Synthesis and Properties of an Amphoteric Polycarboxylic Acid-Based Superplasticizer Used in Sulfoaluminate Cement

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ABSTRACT: A novel amphoteric polycarboxylic (APC) acid-based superplasticizer was prepared by solution copolymerization from maleic anhydride, allyl polyethylene glycol, and methacryloxyethyltrimethyl ammonium chloride (DMC). The cationic monomer DMC was introduced for improving the performances of sulfoaluminate cement (SAC) with APC. The condition on preparation of APC was determined by the orthogonal experiment, and the performances of fresh and hardened superplasticized mortars were assessed. APC was characterized by FTIR spectra. Adsorption amount and dispersing effectiveness of APC were also investigated. Results indicated that APC could improve the fluidity and enhance the mechanical performances of SAC mortars. Adsorption amount of APC in SAC is large. Compared with an anionic PC superplasticizer and a commercial superplasticizer Visco Crete 3390, APC has the better performance. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 283–290, 2012

Key words: amphoteric; superplasticizer; adsorption; sulfoaluminate cement

INTRODUCTION

Superplasticizer, a kind of chemical admixture, is widely used in concrete. It can reduce the water to cement ratio and improve workability of concrete. A variety of superplasticizers have been developed in recent years, e.g., sulfonated naphthalene formaldehyde condensates (BNS) and sulfonated melamine formaldehyde condensates (PMS). Since 1980s, application of a new generation of polycarboxylic (PC) acid-based superplasticizers has been studied.[1] They have excellent fluidity at low water to cement ratios (as low as 0.15) and provide slump retention over a prolonged period.[2]

Although PC superplasticizers show good dispersion and retention properties, they do not have perfect compatibility with different cements, particularly sulfoaluminate cement (SAC). SAC is a special kind of cement invented by Chinese in 1970s, mainly composed of $C_4A_3\bar{S}$ and β-C_2S. It has been widely applied in winter construction, emergency repairs, permeability resistance engineering, offshore and corrosion resistance engineering, etc., due to its properties such as high early strength, short setting time, impermeability, sulfate and chloride corrosion resistance, low alkalinity, etc.[3] SAC is not compatible with PC superplasticizers used for ordinary portland cement because of its fast hydration. That limits the application and development of SAC seriously.

To improve the compatibility of PC superplasticizer with SAC, a cationic monomer was introduced for preparing a novel amphoteric PC superplasticizer. It can be inferred that the PC superplasticizer would show good compatibility with SAC if it could delay the hydration of SAC. The amphoteric PC superplasticizer can reduce the rate of heat evolution, the heat amount of early hydration of cement paste and delay the time to reach highest hydration temperature.[4,5] Li[6] pointed out that the best properties of a PC acid-type superplasticizer may be obtained if the amphoteric and nonionic groups are all in the same molecular structure. Ran[7] prepared an amphoteric PC superplasticizer with high water reduction rate and pointed that the adsorption saturation was improved by the cationic groups.

TABLE I
Chemical Components of SAC 42.5

	Chemical components (wt %)						
Cement	SiO_2	Al_2O_3	CaO	Fe_2O_3	SO_3	MgO	Others
SAC	10.96	28.93	45	25	3.71	8.88	0.99

Furthermore, the introduction of cationic monomer can improve the adsorption capacity and dispersing effectiveness. Adsorbed amount is an important parameter which greatly affects the dispersing effectiveness of a superplasticizer. Sulfoaluminate cement mainly consists of $C_4A_3\overline{S}$ and C_2S. It was reported zeta potential of C_2S was negative, whereas that of $C_4A_3\overline{S}$ was positive.[8,9] It can be inferred the adsorption capacity of the traditional anionic superplasticizer was very limited, and adsorption saturation would be improved by amphoteric superplasticizer. For SAC with amphoteric superplasticizer, anionic groups adsorbed on the surface of $C_4A_3\overline{S}$, whereas cationic groups adsorbed on the surface of C_2S. The performance of SAC with amphoteric superplasticizer would be excellent than that of SAC with traditional anionic superplasticizer, such as PC superplasticizer (PCE) and Visco Crete 3390.

In this article, a novel amphoteric superplasticizer (APC) was prepared by solution copolymerization from maleic anhydride (MA), allyl polyethylene glycol (APEG), and methacryloxyethyltrimethyl ammonium chloride (DMC). The optimal condition on preparation was determined by the orthogonal experiment. Properties of APC used in SAC were investigated. Besides, an anionic PCE reported in our previous study[10] and a commercial anionic superplasticizer Visco Crete 3390 from Sika. Chemical components were also tested to compare with APC. The mechanism for adsorption and dispersion of SAC with APC was investigated.

EXPERIMENTAL SECTION

Materials

MA, potassium persulfate (KPS), and sodium hydroxide (NaOH) were used as received. DMC and

TABLE II
Mineral Components and Surface Area of SAC 42.5

	Mineral components				Specific surface area $(m^2\ kg^{-1})$
Cement	$C_4A_3\overline{S}$	C_2S	C_4AF	f-SO_3	
SAC	57.37	25.55	6.56	1.92	345

Note: $C_4A_3\overline{S}$: $3CaO\cdot3Al_2O_3\cdot CaSO_4$, C_2S: $2CaO\cdot SiO_2$, C_4AF_3: $4CaO\cdot Al_2O_3\cdot Fe_2O_3$, f-$SO_3$: $CaSO_4$.

APEG with three different numbers of ethylene oxide units, i.e., 56, 50, and 32, were supplied from Yantai Xinghuo Chemical and Shandong Dongda Chemical Industry Company, respectively. R·SAC 42.5 was obtained from Zibo Jinhu High-water Material. An anionic PCE was synthesized by the reaction among MA, APEG, and sodium methallyl sulfonated (shown in Fig. 2). Visco Crete 3390 was from Sika. Chemical components, the mineral components, and specific surface area of SAC 42.5 are shown in Tables I and II.

Experimental

Preparation of APC

The synthesis process of APC is shown in Figure 1. MA, APEG, and NaOH were dissolved in degassed, distilled water to prepare a 20.0 wt % solution in 250-mL flask. Nitrogen gas was bubbled for 30 min at 25°C with slow stirring. After heating to 65°C, DMC and KPS aqueous solution were dropped to the reaction mixture. During the polymerization process, the temperature kept 75°C for 4 h. At the end of reaction, the solution of copolymer was neutralized with 20.0 wt % NaOH solution. The optimal condition on preparation was determined by the orthogonal test. Flow of paste assesses the dispersing effectiveness of APC. APC was synthesized according to the optimum condition for the following tests. The experimental factors and levels for APC synthesis are shown in Table III. The structures of monomers and copolymers were confirmed by FTS-165 FTIR spectrometer from PE. The synthesis process of PCE is demonstrated in Figure 2.

Solid content

Dry the weighing bottle in electrothermal thermostatic drying oven at 80 ± 2°C, then, take out the weighing bottle and put it in the desiccator for cooling down. Weigh the weighing bottle accurate to 0.1
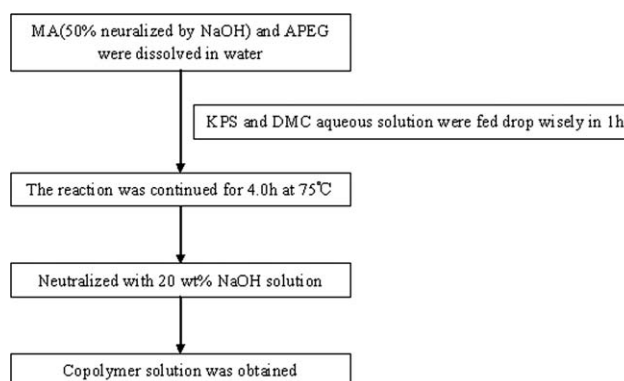

Figure 1 Synthesis process of APC.

TABLE III
Factors and Levels of Orthogonal Experiment

Factors	Levels		
	1	2	3
MA (mol)	3.0	4.0	5.0
APEG (mol)	0.5	1.0	1.5
DMC (mol)	0.2	0.6	1.0
KPS (wt % of all monomers)	2	3	4
n (the number of ethylene oxide units of APEG)	56	32	50

mg. Repeat this procedure until the weight of the weighing bottle become constant. Use the weighing bottle to weigh about 1.0 g solution of APC accurate to 0.1 mg. Gently even out the surface of the specimen and put it in the electrothermal thermostatic drying oven whose temperature has been adjusted to $80 \pm 2°C$. After drying 24 h, remove the weighing bottle and its cover quickly into desiccator for cooling. After cooling down, cover it, weigh the weighing bottle accurate to 0.1 mg. Repeat this procedure until constant weight is obtained. The repeated drying time is around 1 h. Use the following equation for calculation:

$$\omega = \frac{m_1 - m_2}{m_1 - m_0} \times 100 \quad (1)$$

where:

m_0 is the weight of weighing bottle (in grams).

m_1 is the weight of weighing bottle and predrying specimen (in grams).

m_2 is the weight of weighing bottle and after-drying specimen (in grams).

ω is the solid content.

Measurements were repeated three times, and the average values were obtained.

Flow test of cement paste

The optimum preparation condition was determinated by the flow test of cement paste. The tests were carried out according to GB8076 made by Standardization Administration of the People's Republic of China. Fresh cement pastes with APC were prepared at water/cement (W/C) of 0.35. APC was added into the mixing water at solid dosage of 0.3% (the weight percent of the solid of APC to cement. Solid dosage in the other experiments was 0.3%). APC was added and agitated for 1 min at 140 ± 5 r min^{-1} by mixer machine, then stayed for 1 min without stirring and then again stirred for 2 min at 285 ± 5 r min^{-1}. Immediately after the stirring, the cement paste was poured into a minislump cone (60 mm in height, 36 mm in top diameter, and 60 mm in bottom diameter) on a glass plate, and the

cone was vertically removed. The diameter of paste was recorded as the flow of paste. The resulting spread of the paste was measured three times. The optimum condition on preparation was obtained from the differences of the flow values.

Adsorption

Adsorption amount is an important parameter which greatly affects the dispersing effectiveness of a superplasticizer.[11] The adsorption amount of APC on cement was measured according to the depletion method.[12] The initial APC solution and unadsorbed APC (existing in the liquid phase of cement paste after adsorption) concentration were measured by a total organic carbon (TOC) analyzer (Shimadzu TOC-5000A, Japan). Adsorption amount was calculated from the concentrations of the polymer in the initial solution and the liquid phase of cement paste (solid dosage = 0.3%, W/C = 0.35). The liquid phase of cement paste was obtained by centrifugation after APC adsorption for 30, 60, 90, and 120 min. Centrifugal separation was at 10,000 rpm for 8 min. Measurements were generally repeated three times, and the average values were obtained.

Zeta potential

Zeta potential measurement of cement pastes is an effective method to investigate the dispersing
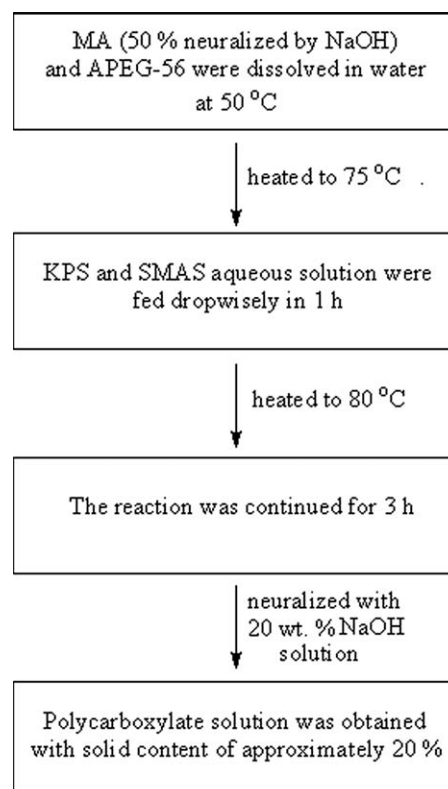

Figure 2 Synthesis process of PCE.

mechanism.[12] Zeta potentials of cement with different dosages of the superplasticizers were measured by Electroacoustic Spectrometer. The cement and the solution containing the superplasticizer were mixed for 5 min. W/C ratio of the mixture was 50/1 and polymer/cement (P/C) ratio was 0.35.

Flow test of cement mortar

Dispersing and retention capability of APC was assessed via the flow test of cement mortar according to GB8076 made by Standardization Administration of the People's Republic of China. The tests were carried out at 10, 30, 60, and 120 min after mixing. The fresh cement mortars with APC were prepared at W/C of 0.45 and C/S (cement/sand) of 1 : 3 (by mass) at 25°C. APC was added into the mixing water at solid dosage of 0.3%, and the flow value was measured by using a cone (60 mm in height, 70 mm in top diameter, and 100 mm in bottom diameter). The method is similar with test of paste.

Compressive strength of hardened mortar

Mix proportion of mortar was given as follows: APC dosage = 0.3% and C/S = 1/3. The flow of mortars was maintained at 180 ± 5 mm by adjusting W/C. The mortars were prepared according to GB8076 made by Standardization Administration of the People's Republic of China. Prism specimens (40 × 40 × 160 mm) were molded, cured in the 20 ± 1°C and =90% relative humidity (RH) environment for 24 h and cured in water at 20 ± 1°C until testing. The compressive strength of mortars cured for 3, 7, and 28 days were measured. The sample of hardened mortar was taken into the machine of compressive strength and fixed on both sides with steel plates of machine. Crush both sides of sample through the steel plates at 2.5 KN S^{-1} until the sample was destroyed by pressure. The number of pressure is the compressive strength of sample.

Comparison with PCE

An anionic PCE was synthesized as displayed in Figure 2. A commercial superplasticizer Visco Crete 3390 and PCE were used to compare with APC. Adsorbed amount, flow of mortar, and mechanical performance of hardened mortar were tested according to the methods described above.

RESULTS AND DISCUSSION

Preparation of APC

Plank[12] has synthesized a copolymer using two kinds of monomers. He proved the copolymers showed an alternating monomer sequence because allylether monomers do not homopolymerize. We
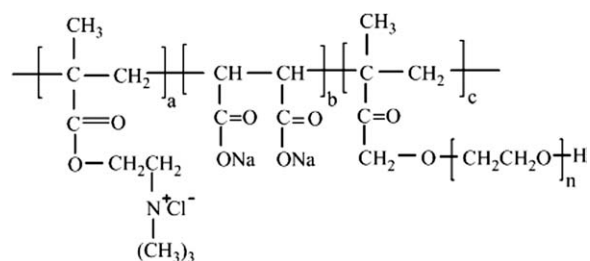
Figure 3 The chemical structure of APC; a, b, and c are the number of each block and positive integers.

synthesized APC by using the same monomers as what he used and adding the third one, namely DMC. The copolymer APC was a random copolymer, and its structure was shown in Figure 3.

For further study, the FTIR spectrum of monomers and APC were shown in Figure 4. The wide absorption band assigned to hydroxyl groups around 3434 cm^{-1} was significantly observed in Figure 4(d). The characteristic absorption bands for the monomers were found in Figure 4(a–c). 1580 and 1350 cm^{-1}, the characteristic ethilenic peak of —CONa, obviously appeared in Figure 4(d).The strong C=C stretch [1717 cm^{-1} (676 in^{-1})], the characteristic ethilenic peak, obviously appeared in the spectrum of monomers. While absorption peaks around 1600–1870 cm^{-1} (630–737 in^{-1}) were not found in Figure 4(d). It indicated that the product was composed of all the three kinds of monomers. And APC did not contain double bonds because the monomers have been copolymerized.

The result of orthogonal experiment

The orthogonal experiment $L_{18}(3)^5$ was designed for determining the optimal condition on preparation of APC. The flow of paste was used as the assessing index for orthogonal experimental, and the highest value of flow was the target. Mean was obtained from the following equation and the maximum of Mean indicated which level was best.

$$\frac{\sum X_{ij}}{n} \qquad (2)$$

X is value of factor i in level j.
$\quad i$ is the factor.
$\quad j$ is the level of factor.
$\quad n$ is the number of X_{ij}.

The impact of each factor on performance of product was shown by Range. The value of Range was calculated through eq. (3).

$$Range = Mean_{max} - Mean_{min} \qquad (3)$$

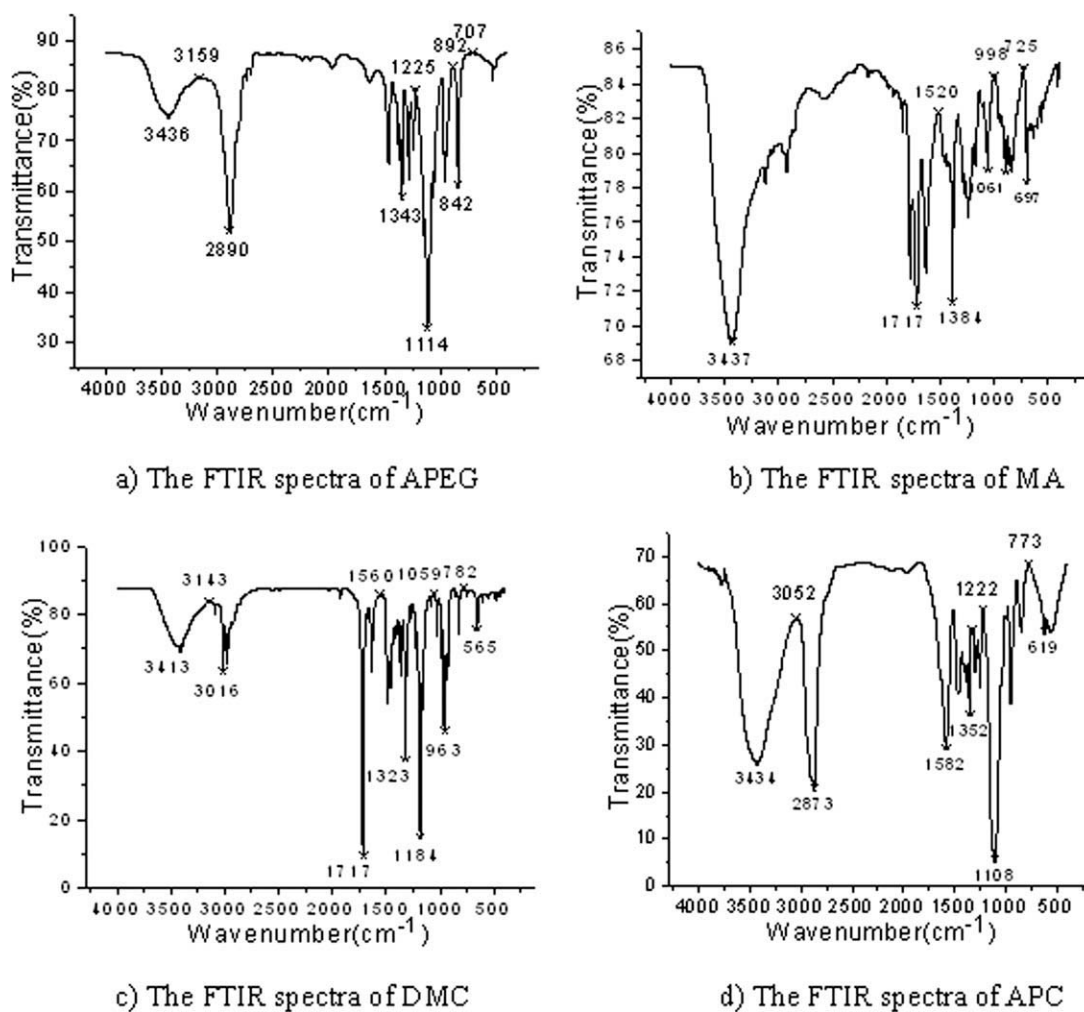The results of orthogonal experiment and the flow of paste are shown in Table IV. The initiator KPS

a) The FTIR spectra of APEG

b) The FTIR spectra of MA

c) The FTIR spectra of DMC

d) The FTIR spectra of APC

Figure 4 The FTIR spectrum.

TABLE IV
The Result of Orthogonal Experiment

Factors	MA (mol)	APEG (mol)	DMC (mol)	KPS (%)	N	Solid content (%)	Flow of paste (mm)
1	3.0	0.5	0.2	2	32	20.8	213
2		1.0	0.6	3	50	19.1	239
3		1.5	1.0	4	56	21.3	279
4	4.0	0.5	0.2	3	50	21.9	198
5		1.0	0.6	4	56	20.7	262
6		1.5	1.0	2	32	20.2	249
7	5.0	0.5	0.6	2	56	21.9	203
8		1.0	1.0	3	32	20.3	268
9		1.5	0.2	4	50	21.8	238
10	3.0	0.5	1.0	4	50	21.2	223
11		1.0	0.2	2	56	21.7	231
12		1.5	0.6	3	32	20.3	228
13	4.0	0.5	0.6	4	32	20.4	276
14		1.0	1.0	2	50	21.2	223
15		1.5	0.2	3	56	20.8	206
16	5.0	0.5	1.0	3	56	20.8	223
17		1.0	0.2	4	32	21.0	268
18		1.5	0.6	2	50	20.5	200
Mean 1	235.500	222.667	225.667	219.833	250.333		
Mean 2	235.667	248.500	234.667	227.000	220.167		
Mean 3	233.333	233.333	244.167	257.667	234.000		
Range	2.334	25.833	18.500	37.834	30.166		

TABLE V
Adsorption Amounts of APC and PCE

	Adsorption amount [mg(superplasticizer) g^{-1}(SAC)]			
	30 min	60 min	90 min	120 min
APC	1.59	1.72	1.78	1.79
PCE	1.02	1.11	1.15	1.15

dosage was wt % in respect to all monomers, and n was the number of ethylene oxide units of APEG. The reaction was continued for 4 h at 75°C. The optimum condition on preparation was that the molar ratio of MA, APEG (with 56 ethylene oxide units), and DMC was chosen as 3.0 : 1.0 : 1.0, and the dosage of KPS was 4.0 wt % through comparing Mean of each factor. In contrast to the strong effect of the dosage of initiator and the number of ethylene oxide units, amount of DMC and MA have little impact on flow of paste by comparing Range.

Adsorption

The most popular mechanism of PC superplasticizer is that many copolymers absorb on the cement particles and form a densely packed polymer layer. The dispersing capability is determined by the steric repulsion of the long side chains. Adsorption amount is an important parameter to assess the dispersing capability of a superplasticizer. The higher the adsorption amount, the better the dispersing capability. The amount of amphoteric copolymer (APC) adsorbed on SAC 42.5 was determined for each example.

It can be obviously seen from Table V that the adsorption amount of APC increased with time and the point of adsorption saturation was much higher than anionic PCE. A potential explanation for this phenomenon is the adsorption saturation was improved by the cationic groups. For SAC with amphoteric superplasticizer APC, anionic groups adsorbed on the cement particles exhibiting positive surface ($C_4A_3\bar{S}$), whereas cationic groups adsorbed on negative surface (C_2S). Therefore, adsorption saturation was improved, and adsorption amount was much higher than that of anionic superplasticizer PCE.

Zeta potential

It can be seen in Figure 5 that zeta potential of cement particles is negative, and the absolute value of zeta potential of cement particles decreased with increase of dosages slightly. Similar result has been reported by Kazuhiro Yoshioka.[8] He found that all

mineralogical components of cement showed negative zeta potential when they were dispersed in a solution with superplasticizer. A strong decline of zeta potential to more negative values indicates electrostatic repulsion is the main mechanism for dispersion. While the decrease of the absolute value of zeta potential of cement particles indicates steric repulsion is the main mechanism for dispersion.[12] Therefore, steric repulsion was found to be the key factor for dispersion to this kind of APC acid-based superplasticizers.

The mechanism for adsorption and dispersion

The mechanism for adsorption and dispersion of SAC with APCs was shown in Figure 6. SAC mainly consists of $C_4A_3\bar{S}$ and C_2S (shown in Table II). It was reported $C_4A_3\bar{S}$ was positive, whereas C_2S was negative.[8,9] The molecular model of APC is shown in Figure 6(a). Both anionic groups and cationic groups exist in APC. The mechanism for adsorption is anionic groups of superplasticizer molecule adsorbed on the surface of $C_4A_3\bar{S}$ and cationic groups adsorbed on C_2S [shown in Fig. 6(b)]. The adsorption was improved compared with traditional anionic superplasticizer. Steric repulsion between the cement particles covered with polymer molecules made cement have better dispersion [shown in Fig. 6(c)].

Flow test of cement mortar

The dispersing and retention capability was measured by flow test of cement mortar. Figure 7 illustrates the loss of cement mortar with APC at 0.3% dosage. The values of flow slightly decreased with elapsed time at first and then decreased rapidly. The
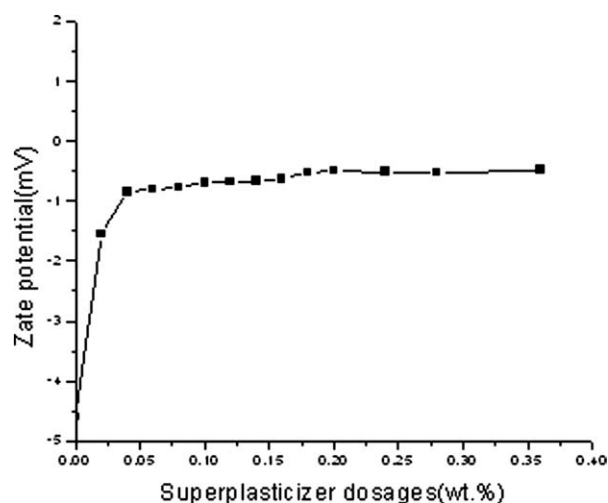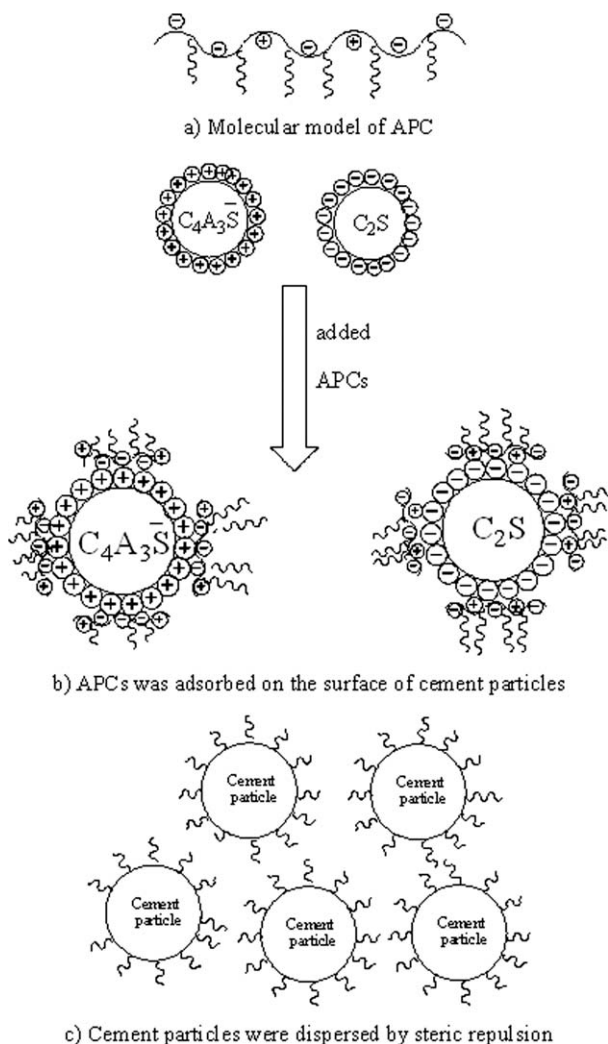
Figure 5 Zeta potential of SAC with APC.

Figure 6 The mechanism for adsorption and dispersion of APC.

Figure 7 Flow of mortars and retention capability.

result shows that APC improved dispersing capability of cement mortar greatly, and low loss was obtained comparing to plain sample.

Adsorption amount was found to be a key factor for dispersing capability. It has been reported that increases in adsorption amount gave more excellent dispersing capability.[11,12] Therefore, good dispersing capability of cement mortar with APC might be attributed to the high adsorption amount. The results indicated that APC is quite compatible with SAC.

Comparison with PCE and Visco Crete 3390

For assessing the properties of APC used in SAC, an anionic PCE synthesized by us and a commercial superplasticizer Visco Crete 3390 were tested. Figure 6 showed the flow of mortars and retention capability with APC, PCE, and Visco Crete 3390. It can be seen from Figure 6 that all the three superplasti-
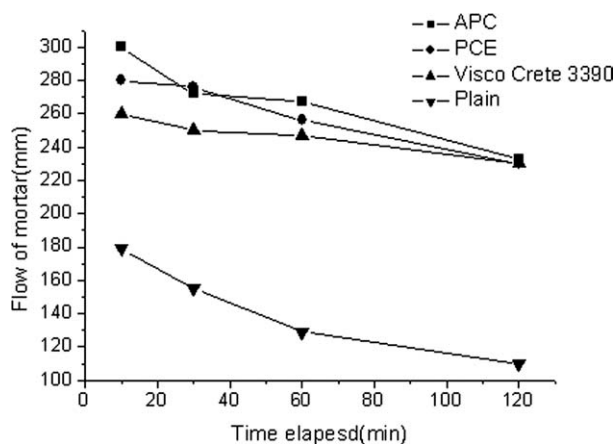
cizers could improve the flow of mortars notably and showed good retention capability comparing to plain sample. Furthermore, APC was better than PCE and Visco Crete 3390. Table VI showed the compressive strength of hardened mortars with APC, PCE, and Visco Crete 3390. The compressive strength of hardened mortars with APC at 3, 7, and 28 days were respectively higher than those hardened mortars with PCE and Visco Crete 3390. The performance of SAC with Visco Crete 3390 was the poorest.

CONCLUSIONS

A novel amphoteric superplasticizer (APC) was prepared by solution copolymerization. The optimum condition on preparation was that the molar ratio of MA, APEG (with 56 ethylene oxide units), and DMC was 3.0 : 1.0 : 1.0 and the dosage of KPS was 4.0 wt %. The reaction was continued for 4 h at 75°C. Adsorption amount of APC in SAC is much larger than an anionic PCE. Zeta potential of APC was also tested. All results indicated steric repulsion between the cement particles covered by polymer molecules made cement have better dispersion.

Mortars with APC showed good dispersing and retention capability and the mechanical performances of hardened mortars were improved notably. Besides, a commercial superplasticizer Visco Crete

TABLE VI
Effect of APC on Compressive Strength of Hardened Mortar

Mortars	Compressive strength (Mpa)		
	3 (days)	7 (days)	28 (days)
Plain	37.4	49.2	65.7
APC	45.3	78.5	81.0
PCE	40.5	67.6	73.0
Visco Crete 3390	42.3	63.4	70.0

3390 was also tested. Results indicated properties of APC used in SAC were better than those of PCE and Visco Crete 3390.

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