EFFECT OF SILANE MODIFIED POLYCARBOXYLIC SUPERPLASTICIZER ON FLUIDITY AND MECHANICAL PROPERTIES OF CEMENT MORTAR

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ABSTRACT

The performance of concrete slurry is a very important factor in the construction engineering. In this paper, based on silane modification, the molecular structure of polycarboxylic superplasticizer was optimized. The siloxane group with reactivity with cement-based materials was introduced, so as to improve the water reducing performance of water reducing agent. The molecular structure of the new superplasticizer was characterized by FIIR, ^{1}HNMR and GPC. The adsorption of the water-reducing agent on the surface of cement particles was determined by TOC. The results show that superplasticizer with silane can obviously improved the working performance of the mortar, but also had obvious fluidity retention ability. Because the introduction of silane significantly increased the adsorption amount of water reducing agent molecules in cement particles. At the same time, the introduction of silane decreased the mechanical properties of hardened cement mortars in 1d, because it delayed hydration. However, there was no negative effect on the mechanical properties after 3d, and even the flexural strength of 28d was increased by 13%-37%.

KEYWORDS: *polycarboxylate superplasticizer (PCE); silane modification; molecular structure; Fluidity; mechanical strength*

1. Introduction

Polycarboxylic acid superplasticizer, as the most widely used superplasticizer, is a polymer with amphiphilic properties. It is usually synthesized by copolymerization of polyoxyethylene ether macromonomer with terminal double bond and unsaturated carboxylic acid small monomer under the action of initiator. It has good hydrophilicity and good compatibility with cement-based materials. It is generally believed that there are two mechanisms of water reduction[1]. On the one hand, the carboxyl functional groups in the polycarboxylic acid water-reducing agent molecules are adsorbed on the surface of cement particles through the electrostatic action generated by themselves or complexing cations, forming electrostatic repulsion, preventing cement particles from gathering, so as to improve the water-reducing performance. On the other hand, it has a comb structure formed by polyether macromonomer, which can produce steric hindrance effect. Through this mechanism, it can be found that the water reducing performance of polycarboxylic acid water reducer is closely related to its adsorption on the surface of cement particles. Therefore, if a group can be introduced into the polycarboxylic acid water-reducing agent molecules that can interact with cement particles better than carboxylic acid groups, it is possible to further improve its water-reducing performance.

Silane coupling agent has been widely used in organic and inorganic composites in recent years. It has the ability to interact with both organic and inorganic materials. Therefore, this study designed and prepared a silane modified polycarboxylic acid water reducer. Acrylic acid, HPEG and silane coupling agent KH-570 were selected as synthetic monomers, and the water reducing agent was prepared by free radical copolymerization. The molecular structure was characterized by FIIR, 1HNMR, GPC and other characterization methods, and the quantitative relationship between molecular structure and water reduction properties was established. Then TOC was used to characterize the adsorption capacity of the water reducing agent on the surface of cement particles, and the mechanism of improving the water reducing performance was explained. All of these has a significant instruction for the design of high performance water reducing agent.

2. Materials and Experiments

2.1 Materials Ordinary Portland cement P.O. 42.5 with a surface area of 360 m2/kg was used to prepare the cement pastes and mortars. River sand with particle sizes of 0.16-4.75 mm were used as fine aggregate to prepare the overlay mortar and substrate. Steel fiber with a length of 13 mm was used to reinforce the substrate. Three monomers (methacryloyloxypropyltrimethoxysilane (KH570), isobutylene polyvinyl ether (HPEG) and acrylic acid) were chosen in this study to synthesize the admixture. Their physical properties were listed in Table 1.

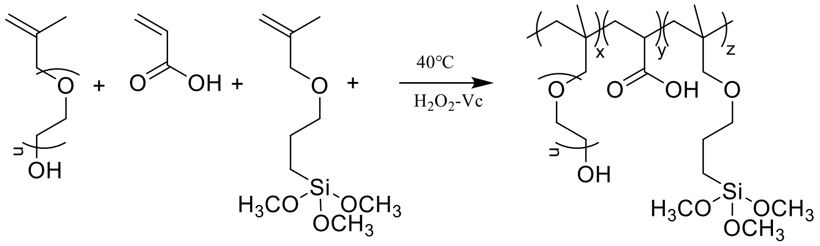
Table 1. Physical properties of three monomers

	S (KH570)	HPEG	AA
Color	Colorless or yellowish	Colorless or yellowish	Colorless
Molecular weight(g/mole)	248.35	1200	72.06
Boiling point	255℃	400℃	139℃
Purity	≥97%	≥90%	≥97%

Note: S refers to methacryloyloxypropyltrimethoxysilane (KH570); AA refers to acrylic acid; HPEG refers to isobutylene polyvinyl ether.

2.2 Synthesis of the silane-modified polycarboxylate superplasticizer

The silane-modified polycarboxylate superplasticizer (S/AA-HPEG) was synthesized through radical copolymerization with methacryloyloxypropyltrimethoxysilane (S), isobutylene polyvinyl ether (HPEG) and acrylic acid (AA). H2O2 and ascorbic acid were used as the oxidants and reductants, while the mercaptoacetic acid was used as a chain transfer agent. The content of solid phases in all mixtures were controlled to be 40%. The synthesis temperature was set to 40℃ by using Oil bath. The corresponding chemical structure of the monomers and obtained polymer is given in Figure 1.



(HPEG) (AA) (S) (S/AA-HPEG)

Figure 1. The molecular formula of synthetic reaction

2.3 Characterization of the silane-modified polycarboxylate superplasticizer

A Fourier transform infrared spectrometer (FTIR, Brooker, Germany) was used to characterize the change of the functional groups, so as to determine whether the free radical polymerization reaction took place successfully. ^{1}H Nuclear Magnetic Resonance (^{1}H NMR) was used to determine the overall reaction degrees of C=C bonds of all monomers. A gel permeation chromatography instrument (GPC Max VE2001, Malvin, UK) was used to determine the average relative molecular weight (Mn) and molecular weight distribution (PDI, Mw / Mn) of the S/AA-HPEG. Meanwhile，It is conceivable that only the free S/AA-HPEG can migrate into the substrate and enhance the interfacial bonding strength, while the S/AA-HPEG adsorbed on the surfaces of cement acts as water reducer. Organic carbon analyzer (TOC-L, Japan) was used to measure the change of organic carbon concentration in pore solution before and after adsorption, so as to calculate the adsorption amount of S/AA-HPEG.

2.4 Effect of S/AA-HPEG on the fluidity of cement mortars

Fluidity test was conducted to evaluate the water reduction efficiency of the synthesized copolymers in cement mortars . The mixtures of mortar with different chemical admixture S/AA-HPEG

(P1, P2, P3) and ordinary commercial PCE (Reference) were showed in Table 2. The w/c ratio was 0.3 and the binder/sand ratio was 1:2. The dosage of S/AA-HPEG used was 0.8% (by weight of cement). After preparation, the mortars were poured into a conical mold with the dimension of top diameter of 70 mm, bottom diameter of 100 mm, and height of 60 mm which was installed on a vibrating table. Then the mold was quickly lifted and the vibrating table vibrated 25 times. The spread diameter of cement mortar was recorded as the average of two perpendicularly crossing diameters and was used to refer the fluidity of cement mortar. In addition, the fluidity retention ability of different chemical additives were determined by the variation of fluidity of the mortar over time.

Table 2. Mix proportions of cement mortars with S/AA-HPEG (P1, P2, P3) and ordinary commercial PCE

Series	cement	sand	water	S/AA_HPEG	Commercial PCE
Cement mortar with S/AA-HPEG	1	2	0.3	0.008	-
Cement mortar with commercial PCE	1	2	0.3	-	0.01

2.5 Effect of S/AA-HPEG on cement hydration and mechanical properties of the new mortars

The mixtures of mortar with different chemical admixture S/AA-HPEG (P1, P2, P3) and ordinary commercial PCE (Reference) were the same as 2.4. For comparison, ordinary commercial PCE with a dosage of 1.0% (by weight of cement) was used to prepare the referenced mortar. Before the mixing of mortar, the chemical admixtures were mixed with water firstly, like the use of ordinary polycarboxylate superplasticizer. The mortar was cast into a cuboid of 40*40*160mm. The specimens were demolded after being curing for 24 h, and then subsequently were cured at 20 ± 2℃/RH>95%. Compressive and flexural strengths were tested at the ages of 1 d, 3 d, 7 d and 28 d. Six parallel specimens were prepared for each test.

3. Results and Discussion

3.1 Molecular structure of the S/AA-HPEG

Figure 2 shows FTIR spectra of the mixture of materials before and after the synthesis reactions for S/AA-HPEG (P1, P2 and P3). The peak at 1100 cm-1, 1727 cm-1 and 951 cm-1 referred to the stretching vibration of C-O bond, C=O bond of carboxyl and Si-O bond respectively[2], which presented the three monomers. The peak at 1638 cm-1 corresponded to the bending vibration of the C=C bond[3]. It can be seen that compared with that of the raw material mixture before reactions, the intensity of the absorption peak at 1638 cm-1 decreased significantly after the copolymerization reactions to form S/AA-HPEG. This indicates that polymerization took place successfully. Note that because of the existence of acyl groups, there were still absorption peak at 1638 cm-1. Moreover, the peaks at 1100 cm-1, 951 cm-1 and 1727 cm-1 still existed after purification, which indicates that all of the three monomers participated in the copolymerization successfully.

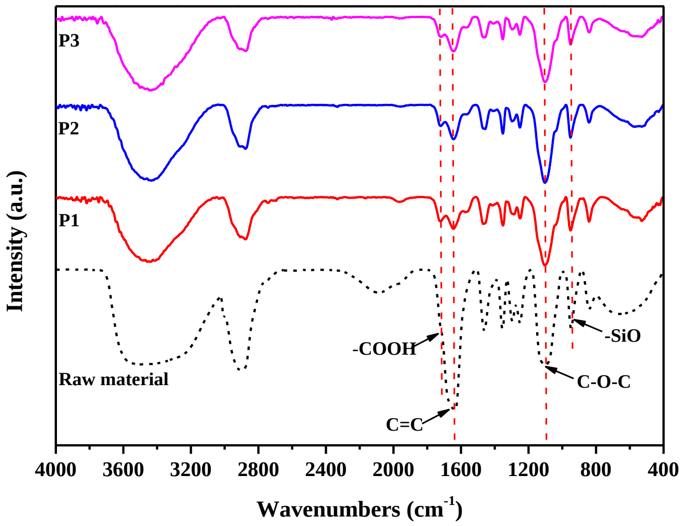


Figure 2. FTIR spectra of S/AA-HPEG and the raw materials

According to the results of 1H NMR and GPC tests, the reaction degree of each monomer, the molecular weight of the obtained copolymers and the molar ratios of their functional groups were determined and given in Table 3. It can be seen that the overall reaction rate of each sample was more than 70%, which means that the free radical polymerization reaction occurred successfully. In general, the overall reaction degrees of the reactants in the mixtures with silane were lower than that of the mixture without silane. As the silane dosage increased, the overall reaction degree of the reactants first decreased and then increased. The reaction degrees of HPEG and AA showed the same trend of the overall reaction degree, while the reaction degrees of S kept increasing from 15.72% to 56.17%. Moreover, as silane was incorporated to the polymer, the molar ratio of AA functional groups in the polymer increased. Among the three products with siloxane, P2 had a relatively higher molar ratio of AA groups and a smaller molecular weight.

Table 3. Synthesis mole ratios and reaction degrees of the monomers used, and the characteristics of molecular structures of copolymers

Note: S refers to methacryloyloxypropyltrimethoxysilane; AA refers to acrylic acid; HPEG refers to isobutylene polyvinyl ether.

3.2 Adsorption of S/AA-HPEG on cement grains in fresh paste and its influence on the fluidity of mortar

The adsorption isotherms of S/AA-HPEG on cement grains in fresh paste are shown in Figure 3. Obvious differences appeared in the adsorption amount of the three S/AA-HPEG. It can be seen that as the siloxane content in the synthesized S/AA-HPEG increased, the adsorption amount of S/AA-HPEG on cement grains increased. It is well known that carboxyl can lead to the adsorption of copolymer on cement surface due to electrostatic action [4].As discussed above, the incorporation of silane in the superplasticizer increased its AA content (see Table 5), which can lead to a higher adsorption possibility. Moreover, after the hydrolysis of silane, the superplasticizer can form chemical bond with cement grains [1]. As present in Table 4, the S/HPEG molar ratio in the superplasticizers increased from 0.03 for P1 to 0.37 for P3. Correspondingly, the adsorption amount of the superplasticizers increased remarkably at the same blending dosage. Moreover, P3 with a highest S/HPEG molar ratio showed an apparent increase in adsorption amount as the blending dosage of this superplasticizer increased from 0.4% to 0.8% by weight of cement.

It is well known that the adsorption of superplasticizer on cement grains influences its water reduction efficiency significantly [5]. As seen in Table 6, the S/AA-HPEG had better effect of water reduction than commercial PCE and this effect was enhanced with the increase of the proportion of silane. In addition, the results also showed that using S/AA-HPEG could lead to a better fluidity retention ability compared to the reference. At 90 min, the losses of fluidity of the samples with S/AA-HPEG were less than 11%, while that of reference sample was more than 18%.

Table 4. The fluidity and its variation over time of cement mortars with S/AA-HPEG or commercial PCE

Time	Fluidity of cement mortars with different admixtures (mm)			
	Commercial PCE	P1	P2	P3
0 min	229 ± 3	233 ± 1	236 ± 1	242 ± 4
15 min	227 ± 4	230 ± 3	232 ± 1	236 ± 1
30 min	219 ± 2	228 ± 0	227 ± 2	235 ± 3
60 min	208 ± 3	225 ± 2	221 ± 0	230 ± 3
90 min	186 ± 3	223 ± 2	211 ± 3	226 ± 2

Note: The dosage of P1, P2 and P3 used was 0.8% by weight of cement, while the dosage of commercial PCE used was 1.0% by weight of cement.

	Molar ratio of monomers (HPEG:AA:S)	Reaction degree				Molar ratio of functional groups in polymers (HPEG:AA:S)	molecular weigh (Mn)	MWD (Mw/Mn)
		overall %	HPEG %	AA %	S %			
P0	1：1.28：0.00	80.36	55.71	99.52	-	1：2.31：0.00	-	-
P1	1：1.28：0.09	73.75	46.73	98.81	15.72	1：2.70：0.03	77871	2.13
P2	1：1.28：0.15	70.12	41.60	97.22	28.03	1：2.99：0.10	42276	1.86
P3	1：1.28：0.29	72.61	44.48	98.35	56.17	1：2.82：0.37	48288	2.70

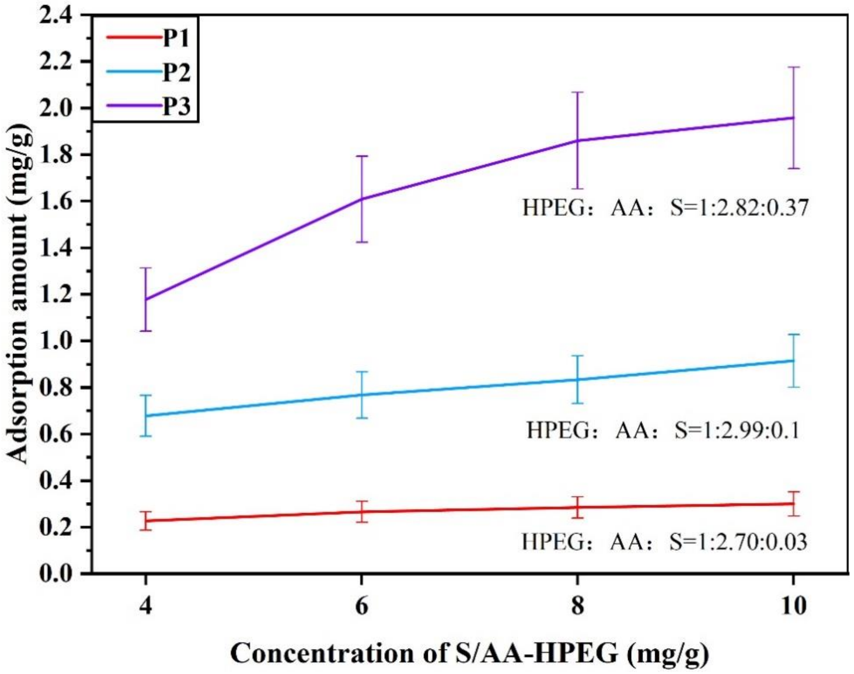
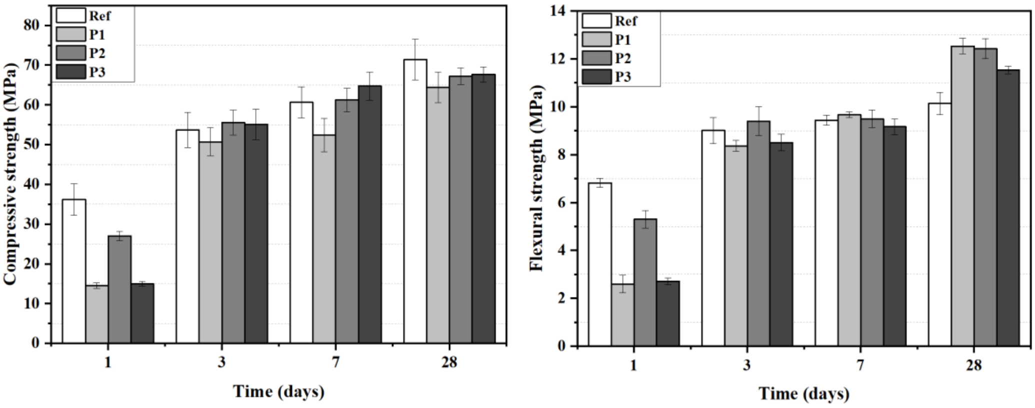


Figure 3. Adsorption of S/AA-HPEG on the cement in fresh paste

3.3 Mechanical properties of cement mortar after adding S/AA-HPEG

Figure 4 shows the compressive and flexural strengths of mortar with the three S/AA-HPEG or commercial PCE. It can be seen that the 1-day compressive and flexural strengths of the mortars with different S/AA-HPEG were lower than that of the mortar with commercial polycarboxylate superplasticizer as the reference. Among the three synthesized superplasticizers, this negative effect by

S/AA-HPEG P2 is smaller than that by the other two. Moreover, at later ages, i.e. 3, 7 and 28 days, the negative effect of the synthesized superplasticizers was hardly seen.



(a) compressive strength (b) Flexural strength

Figure 4. Compressive strength and flexural strength of cement mortars at different ages with S/AA-HPEG or commercial PCE (as reference): (a) flexural strength and (b) compressive strength.

4. Conclusions

superplasticizers with better water reduction and fluidity retention were developed by using silane to modify polycarboxylate superplasticizer. The effects of silane content on the molecular structure of the superplasticizer and its performances were systematically studied. Based on experiments, the following conclusions can be drawn:

(1)Regarding the synthesis of the silane modified superplasticizer, as the silane dosage increased from 0% to 11% by mole, the overall reaction degree of the monomers first decreased and then increased, but was still lower than that without adding silane. Moreover, the incorporation of silane increased the molar ratio of AA in the polymer.

(2)The silane modified superplasticizer exhibited better water reduction efficiency and fluidity retention ability than commercial polycarboxylate superplasticizer. This improvement was enhanced with the increase of silane percentage. The existence of siloxane groups can increase the adsorption amount and stability of the superplasticizer on cement grains.

(3)This novel superplasticizer decreased the mechanical properties of hardened cement mortars in 1d, because it delayed hydration. However, there was no negative effect on the mechanical properties after 3d, and even the flexural strength of 28d was increased by 13%-37%.

Acknowledgements

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References

[1] J. Zhou, G. Ye, K.V. Breugel, Cement hydration and microstructure in concrete repairs with cementitious repair materials, Construction Building Materials, 112 (2016) 765-772.

[2] J.A. Larbi, J.M.J.M. Bijen, Orientation of calcium hydroxide at the portland cement paste-aggregate interface in mortars in the presence of silica fume: A contribution, Cement and Concrete Research, 20 (1990) 461-470.

[3] Y. Li, W. Bai, T. Shi, A study of the bonding performance of magnesium phosphate cement on mortar and concrete, Construction and Building Materials, 142 (2017) 459-468.

[4] A.D. Espeche, J. León, Estimation of bond strength envelopes for old-to-new concrete interfaces based on a cylinder splitting test, Construction and Building Materials, 25 (2011) 1222-1235.

[5] A. Stewart, B. Schlosser, E.P. Douglas, Surface Modification of Cured Cement Pastes by Silane Coupling Agents, ACS Applied Materials & Interfaces, 5 (2013) 1218-1225.