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Clay-Based Materials in Geopolymer Technology

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Abstract

The term “geopolymer” was introduced by Davidovits in the 1970s. The prefix “geo” was selected to symbolize the constitutive relationship of the binders to geological materials, natural stone and/or minerals. Geopolymer is mineral polymers of inorganic polymer glasses with structure resembling natural zeolitic materials. Previously, geopolymer formation used source materials such as clay (e.g. kaolin and calcined kaolin) or industrial by-product (e.g. slag and fly ash). The precursor material plays an important role in the formation of geopolymer. The source material provides silicon (Si) and aluminum (Al) for reaction by an alkali activator solution. The Si and Al contents in the source materials dissolve in the alkaline activator solution and then polymerize to form a polymeric Si-O-Al-O framework which becomes the binder. Geopolymeric materials are attractive because of their excellent mechanical properties; durability and thermal stability can also be achieved. Owing to their low calcium content, they are more resistant to acid attack than materials based on Portland cement. In addition, they are of great interest because of the reduced energy requirement for their manufacture and the higher sustainability. Recently the search for alternative low cost and easily available materials led among others to Clay. Clay generally consists of a mixture of different clay minerals and associated minerals, which are strongly affected by the nature of the parent rocks. These materials are extensively distributed over the surface of the world and may show certain reactivity after a thermal activation process shows a great potential to be utilized in geopolymer technology. This article presents the potential of different types of clay as the source materials for geopolymerization reaction in terms of morphological properties. Moreover, the mechanical and microstructural properties of geopolymer made with various kinds of clay and its potential application are also presented.

Keywords: geopolymer, inorganic polymer, clay

1. Introduction

In 1978, the word “geopolymer” was introduced by Davidovits [1]. In general, geopolymer is an inorganic polymeric material formed through the reaction between aluminosilicate sources and highly alkaline silicate solution, followed by curing at ambient or slightly higher temperature [2]. The formation process is termed as geopolymerization reaction.

Geopolymer has an empirical formula of:

$$M_n\{-(SiO_2)_z-AlO_2\} \cdot w H_2O \tag{1}$$

where M is cation such as K⁺, Na⁺ or Ca²⁺; n is the degree of polycondensation; z is 1, 2, 3 and w is the amount of binding water. It has three-dimensional Si-O-Al polymeric networks ranging from amorphous to semi-crystalline. Tetrahedral SiO₄ and AlO₄ are linked alternately by sharing oxygen atom as shown in **Figure 1**. As refer to **Figure 1**, the terminology of geopolymers can be categorized into three forms which are poly(sialate), poly (sialate-siloxo) and poly (sialate-disiloxo). The Al is in IV-fold coordination [3, 4]. This leaves a negative charge in the IV-fold coordinated Al that is charge-balanced by cations (Na⁺, K⁺, Li⁺, Ca²⁺, Ba²⁺, NH₄⁺ and H₃O⁺). The charge-balancing by cations is important in determining the structural integrity and fragility of geopolymers [5].

The cations is usually contributed by alkaline silicate solution which is a mixture of alkali hydroxides (NaOH or/and KOH) and silicate solution (Na₂SiO₃ or/and K₂SiO₃) [6–8]. The alkali hydroxide is required for the dissolution of aluminosilicates while alkali silicate acts as binder, alkali activator and dispersant or plasticizer [9]. The alkali silicate solution contributes certain amount of SiO₂ for the geopolymerization reaction [10].

Figure 1. Geopolymer systems based number of siloxo Si-O units [2].

2. Aluminosilicates

The aluminosilicate sources are materials rich in alumina and silica content (e.g. ashes [11–14], clays [15, 16] or slag [17, 18]). Some other natural and artificial silicoaluminates such as zeolite [19] and magnesium-contained minerals [20] have also been used as an important source of Si^{4+} and Al^{4+} ions in the geopolymer binding system. Normally, the total composition of Al_2O_3 and SiO_2 is more than 70%, preferable in reactive amorphous phase [3, 21]. In this book chapter, the utilization of clay or clay minerals in geopolymer formation is discussed.

3. Kaolin/kaolinite

Kaolinite is the most common clay mineral used in geopolymer synthesis. It has 1:1 uncharged dioctahedral layer structure (**Figure 2a**) whereby the layers are $(\text{Si}_2\text{O}_5)_n^{2-}$ sheet and the $\text{Al}(\text{OH})_3$ (gibbsite) sheet linked by sharing oxygen atoms. The layers are held together by weak van der Waals and hydrogen bonds leading to the layered structure (**Figure 2b**).

Figure 2. Structure of kaolinite (above) and microstructure of kaolinite (below) [22].

4. Metakaolin

Thermal treatment of kaolinite leads to the transformation of crystalline phases into reactive amorphous phases [7], which is the active constituent that determines the final strength of geopolymers. The thermal treatment is usually carried out at temperature in the range of 550–800°C which accompanied by dehydroxylation of strongly bounded hydroxyl ions on the Al-constitutive layer. Thus, kaolinite is transformed into metakaolin.

Metakaolin also has layered structure as kaolinite even after the thermal treatment process. However, the layer structure appeared more open than kaolinite (**Figure 3**) [23, 24].

Also, the thermal treatment destroys the hexagonal layer of kaolinite and causes atomic arrangement that converted the hexa-coordinated Al ions of kaolinite are converted into penta- and tetra-coordinated Al ions [25]. The amount of penta- and tetra-coordinated Al ions reflects the reactivity of metakaolin [24].

4.1. Clay-based geopolymers

Clays are frequently used as the source materials in geopolymer formation. They have a total composition of Al_2O_3 and SiO_2 in the range between 70 and 90% (**Table 1**) wherein the composition of clay is dependent on the origin and the geology of the location. Initially, in the early stage of geopolymer development, kaolin/kaolinite is mostly used as the aluminosilicate sources [2, 6, 32, 33]. Later, the experimental work has expanded to calcined clays, ashes and slag. This is because kaolin/kaolinite shows low reactivity with alkaline silicate solution causing low strength products. It is deemed that the near zero charge between layers and the layered structure that does not permit the exchange of ions or other element. Hence, kaolin/kaolinite has low surface area for geopolymerization reaction. According to Heah et al. [34], the low surface area limits the dissolution of kaolin/kaolinite to provide Si^{4+} and Al^{4+} ions for further reaction. Comparatively, fly ash has greater surface area as they have spherical-shaped particles.

Figure 3. SEM micrograph of metakaolin (800°C for 2 hours) [23].

Clay/clay mineral	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MgO	P ₂ O ₅	Na ₂ O	CaO	K ₂ O	MnO	SO ₃	LOI
Metakaolin [26]	51.35	44.24	0.98	0.90	0.48	0.45	0.16	0.13	0.08	0.01	—	0.72
Metakaolin [27]	52.1	43.0	0.7	—	0.3	—	0.12		2.5	—	—	1.0
Metakaolin [28]	59.7	34.1	0.9	—		—	0.2	0.1		—	0.1	1.2
Clay sediment from Occhito reservoir, Italy [29]	47.5	15.6	6.7	—	2.4	—	0.3	10.2	1.9	—	—	15.4
Clay sediment from Sabetta reservoir, Italy [29]	50.0	15.9	5.7	—	1.9	—	0.3	6.9	1.7	—	—	17.5
Kaolinite from Hiswa, Jordan [30]	48.92	25.16	7.52	0.86	0.21	0.16	0.21	0.68	1.4	0.01	2.94	11.93
Kaolinite [31]	49.35	36.03	0.20	0.02	0.02	—	0.04	0.02	2.29	—	—	11.94
Kaolinite [31]	40.86	39.87	0.39	0.46	0.12	—	0.01	0.12	0.17	—	—	17.91
Kaolinite [31]	42.66	40.92	1.12	0.45	0.04	—	0.14	0.14	0.09	—	—	14.13
Halloysite [31]	48.12	36.33	0.33	0.16	—	—	0.05	0.04	0.03	—	—	14.8

Table 1. Chemical composition of clays from different origins.

Summary of the compressive strength of geopolymers based on clay/clay minerals is tabulated in **Table 2**. The strength achieved by geopolymers based on clay/clay minerals is low. The addition of kaolinite as secondary source of aluminosilicate is necessary in order to achieve strength. Unfortunately, the use of kaolinite alone in geopolymer is not preferable as it will produce weak structure [35]. The statement is further supported by van Jaarsveld et al. [38] who concluded the strength of fly ash geopolymers degraded as the result of high kaolinite content (41%) addition. The main reason for the deterioration in strength is because not all kaolinite reacted in the reaction.

If the clays/clay minerals are heat-treated, the mechanical strength of the final products would increase [35, 39]. Pre-treatment is crucial to increase the reactivity of clays/clay minerals. The pre-treatment methods include mechanochemical, chemical and thermal treatments. MacKenzie et al. [40] reported that typical characteristic geopolymers are produced with heat-treated (200–1000°C for 2 hours) halloysite. Mechanochemical-treated (high-energy grinding for 20 hours at 400 rpm) halloysite showed less complete geopolymer formation. For acid-treated (0.1 M HCl) halloysite, the resulting geopolymers were poorly set while alkaline-treated (0.1 M NaOH) halloysite caused the formation of crystalline zeolites. Thermal treatment is the most used methods. Successfully calcined clays lead to highly pozzolanic amorphous phase. For instance, geopolymers from clay sediments treated at 750°C for 2 hours showed greater compressive strength (6–12 MPa) than those treated at 400°C (1–4 MPa) [29].

Clay/Clay minerals	Strength (MPa)		Ref.
	KOH	NaOH	
Almandine	10.3 ^c	8.5 ^c	[35]
Grossular	16.7 ^c	14.5 ^c	[35]
Sillimanite	12.7 ^c	6.5 ^c	[35]
Andalusite	11.1 ^c	8.8 ^c	[35]
Kyanite	6.8 ^c	6.3 ^c	[35]
Pumpellyite	10.8 ^c	8.8 ^c	[35]
Spodumene	13.1 ^c	5.0 ^c	[35]
Augite	6.7 ^c	5.0 ^c	[35]
Lepidolite	4.3 ^c	2.5 ^c	[35]
Illite	7.1 ^c	5.8 ^c	[35]
Celsian	9.7 ^c	8.7 ^c	[35]
Sodalite	15.0 ^c	10.3 ^c	[35]
Stilbite	18.9 ^c	14.2 ^c	[35]
Heulandite	7.4 ^c	5.6 ^c	[35]
Anorthite	14.4 ^c	6.0 ^c	[35]
Kaolin	-	2 – 10 ^c	[37]
Clay residues		5.76 – 5.98 ^f	[38]

^ccompressive strength;
^fflexural strength

Table 2. Strength result of clay/clay minerals geopolymers.

According to the author, thermally treated clay sediments exhibited improved surface area toward dissolution and geopolymerization reaction. Apart from the purely clay geopolymers, blended geopolymers are also produced with the addition of other materials such as calcium hydroxide, slag and ashes with the clay materials as the starting source material. When calcium hydroxide is added, the strength of the blended geopolymers does not degrade [41, 42]. Similarly, the addition of 30% slag in metakaolin geopolymers showed improvement in the mechanical strength. Slag acted as filler in the geopolymer structure and enhanced the mechanical properties. However, the slag addition is limited to below 50% as it will greatly deteriorate the strength at content beyond 50% [43]. The high calcium content in both calcium hydroxide and slag caused the formation of geopolymer matrix as the main phases and the calcium silicate hydrates (CSH) phases as the secondary phases [27, 43]. This can be clearly shown in **Figure 4**.

Figure 4: SEM micrographs of (a) pure metakaolin; and (b) metakaolin-50% slag geopolymer (a—Geopolymer matrix and B—CSH phases) [43].

5. Geopolymerization mechanism

Geopolymer formation involves chemical reaction that transforms partially or totally amorphous aluminosilicates into three-dimensional polymeric networks. The geopolymerization reaction is exothermic. Under strong alkaline medium, the aluminosilicate sources dissolve into SiO_4 and AlO_4 tetrahedral units which later on participate in the polycondensation process [44, 45].

The chemical attack of kaolinite starts from the surface and edge and continues layer by layer inside the structure (**Figure 5**) [46]. The Al-substituted silicate layers formed and the structural deformed Al sites transformed into tetra-coordinated Al sites after attack by alkali hydroxide (**Figure 6**) [47].

Davidovits proposed the reaction mechanism as shown in **Figure 7**. The reaction aluminosilicates and alkali silicate solution produced geopolymers with Si-O-Al backbone.

In general, the geopolymerization mechanism is similar for all types of aluminosilicates. Most researchers agreed that the geopolymerization reaction involves dissolution, polycondensation and hardening process. The dissolution of aluminosilicates is initiated by presence of hydroxyl ions in the alkaline silicate solution which releases Si and Al species for further polycondensation reaction [9, 49]. The geopolymerization reaction is deemed occurs in multistep simultaneously [38, 42, 50] such as reorganization and diffusion of dissolved ions with formation of small coagulated structures, solid state transformation and hardening to form hard solid polycondensation to form aluminosilicate gel phases and dissolution of aluminosilicates in highly alkaline medium.

In addition, Xu and Van Deventer [51] suggested that geopolymer is formed through Eqs. (2)–(4). Eq. (1) represents the mixing of aluminosilicates with alkali silicate solution. Geopolymer gel is formed in Eq. (3), while Eq. (4) shows the formation of geopolymer rigid solid.

Figure 5. Reaction of kaolinite under alkaline medium (gray circle denotes the aluminum hydroxyl side groups) [46].

Figure 6. Formation of aluminum substituted silicate layer in metakaolin after attack by NaOH solution [47].

Figure 7. Schematic diagram of geopolymer formation [48].

Figure 8. Graphic model of alkali activation of geopolymers [54].

$$\text{Al-Si material (s)} \left[\text{M}_a ((\text{AlO}_2)_a (\text{SiO}_2)_b)_n \text{MOH} \cdot m\text{H}_2\text{O} \right] \quad (4)$$

According to Provis et al. [52, 53], the final geopolymer gel phase after extended curing process is different from the initial gel phase. The curing process allows continuous rearrangement of geopolymer gel phase toward more crosslinking and some zeolite crystals (more ordered phases) are formed in the geopolymer structure. Similar model is illustrated by Duxson et al. [54] in **Figure 8**. The intermediate product (Gel 1) having high Al contents transformed into

Gel 2 with high Si content as the reaction progresses and finally rearranged forming three-dimensional geopolymer frameworks.

5.1. Clay-based geopolymer formation

Most usual method to form geopolymer is direct mixing of aluminosilicate with alkali silicate solution. After mixing, the geopolymer paste is compacted in molds and cured at room temperature or slightly higher temperature (20–80°C). To avoid extensive loss of moisture, the geopolymer paste is covered with a thin plastic film during the curing process. Besides, other mixing method has also been studied with different mixing sequences. The aluminosilicate is firstly mixed with liquid sodium silicate and the NaOH solution is added afterwards.

Based on Lecomte et al. [25], the normal mixing and separate mixing did not lower the degree of geopolymerization reaction of kaolin/white clay-slag blended geopolymers. However, separate mixing required additional water for mixing and hence detrimental to the mechanical strength. A contradict result is reported by Rattanasak & Chindaprasirt [55] based on fly ash geopolymer. The separate mixing permits more time for dissolution of aluminosilicates providing more dissolved species for the polycondensation process. This in turn leads to formation of stronger geopolymers. On top of that, the homogeneity of the geopolymer mixtures is crucial in order to attain high strength.

Regardless of the different mixing sequence, workability is an important criterion to be taken into consideration during geopolymer formation. Serious workability problem leads to compaction difficulty and produce weak geopolymer structure [23, 34]. For geopolymer based on clay, it usually requires excess water during the mixing process in order to achieve certain consistency. The addition of excess water will definitely decrease the mechanical strength of the final product. Comparison with fly ash geopolymers, the mixture of clay-based geopolymer is usually highly viscous and sticky [56]. The layer structure of clay induces greater inter-particle friction which limits the flowability of mixture. Unlike clay, fly ash has spherical-shaped particles. The imposed inter-particle friction is lesser and can acquire adequate consistency without addition of excess water.

6. Characterization of clay-based geopolymers

6.1. Morphology

As aforementioned, the kaolinite and metakaolin appears plate-like or layer-like structure. After the geopolymerization reaction, this layer-like structure changed. The morphology of clay-based geopolymer appeared sponge-like with globular units (**Figure 9**). The microstructure grows and develops over time starting from the precipitation of loosely-packed globular units on the metakaolin's particle surface and densification of geopolymer matrix inside and outside voids [57, 58]. At the beginning the K/Al and Si/Al molar ratios are high due to leaching of Si from liquid sodium silicate. As time passed, more dissolved Al entered the geopolymer system and lowered the molar ratios [57]. Instead of globular units of geopolymer matrix,

Figure 9. ESEM micrographs of metakaolin geopolymers after (a) 10 minutes, (b) 3 hours, (c) 6 hours, and (d) 9 hours of mixing [57].

fly ash-based geopolymers revealed smooth heterogeneous geopolymer matrix with remnant fly ash particles in the hollow cavities due to partially dissolution (**Figure 10**).

Differently, Wang et al. [59] observed that the metakaolin geopolymers are not compact. The layer structure is remained in the geopolymer matrix after geopolymerization reaction (**Figure 11**). The remnant metakaolin geopolymer might have left and embedded in the geopolymer structure. Based on Rowles et al. [60], the residual raw particles in geopolymer structure may weaken the structure. This is because the residual particles act as stress concentration point that permit propagation of cracks and fractures. To our knowledge, complete geopolymerization reaction is not achieved. There must be some residual raw materials left in the structure after the chemical reaction.

The mechanical strength of geopolymer is affected significantly by the density and porosity in the structure. High strength geopolymer is associated with low porosity, high dense and fine-grained microstructure [61].

6.2. Mineralogy of clay-based geopolymers

The X-ray diffraction (XRD) pattern of kaolinite consists mainly of crystalline phases [34]. The thermal treatment of kaolinite transformed the crystalline phases into amorphous phases.

Figure 10. SEM micrographs of fly ash geopolymers cured at room temperature for 24 hours and at 80°C for another 24 hours [15].

Figure 11. SEM micrographs of metakaolin geopolymers [59].

The metakaolin retains some long-range order as result of stacking of the hexagonal layers [62]. Therefore, metakaolin shows semi-crystalline to amorphous pattern with a halo at 2θ between 15 and 30° [56]. This diffuse halo represents the amorphous silica in metakaolin [63]. Marked shift in the scattering peak is observed after the geopolymer formation. The diffuse halo in metakaolin shifted to higher angle. Generally, geopolymers show completely amorphous X-ray diffraction (XRD) pattern with a diffuse halo peak at 2θ between 27 and 30° [25, 48, 57, 64, 65]. The primary binder phase in geopolymer matrix contributes to the amorphous characteristic and determines the strength of geopolymers. Also, in a study carried out by Wang et al. [59], the halo diffuse peak of metakaolin geopolymer fell at 2θ between 18 and 25°. Increasing Si/Al ratio reduces the angle of diffuse halo [65].

Crystalline phases, particularly zeolites, are usually grown in geopolymers in conjunction with the amorphous binder phases (**Figure 12**) [46, 66]. As zeolites have similar chemical composition with geopolymers, geopolymers are usually deemed as the zeolitic precursor. The

Figure 12. XRD patterns of geopolymers from Algerian metakaolin, activated with alkaline sodium silicate solution and cured at 50°C for 24 h with various Si/Al ratios [66].

main difference between them is that zeolite is crystalline while geopolymer is amorphous. The growth of crystalline phases is facilitated by the high water content, high curing temperature, aging and also extended curing period [4, 67]. Zeolites are highly porous and have poor mechanical properties. Some researches [68, 69] claimed that zeolite crystallites reinforce and improve strength of clay geopolymers. Yet, the long-term strength reduced. Even so, it is strongly believed that there is a tolerance limit on the crystalline phase's content within the geopolymer matrix. Similar trend was reported for fly ash geopolymers [70].

7. Functional group identification

Kaolinite shows FTIR bands around 1113 cm^{-1} (Si-O bonds in SiO_4 molecules); 994 cm^{-1} (Si-O bonds in SiO_4 molecules); 907 cm^{-1} (Al^{IV} -OH vibrations); 799 cm^{-1} (SiO-symmetric stretching) and 537 cm^{-1} (Si-O- Al^{VI}) [24, 38, 71, 72]. On the other hand, as the kaolinite is thermally treated, the band at 1113 cm^{-1} shifted to lower wavenumber ($\sim 1031 \text{ cm}^{-1}$) [23]. This is related to the amorphous SiO_2 [25]. The FTIR bands associated with VI-fold coordinated Al vanished after calcination as a result of distortion of tetrahedral and octahedral sheets of kaolinite [24]. The band at around 781 cm^{-1} appears in metakaolin as the Al-O stretching vibration in AlO_4 tetrahedral [73].

As the geopolymerization reaction progresses, shift of bands are observed. Clay-based geopolymer exhibits main FTIR absorption band at 990 cm^{-1} associated with the asymmetrical

Figure 13. Shifts of FTIR bands from Gel 1 (G1) to Gel 2 (G2) [75].

stretching of Si-O-Si and Si-O-Al bonds [42, 74]. This band is shifted from the band at 1031 cm^{-1} in metakaolin. In addition, this FTIR band becomes more intense as the reaction proceeds indicating more geopolymer networks are formed. The band is usually shifted to lower wavenumber from raw materials and further shifted to higher wavenumber as a consequence of curing process. This is because of the changes in the silicate network with more substitution of non-bridging oxygen and increasing substitution of Al in the silicate sites. This is proved by the model by Duxson et al. [54] who proposed the transformation from Gel 1 to Gel 2 over time, aforementioned. This band shift is also observed in fly ash geopolymers (Figure 13) [75].

Another bands at 720 cm^{-1} (Si-O-Si/ Si-O-Al stretching), 560 cm^{-1} (tetrahedral aluminum stretching bands) and $690\text{--}440\text{ cm}^{-1}$ (Si-O-Si/ Si-O-Al bending vibrations) are also present in clay-based geopolymers [41, 42, 56]. High Si content in geopolymer structure produces stronger geopolymers as the Si-O-Si bonds are stronger than Si-O-Al bonds [76].

8. Properties of clay-based geopolymer

Geopolymers exhibit excellent mechanical and physical properties, such as low density, good chemical, fire and thermal resistance, high mechanical strength, and so on. Therefore, they are widely applied in various fields as new materials with high tech application. Geopolymers harden rapidly. In general, metakaolin geopolymers set and harden within 24 h. Short set time of 4 h has been reported by De Silva et al. [77] cured at 40°C . For fly ash based geopolymer paste, in another way, sets and hardens faster compared to metakaolin geopolymers. Accordance to Hardjito et al., fly ash geopolymer can be hardened up to 2 h when cured at 65 and 80°C [78]. However, setting time is significantly dependent on the curing temperature. The geopolymer will set faster when cured at higher temperature. At 50°C , geopolymerization process required 4 h. Furthermore, geopolymerization process needed 1.5 h and 0.5 h

at 85 and 95°C, respectively [2]. If the geopolymer paste is cured at temperatures lower than ambient temperature, it might need more than 1 day to set. No degradation in the strength of geopolymers at 28 days even they set at a longer time, as reported by Rovnanik [74].

The bulk density of metakaolin geopolymers is reported in the range between 1.20 and 1.80 g/cm³. Thus, lightweight products can be made out of geopolymers. The bulk density reported is lower than ordinary Portland cement paste and almost or even lower than geopolymers based on slag and fly ash. For instance, ordinary Portland cement paste has density of more than 1.80 g/cm³ [35] while coal fly ash geopolymers have density in the range between 1.40 to 1.80 g/cm³ [79, 80]. Bulk density is mainly affected by the curing condition as well as other synthesis parameters, such as the nature of alkali metal silicate, the type of geopolymers and alkali concentration. Bulk density decreases with increasing curing temperature [74]. Compressive strength increases with the increases of bulk density. Almost similar bulk density values were recorded for K-based (1.39–1.82 g/cm³) and Na-based (1.25–1.72 g/cm³) metakaolin geopolymers. Na-based geopolymers are generally lighter than K-based geopolymers. This is due to K-based geopolymers are denser and contain fewer pores as aforementioned [65].

From the result obtained by De Silva et al. [77] in **Figure 14**, high SiO₂/Al₂O₃ ratio in the initial composition shows longer setting and hardening times. Strength development of metakaolin geopolymers with SiO₂/Al₂O₃ of 3.81 became high and stabilized at a later age, even though the setting time was longer. Setting time is short providing that there is high Al₂O₃ content; however, it will deteriorate strength due to low SiO₂ content. Besides, the calcium content in the precursor materials would definitely affect the setting time. This is due to the fact that the Ca content provides extra nucleation sites for precipitation of dissolved species and hence leads to setting and hardening at a faster rate [55].

Figure 14. Final setting times and compressive strength of metakaolin geopolymers with varying SiO₂/Al₂O₃ molar ratios at constant H₂O/Na₂O molar ratio of 13.6 [81].

Geopolymers achieve compressive strength of 20 MPa after only 4 h at 20°C. The 28-day compressive strength of geopolymers could be as high as 70–100 MPa [1]. High strength means the easier or higher dissolution of source materials, generating more aluminosilicate species, which are the most important ingredients for geopolymerization process. The reaction extent of source materials can be measured directly by the compressive strengths of prepared geopolymers. The strength of geopolymers is dependent on the strength of gel phase, the amount of gel phase formed and amorphous nature of the reaction products [73].

On the other hand, geopolymers have excellent thermal stability with low shrinkage (2%). Geopolymers are stable up to 1000–1200°C [4, 58, 82, 83] and have ceramic-like structure [3]. Geopolymers are dimensionally stable in the working range between 250 and 800°C, accordance to Subaer and van Riessen [84]. In order to improve the thermal properties of geopolymers, filler (e.g. granite or quartz) and foaming agents (e.g. Al powder, hydrogen peroxide) have been added during geopolymer mixing. Addition of quartz or granite reduced shrinkage to 1% [85]. In addition, based on Rickard et al. [86], foamed geopolymers reinforced with polypropylene fibers achieved fire rating of at least 1 h (**Figure 15**).

Foamed geopolymers have good potential for ambient application as thermal insulator while exhibiting low density and compressive strength. For fire resistance application, materials must have very low thermal conductivity and resistance to thermal damage as to achieve the similar fire rating. Contradict result was reported by Elimbi et al. [87], whereby metakaolin geopolymers decreased in strength when heated between 300 and 900°C. It was explained due to the progressive transformation of geopolymer matrix into crystalline phases. The metakaolin geopolymers were warped and glazed with cracks at 1000°C.

Figure 15. Cold side temperatures during the fire testing of four mixes of metakaolin geopolymers [86].

Figure 16. SEM micrograph of kaolinite geopolymers subjected to acid attack test after 90 days [30].

Geopolymers possess high perseverance in acidic and alkaline media [68, 88]. Comparatively, they are more stable under alkaline medium. No deterioration in mechanical properties when immersed in sea water ($\text{pH} = 8$) and sodium sulfate solution (5% Na_2SO_4) up to 360 days. On the other hand, geopolymers were severely attacked when immersed in HCl solution for long period. Compression strength decreased while mass loss of samples increased. This was probably due to the de-aluminum of geopolymer structure in highly acidic medium. De-aluminum leads to mass loss of geopolymer structure as the consequences of SiAOAl bonds break that form more silicic acid ions in acid medium. The microstructure of the produced geopolymers became more porous (**Figure 16**) [30].

Drying shrinkage is shrinkage of the geopolymer matrix as a result of the loss of unbounded water during the curing process. As aforementioned, the addition of filler minimizes shrinkage of geopolymer samples. In general, shrinkage occurs in greater tendency in materials with higher content of finer materials than those with high content of coarser materials [89]. For instance, for geopolymers with sand filler, the drying shrinkage recorded was 0.01% at 180 days. However, for geopolymers without sand filler, the drying shrinkage fluctuated between 0.03 and 0.04% [30].

9. Applications of geopolymers

Geopolymers have great potential for variety of applications. Some applications have been successfully commercialized and marketed such as PYRAMENT blended cement and GEOPOLYMITE binders. GEOPOLYMITE binders have been used in several fields such as molding, tooling, foundry work, building's thermal insulation and furnace insulation while

PYRAMENT blended cement has been adapted in civil engineering in the production of pre-stressed and precast concrete [90].

Besides, geopolymers have been used to produce high-quality brick and tiles. Previously, kaolinite geopolymers are formed through low-temperature geopolymeric setting (L.T.G.S.) followed by ultra-rapid fire at 1000–1200°C to form bricks and tiles [4]. Up to now, this similar method has still being investigated by several researchers [91]. The geopolymer ceramics are non-burning and fire resistant. Furthermore, a new development of ceramic materials is compressing geopolymer powder using powder metallurgy method followed by sintering at 1000–1200°C [92].

In 1994, fireproof geopolymer fiber-reinforced composites have been used for aviation applications as aircraft composites and cabin interiors (floor panels, sidewalls, ceiling and partitions) to eliminate cabin fire during the aircraft accidents. The idea was arised from the problem of the existing plastic materials that were combustible and emitted flammable gases when they burnt. Besides, geopolymers have been used by Formula One teams in car manufacturing due to its corrosive, fire and heat resistance [4].

Concern toward lightweight materials for easy transportation and less energy consumption has led to lightweight concrete materials from geopolymers in civil engineering [93]. Furthermore, the lightweight concrete facilitates structural loading bearing and acts as thermal insulator [94]. Studies on foamed geopolymers in thermal insulation materials for housing construction have also been studied [95]. Zhang et al. [96] made reflective and heat insulative coating from geopolymers. With the addition of pigments and fillers (such as hollow glass microspheres, talc powder and titanium dioxide), wetting agent, dispersing agent and water-retaining agent, the coating produced has 90% reflectivity and thermal insulation performance up to 24°C. Apart from thermal insulative properties, the synthesis of geopolymer for acoustic insulation has been reported by Hung et al. [97]. Geopolymers can adequately and potentially become sound insulating materials in construction and buildings. The density of geopolymer matrix affects the noise reduction coefficient.

In addition, according to Temuujin et al. [98], geopolymers are capable of anti-ultraviolet and anti-aging, which made them suitable as coating for exterior wall building to conserve energy. The studies on the thermal and fire performance of geopolymers have also been reported elsewhere [81, 99–101]. As mentioned earlier, geopolymers have molecular structures to resemble zeolitic materials. As such, they are able to immobilize toxic waste or heavy metals as they can absorb and solidify toxic chemical waste. This is beneficial to the immobilization technology [84, 102].

Porous geopolymers were prepared by Okada et al. [89] for use in cooling system. This idea was come about due to high water retention properties or slow water releasing properties of geopolymers. This makes geopolymers suitable for surface cooling by water evaporation that helps to curb the rising earth temperature due to human activities and country development. Potential use of geopolymer in infrastructure rehabilitation was suggested by Pacheco-Torgal et al. [103]. Geopolymer paste can function as sealer for structures and replaced epoxy adhesives in fiber-reinforced polymer retrofitting. Almost similar research was carried out by Geraldine et al. [104], whereby geopolymers are used as restoration materials for tiles. In

order to further enhance the usage of geopolymers in civil engineering, researchers have investigated on one-part geopolymer system [105–107], whereby geopolymer mixture can be prepared by just adding water. The interest of this study is caused by the limitation of geopolymer technology for in-situ application which lowers its economical value.

In recent year, the study on geopolymers moves toward application as biomaterials. As proven by Pangdaeng et al. [28], geopolymer has good bioactivity and it is improved by the addition of white Portland cement. On the other hand, geopolymer as drug delivery system has also been studied by Jamstorp et al. [108] and Cai et al. [109]. Based on them, geopolymers possess variable pore-structure for the release of drug at target cell. This again extends the application of geopolymers in the medical fields.

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