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A novel method for preparation of organic resins reinforced geopolymer composites

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Abstract A novel method for preparation of alkali-activated metakaolin/granulated blast furnace slag (GBFS)-based geopolymer reinforced by organic resins (OR) was reported. The geopolymer composites by doping an amount of 1 wt% OR displayed the highest compressive and flexural strengths at the different curing times. The calorimetry results showed that the reaction heats of the geopolymer composites at the early reaction stage of $1\sim3$d are much higher than that of geopolymer due to the geopolymerization rate to be accelerated by incorporation of OR. A reasonable reinforced mechanism was proposed.

Introduction

Geopolymer is a novel class of inorganic polymer with an amorphous three-dimensional framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ species as building blocks [1–5]. Yip and Deventer et al. [6, 7] recently studied the alkaline activation of the metakaolin/granulated blast furnace slag (GBFS) system. They reported that the geopolymer was the predominant phase at high alkalinity. Alonso and Palomo [8] suggested that there were geopolymer and calcium silicate hydrate formed simultaneously within a metakaolin/calcium hydroxide system. Cheng and Chiu [9] reported that the compressive strength of metakaolin/GBFS-based geopolymer increased with increasing amount of alkaline activator and metakaolin. Qian et al. [10] indicated that the geopolymer obtained by alkali-activating the mixtures of metakaolin and slag could effectively fix radioactive elements. In recent years, the geopolymers have been extensively investigated due to their excellent characteristics including high compressive strength, fire-resistance, immobilization of toxic, hazardous, and radioactive wastes. Besides, geopolymer is also a ‘‘Green Material’’ for its low consumption of manufacturing energy and low emission of waste gases [11–16]. However, the brittle characteristic of geopolymer usually affects its wide applications [17]. Some efforts have been focused on improvements of its mechanical properties. It was reported that short polyvinyl alcohol (PVA) fiber was used to reinforce fly ash/metakaolin-based geopolymer composites and showed a good flexural strength and reasonable toughness [18, 19]. The short PVA fiber could be applied to modify the brittle properties of fly ash-based geopolymer [20]. Zhang et al. [21] reported that five kinds of water-soluble organic polymers, such as sodium polyacrylate (PAANa), polyacrylic acid (PAA), polyacrylamide (PAm), polyethylene glycol (PEG), and PVA were employed to prepare organic polymer reinforced uncalcined-kaolinite geopolymer. It was found that the incorporation of PAA and PAANa could obviously improve the compressive strength, cross-bending strength in the period of cuing time for 1–8 h at temperature of 40–90 °C. Zhang et al. [22] described that calcined kaolin/fly ash-based geopolymer was reinforced by polypropylene (PP) fiber. Dias and Li et al. [23, 24] investigated the mechanical properties of basalt fiber improved geopolymeric concrete. Lin et al. [25, 26] reported that the short carbon fibers were used to increase the strength and toughness of geopolymers.

In the present article, a novel method for preparation of metakaolin/GBFS-based geopolymer composites reinforced by organic resins (OR) which consist of acrylic resin

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emulsion and polyvinyl acetate resin has been firstly reported. Our purposes are: (1) incorporating of OR into geopolymer to improve its brittle characteristic; (2) making use of GBFS as partial replacement of natural kaolin to synthesize geopolymer products with high added value and minimize environmental impacts; (3) exploring on a new pathway to synthesize geopolymer composites reinforced by OR with enhanced compressive and flexural strengths.

Experimental section

Materials

Kaolin came from Yulin Mineral Company. Metakaolin with Blaine specific surface of 738 $m^2\ kg^{-1}$ was obtained by calcined pure kaolin at 800 °C for 6 h. The GBFS with Blaine specific surface of 509 $m^2\ kg^{-1}$ originated from Laiwu Steel Company. The major components of metakaolin and GBFS in mass percentage were listed in Table 1. Sodium metasilicate, $Na_2SiO_3{\cdot}9H_2O$ (A.R.) from Shanghai Chemical Reagent Company is used as an alkaline activator with a modulus of 1.0. A resin emulsion of butyl acrylate and acrylic acid copolymer was purchased from Longrui Company. A resin powder of ethylene–vinyl acetate copolymer was obtained from Tianyun Company.

Preparation of geopolymer composites

The raw materials were blended in the mass ratio of inorganic materials (metakaolin and GBFS in the mass ratio of 1:4):alkaline activator (Na_2SiO_3):OR (the mixture of a resin emulsion of butyl acrylate and acrylic acid copolymer and another resin of ethylene–vinyl acetate copolymer in the mass ratio of 1:4):water = 1:0.15:0.01–0.15:0.36. A typical preparation procedure of geopolymer composites was described as follows: a mixture of metakaolin and GBFS was put into the net paste stirrer to be mingled sufficiently. Subsequently, an aqueous solution of alkaline activator was added to stirrer, and then a mixed aqueous solution of OR was added to stirrer to be interfused adequately. The slurry was cast into a triplicate steel mold measuring 40 × 40 × 160 (mm^3). After demolding, specimens were put into a curing box at 20 °C with 99% relative humidity for 3 days (3d), 7 days (7d) and 28 days (28d), respectively.

Characterization of specimens

The compressive strength of specimen was measured on a YAW-300 automatic pressure testing machine at loading speed of 2.4 kN/s. Flexural strength of specimen was carried out on a DKZ-5000 anti-rupture testing machine with a three-point bend device at loading speed of 50 N/s. Reaction heat of specimen was tested on a SHR-800 calorimetric instrument with an automatic record system according to the standard of GB/T 12959-2008.

Results and discussion

Figure 1 shows the effects of the doping different amounts of OR on compressive strength of geopolymer composites. It can be observed that the compressive strength of geopolymer composites decrease with increase of doping amount of OR at the same curing time. The geopolymer composites by mixing quantity of 1 wt% OR always display the highest compressive strength at the different curing times of 3d, 7d, and 28d, respectively, and the highest compressive strength reaches about 83.7 MPa at curing time of 28d.

Flexural strength reflects the ability of the material to withstand bending forces applied. Figure 2 shows the effects of the doping different amount of OR on flexural strength of geopolymer composites. It can be observed that

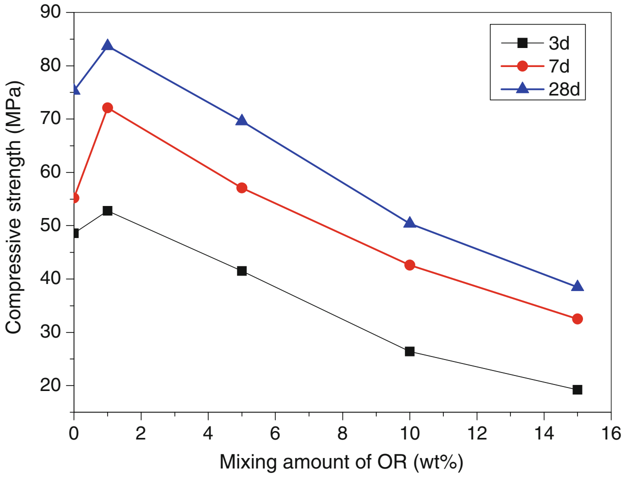


Fig. 1 Effects of the mixing amount of OR on compressive strength of geopolymer composites

Table 1 Chemical compositions of metakaolin and GBFS (wt%)

Component (wt%)	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	TiO_2	Na_2O	K_2O	P_2O_5	SO_3
Metakaolin	44.55	41.46	0.49	0.08	0.47	1.33	0.05	0.12	0.04	0.05
GBFS	28.30	13.16	36.57	7.58	0.83	0.99	0.49	0.50	0.28	1.65

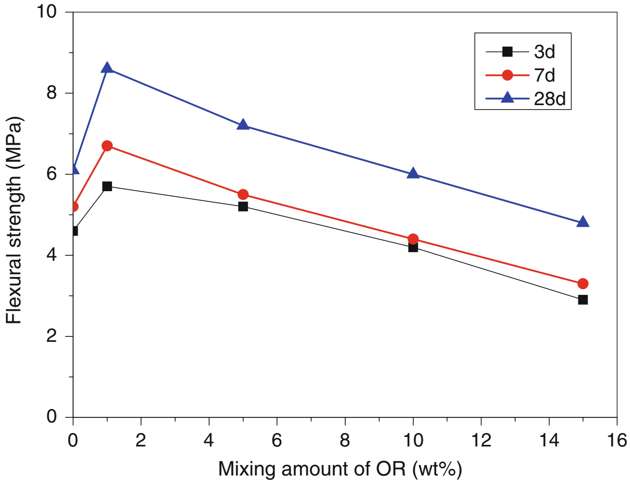


Fig. 2 Effects of the mixing content of OR on flexural strength of geopolymer composites

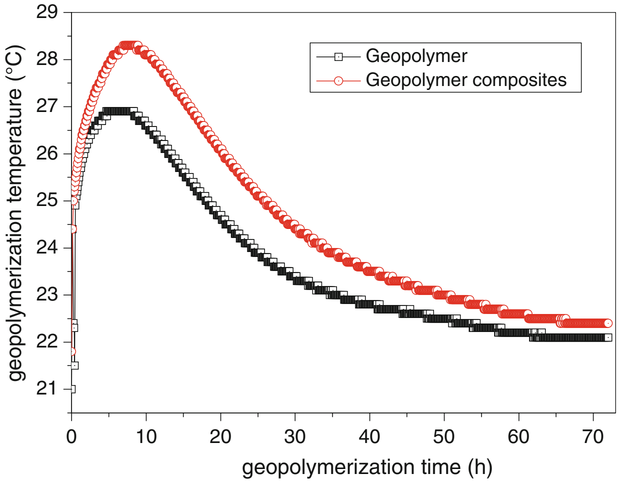


Fig. 3 Geopolymerization heats of specimens

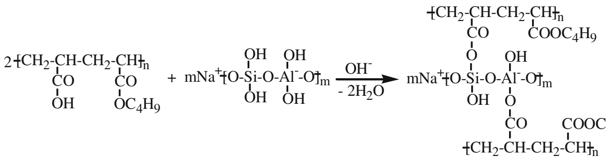
the flexural strength of geopolymer composites gradually dropped with increase of mixing content of OR. However, the flexural strengths in the doping amount of 1 and 5 wt% OR are always higher than that of geopolymer in the absence of OR at curing times of 3d, 7d, and 28d, respectively. Doping an amount of 1 wt% OR shows the highest flexural strength of 8.6 MPa at curing time of 28d.

The compressive strength of geopolymer composites by doping 1 wt% OR increases by 8.6, 30.6, and 11.2% in Fig. 1, and the flexural strength increases by 23.9, 28.9, and 41.0% in Fig. 2, as compared to the specimen without doping OR in the period of curing times from 3d to 28d, respectively. So it is considered that the mechanical properties of metakaolin/GBFS-based geopolymer composites can be remarkably reinforced by doping some amount of OR even small amount of organic modifier also can strongly influence the geopolymerization process.

An adiabatic calorimetric method is used to measure the reaction heat of specimens as shown in Fig. 3. It can be seen that the geopolymerization reaction will start as soon as the metakaolin/GBFS is mixed with alkaline activator due to rapidly raising temperature in initial reaction time. The maximum geopolymerization temperatures for both specimens of geopolymer and geopolymer composites are 26.9 and 28.3 °C, accompanying reaction times of 4.8 and 7.1 h in Fig. 3, respectively. It is noteworthy that the exothermic reaction heats of geopolymer composites reinforced by 1 wt% OR are $Q_{1d} = 65.85\ \mathrm{J\ g^{-1}}$ and $Q_{3d} = 77.96\ \mathrm{J\ g^{-1}}$, whereas the exothermic reaction heats of geopolymer are $Q_{1d} = 50.20\ \mathrm{J\ g^{-1}}$ and $Q_{3d} = 74.65\ \mathrm{J\ g^{-1}}$. The reaction heats for the former are bigger than those of the latter, indicating that the reaction rate is accelerated by doping 1 wt% OR at the early reaction stages. In general, alkali-activated geopolymerization is a complex chemical process involving three kinds of exothermic steps, that is, mineral dissolution, transportation, and polycondensation [27]. We only observed one type of exothermic curve in Fig. 3. Palomo et al. [27] studied that the geopolymerization of alkali-activated fly ash was traced by means of calorimetry test. They reported that the calorimetry could not detect the reaction steps separately due to these steps overlap each other.

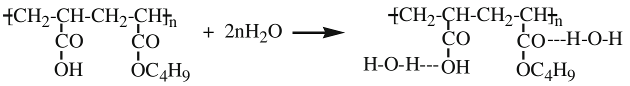
We try to explain why the compressive and flexural strengths of alkali-activated metakaolin/GBFS-based geopolymer are reinforced by mixing of OR. Under alkaline conditions, geopolymer was generated via the cleavages of Si–O–Al covalent bonds, accumulation of intermediates and polycondensation of elimination water between hydroxyl groups [28].

The hydroxyl groups from the chain-like OR and geopolymer together eliminate water by polycondensation to create a continuous gel, and the OR simultaneously acts as the filler to insert the interstices formed by the aggregations of network structures of geopolymers as shown in reaction (1). The OR could prevent cracking growth and hence increases the fracture toughness of the brittle geopolymer matrix through a filling effect.



$$2\,[CH_2-\underset{\underset{OH}{CO}}{CH}-CH_2-\underset{\underset{OC_4H_9}{CO}}{CH}]_n + mNa^+[O-\overset{OH}{\underset{OH}{Si}}-O-\overset{OH}{\underset{OH}{Al^-}}-O]_m \xrightarrow[-\,2H_2O]{OH^-} mNa^+[O-\overset{\overset{\overset{[CH_2-\underset{CO}{CH}-CH_2-\underset{COOC_4H_9}{CH}]_n}{}}{O}}{\underset{OH}{Si}}-O-\overset{OH}{\underset{\underset{\underset{[CH_2-\overset{CO}{CH}-CH_2-\overset{COOC_4H_9}{CH}]_n}{}}{O}}{Al^-}}-O]_m \tag{1}$$

Besides, the polar groups of chain-like OR have a stabilizing effect on water molecules by adsorption of H_2O to form hydrogen bonds and inhibit the evaporation of water so as to benefit the geopolymerization progress as described in reaction (2).



$$-\!\left[CH_2-\underset{\substack{|\\CO\\|\\OH}}{CH}-CH_2-\underset{\substack{|\\CO\\|\\OC_4H_9}}{CH}\right]\!-_n + 2nH_2O \longrightarrow -\!\left[CH_2-\underset{\substack{|\\CO\\|\\H\text{-}O\text{-}H\text{---}OH}}{CH}-CH_2-\underset{\substack{|\\CO\text{---}H\text{-}O\text{-}H\\|\\OC_4H_9}}{CH}\right]\!-_n \qquad (2)$$

Conclusion

The metakaolin/GBFS-based geopolymer reinforced by OR was synthesized here for the first time. The mechanical properties of the geopolymer composites were significantly enhanced by doping of OR. The geopolymer composites showed higher reaction heat than that of geopolymer. The excellent compressive and flexural performance was attributed to the OR preventing cracking growth and increasing the fracture toughness of the geopolymer composites.

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