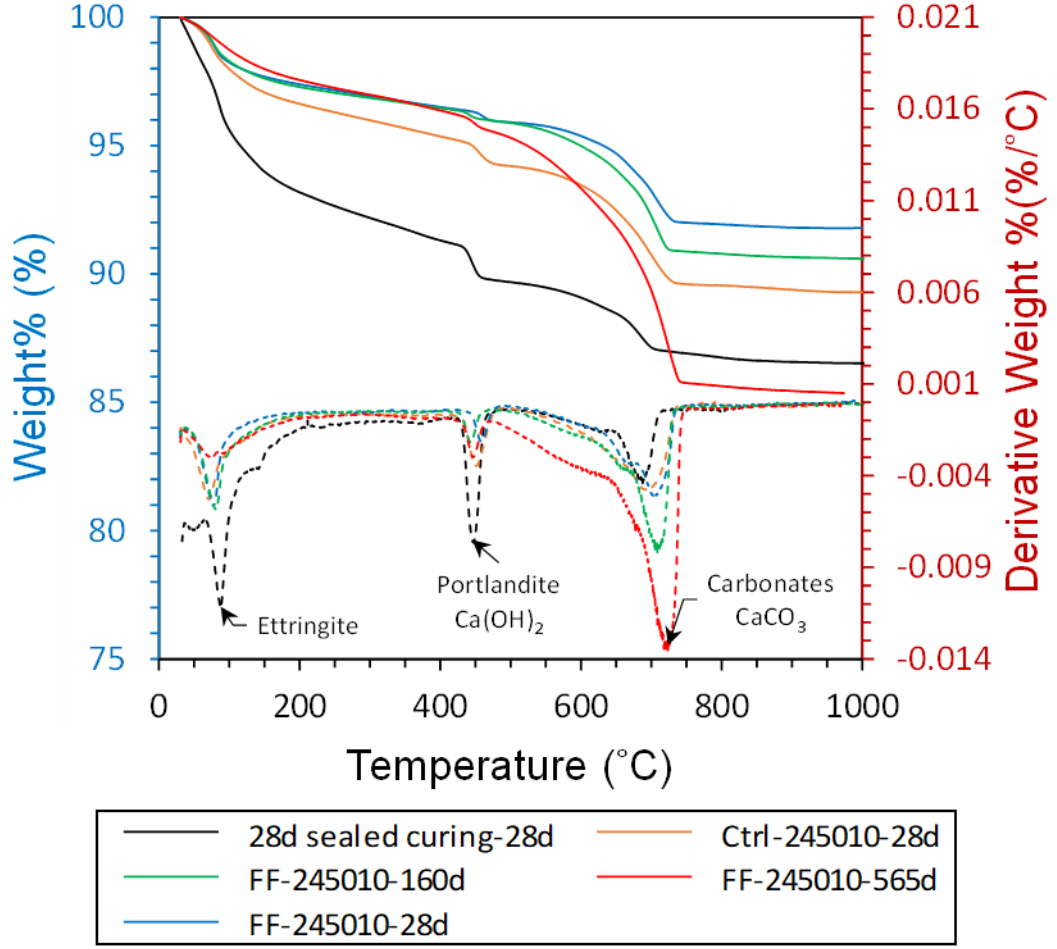
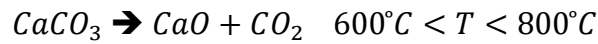


Figure S 3. Variation of TGA of printing mortar with S/C ratio of 1.0 under different initial curing of 28 days sealed curing, 1 day sealed curing (control) and no initial curing (free-formed) conditions, conducted after 28, 160 and 565 days of curing at standard temperature and humidity of 24 °C and 50% RH. Solid lines show the loss percentage of weight and dashed lines are derivative weight loss profile.

Over 600 °C, calcium carbonate (CaCO_3) decomposes into CaO and CO_2 . Using the molecular masses of CaCO_3 ($m_{\text{CaCO}_3} = 100 \text{ g/mol}$) and CO_2 ($m_{\text{CO}_2} = 44 \text{ g/mol}$), this weight loss (WL_{CaCO_3}) can be used to calculate the amount of calcium carbonate as shown in Eq. S1.



$$\text{CaCO}_{3,\text{measured}} = WL_{\text{CaCO}_3} \times (m_{\text{CaCO}_3}/m_{\text{CO}_2}) = WL_{\text{CaCO}_3} \times \frac{100}{44} \quad (\text{S1})$$

As it is shown in Fig. S3, the CO_2 weight loss between 600°C and 800°C (representing the amount of calcium carbonate) of FF-245010 after 28, 160 and 565 days of curing was 16%, 37% and 152% greater than that of Ctrl-245010 after 28 days, respectively. Considering the weight gaining behaviour of printed specimens, as well

as the results of TGA conducted at different ages of free-formed specimen in long term, carbonation has occurred in free-formed condition.