

## Effect of Cross-Linked Polycarboxylate-Type Superplasticizers on the Properties in Cementitious System

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**ABSTRACT:** Fluidity and slump loss are main technical indicators for the quality of concrete. They are related to the dispersion of cement and hydration process, and are greatly affected by the structure of superplasticizers (SPs). For the purpose of obtaining SPs with excellent fluidity and slump retention, water-soluble cross-linked polycarboxylate ether copolymers (CLPCs) of acrylic acid and alkenyl alcohol type polyoxyethylene ether were synthesized. In order to gain full understanding of the effect of cross-linked SPs on the properties in cementitious system, properties of the new SPs in cement paste were compared to those of traditional ones without cross-linking agents. Mortar tests showed that CLPC performed obvious slow-release function and kept about 10 mm higher than its initial paste flow after 150 min, while PC incurred loss of 15 mm after 150 min. Adsorption of CLPC on cement resulted in zeta potential being roughly the same as that in the case of PC, and enabled more effective slump retention to cement suspensions by rheological property tests. Ettringite peaks disappeared for CLPC on 1-day curve and reappeared after 35 days, and the intensity of CH peaks for CLPC appeared weaker than Blank and PC after 1 day. The microstructure of CLPC after 1 day showed a very dense structure of smaller and thinner crystallites, which indicated that the early hydration was greatly delayed. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40856.

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### INTRODUCTION

Comb-type polycarboxylate grafted with poly(ethylene glycol) methyl ether was firstly used as superplasticizers (SPs) in cementitious system in the 1990s.<sup>1</sup> It was considered to enjoy higher compatibility than other SPs, such as lignin sulfonate, naphthalene sulfonate, melamine sulfonate, and amino sulfonate.<sup>2–4</sup>

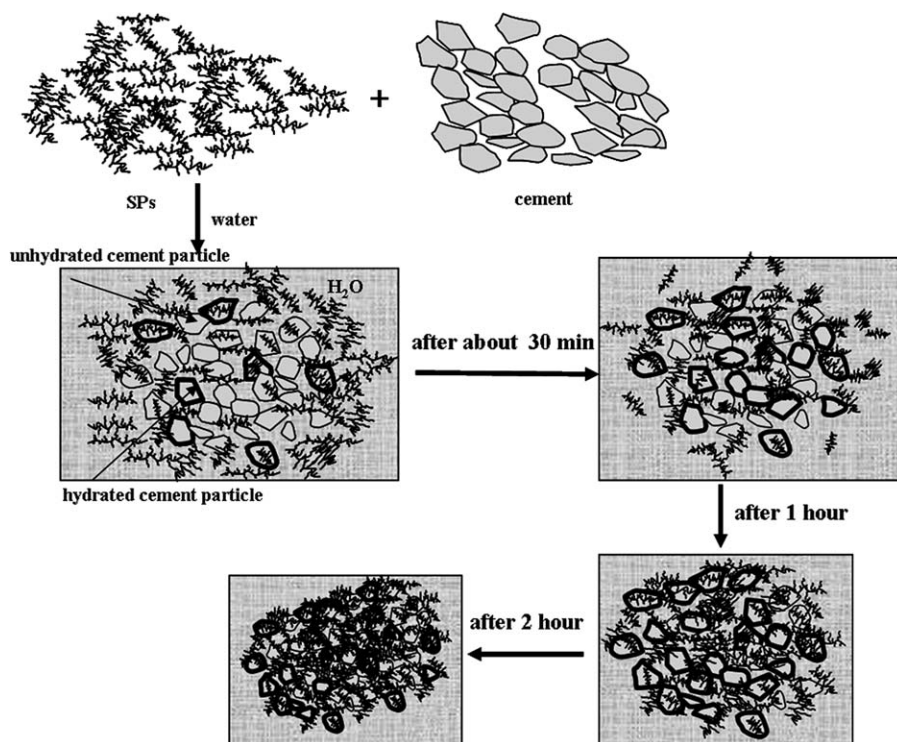
Polycarboxylate type SPs (PCEs) consisted in a linear backbone with carboxylate and long side chains of ether group or ester group. Anchoring and electrostatic repulsion effects of anionic backbone and steric hindrance effects of side chains determined the characteristics of unique structural properties of dispersibility and fluidity.<sup>5–8</sup> Just like all other SPs, PCEs are also subject to slump loss. Slump loss could cause some problems such as difficulties in pouring, defects of honeycomb-like holes, and unacceptable workability.<sup>9</sup>

In the past decade, several methods were proposed for controlling slump loss in cement and concrete.<sup>10–13</sup> One method is

addition of PCEs at the point of saturation, but there are some practical problems associated with this method. For instance, with unpredictably changing chemical composition of cement, it is difficult for PCEs to adapt to kinds of cement with changeable chemical composition. Moreover, no much time is available for adjusting the dosage to control final slump. Another method for controlling slump loss is the use of retardants or composite dispersants. However, there are some drawbacks in this method as sometimes it finally results in unexpected long setting time or low early strength.

Quantifying these difficulties was a hard task and further complicated by the ongoing hydration reactions of cement.<sup>14–19</sup> Fortunately, some polymers could act as both dispersant and slow release agent. It is possible for introducing cross-linked point into monomer chain of SPs to enable excellent slump retention of cement paste without retardants.

Tanaka et al.<sup>20</sup> studied the effects of an AP-based SP, the SP was a cross-linked copolymer of acrylic acid and polyethylene glycol mono-alkyl ether. Tanaka and coworkers demonstrated the

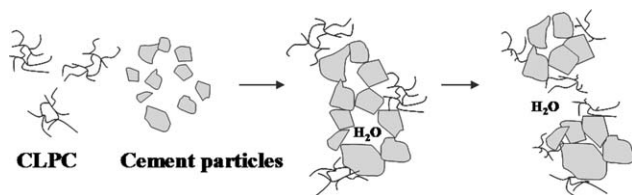


**Figure 1.** Schematic figure for adsorption of SPs on cement particle.

cross-linked polymer was hydrolyzed by alkaline water. Both electrostatic repulsion and steric hindrance effects would account for the action of dispersion and fluidity. The low slump-loss phenomenon might be related to increasing long side chains released by broken cross-linked points through steric hindrance effect.

Cerulli et al.<sup>21</sup> studied a new water-soluble copolymer of methacrylic acid, polyethyleneglycol monomethylether and methacrylate monomers, polypropylene glycol dimethacrylate. The results of the cross-linked dispersant surprisingly showed that the polymer produced an excellent super-plasticizing effect at an exceptionally low dosage, and retained the workability of the mixture based on high alumina cement, which also did not cause any decrease in the strength developments.

Bi et al.<sup>22</sup> studied a bridge PCE of acrylic acid, sodium methylally sulfonate, polyethyleneglycol diacrylate (PEGDA), and polyethyleneglycol mono-acrylate (PEGMA). They used PEGDA as cross-linking agent to replace partial PEGMA. The results indicated that bridge PCs decreased initial dispersity of cement paste, and increased dispersity retention ability.



**Figure 2.** Decomposition of cross-linked points of CLPC by the alkaline solution in cement pores.

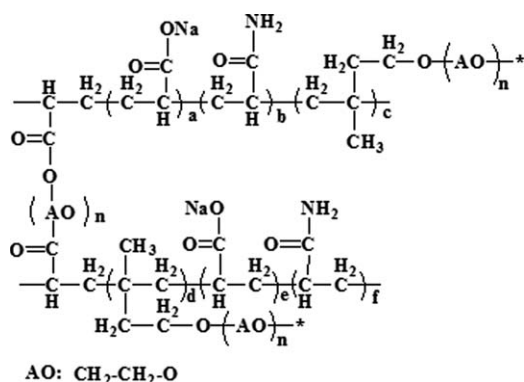
In recent years, researchers have developed various kinds of cross-linked SPs with excellent slump retention, and some related patents were published.<sup>23–26</sup>

Based on the information obtained from these studies of cross-linked polycarboxylate-type SPs, cross-linked polycarboxylate ether copolymer (CLPC), we proposed some hypothesis as showed in Figure 1. When the SPs and water were mixed with cement, cement hydration occurred. The SPs were adsorbed on cement particles, and such adsorption reached saturation in several minutes. At this time, the cement paste delivered the best dispersion. After hydrated for about 1 hour, considerable parts of the SPs were embedded in the hydrated and unhydrated cement particles. The SPs' concentration in pore solution greatly decreased, it led to low cement paste fluidity and slump retention. However, as shown in Figure 2, when CLPCs were adsorbed on cement particles, they were hydrolyzed by cement alkaline pore solution. The cross-linking bonds were hydrolyzed. Electrostatic repulsion and sterical hindrance conditions changed. These were good for slump retention while the cement paste had poor flow behavior after hours.<sup>20</sup>

The present study is designed to gain full understanding of the effect of cross-linked SPs on the properties in cementitious system. For this purpose, we synthesized water-soluble CLPCs of acrylic acid and alkenyl alcohol type polyoxyethylene ether. In order to study slow-release effects of amide group and cross-linked structure in cement alkaline pore solution (Figure 4), the effects of the cross-linking agent in comb-like copolymers on the dispersion, zeta potential, rheology were analyzed. The hardened hydrated cement was then characterized by analyses of

**Table I.** Characteristics of Cement

Phase composition (%)					Volume diameters ( $\mu\text{m}$ )			
$\text{C}_3\text{S}$	$\text{C}_2\text{S}$	$\text{C}_3\text{A}$	$\text{C}_4\text{AF}$	Gypsum	$d_{10}$	$d_{50}$	$d_{90}$	VMD
30.4	39.2	12.9	2.1	13.5	1.74	21.74	52.76	24.9

**Figure 3.** Scheme of CLPC.

X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and compressive strength.

## EXPERIMENT

### Materials

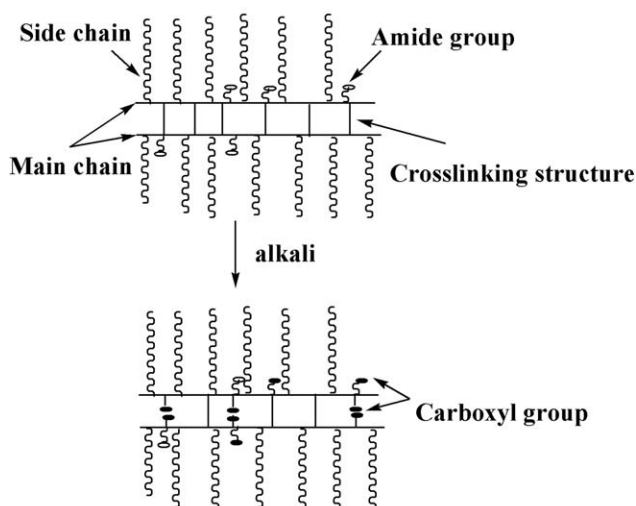
Alkenyl alcohol type polyoxyethylene ether (TPEG,  $M_n = 2400$  g/mol, Shanghai Taijie Chemical), acrylic acid (AA), acrylamide (AM), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30 wt %), ascorbic acid (Vc), thioglycolic acid (TGA), and poly ethylene glycol diacrylate (PEGDA,  $M_n = 575$  g/mol) (Aladdin Reagent (Shanghai), China), cement (Fanglian Cemnet, China) were used as received. The characteristics and composition of cement were illustrated in Table I.

### Synthesis of the SPs

The SP of AA-AM-TPEG was prepared through aqueous free radical polymerization. In a typical experiment,  $\text{H}_2\text{O}_2$  dissolved in deionized water was injected into one reaction vessel containing TPEG. Acrylic acid (AA), Acrylamide (AM), and cross-linking agent PEGDA were dissolved in deionized water to obtain mixed monomer solution. Ascorbic acid and thioglycolic acid were dissolved in deionized water to develop mixed Vc-TGA solution. The mixed monomer solution was added dropwise into the reaction vessel for 3 hours. Meanwhile, the mixed Vc-TGA solution was added dropwise for 3.5 hours. Afterwards, the temperature was kept at  $60^\circ$  for 1 hour. The whole polymerization was carried out at  $60^\circ$  for 4.5 hours. Then the vessel was

**Table II.** Superplasticizers Chemical Composition and Molecular Weight

SP	Molar ratio of different monomers				$M_w$ [Da]	$M_n$ [Da]	Polydispersity index $M_w/M_n$
	AA	AM	TPEG	PEGDA			
PC	3.5	1.5	1	0	783,026	1,006,686	1.29
CLPC1	3.5	1.5	1	0.0125	900,297	1,104,225	1.23
CLPC2	3.5	1.5	1	0.025	2,202,680	3,724,373	1.69

**Figure 4.** The decomposition of the cross-linked structure and amide group in hydration of cement.

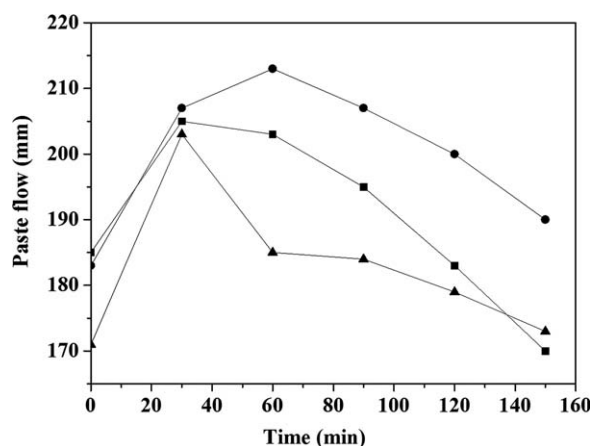
cooled to ambient temperature. The aqueous CLPC was neutralized to  $\text{pH} = 7$  by 30 wt % aqueous NaOH solution. Deionized water was then used to dilute solid content to 40%. The scheme of CLPC was seen in Figure 3. Chemical composition, molecular structure, molar masses,  $M_w$ ,  $M_n$  of PC (SP without cross-linking agent), and CLPC were given in Table II.

### Mortar Tests

Mortar tests were carried out with SPs at a dosage of 0.13% involving cement weight. Standard quartz sand was used as aggregate. Water/cement ratio was 0.29 by mass, Cement/aggregate ratio was 1 : 1. Cement, aggregate, and water were mixed for 30 s. Sand was added progressively during the next 30 s and stirred vigorously in another 30 s, then stopped for 90 s to scrape off the mortars that had been attached to the sides and stirred vigorously for further 60 s.

### Zeta Potential Measurement

Zeta potential measurement was carried out through electrophoresis (Malvern Nano-ZS90 particle size analyzer, UK) at  $25^\circ$ . Water/cement ratio was 10 : 3, and SPs concentrations were 0,



**Figure 5.** SPs paste flow on time in the presence of different PEGDA; ●: CLPC1, ▲: CLPC2, ■: PC.

9, 12, 13, 30, and 160 mg/L, respectively. After mixed for 4 min, the pastes were diluted for 250 times. All suspensions were ultrasonically treated for 10 min before tests. Zeta potential ( $\zeta$ ) of the suspensions was calculated by dynamic mobility.

### Rheology

Dynamic mechanical properties of cement pastes were tested by strain controlled rheometer ARES-RFS using parallel plates with diameter of 25 mm at 25°. The suspensions were prepared by adding 30 g cement, 0.1 g SPs, and 100 g deionized water. After mixed for 4 min, rheological behavior of suspensions was tested from 10 to 120 min after the following process: firstly, shear rate increased from 0 to 250 s<sup>-1</sup> in 180 s, then was kept at 100 s<sup>-1</sup> for 60 s, later decreased to 0 s<sup>-1</sup> in next 180 s. Apparent yield stress and plastic viscosity were calculated according to the Bingham model.

### Analyses of Hydrated Cement by XRD and SEM

In order to examine the effects of SPs on the hydration of cement paste, 0.13 wt % of CLPCs and PC were added into cement paste. Water/cement ratio was 0.29. After mixed for 4 min, the paste was poured into one mould (2.4 cm × 2.4 cm × 2.4 cm). The hardened cement was cured at 25° with relative humidity of 90% for 1, 7, and 28 days, respectively. The samples for XRD and SEM analysis were taken from the center of broken cement blocks. More details about samples' treatment could be seen in Ref. 27. The XRD tests of samples, which were milled to pass through one 200-mesh sieve, were carried out through Cu Ka radiation at the 2-theta range from 0 to 60, with a step-rate of 4 min<sup>-1</sup>. SEM were tested with samples' size of 5 × 10 mm.

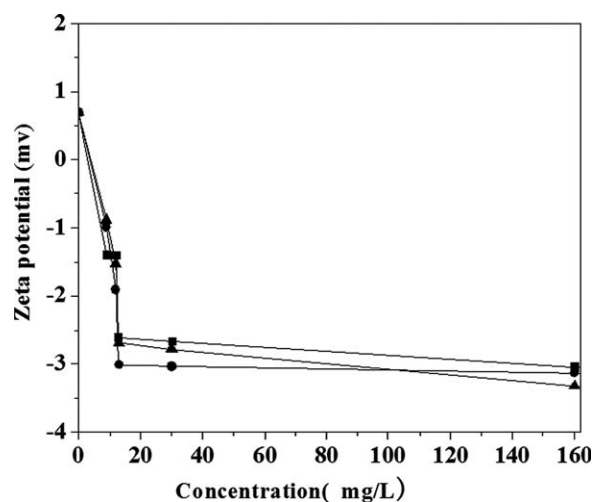
### Compressive Strength

Compressive strength tests were carried out with 0.13 wt % of SPs by TYE-2000B compressive strength testing machine. Standard quartz sand was used as aggregate. Water/cement ratio was 0.29, and cement/aggregate ratio was 1 : 1 by weight. The mixture was made in one blender and then poured to 7 cm × 7 cm × 7 cm mould. After 1 day, the hardened cement was demolded.

## RESULTS AND DISCUSSIONS

### Effect of SPs on Fluidity and Slump-Retaining Ability

The dispersion ability of SPs was evaluated by mortar tests to study slump retention over time.



**Figure 6.** Zeta potential of SPs on the cement suspensions' surface; ●: CLPC1, ▲: CLPC2, ■: PC.

As shown in Figure 5, paste flow of PC and CLPC1 showed good slump retention properties in the first 30 and 60 min, respectively. It was observed that CLPC1 performed obvious slow-release function and kept about 10 mm higher than its initial paste flow after 150 min while PC incurred loss of 15 mm after 150 min. With addition of more PEGDA, the initial fluidity of CLPC2 decreased by about 10 mm, but certain slow-release function was also observed after 150 min. The results showed that CLPC1 had higher fluidity than PC. However, the fluidity of CLPC2 indicated that the initial paste flow slightly decreased as the content of cross-linking agent PEGDA was very low.<sup>22</sup>

The reasons could be summarized as follows:

Firstly, in alkali pore solution of cementitious system, ester groups on cross-linking agent PEGDA were hydrolyzed into carboxyl group. The concentration of carboxyl group became higher. More carboxyl groups could be adsorbed on cement particles while cement paste fluidity got worse.

Secondly, when the ester groups were hydrolyzed, the cross-linked points were broken. The long side chain had more active space, and sterical hindrance of the side chain might be enhanced.

Thirdly, hydrolysable amide groups provided by acrylamide could also be hydrated into carboxyl groups for contributing to slump retention. The behavior based on the three hypotheses effectively improved reabsorption and led to better slump retention.

### Effects of SPs on the Zeta Potential of Cement Paste

To investigate the effects of cross-linking agent, zeta potential of cement paste was measured. Particle charge values at different concentrations for PC-SPs and CLPC-SPs were showed in Figure 6. The initial zeta potential value was positive. Zeta potential decreased with increasing amount of SPs, and then was maintained at a constant value above the concentration of 13 mg/L. Adsorption of CLPC on cement resulted in zeta potential

being roughly the same as that in the case of PC. It seemed that addition of cross-linked structure exerted little impact on zeta potential, and it could not change surface charge of cement suspensions in early adsorption. The experimental results quite coincide with the initial paste flow of PC-SPs and CLPC-SPs.

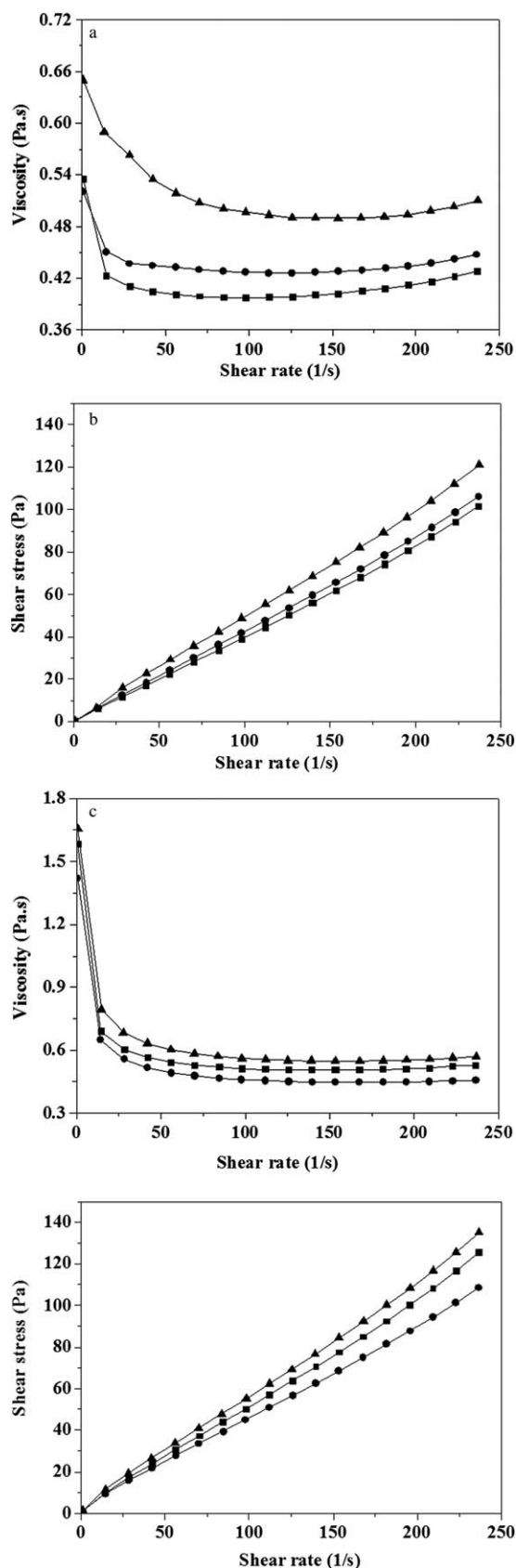
#### Effect of the SPs on Change of Rheological Parameters with Hydration Time

Shear stress and viscosities versus shear rate variations in cement suspensions were shown in Figure 7. Shear stress of cement paste increased with shear rate variation [Figure 7(b,d)]. Shear stress of CLPC1 at 120 min was lower than that of CLPC2 and PC. Generally, high fluidity delivered low shear stress to cement suspensions. Viscosity of cement suspensions with 10 min hydration time gradually decreased with increasing shear rate. The viscosity became slightly higher over  $150 \text{ s}^{-1}$ . This may be explained by the effect of flocculation and shear thinning behavior. Compared with CLPC1 and CLPC2, PC had better dispersibility. With the result of zeta potential analysis, we made explanation of the results based on cross-linked structure that would affect steric hindrance, which restricted the release of free water.

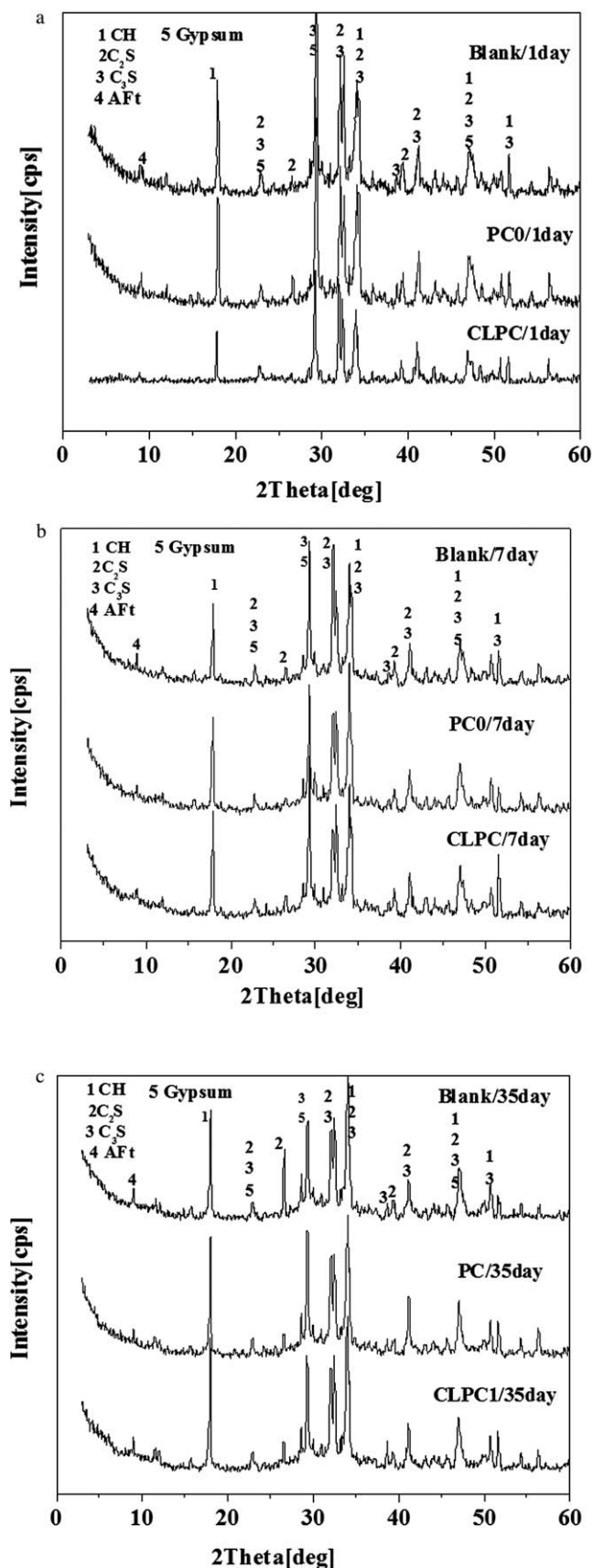
When the shear rate below  $15 \text{ s}^{-1}$ , cement suspensions with 120 min hydration performed as pseudo plastic fluid. When shear rate was higher than  $15 \text{ s}^{-1}$ , the suspensions corresponded to transition from strong shear-thinning to nearly Newtonian flow behavior. Apparent viscosity of CLPC1 was lower than that of PC after 120 min. It indicated that CLPC1 gave more effective slump retention to cement suspensions rheological property tests. It was proposed that ester group and amide group were hydrolyzed under alkaline condition of cement suspension. Increased carboxyl group and enhanced sterical hindrance of side chain made redispersion, which was explained in the analysis of mortar tests. The experimental results quite coincide with that of mortar tests.

#### Effect of SPs on Microstructure of Hardened Cement Pastes

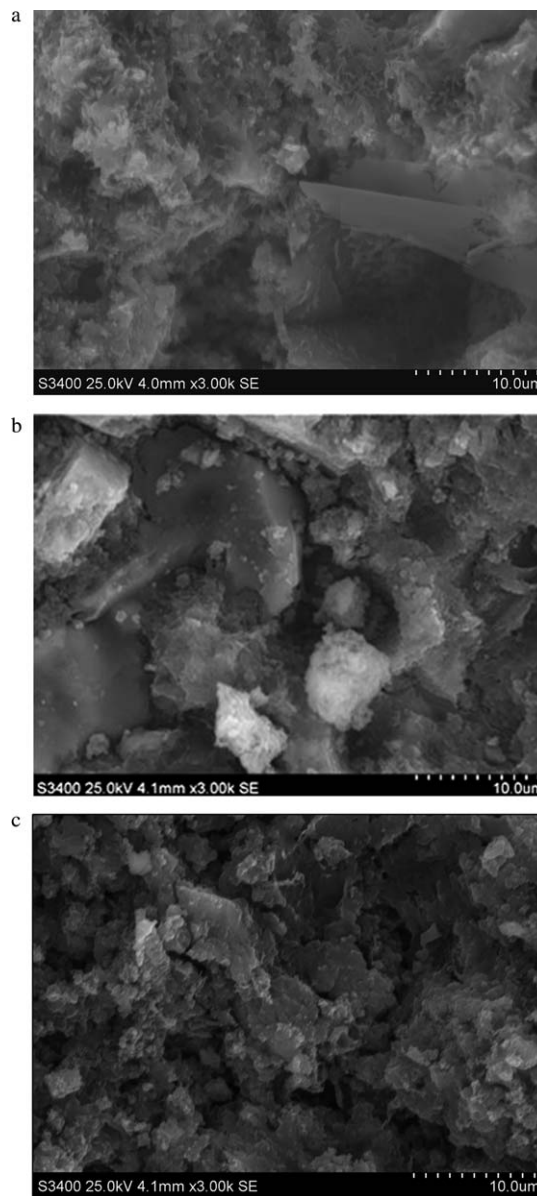
SPs in cement paste affected the formation of hydrated cement phases, such as amorphous C-S-H and crystalline phases, as seen in the results of the XRD analyses. The XRD results of cement paste with SPs were given in Figure 8. The main important phases of portlandite (CH), ettringite (AFt),  $\text{C}_2\text{S}$  (dicalcium silicate), and  $\text{C}_3\text{S}$  (tricalcium silicate) were investigated. The ettringite peaks are clearly seen for Blank (without SPs) and PC at 1 day. Thus, the CLPC1 ettringite peaks disappeared on 1-day curve and reappeared after 35 days. Under alkaline condition of cement suspension, it was concluded that hydrolyzed ester group and amide group released more carboxyl group. Adsorption of carboxyl group might slow down or even stop the growth of ettringite germs. When the SPs had been consumed, normal growth of ettringite resumed.<sup>28</sup> The intensity of CH peaks for CLPC1 appeared weaker than Blank and PC after 1 day. The anions provided by SPs, especially the released carboxyl group of the CLPC1, chelated with  $\text{Ca}^{2+}$  in the hydrated cementitious system. Such tendency indicated more clearly that the early hydration was greatly delayed by the chelation. The intensity of  $\text{C}_2\text{S}$  peaks overlapped with  $\text{C}_3\text{S}$  peaks; however, their trends could be interpreted jointly. The amounts of both



**Figure 7.** Shear stress and viscosity versus shear rate variations with different hydration time in cement suspensions. ●: CLPC1, ▲: CLPC2, ■: PC. (a) 10min, (b) 10min, (c) 120min, (d) 120min.



**Figure 8.** X-ray Diffraction patterns of the hardened cement with or without SPs: (a) 1 day, (b) 7 day, (c) 35 day.



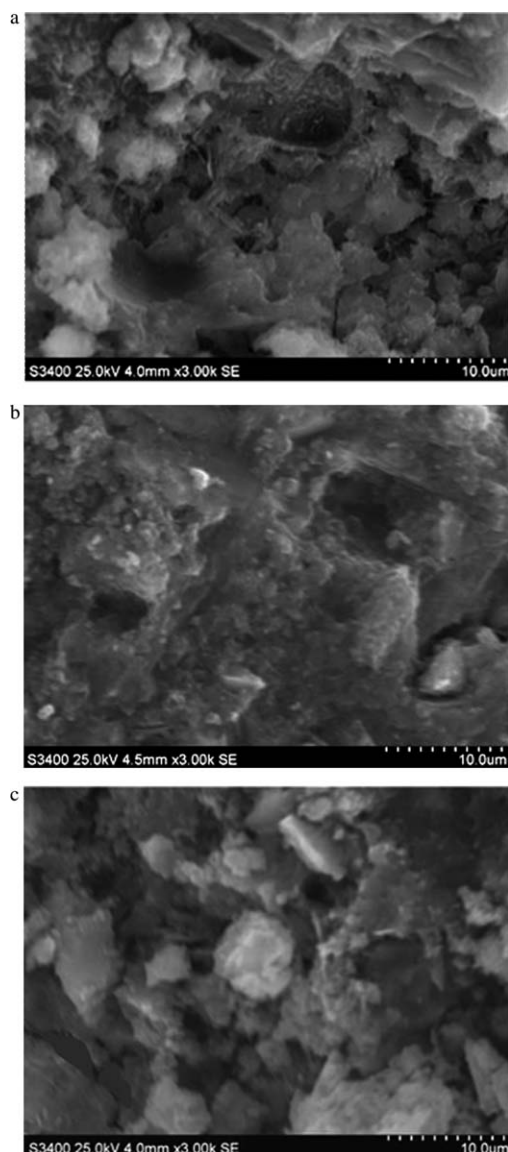
**Figure 9.** SEM micrographs for the hardened cement after 1 day of hydration. (a) Blank, (b) PC, (c) CLPC1.

phases decreased with increasing time for Blank, PC, and CLPC1, for the amorphous calcium silicate hydrates (C-S-H) had been formed.

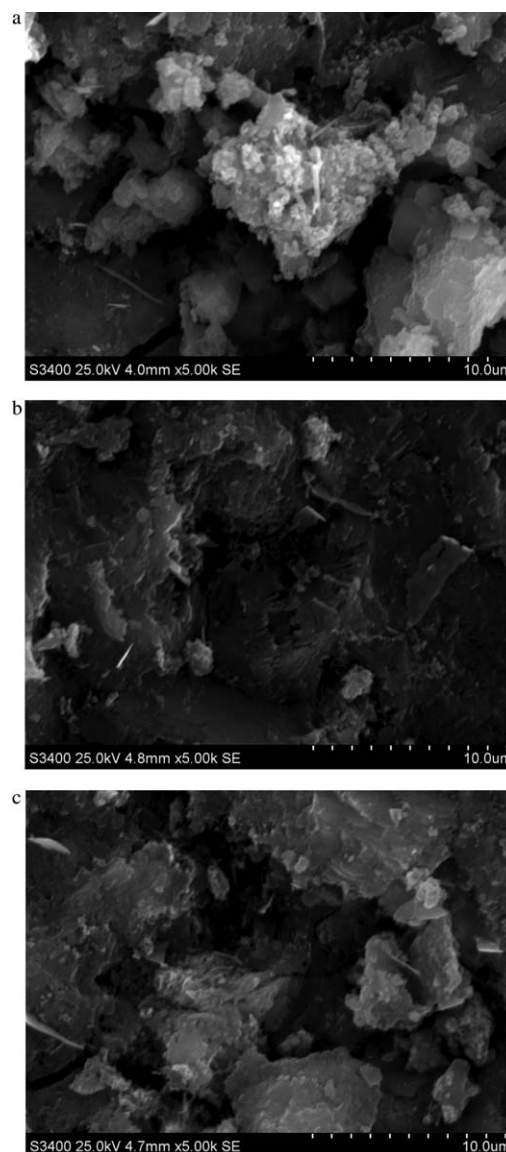
#### SEM Study

The results of SEM observation of microstructure for hardened cement with or without SPs after 1/7/35 days were shown in Figures 9 and 10.

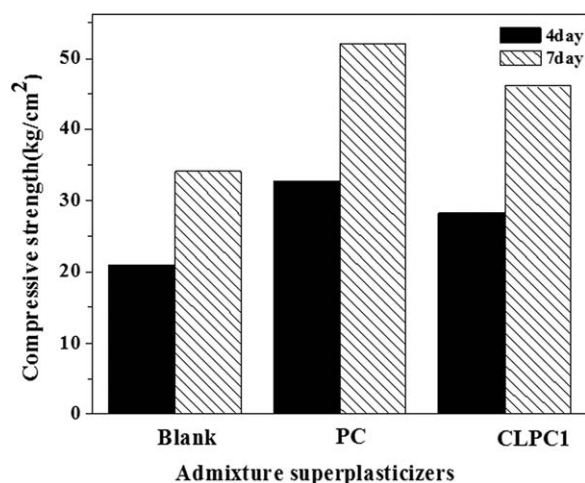
The microstructure of hydrates was composed of main hydration products C-S-H, hexagonal  $\text{Ca}(\text{OH})_2$  and needle-shaped ettringite.<sup>29</sup> The porosity lowered the density of concrete. In Figure 9, it clearly showed that addition of SPs reduced total porosity and homogenized pore size distribution. The microstructure of CLPC1 after 1 day showed a very dense structure of smaller and thinner crystallites. Very little ettringite was seen in



**Figure 10.** SEM micrographs for the hardened cement after 7 days of hydration. (a) Blank, (b) PC, (c) CLPC1.



**Figure 11.** SEM micrographs for the hardened cement after 35 days of hydration. (a) Blank, (b) PC, (c) CLPC1.



**Figure 12.** Variation of compressive strength for the hardened cement after 4/7 days of hydration.

CLPC1. The result quite coincided with XRD in Figure 8(a). Such results clearly indicated that the early hydration was greatly delayed. In Figure 10, the microstructure of the Blank and CLPC1 had thicker and larger  $\text{Ca}(\text{OH})_2$  crystallites after 7 days. However, the microstructure of PC had very dense hydrates. In Figure 11, a dense and closely packed structure of C-S-H was clearly showed. Compared with the others, the microstructure of PC had a denser deposit of C-S-H.

#### Effects of SPs on Compressive Strength of Hardened Cement

Compressive strength of hardened cement with or without SPs was given in Figure 12. Compressive strength of Blank, PC, and CLPC1 showed continuous increase with hydration time up to 7 days. PC pastes had the highest values of strength compared with the Blank and CLPC1 paste. This could be attributable to the formation of calcium silicate hydrates (C-S-H). It was proposed that the cross-linked structures could

affect generation of C-S-H which was beneficial for the density of concrete. The experimental results quite coincide with SEM in Figure 11(c).

## CONCLUSIONS

Water-soluble CLPCs of acrylic acid and alkenyl alcohol type polyoxyethylene ether was synthesized through aqueous free radical polymerization. The cross-linked SP delivered higher performance of slow-release than traditional comb-like polymer. The cross-linked structure exerted little impact on zeta potential, and gave more effective rheological properties to cement suspensions after 120 min hydration. The results showed that ester group and amide group were hydrolyzed under alkaline condition of cement suspension. Released carboxyl group gradually increased with increasing time to enable redispersion during cement hydration. Studies on the hydrated cement by XRD, SEM, and compressive strength indicated that the intensity of CH peaks for CLPC became weaker after 1 day, the chelation of  $\text{Ca}^{2+}$  by the released carboxyl group of CLPC delayed the early hydration in the hydrated cementitious system. The microstructure showed a very dense structure of crystallites and very few ettringite in CLPC. The compressive strength indicated that the cross-linked structures could affect generation of C-S-H.

## ACKNOWLEDGMENTS

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