

Thermo-mechanical and Microstructural Characterization of Geopolymers with α -Al₂O₃ Particle Filler

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Abstract Geopolymers with different content of α -Al₂O₃ particle filler were prepared. The thermo-mechanical and microstructural characterization of the obtained geopolymers were systematically studied by flexural strength and thermal shrinkage measurements, TG-DTA (thermogravimetry and differential thermal analysis), XRD (X-ray diffractometry), and SEM (scanning electron microscopy). The results show that the addition of α -Al₂O₃ particle filler not only increases the onset crystalline temperature but also reduces the crystalline velocity of the geopolymers. The thermal shrinkage of the geopolymers increases with increasing heat treatment temperatures due to the water loss and densification. The flexural strength of the geopolymers increases with the increase of heat treatment temperatures from RT to 1200 °C, and shows a sharp increase in the range from 600 °C to 800 °C due to crystallization and solidification. The increase in content of α -Al₂O₃ particle filler can clearly reduce the thermal shrinkage and maintain a higher porosity at high temperatures. However, it has no distinct influence on the flexural strength after heat treatment. This is mainly attributed to the higher thermal resistance and strength of α -Al₂O₃.

Keywords α -Al₂O₃ particle · Geopolymers · Microstructural characterization · Thermo-mechanical behavior

1 Introduction

Due to their intrinsic fire resistance, low curing/hardening temperatures, environmentally friendly nature, and excellent thermal stability at high temperatures, geopolymers have excellent potential in a variety of applications where high service temperatures

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are anticipated such as engine exhaust systems, offshore drilling platforms, or where fire safety is a critical design parameter such as the interior of an aircraft [1].

Geopolymers can survive a serious fire, and after a proper reconstruction, they can continue their service life for many years due to their inorganic network structure [2]. Therefore, it is useful to study the properties of geopolymers not only in usual conditions but also after thermal load. Thermal loads lead to physical evolution, phase transitions, or microstructural development, which are the critical factors in determining their suitability and performance for applications ranging from construction to refractories and adhesives [3]. At present, the effects of different Si/Al ratios, alkali cations, or raw materials on the thermal-mechanical evolution of geopolymers have been studied [3–9]. In addition, the thermophysical properties of geopolymers can be optimized by adding different categories and contents of ceramic filler [10, 11]. To date, however, studies for geopolymers on the effect of a ceramic filler on thermal evolution, mechanical properties, and microstructural characteristics are relatively rare. Therefore, any measurements of this type would be quite useful for designers and practitioners.

In this paper, geopolymers with different content of α -Al₂O₃ particle filler were prepared, and the effects of the α -Al₂O₃ particle filler on the thermo-mechanical and microstructural characterization of obtained geopolymers were systematically studied.

2 Experiments

The geopolymer resin used here has a composition with SiO₂/Al₂O₃ = R(1.14, 1.6, 2.67, 4, respectively), K₂O/SiO₂ = 0.3, and H₂O/K₂O = 11 (mole ratio). The composition of the mixture for sample preparation is presented in Table 1. A typical processing route for the geopolymer resin is as follows: a potassium silicate solution was made by dissolving silica sol (40 mass%) into a KOH solution with a magnetic stirrer. Kaolin powder (4.08 μ m in average diameter) was calcined at 800 °C for 2 h to obtain metakaolin powder. The metakaolin powder was added to the potassium silicate solution and mixed for 30 min with a high-shear mixer to form a geopolymer resin. Whereafter, α -Al₂O₃ particles (0.75 μ m in average diameter) were added to the geopolymer resin and homogeneously mixed. The mixture was then poured into plastic containers (7 cm in diameter and 0.8 cm in height). Samples were placed in a sealed plastic bag and then cured at 50 °C for 48 h. After demolding, the samples were dried at 50 °C for 24 h. The heating of the samples to the predetermined temperature was carried out at a rate of 5 °C · min⁻¹; then the specimens were left at that temperature for

Table 1 Composition of the geopolymers with and without α -Al₂O₃ particle filler

Materials	KOH (g)	Water (ml)	Silica sol (g)	Metakaolin powder (g)	α -Al ₂ O ₃ particle (g)
A0	25	8	60	44.4	0
A1	25	8	60	44.4	10.2
A3	25	8	60	44.4	30.6
A5	25	8	60	44.4	50.1

a period of 2 h, and finally were slowly cooled. The chosen pre-heating temperatures were 400 °C, 600 °C, 800 °C, 1000 °C, 1200 °C, and 1400 °C.

In this study, the bulk density and open porosity were determined from the following equations:

$$V = \frac{m_w - m_a}{\rho_l} \quad (1)$$

$$\psi_o = \frac{m_w - m_d}{V\rho_l} \quad (2)$$

$$\rho = \frac{m_d}{V} \quad (3)$$

where m_d is the mass of the dry sample, m_w is the mass of the water saturated sample, and m_a is the mass of the immersed water saturated sample. V , ρ , and ψ_o are the volume, density, and open porosity of the sample, respectively. ρ_l is the density of water.

The thermal analysis was performed by means of TG-DTA with a heating rate of 10 °C · min⁻¹. The constitution phases of the obtained geopolymers were determined by XRD. The thermal shrinkage of the geopolymers subjected to different temperatures was obtained from the volume of the geopolymers before and after sintering. Flexural strength measurements were conducted on specimens (4 × 3 × 36 mm³) using a three-point-bending fixture with a span length of 30 mm at a crosshead speed of 0.5 mm · min⁻¹. Six specimens were tested under each test condition. Imaging of the geopolymers was undertaken by SEM.

3 Results and Discussion

TG-DTA curves of A3 and A0 geopolymers show a similar trend despite a little difference in the peak situation, as shown in Fig. 1. This indicates that the addition of α -Al₂O₃ particle filler has little influence on the thermal evolution of the geopolymers at high temperature. The exothermic peaks in Fig. 1 clearly correspond to crystallization of the geopolymers. The exothermic peak moves to the right with α -Al₂O₃ particle addition, probably due to the fact that the distribution of α -Al₂O₃ particles in geopolymers decreases the viscosity of the geopolymers at high temperature. A large endotherm appears from ambient temperature until approximately 300 °C in A0 and A3 specimens. The endotherm can be attributed to evaporation of free water and is also observed for Na-geopolymer [2]. The loss of mass from the geopolymer can be assumed to be entirely from water loss, by either evaporation of free water or condensation of hydroxyl groups [3]. The addition of α -Al₂O₃ particle filler indirectly reduces the content of water in geopolymers. Therefore, the mass loss of A3 geopolymers is slightly less than that of A0 geopolymers as shown from changes of TG in Fig. 1.

The typical XRD traces of A0 and A3 geopolymers treated at different temperatures are shown in Fig. 2. The A0 geopolymers (Fig. 2a) show a characteristic amorphous hump at ~ 28° in 2θ between RT and 600 °C, and a sharp major reflection of quartz is

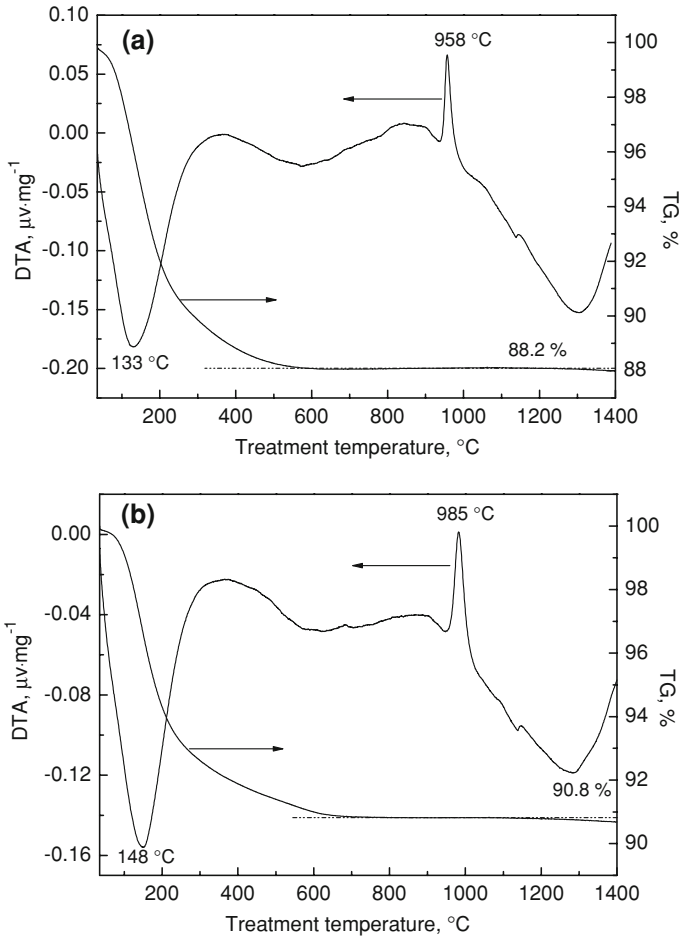


Fig. 1 TG-DTA curves of (a) A0 and (b) A3 geopolymers

present until 1000 °C. The sharp diffraction lines corresponding to leucite (KAlSi_2O_6) are found as the broad amorphous background feature disappears at 800 °C, and undergoes no further change until heating to 1400 °C. This indicates that A0 geopolymers crystallize fully to leucite at 800 °C. However, for A3 geopolymers (Fig. 2b), the sharp diffraction lines of leucite are found at 1000 °C despite the leucite phase is also found at 800 °C. The crystalline velocity of A3 geopolymers is obviously less than that of A0 geopolymers. Therefore, the addition of $\alpha\text{-Al}_2\text{O}_3$ particle filler into geopolymers not only increases the onset crystalline temperature but also reduces the crystalline velocity. The distribution of $\alpha\text{-Al}_2\text{O}_3$ particles in a geopolymer matrix probably generates the “inserted effect” in the amorphous structure of geopolymers and reduces the viscosity of geopolymers at high temperatures, which maybe results in retardance of the onset crystalline temperature and crystalline velocity. The onset crystalline temperatures, indicated by TD-DTA curves, are obviously higher than that indicated by

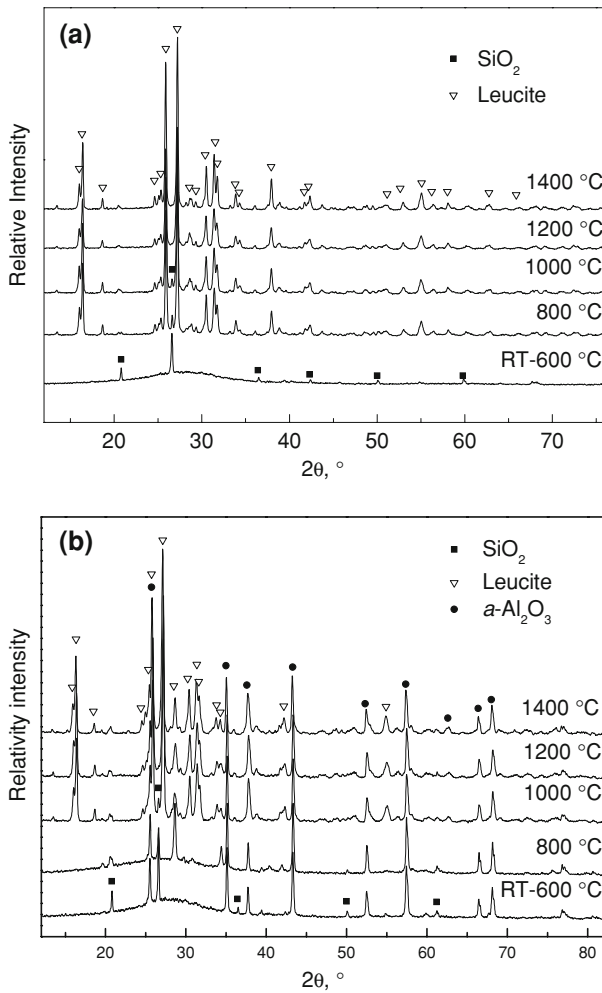


Fig. 2 XRD of (a) A0 and (b) A3 geopolymers treated at different temperatures

XRD patterns due to the fact that the holding time at high temperature, 2 h, is so long before XRD tests that the geopolymers crystallize at relatively low temperatures.

Figure 3 shows variations of the thermal shrinkage of the geopolymers treated at different temperatures. The thermal shrinkage of A0 geopolymers quickly increase at heat treatment temperatures ranging from 400 °C to 800 °C. Especially for 800 °C, the thermal shrinkage value reaches 42.4 %. Beyond 800 °C, the thermal shrinkage gradually increases to 46.5 % for 1400 °C. With the addition of α -Al₂O₃, the thermal shrinkage of the geopolymers, especially for A3 and A5, has a sharp decrease despite they have a similar trend as that of A0 geopolymers. The thermal shrinkage of A3 geopolymers reaches 28.4 % and 34.6 % at 800 °C and 1400 °C, respectively, which is obviously less than that of A0 geopolymers.

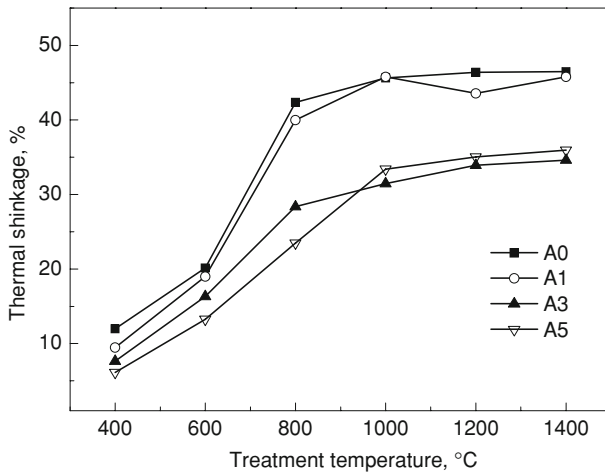


Fig. 3 Variation of thermal shrinkage of the geopolymers treated at different temperatures

The thermal shrinkage of the geopolymers below 600 °C is attributed to a region of capillary strain resulting from large fractional mass loss [12]. A geopolymer matrix after curing retains about 15 mass% water, including free water and hydration water [5]. The free water is lost at low temperatures; however, the hydration water is either bound tightly or less able to diffuse to the surface, and continues to evolve gradually until about 500 °C and beyond [5]. The loss of water reduces the density and increases the porosity of the geopolymers, to some extent, as shown in Fig. 4. Beyond 800 °C, the thermal shrinkage of the geopolymers is mainly attributed to structure densification. The microstructure of a geopolymer matrix has nanoparticulate features and pores which are of the order of 5 nm to 10 nm [13]. The addition of α -Al₂O₃ particles into composites indirectly reduces the content of water and nanopores due to the fact that α -Al₂O₃ has no water and nanopores. Otherwise, the thermal resistance of α -Al₂O₃ is far higher than that of the geopolymer matrix. Therefore, the increase in content of α -Al₂O₃ particles (samples A3 and A5) clearly reduces the shrinkage and keeps the volume stable at high temperature, especially for 800 °C to 1400 °C. Corresponding to the change of thermal shrinkage, the A3 and A5 geopolymers also have relatively lower density and higher porosity than that of A0 geopolymers for 800 °C to 1400 °C, as shown in Fig. 4.

Variation of the flexural strength of geopolymers with respect to the heat treatment temperature and content of α -Al₂O₃ particle is shown in Fig. 5. The flexural strength of the geopolymers gradually increases with increasing heat treatment temperatures from RT to 600 °C (Fig. 5a), although the porosity of the geopolymers increases due to water loss. After heat treatment from 600 °C to 1200 °C, the flexural strength has a sharp increase, especially at 800 °C, which corresponds to the sharp decrease of porosity and increase of density as shown in Fig. 4. The changes in flexural strength are consistent with that of thermal shrinkage. However, the flexural strength of the geopolymers has an unexpected decrease at 1400 °C. This might be attributed to the grain growth. The content of α -Al₂O₃ particles has little influence on the flexural

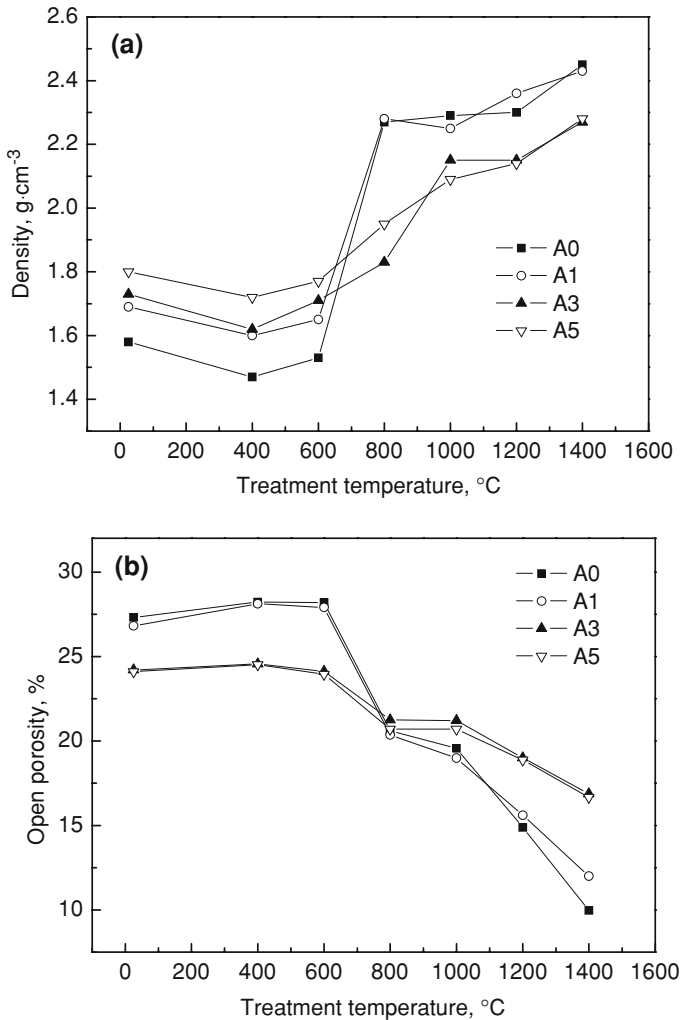


Fig. 4 Density (a) and open porosity (b) of the geopolymers after heat treatment at different temperatures

strength of the geopolymers as shown in Fig. 5b. With an increase of the content of α -Al₂O₃, there is a little increase in the heat treatment range of RT to 600 °C; however, the change of the flexural strength of the geopolymers is complex and small after heat treatment from 800 °C to 1400 °C.

Figure 6 shows the microstructure of A3 geopolymers after heat treatment at different temperatures. Specimens at RT exhibit a loose microstructure; however, the change in the microstructure appears dramatic before and after heat treatment. Specimens show largely homogenous binder containing some isolated pores a few microns in size after heat treatment. The loss of free water and hydration water undoubtedly results in an increase of the open porosity of the specimen as shown in Fig. 6b, although the specimens have little shrinkage from RT to 400 °C as shown in Fig. 3. With the

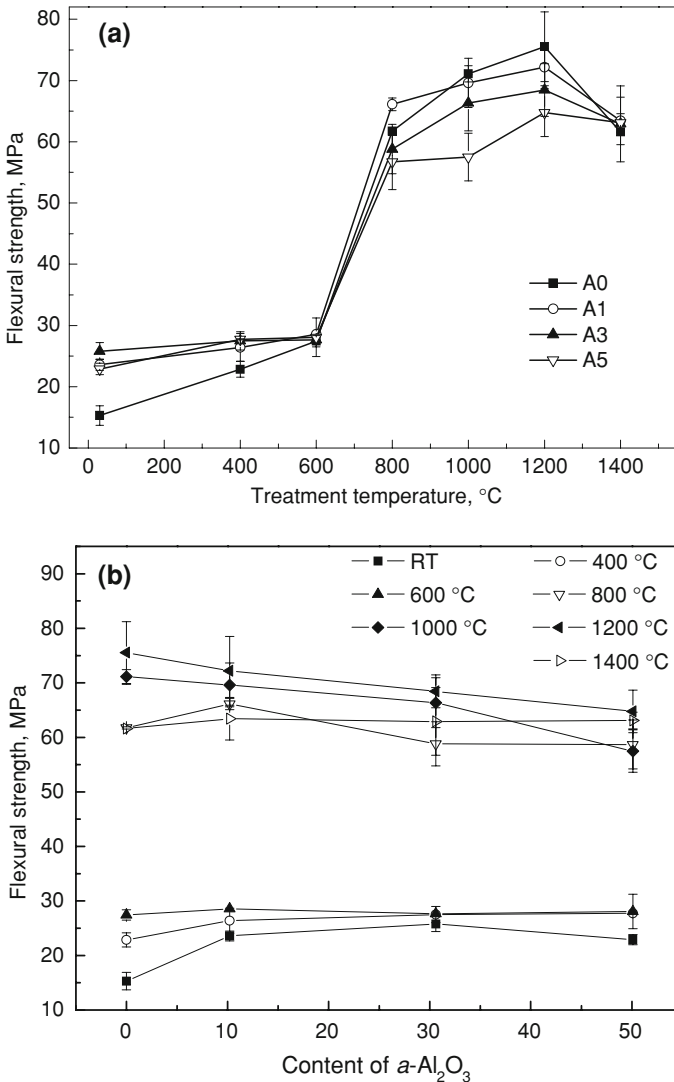


Fig. 5 Variation of flexural strength of the geopolymers with respect to (a) heat treatment temperature and (b) content of α -Al₂O₃ particles

increase of the heat treatment temperature, there is a decrease in the observed porosity on the surface of the specimen. This is consistent with the change of thermal shrinkage.

The fracture surface of geopolymers with different α -Al₂O₃ particle additions after heat treatment at 1000 °C is shown in Fig. 7. With the increase of content of α -Al₂O₃, the fracture surfaces of the geopolymers become rough with an increase in pores. This indicates that the increase in content of α -Al₂O₃ particles has a negative influence on the densification of the geopolymers at high temperature. However, the influence is

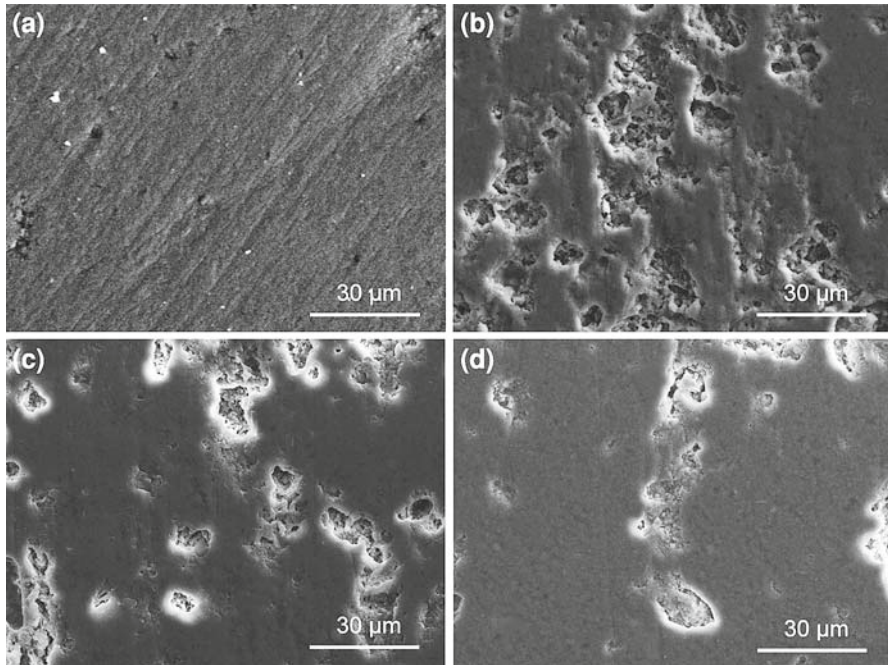


Fig. 6 SEM micrographs of A3 geopolymers after heat treatment at (a) RT, (b) 400 °C, (c) 800 °C, and (d) 1200 °C

very helpful for reducing the thermal shrinkage and keeping the size of the specimen stable at high temperature.

4 Conclusions

Geopolymers fully crystallize to leucite (KAlSi_2O_6) with and without $\alpha\text{-Al}_2\text{O}_3$ particle filler, and undergo no further change until 1400 °C. However, the addition of $\alpha\text{-Al}_2\text{O}_3$ particle filler into geopolymers increases the onset crystalline temperature and reduces the crystalline velocity. The thermal shrinkage of geopolymers increases with an increase in the heat treatment temperature due to water loss and densification. The increase in content of $\alpha\text{-Al}_2\text{O}_3$ particles can clearly reduce the thermal shrinkage, and maintain a relatively lower density and higher porosity than that of geopolymers with no $\alpha\text{-Al}_2\text{O}_3$ particle filler at high temperature due to the higher thermal resistant and strength of $\alpha\text{-Al}_2\text{O}_3$. This is very helpful for keeping the size of the specimen stable at high temperature. The flexural strength shows an increase after heat treatment from RT to 1200 °C, especially for 600 °C to 800 °C due to crystallization and densification of geopolymers, and an unexpected decrease at 1400 °C. The increase in content of $\alpha\text{-Al}_2\text{O}_3$ particles has no distinct influence on the flexural strength after heat treatment despite an increase in the porosity of geopolymers.

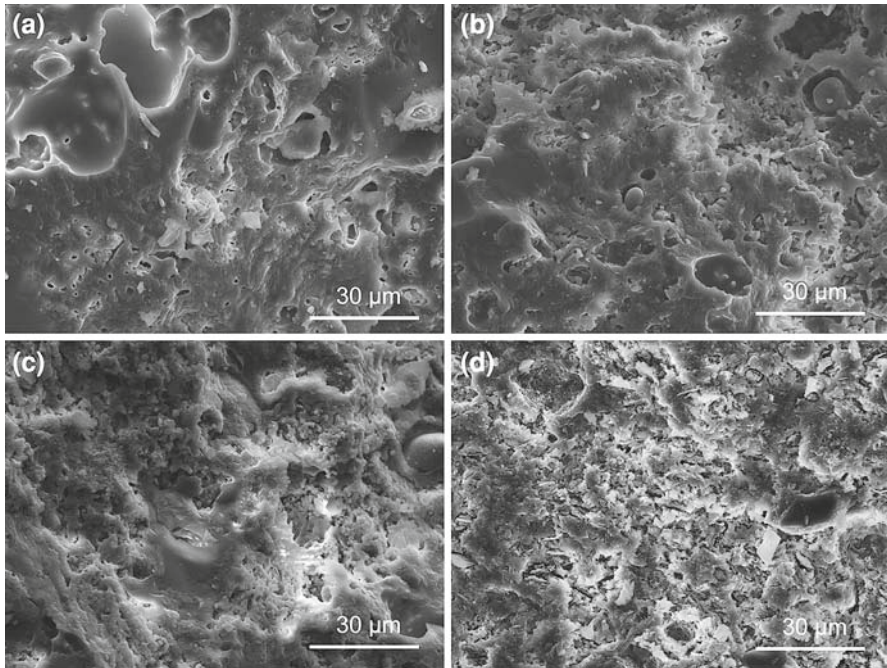


Fig. 7 Fracture surface of the geopolymers after heat treatment at 1000 °C: (a) A0, (b) A1, (c) A3, and (d) A5

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