



Effect of polyacrylic resin on mechanical properties of granulated blast furnace slag based geopolymer

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ABSTRACT

The mechanical performances of alkali-activated granulated blast furnace slag (GBFS) based geopolymer modified with polyacrylic resin were investigated in this paper. The water-to-binder ratio, alkaline activator content (Na_2O wt%) and $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio in this experiment maintained at 0.5, 6% and 0.8, respectively. Geopolymer samples were synthesized by alkaline solution and GBFS with incorporating amount of 0.25, 0.5, 0.75, 1.0, 3.0 and 5.0 wt% polyacrylic resin. The mechanical properties of samples were measured using compression tests, flexure tests and bending toughness tests. The results show that the compressive and flexural strength were both up to the maximum value while doping 1 wt% polyacrylic resin, the ratio of flexural-compressive strength and bending toughness at curing 28 days were increased by 36.3% and 104.6% respectively, compared with the control samples. The structural evolutions of specimen after incorporating polyacrylic resin were characterised by FTIR as well as ^{29}Si NMR spectroscopy. It indicated that a new absorption peak namely Si–O–C bond at wavenumber of about 1180 cm^{-1} in the FRIR spectra appeared while incorporating polyacrylic resin whatever 1 wt% or 5 wt%, the chemical shifts corresponding resonance peaks of siliceous species moved towards to low field, and the polymerization degree of Si transformed from Q^3 , Q^4 to Q^0 , Q^1 , Q^2 .

1. Introduction

Geopolymer is a kind of novel cementitious construction material, composed by amorphous aluminosilicate network containing $[\text{AlO}_4]^{5-}$ and $[\text{SiO}_4]^{4-}$ tetrahedra that derived from the reaction between alkaline activator and aluminosilicates with volcanic activity or potential gelation activity [1,2]. The tri-dimensional silicate configuration mainly formed by four-steps polymerization, including the dissolution of aluminosilicates materials, the formation of Si/Al oligomers, polycondensation of oligomers and the formation of cross-linked geopolymer structure [3,4]. As one of the most promising green building structural materials in the 21st century [5,6], the application fields of geopolymers have been developed fastly especially in terms of road rapidly repaired, immobilization of nuclear wastes and heavy metal ions [7,8,9].

Compared with the traditional cement materials, geopolymers have presented better mechanical performance [10,11], durability [12] and low thermal conductivity [13]. F. Pelisser [14] investigated the mechanical properties of metakaolin based geopolymer. It was shown that the hardness and compressive strength of geopolymer samples after curing 7 days could be up to 0.4 GPa and 64 MPa, respectively. K.A.

Komnitsas [15] synthesized geopolymers by using GBFS, NaOH and water glass at room temperature, and the result elucidated that the compressive strength of samples after curing 4 h was up to about 20 MPa. Y.J. Zhang [11] demonstrated that the compressive strength of alkali-activated metakaolin/GBFS based geopolymer increased progressively with ascending the temperature from $150\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$. However, due to the low flexural strength and notable fragility of geopolymers, the extensive applications of these materials in the construction material industries have still been a big challenge so far. Considering the preparation process, the homogeneous issues of alkaline activators and starting materials have an immense effect on the synthesis of geopolymer, there are also no explicit standards and operation specifications to control and measure the preparation process of geopolymer as well [14].

Some works have paid to illuminate the intimate connection between the mechanical characters with high compressive strength but low flexural strength and internal structure. J. Davidovits [16] had proposed the mechanism model about the formation of geopolymers synthesized by NaOH/KOH activating metakaolin [17]. According to Si/Al ratio of reaction products, geopolymers are composed of three different silicate units: PS ($-\text{Si}-\text{O}-\text{Al}-\text{O}-$), PSS

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(–Si–O–Al–O–Si–O–), PSDS (–Si–O–Al–O–Si–O–Si–O–) [4,18]. The generally existed forms of Si and Al in geopolymer structure are $[\text{SiO}_4]$ and $[\text{AlO}_4]$ tetrahedra respectively, along the three dimension direction extension further forming the tri-dimensional network structure [19,20]. However, due to high bond energy of Si–O and Al–O chains in the structure of geopolymers, it is essential to absorb more energy for the purpose of breaking these bonds, thus performing a high compressive strength in macro-scale. In the meantime, strong directivity and tough to rotate and stretch of the chemical chains due to high key energy result the geopolymers performing low toughness and poor brittleness. It is generally deemed that the formation process of geopolymers is actually that Si–O and Al–O in aluminosilicate structure proceed fracture-reorganization process repeatedly under the affection of alkaline activator solutions, and finally the tri-dimensional network structure of geopolymers is formed [4].

Some effects have been implemented to improve the flexural strength and brittleness of geopolymers. It was reported that the main method researchers domestic and overseas commonly used for modifying geopolymers was adding amount of fibers as toughening agents into the geopolymer slurry while stirring. T.S. Lin [21] and D.P. Dias [22] studied various fibers contained basalt fiber and carbon fiber were employed to reinforce the flexural strength of geopolymers. P.J. Sun [23] also confirmed that the PVA fibers can improve the brittleness and toughness of geopolymers. Besides, J. Davidovits executed a compare experiment to investigate the effect of glass fiber and SiC fiber on the toughening modification of geopolymers. The result manifested that SiC fiber obtained a better modification effect than ordinary glass fiber in the process of synthesizing geopolymer, considering the corrosion impact in the strong alkaline solution. Nevertheless, the above-mentioned methods to implement the toughening modification of geopolymers were just in the level of physical aspects rather than in essence toughening. Meantimes, fibers also can cause an unbeneficial impact on the compressive strength and workability of mortars, thus the modification effect was limited in some degree. In addition, considering the issues of compatibility between fibers and geopolymers, the complicated technologies of mixing and homogenization, the practical applications of fiber toughening modification geopolymer materials were still restricted to some extent.

M. Sumper [24] studied that the mechanical performances of diatom can be improved apparently by doping amount of organic polymers, nevertheless the geopolymer reaction processes above described are considerable similar with the precipitate and polymerization processes of silicic acid to produce diatom with porous shell. Thus, the alike modification methods can also be appropriate for the toughening modification of geopolymer materials. On one hand, the improvement of mechanical properties and structure densification of matrix have been implemented by organic polymer to bind micro-crystals of inner structure and rearrange their orientation; on the other hand, as can be seen through analyzing the distinct internal structure of geopolymers, whatever Si or Al element, there are amount of active hydroxyl groups (–OH) connected with these elements, which provide favorable conditions for introducing external functional groups to react with active –OH, thus improving flexural toughness and reducing brittleness of geopolymer materials. Y.C. Wang [25] took advantage of organic resins to reinforce the alkali-activated fly ash-based geopolymers. The results derived from XRD and SEM detection methods showed that the mortar of geopolymer did not generate any new mineral phases after incorporating amount of resins. However, the amount of micro-fractures in the geopolymer decreased significantly due to filling and cross-linking effect of the resins; S.Z. Zhang [3] investigated the modification effect of four different water soluble organic polymers including polyethylene glycol, polyvinyl alcohol, polyacrylamide and polyacrylate sodium on the mechanical performances of uncalcined kaolinite based geopolymer. It was found that the decrease of micro-cracks and the increase of cross-bending strength and compressive strength had happened coupling with doping these organic polymers.

However, few researches taken GBFS as starting materials to prepare geopolymer products. The investigations on the toughening modification of GBFS based geopolymers reinforced by water soluble organic polymers were not systematical and just limited to the submicro level. And the transformations of inner structure bonding and polymerization degree in GBFS based geopolymers were rarely reported as well. Therefore, GBFS based geopolymers in this work were successfully prepared using GBFS, water glass, sodium hydroxide by alkali-activation reaction. Then the contrast experiments were performed to study systematically the influence of polyacrylic resin content on compressive strength, flexural strength and flexural toughness of modification GBFS geopolymers. The effects of incorporating polyacrylic resin on the microstructure and molecular construction of GBFS based geopolymers were additionally analysed by FTIR and MAS NMR.

2. Materials and methods

2.1. Experimental materials

The S95 grade GBFS used as the main raw aluminosilicate material for this study was derived from Wisco Huaxin Cement Co. LTD. The chemical composition of GBFS in mass percent determined by X-ray fluorescence spectrometer (XRF) is expressed in Table 1. The main mineral phase in GBFS is amorphous, including a handful of Quartz, as shown in Fig. 1. The density of GBFS is 2930 kg/m^3 and the specific surface area measured by CZB-9 Automatic Measuring Instrument is $424.1 \text{ m}^2/\text{kg}$. Sodium hydroxide (AR) of 96% purity purchased from Tianjin Chemical Reagents Company, was used. Sodium silicate solution (SiO_2 -to- Na_2O molar ratio = 3.3, 34% of Na_2SiO_3 , $\rho = 1384 \text{ kg/m}^3$) was obtained from Qingdao Best Line Chemical Technology Co. LTD. Polyacrylic resin (density = 1030 kg/m^3 , viscosity = $250\text{--}2500 \text{ mPa}$, solid content = $55.0 \pm 1\%$, pH = 8–10) was purchased from Tianjin Chemical Reagents Company. The experimental sand meets ISO standard and GB/T17671-1999.

2.2. Composition design and processing

GBFS based geopolymer mortars with and without polyacrylic resin were prepared at ambient temperature and atmospheric pressure (referring to GB/T 17671-1999 [26] and ASTM C1329-1998 [27]). Polyacrylic resin was added at dosages of 0.25, 0.5, 0.75, 1, 3 and 5 wt% of GBFS to produce the series of geopolymer compositions, listed in Table 2. The alkali activator solution with molar ratio of 0.8 was obtained from dissolving the plate-like solid sodium hydroxide in water glass and cooled to room temperature, followed by the addition of water as required. The GBFS was added to the alkali activator solution stirring for 5 min in stirrer until a homogeneous slurry formed. The mixtures, for mechanical properties testing were cast into $40 \text{ mm} \times 40 \text{ mm} \times 160 \text{ mm}$ triplicate stainless steel molds, for microtest were molded into cubic molds with dimensions of $40 \text{ mm} \times 40 \text{ mm} \times 40 \text{ mm}$, respectively. Then put these molds into curing room at $20 \text{ }^\circ\text{C}$ and relative humidity of 97% for 1 day. Hardened specimen after demolding were cured at ambient temperature for additional 27 days until the mechanical performances and microtest measured.

Table 1
Chemical composition of S95 grade GBFS (wt%).

Chemical composition	MgO	Al ₂ O ₃	SiO ₂	SO ₃	CaO	Fe ₂ O ₃	R ₂ O	LOI
Content	9.02	15.01	34.38	2.03	37.51	0.27	0.68	1.10

LOI = loss on ignition.

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