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Factors affecting the shrinkage of fly ash geopolymers

Charoenchai Ridtirud[1)], *Prinya Chindaprasirt*[1)], *and Kedsarin Pimraksa*[2)]

1) Sustainable Infrastructure Research and Development Center, Department of Civil Engineering, Faculty of Engineering, Khon Kaen University, Khon Kaen, 40002, Thailand

2) Department of Industrial Chemistry, Faculty of Sciences, Chiang Mai University, Chiang Mai 50200, Thailand

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Abstract: The shrinkage of fly ash geopolymers was studied in the present study. Fly ash was used as the source material for making the geopolymers. The effects of the concentration of NaOH, sodium silicate-to-NaOH ratio, liquid-to-ash ratio, curing temperature, and curing time on shrinkage were investigated. The geopolymers were cured at 25, 40, and 60°C, respectively. The results indicate that the shrinkage of geopolymers is strongly dependent on curing temperature and liquid-to-ash ratio. The increase in shrinkage is associated with the low strength development of geopolymers. It is also found that NaOH concentration and sodium silicate-to-NaOH ratio also affect the shrinkage of geopolymers but to a lesser extent.

Keywords: fly ash; inorganic polymers; shrinkage; compressive strength

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1. Introduction

The geopolymer is an alkali-activated aluminosilicate material with a much smaller CO_2 footprint than traditional Portland cement products. It has excellent durability and may exhibit many other useful properties such as high compressive strength, low shrinkage, and acid and fire resistance [1-2]. Solid waste and by-products containing silica and/or alumina can, therefore, be used as source materials for making geopolymer. It is environmentally friendly and needs moderate energy to produce. It also provides a major and cost-effective solution to many problems where hazardous residue has to be treated and stored under critical environmental conditions [3].

Fly ash, metakaolin, bottom ash, and rice husk ash have been successfully used as source materials for making geopolymers [4-7]. Fly ash is generally regarded as a good source material because it is the residue from burning coal in a thermal power plant and consists mainly of silica and alumina. Fly ash has a complex microstructure comprising a mixture of amorphous and crystalline components. The structure and physical properties of fly ash geopolymer are dependent upon a variety of parameters including water content, thermal history, particle size, and the degree of amorphicity [8].

Some researches [1-2, 9] have indicated that the shrinkage of geopolymers is relatively small. This is true for a geopolymer with high curing temperature and is similar to the low shrinkage of high temperature-cured Portland cement products. In many cases, the hardening and shrinkage of geopolymers cured at low or room temperature can pose some problems.

The current work focuses on the effects of curing temperature, NaOH concentration, sodium silicate-to-NaOH ratio, liquid-to-ash ratio, and curing temperature on the shrinkage of geopolymer mortars. The findings should lay a

Corresponding author: P. Chindaprasirt E-mail: prinya@kku.ac.th

good foundation for future research on the shrinkage of geopolymer products and their utilization.

2. Experimental

2.1. Materials

High calcium fly ash from Mae Moh Power Station in the north of Thailand was used as a source material. This fly ash has been shown to be a good source material for making geopolymers [4]. The as-received fly ash was rather coarse with 60% passing through a 45-µm sieve and a Blaine fineness of 2000 cm^2/g. Its oxide composition obtained by X-ray fluorescence (XRF) analysis is shown in Table 1. The specific gravity of the fly ash is 2.46 and the loss on ignition is 2.45wt%. The sodium silicate solution with 13.8wt% Na_2O, 32.2wt% SiO_2, and 54.0wt% water, and 7.5, 10.0, and 12.5 M NaOH solutions were used as alkaline activators. The river sand with a specific gravity of 2.62 and a fineness modulus of 2.48 in the saturated surface dry condition was used for making geopolymer mortars.

Table 1. Chemical composition of the fly ash **wt%**

SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	TiO_2	SO_3	Na_2O	MgO	P_2O_5
33.66	18.25	16.35	2.08	19.23	0.35	2.74	1.53	2.84	0.17

2.2. Mix design and mixing of mortar

All geopolymer mortars were made with a sand-to-fly ash ratio of 2.75:1. Three NaOH concentrations of 7.5, 10.0, and 12.5 M and five sodium silicate-to-NaOH mass ratios of 0.33, 0.67, 1.00, 1.50, and 3.00 were used. The mixing was done at a controlled room temperature of 25°C. The mixing procedure started with the mixing of NaOH solution and fly ash for 5 min. Sand was added to the mixture and mixed for more than 5 min. This was followed by the addition of sodium silicate solution with a final mixing of 5 min.

2.3. Preparation of mortar specimens

For compressive strength testing, fresh mortar was placed in a cube mould of 50 mm×50 mm×50 mm. The specimens were compacted with two-layer placing and tamping as described in ASTM C109 [10]. For drying shrinkage testing, fresh mortar was placed in 25 mm×25 mm×285 mm prisms. The prisms were compacted in accordance with ASTM C 490 [11]. The samples were wrapped with cling film to avoid moisture evaporation. One hour after mixing, the samples were cured at different temperatures and durations. After 24-h temperature curing, the compressive strength specimens were demoulded and left in a 25°C controlled room until the test age. The compressive strength tests were performed at the ages of 7, 28, and 90 d in accordance with ASTM C109. The reported strengths are the average of three tests.

The shrinkage specimens were demoulded after temperature curing for 24 h. The first length measurement was made at 0.5 h after demoulding and the specimens were then left in a room of 23±2°C with a relative humidity of 50%±5%. Measurements were carried out every day for the first 2 weeks and then 3 times a week.

2.4. Test series

A number of tests were designed to test the influence of various variables on the shrinkage of geopolymer mortars. The variables were curing temperature, NaOH concentration, sodium silicate-to-NaOH ratio, and liquid-to-ash ratio.

(1) Curing temperature. In this test, the geopolymer mortars with 10 M NaOH, a sodium silicate-to-NaOH ratio of 0.67, and a liquid-to-ash ratio of 0.6 were used. The curing at 25, 40, and 60°C for 24 h was adopted for this test.

(2) NaOH concentration. To test the influence of NaOH concentration, geopolymer mortars with a sodium silicate-to-NaOH ratio of 0.67 and a liquid-to-ash ratio of 0.6 were used. The curing temperature of 40°C was selected for this test as it produced relatively high strength mortar and substantial drying shrinkage. Three NaOH concentrations of 7.5, 10.0, and 12.5 M were tested.

(3) Sodium silicate-to-NaOH ratio. For this test, the geopolymer mortars with 10 M NaOH, a liquid-to-ash ratio of 0.6, and a curing temperature of 40°C were used. Sodium silicate-to-NaOH ratios of 0.33, 0.67, 1.0, 1.5, and 3.0 (1:3, 2:3, 3:3, 3:2 and 3:1) were tested.

(4) Liquid-to-ash ratio. The comparison of strength and shrinkage performance in terms of liquid-to-fly ash ratio was made similar to the study on the water-to-cement ratio for the Portland cement system. The total mass of the liquid is a combined mass of sodium silicate and NaOH. The geopolymer mortars with 10 M NaOH, a sodium silicate-to-NaOH ratio of 0.67, and a curing temperature of 40°C were used. Liquid-to-ash ratios of 0.4, 0.5, 0.6, and 0.7 were tested.

3. Results and discussion

3.1. Effects of curing temperature

The compressive strengths of geopolymer mortars at the ages of 7, 28, and 90 d are shown in Fig. 1(a). In general, the strength of the geopolymer mortars increases with the increase in curing temperature. The strengths at 7 d of geopolymer mortars cured at 23, 40, and 60°C are 18.0, 28.0, and 43.0 MPa, respectively. At a low curing temperature of 23°C, the strength development from 7 to 28, and 90 d is clearly observed. For the higher curing temperatures of 40 and 60°C, the strength development between 7 and 28 d is also significant. The strength development after 28 d is small for 40°C curing and is insignificant for 60°C curing. At ambient temperature, the reaction of fly ash is extremely slow [12]. The initial curing at an elevated temperature improves the geopolymerization and the strength of the geopolymer.

Fig. 1(b) indicates that the shrinkages of geopolymer mortars are dependent on the curing temperature. For curing at high temperature, the reaction of the geopolymer is a rapid polymerization process and about 70% of its strength is gained within the first 3-4 h of curing [13-14]. The increase in compressive strength with the age is small since the specimens undergo accelerated heat curing for 24 h. For curing at 60°C, the geopolymerization process is quite advanced and the shrinkage at 60 d is very low at 450×10^{-6} mm/mm. For curing at low temperature, the reaction is slow and the increase of strength over time which is similar to that of Portland cement is therefore observed. For curing at 23°C, the geopolymerization process is quite slow and the shrinkage at 60 d is very high at 6500×10^{-6} mm/mm. The effect of curing temperature on the shrinkage of mortars is therefore very significant.

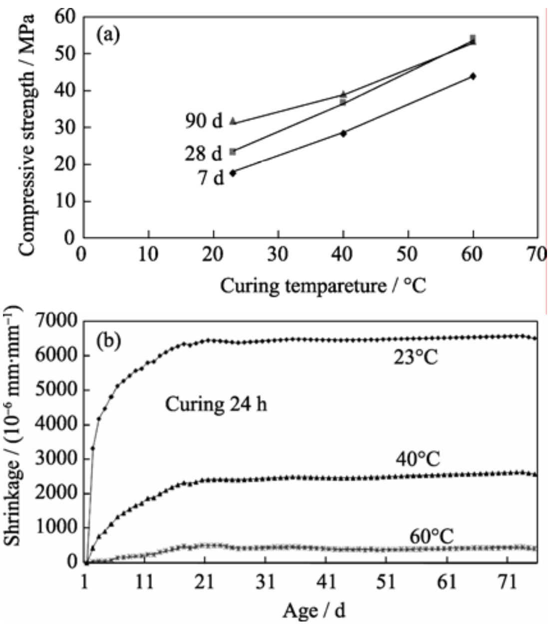

Fig. 1. Compressive strength of mortars at various curing temperatures and ages (a) and shrinkage of mortars at various curing temperatures (b).

One feature worth mentioning is the shrinkage rate of geopolymer mortars. The shrinkages of geopolymer mortars cured at the three temperatures after three weeks are very small. This behavior can be very useful for the precast industry in commercializing these geopolymer products.

3.2. Effects of sodium silicate to sodium hydroxide ratio

Fig. 2(a) shows the 7-d compressive strength of geopolymer mortars prepared at a curing temperature of 40°C. The strength of geopolymer mortars at the sodium silicate-to-NaOH (S/N) ratio of 0.33 is low at 25.0 MPa. The strength increases to 28.0, 42.0, and 45.0 MPa as the S/N ratio increases to 0.67, 1.0, and 1.5, respectively. The increase in the Na_2SiO_3/NaOH ratio results in the increase of Na content in the mixture. Na is important to the formation of geopolymers as it acts as charge balancing ions. However, the compressive strength decreases as more silicate is added into the system since excess sodium silicate hinders water evaporation and structure formation [15].

The shrinkages of geopolymer mortars with different S/N ratios are shown in Fig. 2(b). The mortar with a low S/N

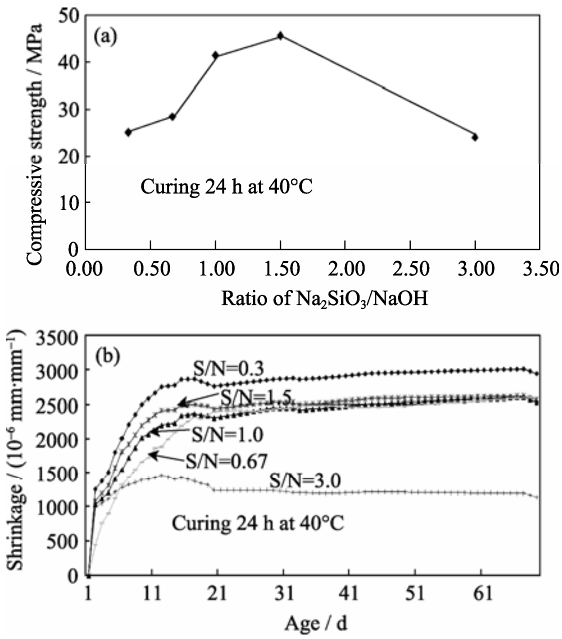

Fig. 2. Compressive strength (a) and shrinkage (b) of mortars with various Na_2SiO_3/NaOH ratios.

ratio of 0.33 shows a high shrinkage of 3000×10^{-6} mm/mm at the age of 60 d. The high shrinkage is due primarily to the low strength of this mortar. Geopolymer mortars with higher S/N ratios of 0.67, 1.0, and 1.5 show the similar shrinkage values of 2500×10^{-6}-2600×10^{-6} mm/mm. The increase in S/N ratios to 0.67, 1.0, and 1.5 improves the strength of mortars and reduces the shrinkage. At a high S/N ratio of 3.0, shrinkage is relatively low at 1200×10^{-6} mm/mm. The increase in S/N ratios also results in the increase in the silicate content of the mixture. At high silicate content, although the strength is low, the geopolymer matrix is high in the silica-to-alumina ratio. The reaction or condensation of the geopolymer with a high silica-to-alumina ratio is fairly quick [16]. The relatively low shrinkage of geopolymer mortars with a high S/N ratio is associated with the fairly quick reaction.

3.3. Effects of NaOH concentration

The strength and shrinkage of geopolymers with different concentrations of NaOH solutions cured at 40°C are shown in Fig. 3. The effect of NaOH concentration on strength is small while that on shrinkage is significant. The strengths at 7 d of 7.5, 10, and 12.5 M geopolymer mortars are 31.0, 30.0, and 29.0 MPa with the corresponding shrinkages at 60 d of 1950×10^{-6}, 2500×10^{-6}, and 2800×10^{-6} mm/mm, respectively. Low strength variation within this range of the NaOH concentration of 7.5-12.5 M for bottom ash geopolymer with the S/N ratio of 1.5 was also reported in Ref. [17]. The shrinkage of the geopolymer mortar with 12.5 M NaOH is high due partly to its low strength.

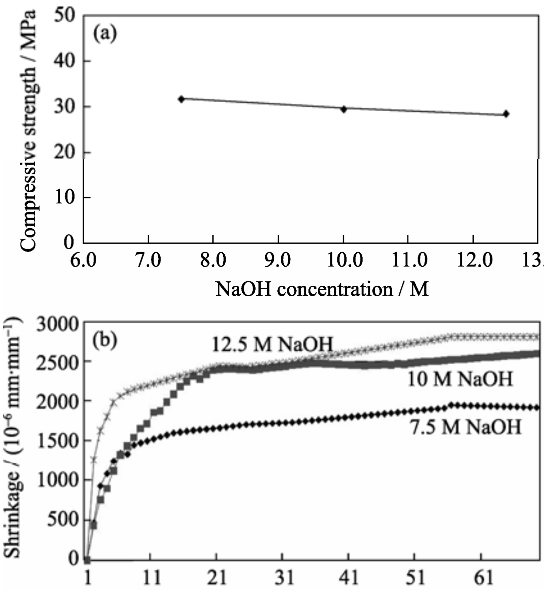

Fig. 3. Compressive strength (a) and shrinkage (b) of mortars with various NaOH concentrations.

3.4. Effects of liquid-to-ash ratio

The strength and shrinkage of geopolymer mortars with different liquid-to-ash ratios (L/A) are shown in Fig. 4. The strength of geopolymer mortars increases with the reduction in L/A ratios from 0.7 to 0.4. The high L/A ratio contributes to the high porosity of the hardened geopolymer. Increased porosity causes a decline in strength [5, 18]. The shrinkage, however, increases with the increase in L/A ratios. The excess water content from the increased activator content results in a geopolymer mortar with high porosity, low strength, and high shrinkage as shown in Fig. 4(b).

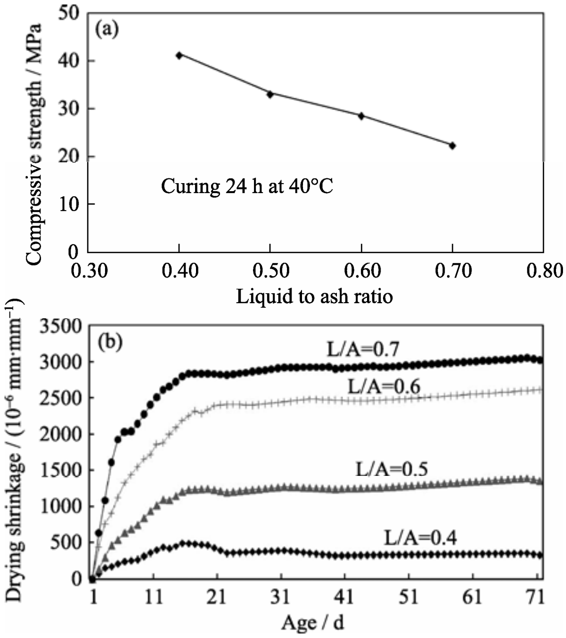

Fig. 4. Compressive strength (a) and shrinkage (b) of mortars with various L/A ratios.

4. Conclusion

The shrinkage of geopolymers is primarily affected by curing temperature and liquid-to-ash ratio. A strong geopolymer with a smaller shrinkage can be produced at high curing temperature. The shrinkage is also found to increase significantly with the increase in liquid-to-ash ratios from 0.4 to 0.7. In general, the increase in shrinkage is associated with the low strength development of geopolymers. NaOH concentration and sodium silicate-to-NaOH ratio also have some effects on the shrinkage of geopolymers. The effect of NaOH concentration on strength is small but that on shrinkage is quite significant. High NaOH concentration of 12.5 M produces a geopolymer with high shrinkage comparing to that with a low NaOH concentration of 7.5 M. The geopolymer with a high sodium silicate-to- NaOH ratio of

3.0 gives low drying shrinkage comparing to other geopolymers with the sodium silicate-to-NaOH ratios of 0.3-1.5. At high silicate content the reaction or condensation is fairly quick which results in relatively low shrinkage.

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