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Effect of PCEs with Different Functional Groups on the Performance of Cement Paste

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Abstract: The adsorption behaviors and dispersing properties of polycarboxylate superplasticizer (PCE) with different functional groups were systematically analyzed to reveal the theory and methods of modifying PCE molecular structures and regulating PCE performances. By substituting carboxylic groups with sulfonic groups, ester groups or acylamino groups, respectively, modified PCEs with different functional groups were synthesized. Results show that introducing low amount of ester groups or sulfonic groups into the PCE molecules has no negative effects on the fluidity of cement paste, while introducing acylamino groups into PCE molecules significantly weakens the fluidity of cement paste. At low amount (when the molar ratio of sodium methallyl sulfonate to TPEG is lower than 0.4), the rapid adsorption of sulfonic groups onto the cement particles contributes to the high dispersing performance of the sulfonic group modified PCEs. When the substitution ratio of acrylic acid by sulfonic acid is higher than 0.4, the viscosity and the yield stress of cement paste increases sharply. Redundant sulfonic groups lead to the excessive charge density of the PCE, which contributes to the inhomogeneous adsorption on the cement grains and hence results in the decline of the dispersing performance. Substitution of carboxylic group by acylamino group or ester group slightly changes the viscosity as well as the yield stress of cement paste. Introducing sulfonic group into PCE molecule improves the adsorption behavior of PCEs, while introducing ester group or acylamino group into PCE depresses the adsorption properties.

Key words: polycarboxylate superplasticizer; functional group; adsorption behavior; rheological properties; cement hydration

1 Introduction

Recently, polycarboxylate superplasticizers (PCEs) have been widely adopted into concrete, due to its high dispersing performance as well as prominent water reducing ratio[1-6]. The dispersing mechanism of PCE is usually attributed to the adsorption onto cement particles via functional groups in backbones and the steric hindrance effect created through polyethyleneglycol (PEG) side chains[7-9]. Typically, the molecular structure of PCEs can be modified, because PCE is a kind of polymer and the chemical structure constitutes a series of components [10]. There are many studies concerning the modification of the PCE molecules and the working mechanisms of PCEs[11,12]. Through changing PEG side chain length, PCEs can generate different steric hindrance effects. On the other hand, by insertion various functional groups into PCE backbones, the adsorption behaviors of PCE vary.

Hou *et al*[13] found that PCEs with longer polyethylene oxide (PEO) side chains, lower degree of backbone polymerization and higher content of sulfonic groups exhibit better dispersing properties. Felekoğlu *et al*[14] modified the bond structures between the backbone and side-chains of copolymers of PCEs and studied the effect of these modifications on workability of cement paste. Results show that PCE with ester bond structure is not appropriate to obtain long workability

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retention period. Y Zhang *et al*[15] studied the effects of PCE charge density on the adsorption behaviors and retardation effects. By co-polymerizing the macro-monomer with anionic and cationic monomers, PCEs with various charge species were synthesized. It was found that charge characteristics of PCEs mainly decide their adsorption behavior as well as retardation effects, in order of $\text{-COO}^- > \text{-SO}_3^- > \equiv\text{N}^+\text{-}$.

However, previous insights primarily involved the influence of PCE molecular structures on the adsorption, zeta potential, and rheological behaviors of cement paste. There are few studies dedicated to detailed analysis on the effects of functional groups in the backbone of PCE on the adsorption behavior as well as dispersing properties, and less is about their impacts on cement hydration properties. In this paper, a series of functional groups, including ester group, sulfonic group, acylamino group, *et al* were inserted into PCE molecules by substituting these groups with carboxylic groups at various molar ratios. Effects of PCEs inserted with these functional groups on the adsorption performance, dispersing properties and cement hydration properties were systematically investigated. This study aims to bring new insights about the impacts of functional groups on the PCE performance, and lay theoretical foundation for the molecular design as well as modification of high-performance PCEs in concrete industry.

2 Experimental

2.1 Materials

Portland cement 42.5R complying with Chinese standard GB 175-2007 was adopted in this research. The chemical composition and physical properties of the cement are shown in Table 1.

In order to synthesize PCEs with different molecular structures, industrial grade methyl allyl polyethenoxy ether (TPEG, M_n about 2 400 g·mol^{-1}, average polymerization degree about 35) manufactured by Yangzi Aoke Chemical Company, analytical grade of acrylic acid (AA), sodium methyl acryl sulfonate (SMAS), 2-acrlamide-2-methylpropanesulfonic (AMPS), acrylic acid methyl ester (AAME), acrylamide (AM), ammonium persulfate (APS), hydrogen peroxide, 3-mercaptopropionic acid as well as L-ascorbic acid were used, which were manufactured by Shanghai Guoyao Chemical Company.

2.2 Synthesis and purification of PCEs

Self-synthesized PCEs were employed in the experiment. The reference PCE is a comb-like copolymer of AA and TPEG, and the molar ratio of acrylic acid to TPEG is 4:1. To modify the functional groups in PCE backbone, different monomers, such as SMAS, AMPS, AAME, AM, were respectively applied to substitute part of AA in the synthesis system. APS, hydrogen peroxide, and L-ascorbic acid were used as initiators, with a molar ratio of 1:0.7:1.4. 3-mercaptopropionic acid was adopted as chain transfer agent in the synthesis system. The content of initiator was 2.45% of the total weight of monomers, including TPEG, AA, SMAS, AMPS, AAME, AM, while the content of chain transfer agent was 0.56% of the total weight of monomers.

Before synthesis, 80 g TPEG was dissolved with 100 g deionized water in a bottle flask. Then APS and hydrogen peroxide were placed into the synthesis system, and stirred until total dissolution. AA and 3-mercaptopropionic acid were mixed together with 50 g deionized water. The extra monomers were mixed with L-ascorbic acid using 50 g deionized water. Water bath was used to provide stable heat for the synthesis system at 60 ℃. Peristaltic pump was used to titrate the above dissolved solutions for 2.5-3 h. After that, the copolymers were cooled to 30 ℃ and then neutralized to pH=6-7 with NaOH solution.

To remove un-reacted monomers from the samples, a cellulose ester semipermeable membrane with nominal molecular weight cut-off of 7 000 Da was used to purify co-polymers. The synthesized polymers were introduced into the dialysis bag. Then the sealed dialysis bags were put in a vessel full of deionized water for 7 days[8,15].

Table 1 Characteristics of the cement

CaO/%	SiO_2/%	Al_2O_3/%	Fe_2O_3/%	MgO/%	SO_3/%	TiO_2/%	K_2O/%	Na_2O/%	(Na_2O)eq./%	LOI/%
62.9	20.9	5.5	2.8	2.0	3.3	0.5	0.6	0.13	0.57	0.8

Specific gravity /(g/cm^3)	Mean size /μm	Fineness /(cm^2/g)	Setting time /min		Mortar compressive strength/MPa		Mortar flexural strength/MPa	
			Initial	Final	3 days	28 days	3 days	28 days
3.14	27.1	3 565	92	174	34.0	59.3	6.3	9.1

2.3 Measurements on cement paste

2.3.1 Fluidity and rheological properties of cement paste

The mass ratio of PCE to cement (PCE/C) was 1% and the mass ratio of water to cement was fixed at 0.29. The fluidity of cement paste was measured using a mini-slump cone, 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 adopted. The measurements were conducted 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 to 1 s^{-1} during 200 s. The yield stress was calculated by fitting the rheogram data according to the Hershey-Buckley model[8].

2.3.2 Adsorption amount

The adsorption amount of PCE was measured by a TOC-VCPH TOC analyzer. After mixing, the cement paste was centrifuged at 4 000 rpm for 15 min, and then the supernatant solution was collected, diluted with deionized water, and subjected to TOC test. The adsorption amount of PCE on cement of per unit mass can be calculated by subtracting the amount of PCE remaining in the aqueous solution from the amount initially added into cement paste[16,17].

2.3.3 Hydration properties analysis

The solid ratio of PCE to cement (PCE/C) was 1% and the mass ratio of water to cement was fixed at 0.29. At certain ages, the small pieces of hardened cement paste were firstly immersed into alcohol for 24 h, and then dried through vacuum desiccator. The dried samples were further ground to less than 63 μm. To analyze the hydration degree, XRD analysis was conducted with a graphite-mono-chromatized Cu-Kα radiation generated at 40 kV and 200 mA[18-20]. Scanning was performed at the 2θ range of 5°-65°, and the step length is 0.02° and the settle time of each step is 3 s.

3 Results and discussion

3.1 Effects of different PCEs on rheological performance of cement paste

3.1.1 Fluidity of cement paste

Effects of PCEs with various functional groups on the fluidity of cement paste were investigated. Ester group, acylamino group, and sulfonic group were respectively introduced into the PCE backbones by substituting part of the acrylic acid with acrylic acid methyl ester, acrylic amide, and sodium methallyl sulfonate, respectively. With different functional groups introduced into PCE backbones, the adsorption and dispersing properties of PCEs have greatly changed. And Fig.1 shows the fluidity of cement paste with various molecular PCEs.

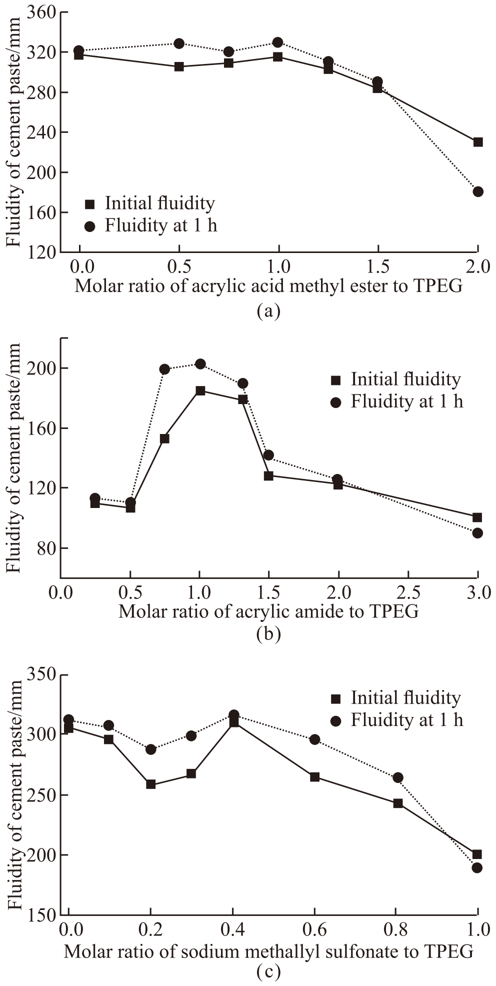


Fig.1 Fluidity of cement paste containing various molecular PCEs

With ester group introduced into PCE molecules, the dispersing properties of PCE keep stable when the substitution ratio of acrylic acid by acrylic acid methyl ester is lower than 1:3 (*i e*, molar ratio of acrylic acid methyl ester to TPEG is lower than 1.0). However, when the substitution ratio increases to higher than 1:3, the dispersing capability and the fluidity retainability of PCE decrease sharply.

Diversely, introducing acylamino group into PCE architecture greatly weakens the dispersing capability of PCE. However, when the molar ratio of acrylic amide to TPEG is approximately 1.0, cement paste shows highest fluidity as well as fluidity retainability.

Similar to ester group, introducing sulfonic group into PCE architectures has slight effects on the initial fluidity of cement paste when the molar ratio of sodium methallyl sulfonate to TPEG is lower than 0.4. However, when the molar ratio of sodium methallyl sulfonate to TPEG is higher than 0.4, the dispersing property of PCE declines steeply.

3.1.2 Viscosity and yield stress of cement paste

Rheological behaviors are vital indicators for the rheological characterization of cement paste. Rheological behaviors can be adopted to characterize the internal structure features. The changes in internal structures can be analyzed through the rheological parameters, including shear rate, shear stress, viscosity and thixotropy.

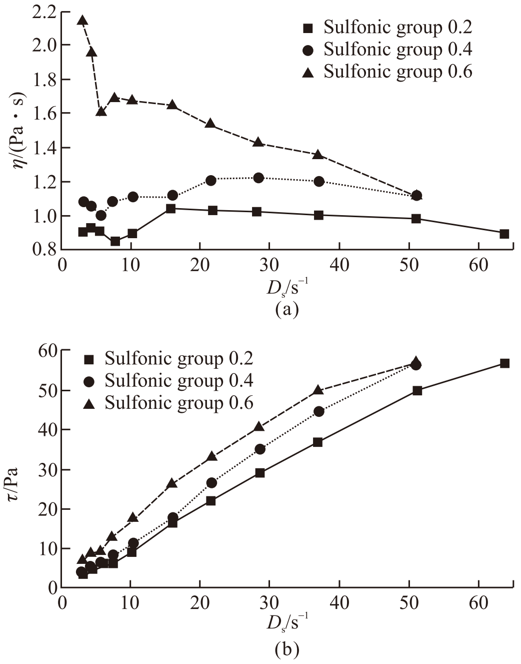


Fig.2 Rheological characteristics of cement paste containing PCEs with sulfonic groups

According to the multistage flocculation structure theory model, in fresh flocculation structure, the flocculation and deflocculation process of cement grains and hydration products are reversible. 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 cannot be destroyed by external forces. The non-persistently connective flocculation structure will be gradually destroyed by adding PCEs, and hence the cement paste keeps in dispersion state. As PCEs adsorb onto the mineral surface, the adsorption layer hinders the cement hydration kinetics. The hydration retardation effect in a certain extent contributes to a stable dispersing state of cement paste. With time evolution, PCEs will gradually be covered by hydration products and will be ineffective in dispersion. The internal structure of cement paste converts from dispersion state into non-persistent flocculation structure, and then gradually reaches persistent flocculation state. Cement paste finally condenses with the growth of hydration product crystals.

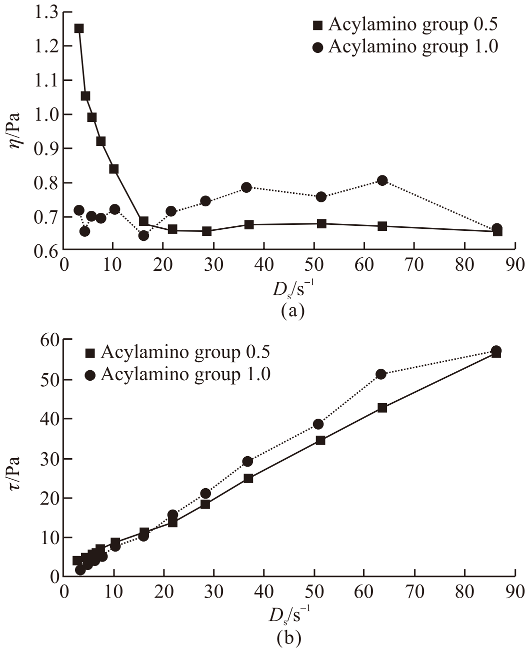


Fig.3 Rheological characteristics of cement paste containing PCEs with acylamino groups

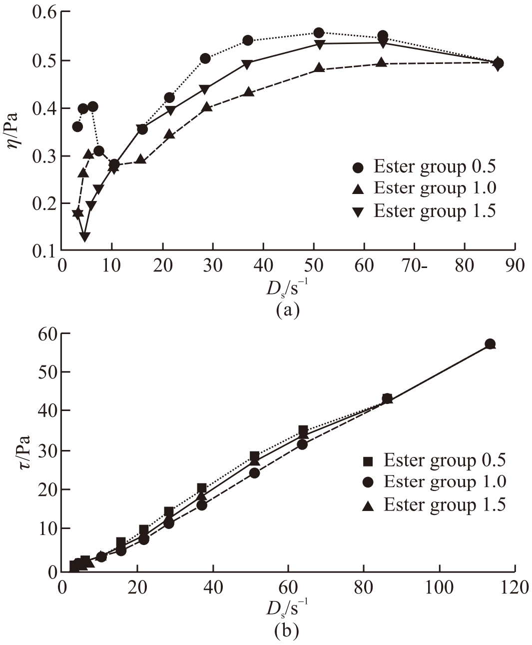


Fig.4 Rheological characteristics of cement paste containing PCEs with ester groups

In the multistage flocculation structure theory model, different molecular PCEs may cause different degree 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, the rheological characteristics of cement paste added with different molecular PCEs were investigated, and the results are shown in Fig.2-4. As shown in Fig.2, the higher substitution ratio of acrylic acid by sulfonic acid increases the viscosity as well as yield stress of cement paste. However, the substitution ratio of carboxylic group by acylamino group or ester group slightly changes the viscosity and the yield stress of cement paste (shown in Fig.3-4). The results are greatly coherent with the dispersing properties of PCEs with various molecular structures.

3.2 Adsorption behavior of different PCEs

PCEs that adsorb onto mineral surfaces impede the flocculation as well as water entrapment[19,20]. The adsorption isotherms of different PCEs are shown in Fig.5. Adsorption of PCEs onto cement grains exhibits exponential behavior, as seen by linear adsorption onto cement particles at initial concentrations of PCEs at relatively low content, followed by gradually reaching a maximum amount of adsorbed PCEs.

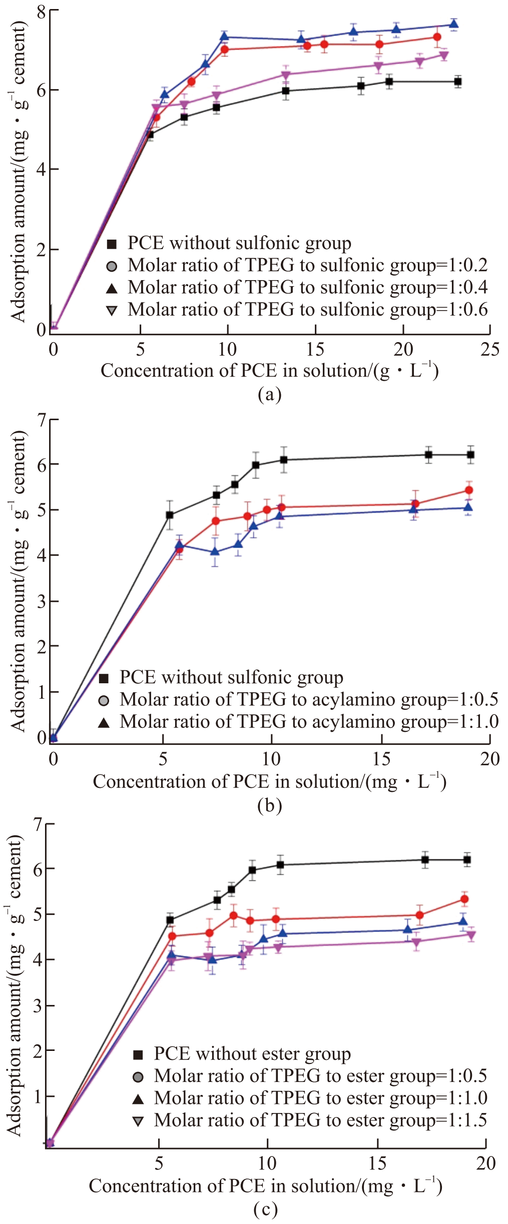


Fig.5 Adsorption behavior of different molecular PCE

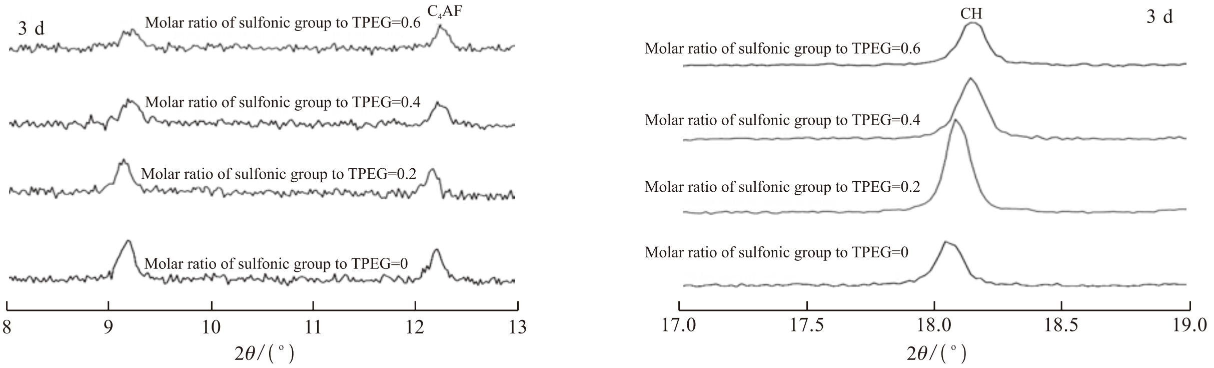
Because of anion group and the positively charged sites on cement particles, certain architectural PCEs seem to have higher adsorption values. However, due to the deviation test, the adsorption amount of PCEs is not only accounts for the part of PCEs adsorbed onto the mineralogical anhydrous phases, but a certain proportion of the PCEs consumed by C_3A minerals, forming the intercalated organo-mineral phases (OMP). As shown in Fig.5, introducing sulfonic group into the PCE backbones improves the adsorption behavior of PCEs, while introducing ester group or acylamino groups into PCEs depresses the adsorption properties.

Analyzing the adsorption amounts with the dispersing properties of various structural PCEs, it is evident that at low amount (when the molar ratio of sodium methallyl sulfonate to TPEG is lower than 0.4), the rapid adsorption of sulfonic groups onto the cement particles contributes to the high dispersing performance of the sulfonic group modified PCEs. However, when the substitution ratio of acrylic groups by sulfonic groups is higher than 0.4, the redundant sulfonic groups results in the excessive charge density, which leads to the inhomogeneous adsorption on the cement grains and hence results in the decline of the dispersing performance.

3.3 Effects of different PCEs on cement hydration process

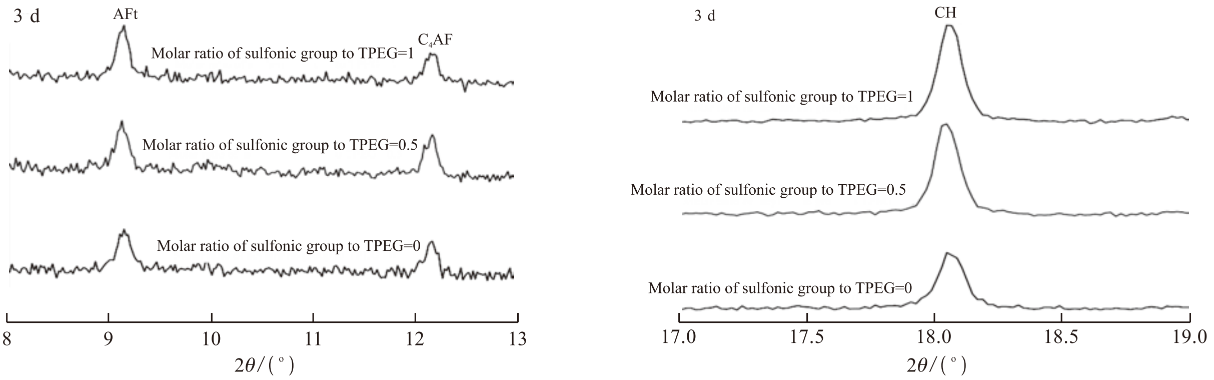
The adsorption of PCEs onto cement surfaces results in significant changes in cement hydration kinetics[15,21,22]. In this research, the main hydration products, $Ca(OH)_2$ (CH) as well as ettringite (AFt), were detected by XRD, and the effects of different molecular PCEs on the cement hydration performance determined by XRD are presented in Fig.6-8.

In comparison with reference PCE, introducing sulfonic group into PCE backbones significantly promote the cement hydration process at early age (3 d). When molar ratio of sulfonic group to TPEG is 0.2, the amount of CH is the highest, but the amount of AFt slightly varies. Introducing sulfonic group into PCE backbones seems to depress the formation of AFt. Introducing acylamino group into PCE backbone changes the amount of CH, in comparison with the reference PCE. Moreover, introducing acylamino group into PCE backbone promotes the formation of AFt. By contrast, introducing ester group into PCE architecture



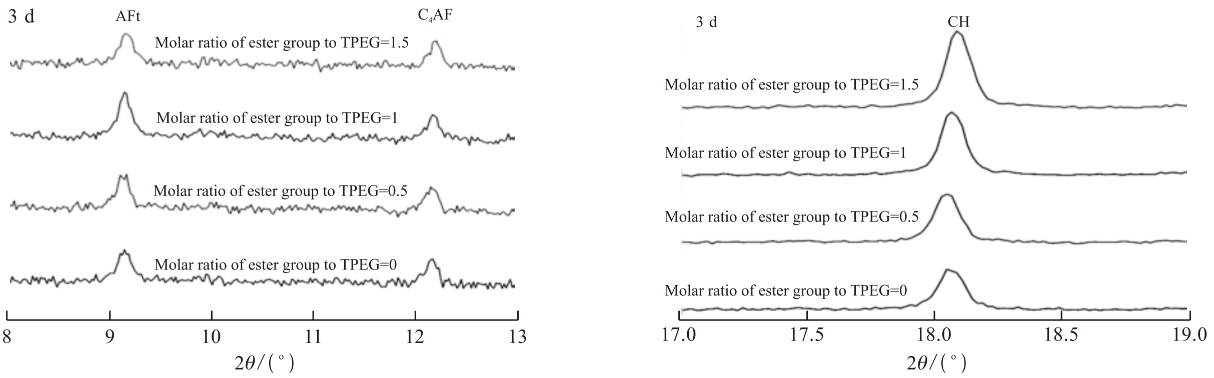
(a) (b)

Fig.6 XRD spectrum of cement paste containing sulfonic group modified PCEs



(a) (b)

Fig.7 XRD spectrum of cement paste containing acylamino group modified PCEs



(a) (b)

Fig.8 XRD spectrum of cement paste containing ester group modified PCEs

slightly influences the cement hydration process, for the formulation amount of CH slightly changes. The results reflect that inserting acylamino groups into PCE backbone can accelerate the cement hydration process due to the agglomerative effect as well as the dilution effect of the ion exchange. The high valence ions entry the diffusion layer and the fixed layer, exchange with the low valence ions, and leads to the decline of the ion amount. Less amount of ions in the diffusion layer and the fixed layer leads to the reduction of the diffusion layer thickness as well as the fixed layer thickness. By the way, the dispersing performance of PCE also influences the cement hydration process. When the cement paste is well dispersed by PCE, cement particles can contact water more adequately, which contributes to the promoted cement hydration process.

4 Conclusions

PCEs imbedded with various functional groups exhibit different adsorption behavior and dispersing properties. Introducing low amount of ester group or sulfonic group into PCEs has no negative effects on the fluidity of cement paste, while introducing acylamino group into PCEs greatly decreases the fluidity of cement paste. When the substitution ratio of acrylic acid by sulfonic acid is higher than 0.4, the viscosity and the yield stress of cement paste increases sharply. The substitution of carboxylic group by acylamino group or ester group slightly changes the viscosity and yield stress of cement paste. Introducing sulfonic group into the backbone of PCE improves its adsorption behavior, while introducing ester group or acylamino group into PCEs depresses the adsorption properties.

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