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Influence of Polycarboxylate Superplasticizer on Rheological Behavior in Cement Paste

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Abstract: Molecular structures of polycarboxylate (PCE) superplasticizer significantly affect the rheological properties of cement paste. Consequently, we employed self-synthesized PCE copolymers with different carboxylic densities to investigate their influence on the rheological behavior of cement paste. Three typical rheological models were applied to analyze the rheological properties, including Power-law model, Bingham model as well as Herschel-Buikley model. In addition, the thixotropical performances of cement paste in the presence of PCE with different carboxylic densities were investigated. The results show that the carboxylic density of PCE greatly influences the dispersing performance of PCE superplasticizers. As carboxylic density increases, the dispersing capability of PCE improves, and P(PEG1-AA6) possesses the strongest dispersing capability, the initial fluidity and 1 h fluidity of cement paste are both the highest, and cement paste has the lowest viscosity and the smallest hysteresis loop.

Key words: polycarboxylate superplasticizer; carboxylic density; fluidity; rheology; thixotropy

1 Introduction

Nowadays, polycarboxylate (PCE) superplasticizers are used extensively for the production of high performance concrete[1-3]. It is widely accepted that the rheological performance of fresh concrete is improved through the dispersion of agglomerated cement and hydrated cement particles[4,5]. When added into cement paste, PCE polymers adsorb onto the cement particle surface and disperse cement particles through steric hindrance effects[2]. The dispersing effects of PCE polymers significantly depend on the molecular structures[5]. Extensive research has been carried out on the relationship between the molecular structure and the dispersing properties of PCE superplasticizer. PCEs with long side chains have stronger dispersing capability. PCEs superplasticizers with higher molecular weight, lower side chain density and shorter side chains present higher dispersing performance[6,7]. Puertas *et al* put forward that the carboxylic density makes a great effect on the dispersing performance of PCE superplasticizers[8,9]. Overall, the relationship between PCE molecular structures and the dispersing performance is still a vital concern.

Moreover, the addition of superplasticizers undoubtedly changes the rheological properties of cement paste[5]. Krieger-Dougherty equation was used to reflect the quantitative relationship between the viscosity and the concentration of Portland cement pastes. Yodel model was uded to characterize the rheological behaviors of fresh mortar and concrete, and this method can accurately predict the dependence of yield stress on the volume fraction of solids[3,10,11]. This study mainly focuses on the rheological properties of cement paste in function of PCEs with different carboxylic densities. Self-synthesized PCE copolymers with variation of carboxylic density were applied to investigate the effects of charge density on the rheological behavior of cement paste. Three rheological models were employed to fit the relationship between the shear rate and shear stress of cement paste. And the thixotropic performance of cement paste was also studied. This research is expected to bring new insights about the influence of the molecular structure of PCE superplasticizers on the rheological properties of cement paste and to lay a

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Table 1 Chemical composition and mineral composition of cement/wt%

Chemical composition								Mineral composition			
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O_{eq}	f-CaO	C_3S	C_3A	C_2S	C_4AF
21.84	4.27	2.65	63.64	2.16	2.43	0.56	0.54	53.45	5.98	23.96	8.09

Table 2 Structural characteristics of synthesized polymers

Sample No.	Initial/mol%		^{1}H NMR	Acid-based titration	M_w/kDa	PDI M_w/M_n
	HPEG	AA	PEG/mol%	COOH/mol%		
P(PEG1-AA2)	33.33	66.67	35	68	84	1.8
P(PEG1-AA4)	20.00	50.00	21	53	89	1.5
P(PEG1-AA6)	14.29	85.71	17	87	74	1.3
P(PEG1-AA8)	11.11	88.89	10	90	86	1.7

theoretical foundation for the development of higher performance PCE superplasticizers.

2 Experimental

2.1 Materials

Ordinary Portland cement classified by 42.5R was used in this research. Chemical composition and mineral composition of the cement are shown in Table 1. The contents of oxides were measured through X-ray fluorescence. The content of *f*-CaO was analyzed by the Franke method. The mineral phases were investigated by the Bogue method.

Analytical grade of chemicals, acrylic acid (AA, 99%, Acros, stabilized with 250 ppm of methylethylhydroquinone), ammonium persulfate (APS), 3-mercaptopropionic acid (MPA) and methyl allyl polyethenoxy ether (HPEG, Mn 1 600 g·mol^{-1}) were used without further purification.

2.2 Synthesis and characterization of PCE polymers

In the synthetic reaction of a PCE copolymer, the molar ratios of AA to HPEG were controlled to 2.0, 4.0, 6.0, and 8.0. APS was used as initiator and MPA was used as chain transfer. The contents of APS and MPA were respectively 0.5wt% and 0.02wt% of the amount of monomers. The synthesis procedure is listed as follows. Firstly, certain weight of HPEG was mixed with 40 g deionized water in a glass flask, and stirred by a mixer. The flask was then immersed in a water bath thermostated at 60 ℃ and the reaction was maintained for 3 h in nitrogen. During the period, AA, APS and MPA were respectively injected into the mixture through micro-syringes respectively. After reaction, NaOH solution was applied to neutralize the solution to pH=7. To remove un-reacted monomers from the samples, a cellulose ester semipermeable membrane with nominal molecular weight cut-off of 7000 Da was used to purify the co-polymers. The synthesized polymers were introduced into the dialysis bag. Then the sealed dialysis bags were put into a container filled with deionized water for 7 days.

The weight-average molar masses (M_w) and their distribution (PDI=M_w/M_n, the polydispersity index) were measured by size exclusion chromatography (Viscotek GPCmax) coupled with three detectors (light scattering, viscosity and refractive index). The measurements were performed at 35℃ using a 0.5 mol·L^{-1} $NaNO_3$ aqueous solution (pH adjusted to 12.6 with NaOH) as eluent. Polyethylene oxide (M_w=21.917 kg·mol^{-1}, PDI=1.03 and Intrinsic Viscosity=0.384) was used as the reference.

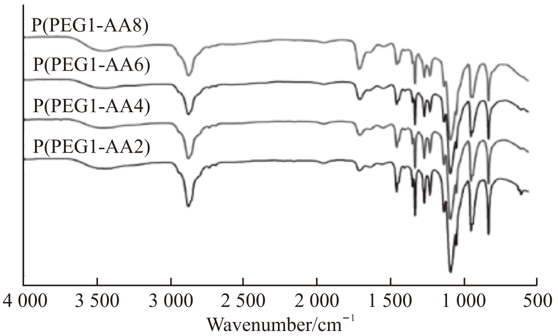

Fig.1 IR spectra of self-synthesized PCE superplasticizer

FTIR (Fig.1 and Table 2) structural analysis suggests that the PCE copolymer comprises molecular chains consisting primarily of carboxylic and ether groups.

2.3 Rheological property test

Cement paste with a *w/c* ratio of 0.29 was prepared. The concentration of PCE was 0.15% by the weight of cement (in solid content).

The fluidity of cement paste was measured using a mini-slump cone (with a height of 60 mm, upper diameter of 36 mm and a bottom diameter of 60 mm). The processes were performed according to the Chinese standard GB/T 8077-2000.

For the rheology experiments, a Bohlin C-VOR shear rheometer equipped with a Vane geometry was used. The Vane tool diameter was 25 mm, the outer cup diameter was 50 mm whereas its depth was 60 mm. The cup of the rheometer was filled with the tested cement paste and the measurement sequence was started. The measurements were performed 15 min after mixing by preshearing the paste at a shear rate of 100 s^{-1} for 1 min. A decreasing shear rate was then directly applied from 100 s^{-1} to 1 s^{-1} (with a logarithmic distribution of shear rates) during 200 s. The yield stress was calculated by fitting the rheogram data according to the Hershey-Buckley model. The detection limit was estimated to 1 Pa.

3 Results and discussion

3.1 Fluidity of cement paste

The dispersing capability of PCE superplasticizers as well as the retarding effects may be significantly attributed to the content of carboxylic groups. This study investigated the initial fluidity and the 1h fluidity of cement paste containing PCE with different carboxylic densities. The fluidity measurement results are shown in Fig.2. From Fig.2, we can see that when the molar ratio of acrylic acid to HPEG is 2, the dispersing capability of PCE is quite weak. However, as the molar ratio of acrylic acid to TPEG increases, the dispersing capability of PCE improves, and P(PEG1-AA6) possesses the strongest dispersing properties, for the initial fluidity and 1 h fluidity of cement paste are both the highest.

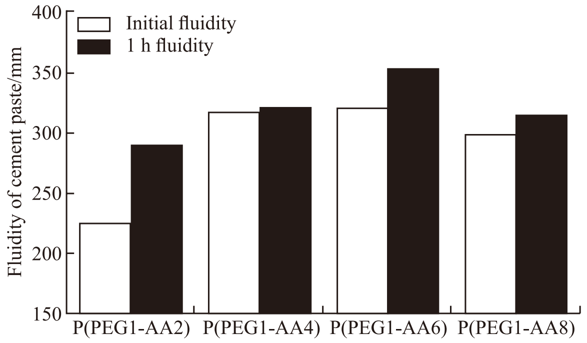

Fig.2 Influence of polycarboxylates with various carboxylic densities on the fluidity of cement paste

3.2 Rheological behavior of cement paste

3.2.1 Rheological models

Many models have been developed to describe the rheological behavior of cement paste, such as Bingham, Herschel-Bulkley, and Power-law models[5]. Rheological parameters are vital indicators for the characterization of mixability and workability of fresh cement mixtures. Rheological behaviors can be well used to characterize the internal structure features. The changes in internal structures are always analyzed through these rheological parameters, shear rate, shear stress, viscosity as well as thixotropy.

According to the multistage flocculation structure theory model, in fresh flocculation structure, the flocculation and deflocculation processes of part cement grains and hydration products are reversible. That is to say, the connections between the particles are non-persistent, and the connections are influenced by external forces. On the other hand, a small part of cement grains will form permanent connection. This kind of connection can not be destroyed by external forces. The non-persistently connective flocculation structure will be gradually destroyed with the addition of chemical admixtures, and hence the cement paste will be in dispersion state. As chemical admixtures adsorb on the surface of cement particles, the adsorption layer will hinder the cement hydration kinetics. The hydration delay effect in a certain extent contributes to a stable dispersing state of cement paste. With time evolution, chemical admixtures will be covered by hydration products and be ineffective in dispersion. The internal structure of cement paste converts from dispersion state into non-persistent flocculation structure, and gradually reaches persistent flocculation state. Cement paste finally condenses with the growth of hydration product crystals.

In the multistage flocculation structure theory model, different kinds of chemical admixtures may cause different degrees of deflocculation according to their water reducing capability. The variation in molecular structures will also make a difference in multistage flocculation structure.

In this study, we analyzed the rheological charateristics of cement paste containing different molecular PCE superplasticizers. The rheological charateristics were matched through three rheological models, including Power-law model, Bingham model as well as Herschel-Buikley model.

(a) Power-law model:

Power-law model can be expressed as follows:

$$\tau=K\gamma^{n} \qquad (1)$$

where, τ is the shear stress; K is the consistency coefficient; higher consistency coefficient suggests higher viscosity; γ is the shear rate; and n is the flow behavior index; When n=1, Power-law fluid is Newtonian fluid; when n<1, Power-law fluid is pseudoplastic fluid; when n>1, Power-law fluid is dilatant fluid.

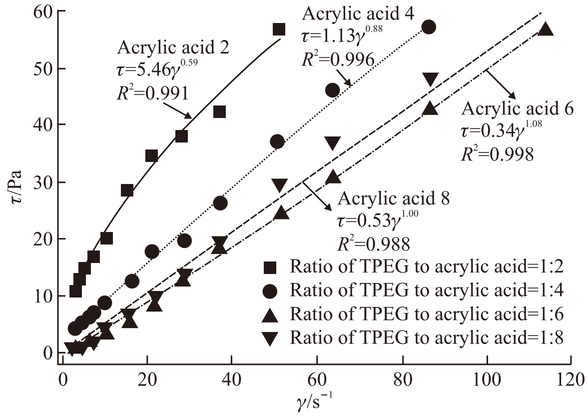

Fig.3 Rheological fitting according to Power-law model

This study fitted the rheological parameters according to Power-law model, including shear rate (γ) and shear stress (τ). The fitting results are shown in Fig.3 and Table 3. We can see that with the increase of carboxylic density in PCE molecules, the consistency coefficient (K) of the Power-law model decreases, and when the molar ratio of acrylic acid to TPEG is 6, the value of consistency coefficient reaches the lowest. We can also see that when the molar ratio of acrylic acid to TPEG is 6, the flow behavior index is the largest, which is larger than 1. This result indicates that when the molar ratio of acrylic acid to TPEG is 6, PCE superplasticizer causes cement paste to be dilatant fluid, while when the molar ratio of acrylic acid to TPEG is less than 6, cement paste added with PCE superplasticizer is pseudoplastic fluid. However, when the molar ratio of acrylic acid to TPEG is 8, PCE superplasticizers lead cement paste to be Newtonian fluid, because n=1. Overall, the fitting optimization index all approaches 1.00, which demonstrates the correctness of fitting.

(b) Bingham model:

Bingham model is the most commonly used model for rheological investigations on cement paste. In Bingham model, two intrinsic rheological parameters, yield stress and plastic viscosity , are involved to roughly describe the rheological properties of cement paste.

The Bingham model can be described as follows:

$$\tau = \tau_0 + \mu\gamma \tag{2}$$

where, τ is the shear stress; τ_0 is the yield stress, which means that when the shear rate is 0, a certain shear stress can start the flow; γ is the shear rate; and μ is the stiffness coefficient.

Fresh cement paste is a kind of plastic fluid. In cement paste, μ is used to characterize the resistance or internal friction of fluid. In plastic fluid, μ does not change with the change of velocity gradient. In Bingham model, when $\tau<\tau_0$, the break-up velocity and the recombination velocity of the particles are in a balanced condition. Hence, the cement paste can stably flow, and only form elastic deformation. However, when $\tau>\tau_0$, the break-up velocity of cement particles is larger than the recombination velocity. The shear rate (γ) is linearly correlated with the shear stress (τ). As the shear stress is removed from the system, the particles will rejoin together.

Rheological performances of cement paste were also fitted according to Bingham model, and the results

Table 3 Fitting results according to power-law model

Fluid model	Molar ratio of AA to TPEG	Equation	Regression coefficient		Fitting optimization index
			K	n	R^2
Power-law model	2.0:1.0	$\tau=K\gamma^n$	5.46	0.59	0.991
	4.0:1.0		1.13	0.88	0.996
	6.0:1.0		0.34	1.08	0.998
	8.0:1.0		0.53	1.00	0.988

Table 4 Fitting results according to Bingham model

Fluid model	Molar ratio of AA to TPEG	Equation	Regression coefficient		Fitting optimization index
			τ_0	μ	R^2
Bingham model	2.0:1.0	$\tau=\tau_0+\mu\gamma$	10.73	0.93	0.975
	4.0:1.0		2.21	0.66	0.996
	6.0:1.0		-1.39	0.51	0.999
	8.0:1.0		-0.99	0.55	0.989

of rheological fitting are shown in Fig.4 and Table 4. We can see that with the increase of carboxylic density in PCE molecules, the yield stress (τ_0) of Bingham model decreases, and when the molar ratio of acrylic acid to TPEG is 6, the value of yield stress (τ_0) reaches the lowest. Low yield stress means that less external force is needed to start the flow of cement paste when the shear rate is 0. Moreover, when the carboxylic density increases, the stiffness coefficient (μ) decreases. And when the molar ratio of acrylic acid to TPEG is 6, the value of stiffness coefficient (μ) is the lowest. The decrease in stiffness coefficient (μ) someway reflects that the viscosity of the cement paste declines. The results suggest that PCE superplasticizer with different carboxylic density will contribute to different rheological performance of cement paste, in which the flocculation structure changes.

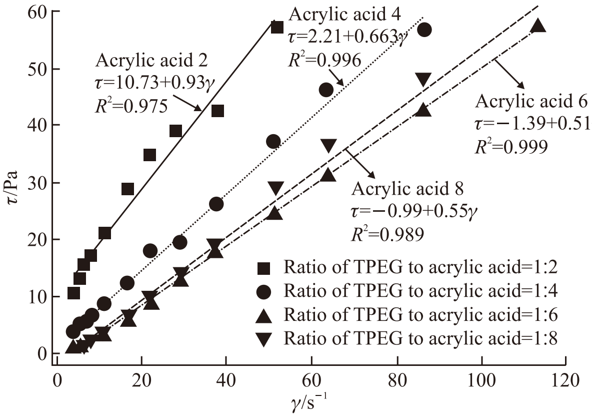

Fig.4 Rheological fitting according to Bingham model

(c) Herschel-Buikley model:

Herschel-Buikley model is a modified power-law model, which can be described as follows:

$$\tau = \tau_0 + K\gamma^n \qquad (3)$$

where, τ is the shear stress; τ_0 is the yield stress; γ is the shear rate; K is the consistency coefficient; higher consistency coefficient suggests higher viscosity; n is the flow behavior index; when n=1 and $\tau_0 \neq 0$, Herschel-Buikley fluid is plstic fluid; When n<1, τ_0=0, Herschel-Buikley fluid is pseudoplastic fluid; When n>1, τ_0=0, Herschel-Buikley fluid is dilatant fluid.

Rheological performances of cement paste were also fitted according to Herschel-Bulkley model, and the results of rheological fitting are shown in Fig.5 and Table 4. We can see that with the increase of carboxylic density in PCE molecules, the yield stress (τ_0) of Bingham model decreases. However, compared with Bingham model, in Herschel-Buikley model, the value of yield stress (τ_0) reaches the lowest when the molar ratio of acrylic acid to TPEG is 8. When the molar ratio of acrylic acid to TPEG is 6, the flow behavior index (n) is the largest, which is larger than 1. This result indicates that when the molar ratio of acrylic acid to TPEG is 6, PCE superplasticizer causes cement paste to be dilatant fluid, while when the molar ratio of acrylic acid to TPEG is less than 6 or larger than 6, cement paste added with PCE superplasticizer is pseudoplastic fluid. On the other hand, with the increase of carboxylic density in PCE molecules, the consistency coefficient (K) of the Power-law model decreases, and when the molar ratio of acrylic acid to TPEG is 6, the value of consistency coefficient reaches the lowest.

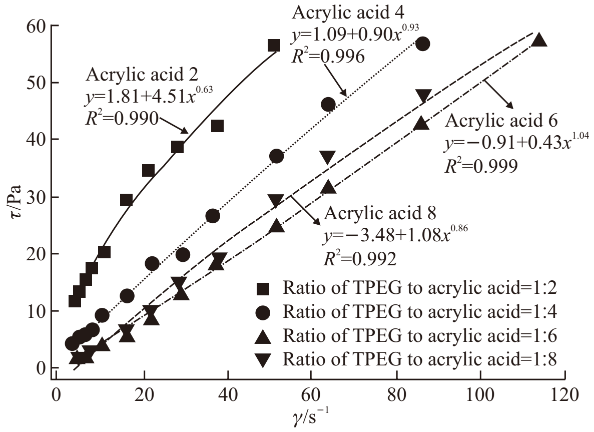

Fig.5 Rheological fitting according to Herschel-Buikley model

Overall, all the three rheological models are coincident in obtaining the preferred PCE molecular structure for better dispersion capability, for all the fitting optimization indexes are quite low. Moreover, the Bingham model is the best model since it can significantly reflect the rheological properties of cement paste.

Table 5 Fitting results according to Herschel-Buikley model

Fluid model	Molar ratio of AA to TPEG	Equation	Regression coefficient			Fitting optimization index
			τ_0	K	n	R^2
Herschel-Bulkleymodel	2.0:1.0	$\tau=\tau_0+K\gamma^n$	1.81	4.51	0.63	0.990
	4.0:1.0		1.09	0.90	0.93	0.996
	6.0:1.0		-0.91	0.43	1.04	0.999
	8.0:1.0		-3.49	1.08	0.86	0.992

3.2.2 Thixotropic behavior

Thixotropy indicates that under external force, temporary liquidity increases, while the external force is once removed, fluid has slow reversible recovery performance. Thixotropy is caused by the change in flocculation degree of internal structure. Generally, cement paste can ether behave as thixotropy or anti-thixotropy, which can be analyzed through double-line methods. The phenomenon of thixotropy shows that rising curve of shear stress-shear rate is located in right side of the descending curve. Conversely, the anti-thixotropy manifests that the rising curve is located in left side of the descending curve. The rising curve and the descending curve of the relationship between shear stress and shear rate can form a circle. This circle is so-called hysteresis loop. Hysteresis loop is caused by the difference in shear rates at different period. Commonly, the area of the hysteresis loop can be applied to reflect the degree of thixotropic apart and hence to measure the degree of thixotropy of certain cement paste.

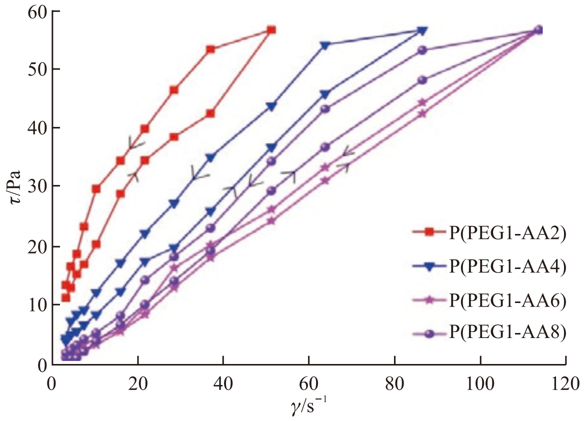

Fig.6 Thixotropic behavior of cement paste containing PCE superplasticizer

This study investigated the thixotropic properties of cement paste containing PCE superplasticizers with different carboxylic densities, and the results are shown in Fig.6. From Fig.6, it is clear that with PCE superplasticizer added into cement paste, cement paste presents thixotropy performance. When the molar ratio of acrylic acid and TPEG is 6, the hysteresis loop is the smallest. The smallest hysteresis loop means less difference in shear rates at different period. That is to say, the degree of thixotropy is tiny. The results are in good accord with the rheological properties. Overall, when the molar ratio of acrylic acid and TPEG is 6, PCE superplasticizer has the best dispersing performance.

4 Conclusions

In this study, self-synthesized PCE copolymers with different carboxylic densities were employed to investigate their influence on the rheological behavior of cement paste. Three typical rheological models were applied to analyze the rheological properties, including Power-law model, Bingham model as well as Herschel-Buikley model. In addition, this study also investigated the thixotropical performance of cement paste in function of PCE with different carboxylic densities.

The carboxylic density of PCE makes great effects on the dispersing performance of PCE superplasticizers. As carboxylic density increases, the dispersing capability of PCE improves, and P(PEG1-AA6) possesses the strongest dispersing properties, for the initial fluidity and 1 h fluidity of cement paste are both the highest.

Rheological model fitting analysis suggests that the flocculation structure of cement paste is changed due to the addition of PCE superplasticizers with different carboxylic densities. When the molar ratio of carboxylic acid to TPEG is 6, cement paste has the lowest viscosity and the smallest hysteresis loop.

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