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# Microstructural and mechanical characterization of fly ash cenosphere/metakaolin-based geopolymeric composites

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**Abstract**

Novel fly ash cenosphere (FAC)/metakaolin (MK)-based geopolymeric composites were prepared by adding FAC to the MK-based geopolymeric slurry. Microstructure, mechanical property, thermal conductivity, and bulk density of the FAC/MK-based geopolymeric composites were investigated. It was confirmed by the scanning electron microscope (SEM) and transmission electron microscopy (TEM) that the FAC did not dissolve in alkaline condition, but element diffusion took place around the interface between geopolymeric matrix and FAC. The compressive strength, thermal conductivity and bulk density of FAC/MK-based geopolymeric composites decreased monotonically with the increase of the FAC content from 15 vol.% to 40 vol.%, and the minimum values for the 40 vol.% FAC/MK-based geopolymeric composite reached 36.5 MPa, 0.173 W $m^{-1}$ $K^{-1}$ and 0.82 g $cm^{-3}$, respectively, in the range of FAC content from 15 vol.% to 40 vol.%. The results showed that the FAC could lower thermal conductivity effectively and bulk density of FAC/MK-based geopolymeric composites at a cost of slight decrease of mechanical properties. The 40 vol.% FAC/MK-based geopolymeric composite was a promising candidate material for intermediate-temperature thermal insulation applications due to its low thermal conductivity and low density.


*Keywords:* B. Composite; C. Mechanical properties; C. Thermal conductivity; Geopolymer; Microstructure

## 1. Introduction

Geopolymer is an artificial synthetic aluminosilicate material. During recent years, there are mainly three kinds of aluminosilicate sources materials for the preparation of geopolymeric matrix: (i) natural metakaoline (calcined kaolin) [1–3]; (ii) fly ash [4–9]; (iii) chemically synthesized metakaolin [10,11]. The obtained geopolymeric materials possess excellent properties including impressive acid and fire resistance, low production cost, environmentally friendly nature and good heat resistance properties [12–15]. Recently, some researchers have drawn their attention on the effect of high-temperature heat treatment on the properties of geopolymer and its composites. Kong et al. reported that the strength of geopolymer made with fly ash increased after exposure to 800 °C, while the strength of geopolymer/aggregate composite decreased after the same exposure due to the great thermal incompatibility [16]. The addition of $\alpha$-$Al_2O_3$ particles increased the strength of geopolymer composites, and after exposure at the temperature range between 800 and 1200 °C, both geopolymer and composites got significant gain in strength due to the viscous sintering [17]. Researches made by He et al. [18] proved that high-temperature heat treatment is an efficient method to improve the mechanical properties of carbon fiber reinforced geopolymer composites and the resulted composites showed much higher flexural strength under 700–900 °C than that at room temperature. The literatures suggest that geopolymer or their composites show much more desirable properties under or after high-temperature exposure, so they are a kind of very promising materials for thermal insulation applications [19,20].

According to the standard of the fire industry [21], the compressive strength of MK-based geopolymeric matrix is about 40–80 MPa [22,23], which can meet the demand of the fire industry. While the thermal conductivity of MK-based geopolymeric matrix is about 0.8 W $m^{-1}$ $K^{-1}$ at 40–100 °C [24], which is higher than that of the requirement in the fire industry. Incorporation of the second phase with low thermal

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Table 1
Chemical compositions of metakaolin and fly ash cenosphere in weight percent.

| Composition (wt.%) | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | CaO | $K_2O$ | Balance |
|---|---|---|---|---|---|---|---|
| Metakaolin | 51.906 | 45.392 | 0.921 | 0.763 | 0.113 | 0.455 | 0.450 |
| Fly ash cenosphere | 62.212 | 29.704 | 3.531 | 1.201 | 0.902 | 1.702 | 0.749 |

conductivity is an efficient method to decrease the thermal conductivity of the final product.

Fly ash cenospheres (FAC) are hollow spheres and are filled with air or gases. FAC have been found tremendous applications in various industries due to their low densities (0.2–0.8 g $cm^{-3}$), low thermal conductivities (about 0.065 W $m^{-1}$ $K^{-1}$), and excellent stability in alkali solution and at high temperatures [25–27]. Meanwhile, preliminary study proved that FAC used in our laboratory did not react with the geopolymer slurry. Thus the addition of FAC into the geopolymeric material may significantly reduce its thermal conductivity based on satisfying integrity of the FAC.

In this paper, fly ash cenospheres (FAC) were added into MK-based geopolymeric materials as a second phase. The content of the FAC were optimized based on the strength and thermal conductivity tests. Moreover, SEM and TEM were used to characterize the microstructure and interfacial conditions. Relevant studies were rarely reported before.

## 2. Experimental

Metakaolin (95%, Fengcheng Reagent Factory, China) and fly ash cenosphere (FAC) (Pindingshan Yaodian fly ash Co., China) were used as the starting materials. The particle size distribution of metakaolin was 9.1 μm ($d_{50}$), as determined by a Horiba LA-920 laser scattering particle size distribution analyzer. The bulk density and thermal conductivity of FAC with a mean diameter of 180 μm were around 0.364 g $cm^{-3}$ and 0.065 W $m^{-1}$ $K^{-1}$, respectively. The chemical compositions of metakaolin and FAC were determined by the X-ray fluorescence (XRF) spectrometer (Table 1).

First, the metakaolin was calcined at 800 °C for 4 h as the starting materials. Then, MK-based geopolymer with theoretical composition of $SiO_2/Al_2O_3$ = 4.0, $K_2O/Al_2O_3$ = 1.0 and $H_2O/K_2O$ = 11.0 (molar ratio) was obtained by mixing the as-calcined metakaolin powder with potassium silicate solution. Finally, FAC was added into the as-prepared geopolymeric slurry and cured at 80 °C for 6 days to get the FAC/MK-based geopolymeric composites.

The as-prepared composite specimens were examined at high magnifications using a Hitachi S-4700 scanning electron microscope (SEM, Hitachi Co., Tokyo, Japan) to ensure an accurate measurement. The microstructures of the obtained composites were characterized by transmission electron microscopy (TEM: FEI Tecnai F 30, America) and selected area electron diffraction (SAED) patterns operated at 300 keV. Specimens were prepared by grinding with mortar and pestle, embedding in G-1 gatan epoxy, cured at 90 °C for

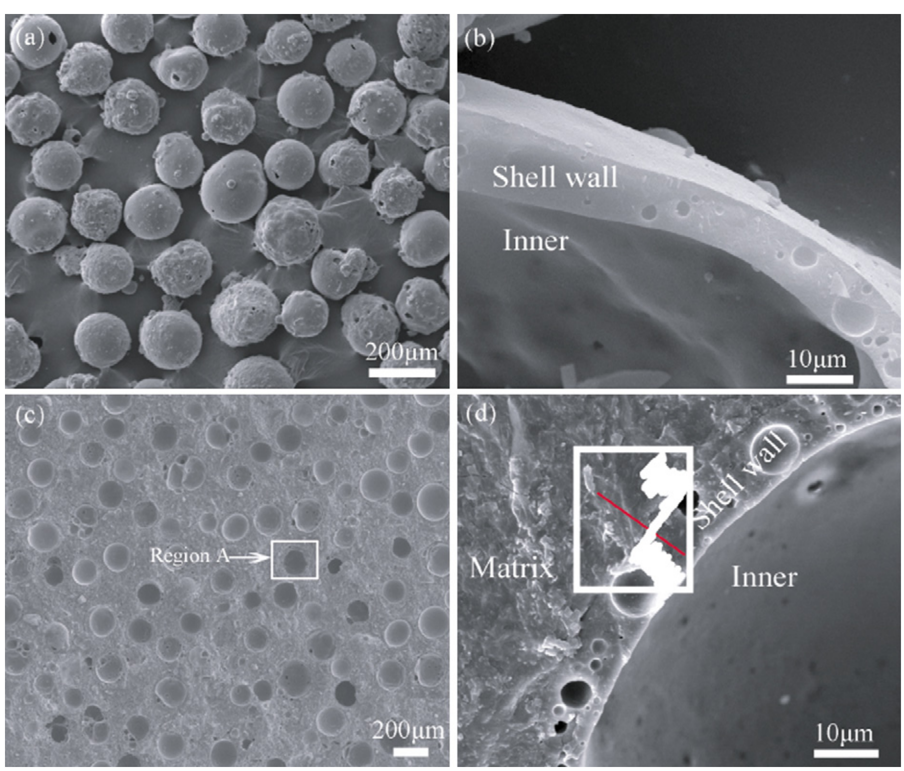


Fig. 1. SEM of (a) FAC, (b) Fractured wall of FAC, (c) 40 vol. % FAC/MK-based geopolymeric composite, (d) Interface between FAC and geopolymeric matrix.

20–25 min in a standard curing box, mechanically polished to a thickness of less than 50 μm, and then ion-milling the sample to perforation at 4 keV and at an incident angle of about 6°. Compressive strength of specimens was measured on Instron-500 type testing machine with a crosshead speed of 1 mm min$^{-1}$ using solid cylindrical specimens of $\phi$ 20 mm × 20 mm. A mean of five specimens was used for each determination. The relative bulk densities of FAC/MK-based geopolymeric composites were determined by Archimedes method. Thermal conductivity measurements of specimens were carried out on disk shape specimens, coated with carbon, using a laser flash diffusivity technique (Netzsch LFA-427, Laser Flash Thermal Constant Analyzer, Germany) at room temperature in an argon atmosphere. The samples were about 12.60 mm in diameter and about 2.55 mm in thickness. The thermal conductivity ($\lambda$) of specimen was calculated by Eq. (1)

$$\lambda = \rho a c_p \quad (1)$$

where $\rho$, $a$, $c_p$ were the density, thermal diffusivity and the heat capacity of specimen, respectively. The value of thermal conductivities was determined by averaging data acquiring from three measurements of each specimen.

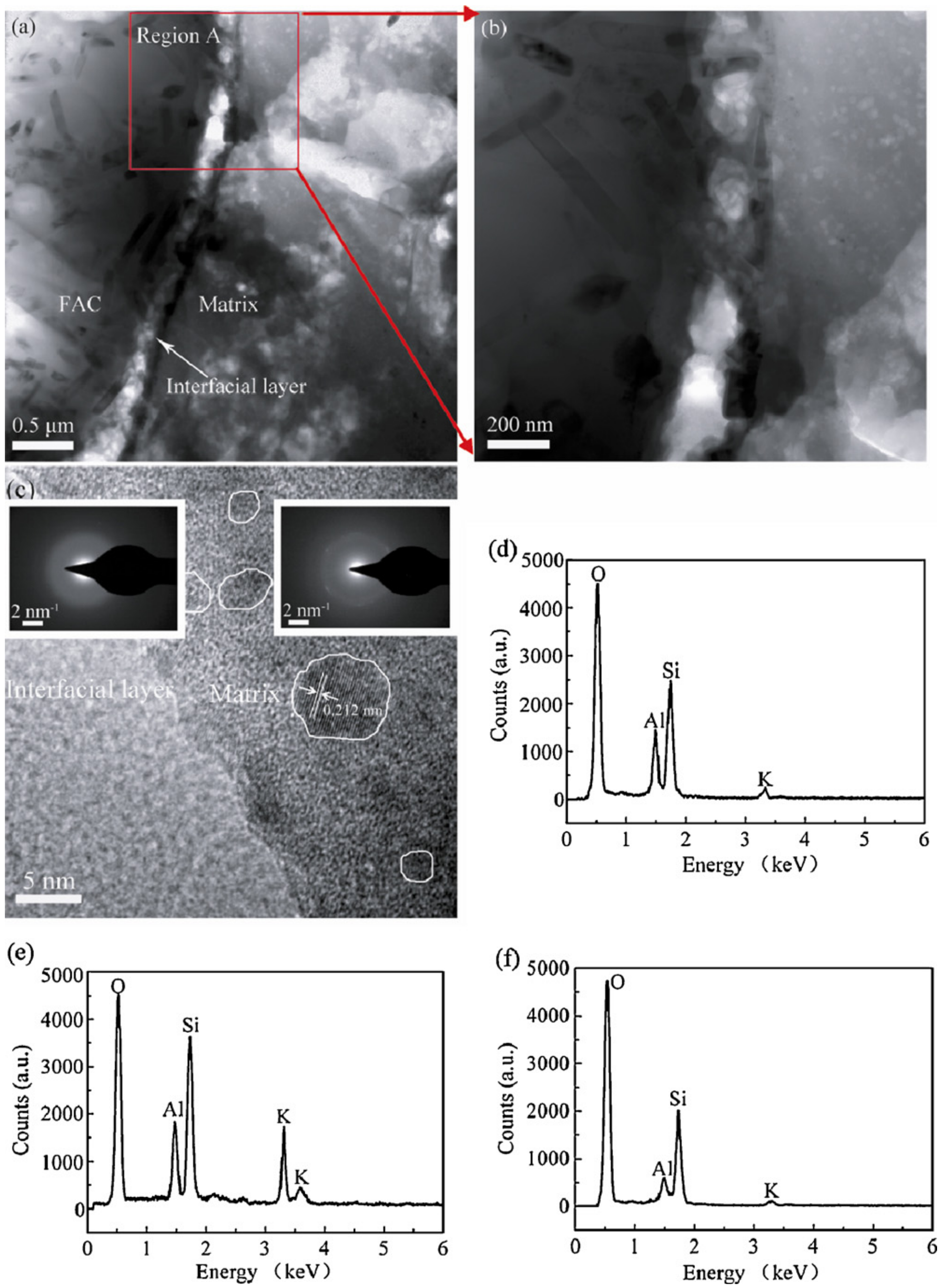


Fig. 2. TEM analysis of FAC/MK-based geopolymeric composite. (a) The interfacial layer between FAC and geopolymeric matrix, (b) Magnification micrograph of Region A, (c) HRTEM of interfacial layer and geopolymeric matrix, (d) EDS of interfacial layer, (d) EDS of geopolymeric matrix, (d) EDS of FAC.

## 3. Results and discussions

Fig. 1 shows micrographs of FAC and 40 vol.% FAC/MK-based geopolymeric composites. It could be found from Fig. 1a and b that the average diameter and the shell wall thickness of FAC were about 180 μm and 10 μm, respectively. Many pores of several micrometers were observed on the fractured shell wall of FAC in Fig. 1b. Fig. 1c indicated the FAC were uniformly dispersed in the MK-based geopolymeric matrix and FAC did not dissolve in the high alkaline condition. However, fly ash mostly reacted in alkaline solution with a constant $Al_2O_3/K_2O$ molar ratio of 1.0 according to the literature [28] and amounts of unreacted fly ash decreased with increasing concentration of alkaline metal hydroxide [29]. As revealed in Fig. 1c, a clear interface could be observed between geopolymer and FAC. Fig. 1d, which was a high-magnification image of region A in Fig. 1c, also confirmed this point. Energy dispersive spectrum (EDS) analysis of the inset in Fig. 1d showed that there was a steep decrease in potassium element amount from geopolymer to the FAC, indicating that the no potassium element penetrated the remnant outside. Meanwhile, MK-based geopolymeric matrix in our investigation showed a much more compact microstructure as compared with the results in another literature [31].

TEM analysis was carried out on all specimens to further investigate the interface between geopolymer and the FAC. Fig. 2 represents a TEM micrograph of a FAC/MK-based geopolymeric composite specimen. An interfacial layer of about 100 nm in thickness was clearly observed between the geopolymer matrix and FAC, as indicated in Fig. 2a and b. Fig. 2c demonstrates the high-resolution transmission electron micrograph of interfacial layer and geopolymer matrix. The typical amorphous halos (left in Fig. 2c) implied that the interface layer was amorphous. The geopolymer matrix (right inset in Fig. 2c) was a glassy phase, which has been observed by other researchers [19,30,31]. However, a few scattered lattice fringes with a size of 2–5 nm were found in the matrix. The ordered regions by the fast Fourier transformation (FFT)-filtered images determined that the lattice constant was 0.212 nm, which corresponded to the α-quartz phase. Energy dispersive spectrum (EDS) analysis (Fig. 2d–f) showed that the composition of the interfacial layer was $Si_{19.33}Al_{9.67}O_{69.96}K_{1.02}$, which was different from those of geopolymer matrix ($Si_{21.08}Al_{10.59}O_{57.85}K_{10.49}$) and FAC ($Si_{26.47}Al_{6.90}O_{65.29}K_{0.44}$). These results proved unambiguously that the interfacial layer was formed by the diffusion of elements rather than reactions between FAC and the MK-based geopolymer. It could be concluded that the geopolymer, interfacial layer and FAC bonded very well to each other.

The compressive strength of MK-based geopolymer is shown in Fig. 3. The compressive strength of geopolymeric matrix was 106.2 MPa. The compressive strength values decreased with increasing FAC contents, and the minimum compressive strength of composite for 40 vol.% FAC/MK-based geopolymeric composite, was 36.5 MPa, which satisfied the requirement of insulation material industries [21]. The mechanical properties of FAC used in our study were much lower than those of geopolymer matrix. Therefore, the mechanical properties of FAC/MK-based geopolymeric composites decreased monotonically with increasing FAC contents and exhibited a minimum at the FAC content of 40 vol.%.

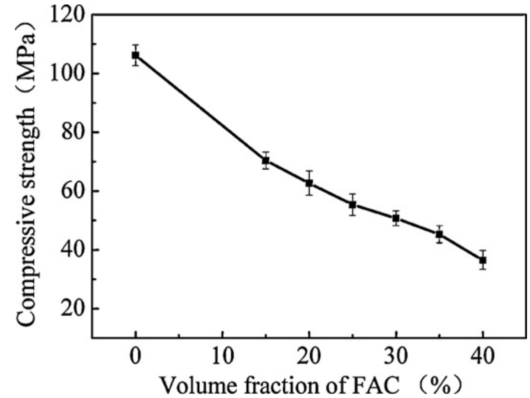


Fig. 3. Compressive strength of the composites vs. volume fraction of FAC.

Thermal conductivities and densities of FAC/MK-based geopolymeric composites with different FAC contents are shown in Fig. 4. It could be observed that the thermal conductivity and bulk density of the pure geopolymer were 0.361 W $m^{-1}$ $K^{-1}$ and 1.37 g $cm^{-3}$, respectively. As the addition of FAC increased from 15 vol.% up to 40 vol.%, thermal conductivities of FAC/geopolymer matrix composites decreased monotonically. The minimum thermal conductivity of 0.173 W $m^{-1}$ $K^{-1}$ and minimum bulk density of 0.82 g $cm^{-3}$ were achieved for FAC/geopolymer matrix composites with 40 vol.% FAC addition, which were 52.1% and 40.1% lower than those of the pure geopolymer, respectively.

So far, thermal conductivity of geopolymer materials was only measured by Duxson et al. [24]. While FAC/MK-based geopolymeric composites has not been investigated in open literature. The mechanism of heat transfer in FAC/MK-based geopolymeric composites for three-phase systems was complicated. According to Woodside [32], the effect of convection became significant for particles with diameters larger than 1 cm, convective heat transfer in pore can be neglected. At temperatures above 200 °C, as well as for larger grains, radiation also contributed to thermal conductivity in granular materials [33]. In this paper, inner diameter of hollow spheres was about

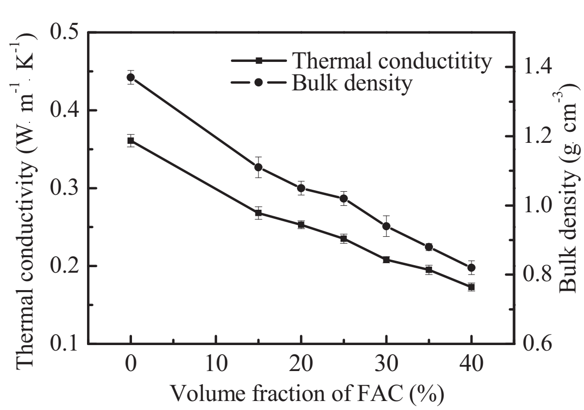


Fig. 4. Thermal conductivity and bulk density vs. volume fraction of FAC.

160 μm and thermal conductivity measurements were carried out at room temperature, thus the effects of convection and radiation were both neglected and only thermal conduction between solid and gas was taken into account. On one hand, the relatively low thermal conductivity of FAC/MK-based geopolymeric composites was attributed to the addition of FAC with low thermal conductivity. On the other hand, the presence of interface thermal resistance across the FAC–matrix interface resulted in a decreased in the thermal conductivity of composites [34,35]. In addition, the porosity of FAC/MK-based geopolymeric composites increased with increasing FAC contents. Generally, the thermal conductivities and densities of materials were mostly influenced by the porosity of the materials. Thus FAC/MK-based geopolymeric composites showed lower thermal conductivity than the MK-based geopolymeric matrix. The low thermal conductivities and densities of FAC/geopolymer matrix composites suggested their potential light-insulation applications. It can be concluded that the addition of FAC was an effective way for decreasing thermal conductivity of geopolymer matrix while preserving sufficient mechanical properties.

## 4. Conclusions

In this study, FAC/MK-based geopolymeric composites with various FAC contents were prepared. Compressive strength, thermal conductivities and bulk densities of the composites decreased with increasing FAC contents, which primarily were due to the addition of FAC with high porous nature. In addition, increase of interface thermal resistance for interfacial layer played a certain part in lowering thermal conductivity. Moreover, in the range of FAC content from 15 vol.% to 40 vol.%, the compressive strength of 36.5 MPa, the minimum thermal conductivity of 0.173 $W\ m^{-1}\ K^{-1}$ and bulk density of 0.82 $g\ cm^{-3}$ were reached for the composites with 40 vol.% FAC which satisfied the requirement of insulation material industries. Therefore, the 40 vol.% FAC/MK-based geopolymeric composite was a promising candidate material for intermediate-temperature thermal insulation applications due to its low thermal conductivity and low density while retaining enough mechanical properties.

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