Study on the microstructure of metakaolin-based geopolymer enhanced by polyacrylate

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In order to explore the microscopic mechanism of the remarkable improvement of the organic polymer on the mechanical properties of the geopolymer, Fourier transform infrared spectroscopy, ²⁹Si nuclear magnetic resonance, scanning electron microscope and molecular imprinted polymer were used to investigate the effects of polyacrylate (PAAS) on the microstructure of the metakaolin-based geopolymer (MKG). The load-deflection curves were also tested to confirm the toughing effect. The results show that the organic polymer can modify the structure of the geopolymer at the molecular scale and submicroscopic scale. At the molecular scale, Si-O-C bonds formed in MKG after the incorporation of PAAS and the polymerization degree of [SiO₄] tetrahedra reduced resulting in the mean chain length of [SiO₄]/[AlO₄] tetrahedra change. At the submicroscopic scale, the MKG became denser after adding PAAS because PAAS could fill the cracks and capillary pores of MKG. Also, PAAS formed a film with an interconnected network structure, which interpenetrated to geopolymer. The load-deflection curves confirmed increase by 50% in the flexural toughness coefficient of the MKG with the incorporation of 0.8 wt% PAAS.

Key-words: Organic polymer, Geopolymer, Microstructure, Polymerization degree, Flexural toughness

1. Introduction

As an innovative material, geopolymer is an alternative to traditional Portland cement used in building, transport infrastructure and offshore engineering.¹) Compared to Ordinary Portland cement, the production of geopolymer needs less energy and discharges less greenhouse gas emissions.²) It also can use a variety of industrial solid wastes such as fly ash, blast furnace slag,³) etc. A solid aluminosilicate material activated by an alkali activator solution at room or slightly elevated temperature to form geopolymer, which belongs to a kind of amorphous aluminosilicate binding materials.⁴) Geopolymer has many excellent properties such as high compressive strength, low shrinkage, short setting and curing time, high acid resistance and high heat resistance,⁵) but the problems of low flexural strength and poor toughness limits its application in a wide range.⁶) It is very popular to use organic polymers for improving the toughness of cement-based materials such as cement mortar⁷) and concrete.⁸) Over the past few decades, the attention has been attracted to use organic polymers like polyacrylate (PAAS), polyacrylamide, and polyethylene glycol (PEG) to modify geopolymer. Shuzheng Zhang et al. studied the effects of several water-soluble organic polymers on mechanical and physical properties of the uncalcined-kaolinite geopolymer, and found that compared with the reference sample, compressive and flexural strength of the control samples reinforced by polyacrylic acid and PAAS increased markedly.⁹) The study of YaoJun Zhang et al. suggested that the dosage of 1% organic polymer resin could increase the flexural strength of the geopolymer from 3.8 to 7.5 MPa, and could also improve its heat resistance.¹⁰) Z. Li et al. found that the toughness of the geopolymer increased with the incorporation of N-carboxymethyl chitosan (maximum of 35%, when the chitosan dosage was 0.1 wt %).¹¹) The styrene-butadiene (SB) latex was also used to modify the mechanical properties of geopolymers, and the flexural strength of geopolymer improved 50% with the incorporation of SB latex.¹²) Brayden E. Glad et al. investigated geopolymer with hydrogel characteristics via silicone coupling agent additives and got similar results.¹³)

Since the material structure determines its performance, several studies of the microstructures of geopolymers modified by organic polymers have been executed simultaneously. Z. Li et al. suggested that the fly ash particles were coated and bridged (depolymerized) by chitosan biopolymer, which led to the formation of a relatively condensed geopolymer matrix.¹⁴) Some studies argued that PEG could lead to an enrichment of the network by Al–O–
Si bonds and the formation of H-bonds between the organic and inorganic phases.\(^{14}\) However, other studies found that there was no obvious change in the structure of the geopolymer after modifying by organic polymer.\(^{15,16}\) Obviously, the above conclusions are not univocal and it is difficult to explain the reason for a markedly toughing effect of the organic polymer on the geopolymer.

Metakaolin is a kind of aluminosilicate material used for large-scale geopolymer production and also is an environmentally friendly material comparing to Portland cement.\(^{17}\) It is generally considered that the metakaolin-based geopolymer (MKG) has a typical structure of the three-dimensional network and typical geopolymer characteristics.\(^{18}\) There are many studies concerning the formation mechanism and affecting factors of MKG.\(^{19–22}\) It is a relatively unified conclusion that the formation of MKG include two steps: (1) dissolution of a reactive silicate and aluminate monomers from the metakaoline (MK) and (2) condensation of an aluminosilicate gel.\(^{23}\) The aluminum and silica tetrahedrally interlink alternately by sharing the oxygen atoms to form the Al–O–Si or Si–O–Si structures, and then build up the structure of geopolymer.\(^{24}\) \(^{29}\)Si and \(^{27}\)Al MAS-NMR spectroscopy was used to characterize the change in polymerization degree of Al and Si. It was found that after alkali activator reaction, the coordination number of aluminum in MK matrix transformed from 8 into 4 and 5 eventually, meanwhile, the polymerization degree of Si increased.\(^{23,25}\)

Therefore, it can be speculated that the formation of bonds between aluminum, oxygen and silica atoms, the polymerization degree of Al and Si, and the characteristics of micro-structure changed after modification of by an organic polymer, which improves the toughness of MKG significantly. In order to reveal the mechanism of geopolymer modification by the organic polymer, we investigated the bonding, the polymerization degree of [SiO\(_4\)], the pore diameter distribution and micromorphology of MKG modified by PAAS by fourier transform infrared spectroscopy (FT-IR), \(^{29}\)Si nuclear magnetic resonance (\(^{29}\)Si NMR), molecular imprinted polymer (MIP) and scanning electron microscope (SEM) methods in this paper. The Load-deflection curves of MKG modified by different dosage of PAAS were tested and the flexural toughness coefficients were calculated to verify the modification effect.

2. Materials and methods

The chemical formula of MK is Al\(_2\)O\(_3\)·2SiO\(_2\), which is formed by dehydration of kaolinite at 750°C. It was produced in Maoming, China. The chemical composition of MK is shown in Table 1. The alkali activator applied for the experiment was a mixed solution of NaOH and water glass (WG, Na\(_2\)O = 7.8 wt %, SiO\(_2\) = 26.2 wt %, H\(_2\)O = 66 wt %). NaOH was granular and with a purity of 96 wt %, supplied by Sinopharm Chemical Reagent Co., LTD; the SiO\(_2\)/Na\(_2\)O ratio (by mole) and Baume degrees of WG were 3.3 and 40° respectively, supplied by Qingdao Best Line Chemical Technology Co., LTD; PAAS was used as a toughness modifying material, its chemical formula is [C\(_3\)H\(_3\)O\(_2\)Na\(_n\)]. The ISO standard sand was also used for the mortar experiment.

In this experiment, MK was used as an aluminosilicate material, the mixed solution of NaOH and WG was used as an alkali activator, to prepare MKGs. The ratio of water/powder, the mole ratio of Na\(_2\)O/SiO\(_2\) and the Na\(_2\)O content of alkali-activator were fixed at 0.5, 0.8 and 6 wt %, respectively. Then, the contents of PAAS were 0, 0.4, 0.8, and 1.2 wt % (relative to MK). The detailed experimental proportions are listed in Table 2. According to Table 2, first of all, a certain amount of WG and NaOH were weighed and dissolved in a beaker, thoroughly stirred and then cooled to room temperature; MK was mixed with sand in a stirring pot by a planetary mixer. During this process, the cold alkali activator solution and PAAS were then slowly added in the pot with the organic polymer, at permanent stirring for 4 min; further, the homogeneous geopolymer slurries were ultimately poured into a mold with the dimensions of 40 mm × 40 mm × 160 mm, and compacted for 3 min on a vibration stand; the mold was placed in a curing box at 40°C for 6 h, then cured at room temperature for 18 h, and finally the mold was removed. Immediately after that samples were put in a standard curing box at 20°C with 95% relative humidity. After demolded, the samples were cured until the mechanical properties were tested. The geopolymer pastes were applied for the microscopic performance test. The experimental procedure was the same as described above. The cube molds (40 mm × 40 mm × 40 mm) were used for the molding, and the samples were cured under the same curing conditions for 28 days. Before the microscopic tests were performed, the hydration reaction of all samples was stopped by ethanol washing, and then they were dried in a vacuum desiccator. After that, the testing procedures were executed.

A Nicolet 6700 spectrometer was used for FT-IR spectra investigations in the measurement range was over 400–4000 cm\(^{-1}\), the signal-to-noise ratio of the spectrometer used in this study is 33000/1. Powdered specimens were examined with the Bruker ASX 500 spectrometer (11.7T magnetic field) spectrometer operating at 99.36 MHz to get the information of \(^{29}\)Si NMR spectra of specimens. The microstructure of the sample was observed using a JSM

| Table 1. Composition of MK |
|---------------------------|
| Composition | SiO\(_2\) | Al\(_2\)O\(_3\) | TiO\(_2\) | Fe\(_2\)O\(_3\) | Na\(_2\)O | CaO | P\(_2\)O\(_5\) | K\(_2\)O | LOI |
| Content (wt%) | 58.26 | 37.81 | 0.31 | 0.40 | 0.36 | 0.05 | 0.50 | 0.50 | 1.71 |

| Table 2. Experimental proportions of MK-based geopolymers modified with PAAS |
|-----------------------------|
| PAAS/wt% | MK/g | Sand/g | WG/g | NaOH/g | Water/g |
|-----------------------------|
| 0 | 450 | 1350 | 423.83 | 62.69 | 170.26 |
| 0.4 | 450 | 1350 | 423.83 | 62.69 | 170.26 |
| 0.8 | 450 | 1350 | 423.83 | 62.69 | 170.26 |
| 1.2 | 450 | 1350 | 423.83 | 62.69 | 170.26 |
4800f scanning electron microscope and the X-ray energy dispersive spectrometer, manufactured in Japan, and the elemental distribution, qualitative and quantitative analyses of the microscopic component analysis were carried out. The pore structure of geopolymer was determined by means of MIP using auto-pore IV 9500 produced from Micromeritics Instrument Corporation, which can generate a maximum pressure of 228 MPa and can evaluate a pore diameter measuring range of ~1000 μm. The flexural toughness of samples (40 mm × 40 mm × 160 mm) was measured according to the Japanese concrete standard JSCE-SF4 (JSCE 1984). A universal servo (Instron 1394 instrument model) was used to test the flexural toughness of the geopolymers modified with PAAS, and the loading rate was set as 0.05 mm/min. The relative loaded strength and deflection values were recorded.

3. Results and discussion

3.1 FT-IR analysis

Figure 1 shows FT-IR results of MK and MKGs modified with different dosage of PAAS (0, 0.4, 0.8, 1.2 wt %). MK showed some peaks centered at 465, 800 and 1086 cm⁻¹, corresponding to the bending vibration of Si–O–Si, symmetric stretching vibration of Si–O–Si, symmetric vibration of Si(Al)–O. After geopolymerization, the typical peak at 1086 cm⁻¹ in MK shifted to lower frequencies, which indicated that new products with different chemical environment had been formed from MK. It was noted that new absorption peaks around 1180 cm⁻¹, corresponding to the stretching vibration of Si–O–C, and appearing in the IR spectra of MKG added with PAAS, due to the bonding reaction between the –COO⁻ in PAAS and –OH of [SiO₄] tetrahedra of MKG, just as Eq. (1). According to Fig. 1, the peak at 1010 cm⁻¹ shifted to higher frequencies (i.e., 1037, 1039 and 1046 cm⁻¹) as the dosage of PAAS increased from 0 to 1.2 wt %, and the peak at 447 cm⁻¹ did show the same trend. It means that the chemical environment of Si and Al in MKG changed after modification with PAAS. From these changes, it can be drawn that the chemical reaction between carboxyl and Si–OH took place. The aluminosilicate tri-dimensional network structure formed through the links between the newly formed bonds Si–O–C and the already existing Si–O–Si (Al–O–Si). The chemical bonds in PAAS have a chain structure and flexible to bend, rotate and stretch, while the bonds of Al–O and Si–O in MKG are rigid, containing highly energetic and strongly directed. The properties of chemical bonds in MKG were modified by adding PAAS, and the formed Si–O–C bonds took part in the geopolymerization, and improved the structure of MKG at the molecular scale. This may be one main reason for remarkable improvement of MKG toughness modified by PAAS.

![Figure 1. FT-IR of MK, MKG, and MKG modified with PAAS, 28d.](image)

3.2 ²⁹Si NMR analysis

The ²⁹Si NMR spectra of MKG modified with 0, 0.4, 0.8, and 1.2 wt % of PAAS at 28 days are shown in Fig. 2, and Table 3 are the corresponding results of deconvolution. The MCL were determined using the formula from Ref. In ²⁹Si NMR spectra, the polymerization degree of [SiO₄] can be indicated by using Qⁿ(mAl). n represents the quantity of bridge oxygen atoms among [SiO₄], m represents the quantity of Al atoms existing around [SiO₄]. Q⁰, Q¹, Q², Q³, and Q⁴ indicate the isolated [SiO₄] group, the chain-end group, the chain-middle group, the layer group, and the tri-dimensional network group. It was found that the density of Q³ species decreased and densities of Q⁰, Q¹, and Q² species increased with the incorporation of PAAS, indicating that the polymerization degree of the [SiO₄] tetrahedral decreased. This agrees with the results of FT-IR. Moreover, it reduced with the dosage of PAAS from 0 to 0.8 wt % and there was no significant change from 0.8 to 1.2 wt %, following the results of the MCL of [SiO₄]/[AlO₄]. As the contents of PAAS vary from 0.4 to 1.2 via 0.8 wt %, the growth rates of MCL vary from 14.8 to 15.1% via 16.8%. It can be explained that the carboxyl of PAAS react with the hydroxyl of MKG to form C–O–Si (revealed by FT-IR), which took part in forming the network of MKG. Thus, the number of chain structure increases. This may explain the improvement of the flexural toughness of MKG with doping PAAS.

3.3 SEM analysis

Figure 3 shows the micromorphology of MKG modified with PAAS (0.8 wt %) and blank sample (without PAAS) after curing for 28 days. There are some micro-cracks on the surface of the MKG without PAAS [Fig. 3(a)], while the number of micro cracks decreased and the structure became solid and compact after the MKG being modified by PAAS [Fig. 3(b)], which is consistent with the results of. This is because PAAS can fill micro-cracks and large capillary pores of MKG. According to the results of FT-IR
and $^{29}$Si NMR, the PAAS can react with the MKG during geopolymerization of MK to form a microstructure which is composed of the continuous matrix and the organic polymer embedded in it.\(^{36}\) Although some ions, those released at the hydration of cementitious materials, could affect the formation of the continuous polymer network structure,\(^{37}\) it can be observed that PAAS forms a polymer film interspersed into the MKG in MKG modified with 0.8 wt% of PAAS [Fig. 3(c)]. In order to further verify the chemical composition of the film-like substances in Fig. 3(c), the energy dispersive X-ray spectrometry (EDS) analysis was done at 2 characteristic spots, and the results are as shown in Fig. 3(d). The content of carbon at Spot 1 is much higher than at Spot 2, while contents of Si and Al are much less than at Spot 2, that may confirm that the substance in area 1 is PAAS, and the substance in area 2 is MKG. Therefore, EDS analyses at Spot 1 and 2 proved that the polymer forms films which can intersperse into the geopolymer. This special structure can improve the toughness of MKG because the polymer films can increase interface adhesion and can absorb the plastic deformation energy to some extent.

### 3.4 Pore structure

The pore diameter distribution can be used to indicate the structure of geopolymer because it may characterize the relationship between microstructure and mechanical performances of materials.\(^{30}\) The variation of the pore diameter distribution of MKG with different dosage of PAAS (0, 0.4, 0.8, 1.2 wt%) is shown in Fig. 4. Figure 4 displays that there are many large capillary pores with diameters of 100 nm in MKG without PAAS, which are harmful to performances of materials.\(^{31}\) As the dosage of PAAS increased from 0 to 0.4 wt%, the pore diameter in MKG reduced remarkably. The same conclusion was derived in.\(^{30},^{32}\) The reason is that PAAS can promote the formation of more reaction products (especially some small size products, just like Q0, Q1, Q2 in $^{29}$Si NMR analysis), and these products and PAAS can fill into some capillary and make the geopolymer denser. It could also be found that the pore diameter reduced with the increase of the PAAS proportion. When the addition of PAAS increased to 1.2 wt%, the pores size in geopolymer was mainly less than 10 nm, which being good for mechanical characteristics.

### Table 3. Deconvolution for $^{29}$Si NMR of MKG reinforced by PAAS

| Content of PAAS (wt%) | Relative strength of Q'(mAl) (I/%) | MCL |
|----------------------|-----------------------------------|-----|
|                      | n 0 1 2 2 3 3                      |     |
| 0                    | 6.28 22.21 8.50 15.92 37.30 4.65 4.58 |
| 0.4                  | 9.54 22.02 11.85 18.08 24.83 6.25 5.26 |
| 0.8                  | 12.64 23.07 11.24 21.76 25.81 4.26 5.35 |
| 1.2                  | 10.54 24.01 11.80 21.52 24.40 9.27 5.27 |

Fig. 2. $^{29}$Si NMR spectra of MKG reinforced by PAAS, 28d.
3.5 Effect of PAAS on the microstructure of MKG

The formation of microstructure of MKG includes dissolution, nucleation, gelation and polymerization. The aluminosilicate material generates silanol Si–OH groups and isolation of ortho-sialate molecules (as shown in Fig. 5), which is the basic unit in the formation of geopolymer, through the processes of dissolution, nucleation and gelation. It is at this stage that PAAS begins to act on the microstructure of MKG. The dehydration condensation reaction of the carboxyl functional group in the PAAS with the hydroxy of the silanol Si–OH group forms Si–O–C bonds in the structure of geopolymer (just like the results of FT-IR in Fig. 1), which is shown in Fig. 5, and PAAS participates in the formation of the structure of geopolymer. The above basic units carrying the PAAS are polycondensed, and the ortho-sialato-disiloxo cyclic structure is gradually formed in the presence of water glass in the alkali activator solution, just as shown in Fig. 6. Finally, the ortho-sialato-disiloxo cyclic structure undergoes a further condensation reaction to form a geopolymer structure of PAAS- poly (sialate-disiloxo) framework (Fig. 7).

In addition to participating in the construction of microstructures of MKG in molecular scale, PAAS also has a modification effect on its mesoscopic structure. Figure 8 shows a mesoscopic structures of MKG [Fig. 8(a)] and MKG modified by PAAS [Fig. 8(b)] based on the results of SEM-EDS and MIP. The organic polymer film (PAAS film) interpenetrates into the geopolymer, and form a cross-linked network (just like the results of SEM-EDS in Fig. 3). The PAAS fills into the capillary pores and the compactness of geopolymer increases, which is according to the results of MIP in Fig. 4.

Therefore, it can be said that the PAAS, which is as a kind of organic polymer, has a significant influence on the formation of structure of metakaolin based geopolymer both at the molecular and mesoscopic levels, and can also
Fig. 5. PAAS participates in the gelation of MKG.

Fig. 6. Formation of ortho-sialato-disiloxo cyclic structure.

Fig. 7. Formation of MKG modified by PAAS structure.
affect the mechanical properties (especially flexural toughness) of this materials.

3.6 Load-deflection curves

Load-deflection curves can characterize the ability to absorb energy of materials from load to fracture. The load limit value correlates with the flexural strength, the deflection limit characterizes the ductility of materials, and the flexural toughness value is calculated according to formula (1). Figure 9 indicates the load-deflection curves of MKG mortars with different dosage of PAAS (0, 0.4, 0.8 and 1.2 wt %). The flexural toughness coefficients were listed in Table 4.

\[ \sigma = \frac{T_b}{\delta_{tb}} \cdot \frac{l}{bh^2} \]  

Where \( \sigma \) is the flexural toughness (MPa); \( T_b \) is the area surrounded by curves and abscissas (N·mm); \( \delta_{tb} \) is a fixed value, which is equal to the span length divided by 150 (mm); \( l, b, h \) are the span length (mm), the width (mm) and the height (mm) of the sample, respectively.

Figure 9 and Table 4 indicated that the load limit increased from 3710 to 4172 N with the content of PAAS increased from 0 to 0.8 wt %, and then reduced at PAAS content above 0.8 wt%, which was consistent with other studies conclusions. Compared with the black sample (MKG mortar without PAAS), the deflection limits of MKG with 0.4 and 0.8 wt % PAAS increased substantially, which meant the ductility of MKG was improved. It is noted that the flexural toughness coefficients of MKG mortars reinforced by 0.4 wt % PAAS and 0.8 wt % increased by 37.1 and 50%. Combining with the results of microstructure analysis, it can be drawn that the organic polymer can improve the toughness of geopolymer due to a reduction in the polymerization degrees, Si–O–C bond formation, and better pore diameter distribution.

4. Conclusions

In this work, the bonding, the polymerization degree of [SiO₄] tetrahedron, the micromorphology and the pore diameter distribution of MKG modified by different dosages of PAAS were investigated by FT-IR, ²⁹Si NMR, SEM (EDS) and MIP to explore the influence of the organic polymer on the toughness of the geopolymer and the load-deflection curves were also tested to confirm the toughening effect. The main conclusion of this study can be summarized as follows:

(1) The bonding reaction between the –COO⁻ in PAAS and –OH around [SiO₄] or [AlO₄] tetrahedron takes place, and the Si–O–C bonds forms after adding PAAS into MKG. Therefore, PAAS links to MKG through Si–O–C bonds at a molecular scale and constructs an alumino-silicate 3-dimensional network structure with MKG together. Thus, the polymerization degree of [SiO₄] reduces as the content of PAAS increasing.

(2) The organic polymer fills cracks and capillary pores in geopolymer and made it more compact. SEM and EDS showed that PAAS can form a film interpenetrating
with the geopolymer, which improves the toughness of geopolymer at a submicroscopic scale.

(3) The organic polymer changes the structure of the geopolymer at the molecular scale and submicroscopic scales, which both improves the flexural toughness of the geopolymer. The flexural toughness of MKG initially increases with the addition of PAAS, and then reduced at PAAS content over 0.8 wt.

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Compliance with the ethical standards Conflict of interest All the authors declare that they have no conflict of interest.

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