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Extrusion and rheology characterization of geopolymer nanocomposites used in 3D printing

Biranchi Panda¹, Cise Unluer^{2*}, Ming Jen Tan¹

¹ Singapore Centre for 3D Printing, School of Mechanical & Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

² School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

* Corresponding author. Tel.: +65 91964970, E-mail address: ucise@ntu.edu.sg

Abstract

This study focused on the suitability of geopolymer mixes for extrusion-based additive manufacturing applications. Geopolymer mixes including alkaline potassium silicate activator with different molar ratios were prepared and evaluated for their rheological responses (e.g. yield stress, viscosity and thixotropy) that influenced their extrudability and buildability. Due to the low yield stress of geopolymers, nanoclay was introduced to enhance their thixotropy, which was assessed by structural breakdown and viscosity recovery tests. An activator-to-binder ratio of 0.35 and water-to-solid ratio of 0.30 were found to work well with a clay addition of 0.5% (i.e. by mass of total binder component). The addition of nanoclay led to an improvement in the rheological properties of geopolymer nanocomposites, which was attributed to the flocculation characteristic of the clay particles. A small-scale bathroom unit was printed by using the developed geopolymer nanocomposite, indicating the suitability of the proposed mix design to be used in 3D printing applications.

Keywords: 3D printing; extrusion; geopolymers; nanoclay; rheology

1. Introduction

Additive manufacturing of concrete, also known as 3D concrete printing, has gained a significant attention in the last few years due to its potential to change traditional building practices via the use of digital modelling and associated technologies to produce freeform building components. This approach is based on the fused deposition modelling (FDM) process, without requiring heating during the extrusion process. This is associated with the rheological behaviour of concrete, which is influenced by the flocculation of particles and hydration reaction rather than temperature effects, as described by Tay et al. [1] and Bos et al. [2]. Concrete printing starts with the 3D modelling of a component, followed by the depositing of the fresh mortar layer-by-layer until completion. Unlike plastic and metal printing, in concrete printing, the deposited material is not allowed to harden instantaneously to avoid cold joint between the layers. A thixotropic material is most suitable for such applications as it can be smoothly extruded and possesses the ability to hold the weight of the subsequent layers by providing shape stability [3-8].

Roussel [9] discussed the thixotropy property of printable materials, which originates due to the colloidal flocculation of particles and ongoing nucleation in Portland cement (PC)-based cementitious materials. Once a thixotropic material is developed by optimising the mix design, the structural build-up (i.e. hardening) rate can be controlled using various combinations of admixtures, as described by Marchon et al. [10]. The effect of admixtures on cement rheology and structural build up was previously reported by Reiter et al. [11], where the need for evolving yield stress to support the vertical buildability in concrete printing was highlighted. As shown in Equation 1, suggested by Wangler et al. [12], where ρ , g and h represent the density, gravity and extruded layer height, respectively; the initial yield stress (τ) for a single layer at the time of extrusion should be approximately 180 Pa to self-support a typical layer with a height of 15 mm. For the addition of more layers, the yield stress must increase over time with respect to the final height (e.g. one meter). As shown in Fig. 1, a yield strength of 180-1000 Pa is required for the stability of a single layer, whereas the bottom layer requires a yield strength of ~12 KPa to support a one-meter structure. However, even with the addition of accelerators shortly before placing the material, the limited strength gain rate in some mixes can constrain buildability, which can lead to a limited height (e.g. two meters).

$$\tau = \rho g h / \sqrt{3} \quad (1)$$

Fig. 1 Schematic representation of the evolution of the bottom layer yield strength with build height

Current practices have involved the use of a wide range of PC-based materials that have been developed for concrete printing applications, as described by Le et al. [13], Kazemian et al. [14] and Panda et al. [15]. One aspect that is considered during this process are the layer interface properties, which can change in line with the unique requirements of each concrete formulation used in 3D printing. Despite the advances made in this area, the use of alternative cementitious materials in 3D printing and associated processes have not been fully assessed until now. While the properties of different 3D printable geopolymers have been reported in previous studies by Panda et al. [16] and Nematollahi et al. [17], the proper material selection that affects the flow properties during and after the extrusion process still remains unexplored.

Accordingly, this study aims to investigate the fresh properties of fly ash-slag based geopolymers, which can be considered as an alternative cementitious binder, to evaluate their suitability for

extrusion-based 3D concrete printing. This is to be achieved by first understanding the rheology (i.e. yield stress, viscosity and thixotropy) of geopolymer mixes, with respect to different controlling factors such as activator concentration, water-to-solid ratio and activator-to-binder ratio. The second step involves the further improvement of these properties via the introduction of nanoclay (i.e. attapulgite clay), which is a thixotropic material, to the mix design. This approach led to the development of a printable geopolymer nanocomposite with an improved thixotropic property, based on a rheological assessment. The improved geopolymer involving the use of clay was further characterized for its strength development and microstructural properties. This developed binder was then used in the printing of a small-scale bathroom unit to demonstrate its potential to be used in 3D printing applications.

2. Materials and Methodology

2.1 Materials and sample preparation

Class F fly ash (FA) conforming to ASTM C 618 was used as a solid precursor with blast furnace slag (GGBS), obtained from Engro Ltd. (Singapore). The specific surface area (SSA) of FA and GGBS was measured as 455 and 465 m²/kg, respectively. Fig. 2 shows the particle size distributions (PSD) of FA and GGBS. Nanoclay, a thermal treated, highly purified attapulgite clay supplied by Actigel® (USA), was used to improve the thixotropy of the geopolymer binder. When dispersed in water, the nanoclay was needle-shaped, with an average length of 1.75 µm and a diameter of 3 nm. The chemical compositions of FA, GGBS and nanoclay, determined by using x-ray fluorescence (XRF), are shown in Table 1.

Fig. 2 Particle size distribution (PSD) of FA and GGBS

Table 1 Chemical composition of FA, GGBS and nanoclay

Material	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	Na ₂ O	K ₂ O	TiO ₂	LOI
FA	51.1	5.8	28.8	6.4	1.0	1.1	0.3	1.2	2.5	1.2
GGBS	29.6	39.3	15.5	0.35	4.32	7.54	0.45	0.51	1.76	-
Nanoclay	65.3	2.26	15.04	4.94	0.07	9.38	0.62	0.75	0.59	-

Hydroxide and silicate solutions of potassium (K) were used as the activating solution to formulate the geopolymer binders. The K-silicate was characterised by its molar ratio (MR), which was 1.56 times the weight ratio (WR) of SiO₂ and K₂O present in the liquid solution. Accordingly, activators with two different MR values (i.e. 1.8 and 2) were used in this study. A commercial grade K-silicate solution (MR= 2) with a solid content of 43% (i.e. SiO₂:K₂O = 24.32:18.71) was modified with KOH to adjust the MR to 1.8. The MR values used in this study were selected in line with the findings of Ravikumar and Neithalath [18] to induce sufficient activation and strength

development. A comparison of the viscosities of K-silicates with regular tap water, as shown in Fig. 3, revealed their increased viscosities at higher MR values, in line with the findings of Vance et al. [19]. NMR studies of silicate solutions by Tognonvi et al. [20] have indicated that the presence of colloidal Si-O-H-K complexes, which form nano-aggregates, increased the viscosity of the solution. These aggregate sizes increased with MR, which further increased the viscosity.

Fig. 3 Influence of molar ratio (MR) on the viscosity of potassium silicate activator

Two water-to-solid (w/s) ratios of 0.30 and 0.35 were used to investigate the rheological properties of the geopolymer mixes, at a constant activator solution-to-binder ratio of 0.35. The total water component included the water used in the preparation of the activator solution and the water added to achieve the desired consistency. Alternatively, the solids component consisted of FA, GGBS and the solid fraction of the K-silicate activator. Another investigation was also carried out by changing the activator-to-binder ratio from 0.35 to 0.40, while the w/s ratio was kept constant at 0.30. All the combinations of liquid activators were prepared prior to their mixing with the binder

(FA+GGBS) and were allowed to cool down to an ambient temperature (23 ± 2 °C) for a period of 24 hours.

For rheology studies, geopolymer mortars were prepared by mixing 85% FA and 15% GGBS (i.e. by mass) with a required amount of K-silicate activator, with a range of different MR values and activator-to-binder ratios. Fine aggregates (i.e. river sand with a maximum particle size of 2 mm) were also added to this mix at a sand-to-binder ratio of 1.5, in line with the findings of a previous study by Panda et al. [21]. Nanoclay was introduced to some of the selected mixes at up to 0.5% (i.e. by mass) of the total binder content to improve the thixotropy of the developed mixes. To achieve this, the clay was first dispersed in water and added to the geopolymer mortar at the end of the mixing procedure, followed by mixing for one minute at a high speed. The prepared mixes were cured in room temperature (23 ± 2 °C) prior to mechanical and microstructural analyses at the age of 28 days.

2.2 Methodology

2.2.1 Measurement of static yield stress

To measure the evolution of static yield stress, the stress growth test was performed by applying a small amount of deformation at a constant shear rate of 0.5 s^{-1} , as described by Panda et al. [22]. The shear stress progressively developed to a maximum value, followed by its reduction to an equilibrium value. The static yield stress was defined as the peak shear stress value obtained during this process.

2.2.2 Thixotropy evaluation via structural breakdown and viscosity recovery

Thixotropy is an essential property of printable materials and it can be characterized by combining shear thinning (i.e. structural breakdown) and viscosity recovery tests, as described by Panda et al. [22]. In this study, the viscosity recovery test was carried out in three stages by applying: (i) a low

shear rate of 0.5 s^{-1} for 60 seconds, followed by (ii) a high shear rate of 300 s^{-1} for 30 seconds and (iii) a low shear rate of 0.5 s^{-1} for 60 seconds. The shear rates and time of shearing were selected by mimicking the 3D printing process, where the material starts flowing from a state of rest (stage 1) and comes to rest (stage 3) after moving through a high shear zone pumping (stage 2). The recovery percentage was calculated by comparing the apparent viscosities at stages (i) and (iii). Shear thinning and the thixotropy parameter (λ) were determined using the procedure previously described in [16].

2.2.3 Compressive strength

The compressive strength of geopolymer mortars were assessed at 28 days by subjecting the prepared cubic samples (50x50x50 mm) to uniaxial loading, according to BS EN 196-1:2016 [23]. The equipment used for this purpose was an ALPHA 3-2000A machine, operated at a loading rate of 100 KN/min. Three samples were tested for each set and their average and standard deviation were calculated and reported for each data point.

2.2.4 Vicat set-time test and initial strength evolution

A standard method to estimate the setting time is the Vicat test, as described in ASTM C191 [24]. Accordingly, a needle weighing 300 g with a diameter of $1 \pm 0.05 \text{ mm}$ was lowered into the fresh geopolymer paste and the penetration depth was recorded. Initial setting time was marked when the needle penetration was $25 \pm 0.5 \text{ mm}$.

The initial strength of the prepared geopolymer mortars was measured by considering the increase in their static yield stress, as explained by Yuan et al. [25]. Starting from the initial mixing process, the static yield stress was plotted against resting time to assess the development of strength, before the initial setting occurred.

2.2.5 Isothermal calorimetry

The heat flow and cumulative heat evolved during the geopolymer reaction was studied at 26 °C by an I-Cal 8000 high precision calorimeter, in accordance with ASTM C1702-15a [26]. To prepare the paste samples, the dry powders were mixed with the activator solution. The paste was placed into the isothermal calorimeter channel within 30 seconds to measure the heat of reaction.

2.2.6 Microstructural analysis

Field Emission Scanning Electron Microscopy (FESEM) analysis was performed on a JEOL JSM-7600F electron microscope, equipped with an energy dispersive analyser to examine the geopolymer paste samples after 28 days of curing.

2.2.7 3D concrete printing

The printing process involved the use of a 4-axis gantry concrete printer, also previously used in Panda et al. [27], operated at a speed of 80 mm/sec. The pump flow rate was adjusted accordingly to ensure the smooth deposition of the geopolymer mortar. A 20-mm square nozzle was used to deposit the fresh geopolymer, as shown in Fig. 4. The determination of shape retention factor (SRF) was performed via the use of a 30x10 mm rectangular nozzle, in line with Equation 2.

$$\text{Shape retention factor (SRF)} = \frac{\text{cross section area of extrudates after printing}}{\text{cross section area of the orifice}} \quad (2)$$

The gantry printer was used to print a small-scale model of the bathroom unit at a speed of 90 mm/sec. The print speed was selected to avoid strength-based failure. Accordingly, the build rate, calculated according to Equation 3, was carefully controlled to ensure that the yield stress of the bottom layer was higher than $\frac{\rho gh}{\sqrt{3}}$ [9].

$$\text{Build rate (in mm/sec)} = \frac{\text{Print speed} \times \text{layer thickness}}{\text{Extrudate perimeter}} \quad (3)$$

Fig. 4 The depositing of the geopolymer mortar via 3D printing

3. Results and Discussion

3.1. Effect of MR and w/s ratio

Assessment of the rheological properties of the prepared geopolymer mortars was performed using a K-silicate activator with two different MR values (i.e. the originally used MR value of 2 was later adjusted to 1.8 via the addition of KOH) at w/s ratios of 0.30 and 0.35. Fig. 5(a) and (b) show the influence of MR and w/s ratio on the yield stress and apparent viscosity of geopolymer mortars, respectively. An increase in the w/s ratio resulted in a drastic decrease in the yield stress and plastic viscosity. This was because increasing the amount of suspending fluid in a suspension increased the particle spacing, thereby increasing the fluid film thickness around the particles and decreasing the yield stress and plastic viscosity. Increasing the water content also reduced the alkali ion concentration in the solution, which led to an activation solution with a lower viscosity, further contributing to a decrease in the values of the rheological parameters. However, increasing the MR

value increased the yield stress and apparent viscosity, which could be due to the increase in activator viscosity, as shown in Fig. 3.

Fig. 5 Influence of MR on the (a) yield stress and (b) viscosity of geopolymer mortars at an activator solution-to-binder ratio of 0.35

3.2. Effect of activator solution-to-binder ratio

Activator solution-to-binder ratio is a mass-based ratio of the activation solution to the binder, which is an appropriate proportioning parameter for practical applications. The rheology of the geopolymer mortar varied depending on the volume of the activating solution and its viscosity, in line with the findings of Palacios et al. [28] and Alonso et al. [29]. Fig. 6(a) and (b) illustrate the influence of the activator solution-to-binder ratio on the yield stress and viscosity of geopolymer mortars, at a constant w/s ratio of 0.30, respectively. In general, the yield stress and plastic viscosity decreased with an increase in the solution-to-binder ratio for all mixtures due to the reduction in particle concentration. It was further revealed that both the yield stress and plastic viscosity increased with an increase in MR at a constant solution-to-binder ratio. At a MR value of 2, the yield stress and viscosity values demonstrated a more dramatic decrease (i.e. in comparison to a MR value of 1.8) when solution-to-binder ratio increased from 0.35 to 0.40.

Accordingly, the yield stress reduced to 70% of its original value, while the viscosities for both samples (i.e. at MR values of 2 and 1.8) merged into a single value when the solution-to-binder ratio was 0.40. These results indicated the dominant influence of the activator viscosity on the geopolymer viscosity. On the other hand, particle interactions and volume fraction played a key role in the determination of the yield stress, which was in agreement with the findings of Vance et al. [19].

Fig. 6 Influence of activator-to-binder ratio on the (a) yield stress and (b) viscosity of geopolymer mortars at a w/s ratio of 0.30

3.3. Effect of nanoclay addition

Nanoclay can play a key role within geopolymer mixes due to their low yield stress property, which needs to be improved for 3D printing applications. Although nanoclay was identified as an effective additive for improving the 3D printability of various cementitious materials in previous studies [30], it has not yet been used widely in geopolymer mixes. Fig. 7(a) and (b) show the shape retention ability of geopolymer pastes prepared using a K-silicate activator with MR values of 2 and 1.8, respectively. It is apparent that due to the higher viscosity of the silicate at a MR of 2, the yield stress and viscosity of the resulting geopolymer was also higher, which led to a better shape

retention when compared to the paste prepared at a MR of 1.8. However, as the printability of geopolymers could not be accurately concluded based on a single line extrusion, which only revealed the extrudability aspect, the 3D printing of a cylinder structure was also carried out to assess the buildability of this binder at a MR of 2, as shown in Fig. 8. As there is no standard for measuring buildability, the layer slump in terms nozzle standoff distance was used to evaluate the buildability. Within this demonstration, an increase in the slump value was observed with additional layers, which was reflected by the large standoff distance after the placement of the 18th layer. This standoff distance was also an indication of the low yield stress (and stiffness) of the extruded layers, which could easily collapse under the loading imposed by the subsequent layers.

Fig. 7 Differences in the shape retention of geopolymer samples based on MR values of (a) 2 and (b) 1.8; at an activator-to-binder ratio of 0.35 and w/s ratio of 0.30

Fig. 8 3D printing of geopolymer mixes depicting a gradual increase in standoff distance at a MR of 2

Although a reduction in the MR of the activator was reported to lead to geopolymer mixes with higher compressive strengths by Palacios et al. [28], other aspects such as the rheology, yield stress and viscosity need to be sufficient for 3D printing applications. Therefore, the rheology of the geopolymer sample at a MR of 1.8 was aimed to be improved via the addition of nanoclay. Based on the findings of previous studies [30], nanoclay was added at an amount corresponding to 0.5% of the total binder component (i.e. by mass) to investigate the rheology of the prepared geopolymer mixes at different w/s and activator-to-binder ratios. Fig. 9(a) and (b) show the yield stress and viscosity of geopolymer mortars at a constant activator-to-binder ratio of 0.35, while the w/s ratios were set at 0.30 and 0.35, respectively. It can be noted from Fig. 9(a) that a small amount of nanoclay addition significantly improved the yield stress of the geopolymer sample. Alternatively, an increase in the w/s ratio led to a 40% decrease in the yield stress. During material flow, nanoclay particles, which hold a positive charge in one end and negative in the other, aligned themselves in the direction of the flow due to the repulsion between similar charges. On the other hand, while the material was at rest, the opposite charged ends attracted each other and flocculated to form a colloidal network. Kawashima et al. [31] reported that the addition of nanoclay in fresh mortars increases the apparent viscosity due to enhanced flocculation and this phenomenon can be more effective in the presence of extra free water to enable the proper dispersion of clay within the mix, was associated with an increase in the yield stress.

Fig. 9 Influence of w/s ratio with and without the addition of nanoclay on the (a) yield stress and (b) viscosity of geopolymer mortars at a MR value of 1.8

Fig. 10(a) and (b) illustrate the effect of clay on the yield strength and viscosity of geopolymer mortar at a constant w/s ratio of 0.3, while the activator-to-binder ratio was varied at 0.35 and 0.4. As expected, both the yield stress and viscosity decreased with an increase in the activator dosage, even in the presence of nanoclay. Although the addition of nanoclay improved the yield stress when compared to samples in which it was omitted, the activator dosage and high viscosity of the silicate seemed to dominate this property. On the other hand, the clay revealed a minimal impact on the viscosity of the geopolymer, when compared to its effect on the yield stress. This can be attributed to the fact that yield stress was associated with the particle-to-particle interactions, whereas viscosity was mainly regulated by the viscosity of the alkali activator. Results shown in Fig. 10(a) demonstrated that the effect of clay addition was not as significant when the activator-to-binder ratio was 0.4. This could be attributed to the higher pH of the solution under increased activator dosages. At high pH, the negatively charged clay particles were not strongly aggregated due to the electrostatic repulsive forces [38-39].

Fig. 10 Influence of activator-to-binder ratio with and without the addition of nanoclay on the (a) yield stress and (b) viscosity of geopolymer mortars at a molar ratio of 1.8

The effect of the improved yield stress of clay modified geopolymer samples on their ability to be used in 3D printing can be seen in Fig. 11. The printing process revealed the stability of the extruded geopolymer layers even under a continuous loading of 18 layers, which were produced at a w/s ratio of 0.3 and activator-to-binder ratio of 0.35. The printed layers led to no visible standoff distance during this process. This was an indication of the zero-slump behaviour of the designed geopolymer mix, thus confirming it as an ideal material to be used in 3D concrete printing applications.

Fig. 11 3D printing of clay modified geopolymers to indicate their buildability aspect (i.e. no visible standoff distance)

3.4. Thixotropy of geopolymer nanocomposite

Apart from yield stress and viscosity, one of the key parameters controlling the stability of the geopolymer extrudates was their viscosity recovery ability (i.e. thixotropy), which could indicate the material rheology before and after extrusion-based 3D concrete printing. Accordingly, the recovery time may need to be adjusted to avoid cold joints in the printed specimen, depending on the print size and time gap between the layers [32]. Unlike PC-based mixes, geopolymers do not present thixotropic behaviour, which, despite of their high initial viscosity, can cause a low final viscosity that results in a lack of shape stability within the deposited layers. This can be potentially overcome via the addition of nanoclay in the initial mix design to enhance the thixotropy property of geopolymer samples.

Fig. 12(a) shows a comparison of the recovery ability of geopolymers made using two different MR values of 1.8 and 2 (i.e. labelled as GEO 1.8 and 2.0), along with the geopolymer mix including clay (i.e. labelled as GEO 1.8+0.5% clay). The obtained results indicated that none of the mixes were able to fully recover their initial viscosity after printing. Furthermore, the addition of clay improved the recover ability within 60 seconds of extrusion. Recover ability was an indication of the material viscosity after it went through shearing/printing. When the initial viscosity values were compared, it was found that the geopolymer samples involving a MR of 2 had a higher initial viscosity and better recover ability (i.e. ~36% higher) than those involving a MR of 1.8. As discussed earlier, the higher viscosity in the presence of higher MR and clay addition could be associated with the flocculation effect, in line with the findings of previous studies [30].

A constant shear rate of 600 rpm was applied to both GEO 1.8 and GEO 1.8 + 0.5% clay mixtures to determine the structural parameter (λ) and characteristic time. The higher structural parameter obtained in the presence of clay, as displayed in Fig. 12(b), indicated the role of clay in modifying the shear thinning behaviour of geopolymers. This was possibly associated with the stiffening mechanism of nanoclay, which increased the bonding strength amongst different phases, therefore leading to a higher equilibrium stress and λ value. Considering its shorter time required to reach

equilibrium (i.e. shorter characteristic time), the clay added mix (GEO 1.8+0.5% clay) could be easily broken down during the extrusion process, thereby eliminating the need for high extrusion pressure.

Fig. 12 The thixotropy behaviour of geopolymer mortars, showing the (a) viscosity recovery and (b) structural breakdown

3.5. Setting time and early-age strength evolution

Fig. 13(a) and (b) show the setting time and yield stress curves of the printable geopolymer samples with and without the addition of clay. It is evident that the use of clay has a very negligible effect on the initial setting time, which is often regarded as the “open time” in concrete printing. A short open time can present both an advantage and disadvantage, depending on the printing process and the mode of material delivery (i.e. transport of material from the mixer to the nozzle head). For instance, in the case of batch mixing, a material with a short open time may not be ideal as depending on the batch volume, a majority of the wet mix can rapidly harden and therefore present challenges during the printing process. Nevertheless, the use of continuous mixing may present the best option as the freshly mixed material can rapidly harden, while allowing more layers to build on it.

Another important parameter of concrete printing process is the yield stress (i.e. in addition to the stiffness), which represents the early-age load bearing capacity and can be used to characterize the material behaviour before its initial setting. After extrusion, a fast strength development is preferred to enable the depositing of subsequent layers on top of the initial one. However, fast setting materials can also cause a weak interlayer bond strength (i.e. cold joint) in between the layers. Therefore, the rate of setting/strength development must be aligned with the speed of layer deposition to avoid any problems related to bond strength, as reported by Sanjayan et al. [33] and Panda et al. [34]. As can be seen in Fig. 13(b), both geopolymer mixtures revealed a continuous development in yield stress. While the addition of clay led to a higher initial yield stress, it had a minimal effect on the rate of strength development, which was mainly controlled by the chemical reaction that took place during the hydration process. In this respect, the presence of nanoclay was not very effective in accelerating the rate of strength development, which was also in line with the findings of previous studies [30].

Fig. 13 Influence of nanoclay addition on the (a) setting time and (b) yield stress of printable geopolymer mortars

3.6. Reaction mechanism, mechanical performance and microstructure

Fig. 14(a) shows the negligible effect of nanoclay on the heat flow and cumulative heat of geopolymer mixes, as analysed by isothermal calorimetry. This was an indication that the use of clay did not alter the reaction mechanisms within geopolymer mixes. A ~17% reduction in compressive strength was seen in samples containing clay, as shown in Fig. 14(b). Differing from these results, Assaedi et al. [35] reported an improvement in the mechanical properties (i.e. flexural strength) of geopolymer samples involving the use of 0-3% nanoclay, which was associated with the space filling ability of nanoclay that densified the sample microstructure. In another study by Joshi et al. [36], nanoclay added at an amount of 3-6% of binder (i.e. fly ash) was used to improve the rheology of geopolymers by coating fly ash microparticles, which in return decreased the compressive strength, similar to the findings of the present study. As the clay used here was hydrophilic in nature, it may have led to some water adsorption, which could slow down the geopolymer reaction, as reported earlier by Zuhua et al. [37].

Fig. 14 Influence of nanoclay on the (a) heat flow and cumulative heat and (b) 28-day compressive strength of geopolymer mixes

To further investigate the influence of nanoclay on sample microstructure, the SEM images of the prepared geopolymer samples taken at the age of 28 days are displayed in Fig. 15. A heterogeneous aluminosilicate gel matrix accompanied with unreacted or partially reacted FA particles was observed in the geopolymer mix involving the additional of clay. These unreacted FA particles were separated from the geopolymer binder, thus indicating a weak adhesion between them and

the surrounding gel. Several micro-cracks formed on the surface of the unreacted/partially reacted FA grains, which could be linked with the reduction in the compressive strength of this sample, as observed in Fig. 14(b). Alternatively, the geopolymer sample that did not include nanoclay demonstrated a more homogenous microstructure without a widespread formation of visible cracks.

Fig. 15 Microstructure of geopolymer paste samples (a) GEO 1.8+0.5% clay and (b) GEO 1.8

4. Conclusions

This paper presented an assessment of the suitability of geopolymer mixes to be used in 3D printing applications. Geopolymer mixes including an alkaline potassium silicate activator with different molar ratios were prepared and evaluated for their fresh properties that determine their printability. The following conclusions could be drawn from the presented findings:

- The viscosity of the activator affected the resultant viscosity of the geopolymer.
- The yield stress and viscosity were found to increase with molar ratio. At a low molar ratio (i.e. 1.8), the obtained yield stress was not sufficient to maintain the shape retention of the printed layers.

- Modifying the geopolymer with the addition of a small amount of nanoclay led to an improvement in the rheological properties necessary for 3D printing applications. These enhancements were attributed to the flocculation characteristic of the clay particles.

- The influence of clay on the fresh and hardened properties significantly depended on the water-to-solid and activator-to-binder ratios used in the production of the geopolymer binders. Higher activator dosages were found to nullify the thixotropy effect of the clay. Therefore, an activator-to-binder ratio of 0.35 and water-to-solid ratio of 0.3 were found to work well with a clay addition of 0.5% (i.e. by mass of total binder component).

- The enhancement of the viscosity recovery property (i.e. thixotropy) of the developed geopolymer binders via the addition of nanoclay was also reflected by the low slump behaviour (i.e. zero standoff distance) recorded during the 3D printing process.

While the addition of clay did not have a major influence in the reaction kinetics, the overall results were an indication of the improved fresh property of geopolymer binders modified with nanoclay. Accordingly, a small-scale bathroom unit, as shown in Fig. 16, was produced by using this composition to demonstrate the suitability of the proposed mix design in practice.

Fig. 16 Demonstration of geopolymer 3D printing, showing the (a) digital render and (b) actual printed structure

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