Preparation of Amphoteric Polycarboxylate Superplasticizers and Their Performances in Cementitious System

Lingfei Jiang,[1] Xiangming Kong,[1] Zichen Lu,[1] Shanshan Hou[2]

[1]Key Laboratory of Structural Engineering and Vibration of China Education Ministry, Department of Civil Engineering, Tsinghua University, Beijing 100084, China
[2]School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China
Correspondence to: X. Kong (E-mail: kxm@tsinghua.edu.cn)

ABSTRACT: A series of amphoteric polycarboxylate (PC) polymers were synthesized by radical copolymerization of acrylic acid (AA), [3-(methacryloylamino) propyl] trimethylammonium chloride (MAPTAC) and ω-methoxypolyoxyethylene methacrylate ester (MPEGMA). Cationic groups were introduced in to PC molecules with expectation of less retardation effect on cement hydration compared to the traditional anionic PC superplasticizers. The content of cationic groups in polymer was varied by changing the monomer ratio of MAPTAC to AA in the synthesis recipes. The structure of the synthesized amphoteric PCs was verified by gel permeation chromatography (GPC) and Fourier transform infrared spectroscopy (FTIR). The performances of the amphoteric PCs were evaluated by measurement of flowability and zeta-potential of cement pastes and adsorption amount of PC in cement pastes. Impacts of the PCs on cement hydration were studied by isothermal calorimetry. It is concluded that both anionic and cationic PC polymers can be effectively adsorbed onto the surface of cement particles and thus change the zeta potential of cement pastes. The adsorption amounts of the amphoteric PCs decrease with increasing content of cationic units. A proper incorporation of cationic units into PC polymers may lead to a higher fluidizing performance in fresh cement pastes. The amphoteric PC polymers with higher content of cationic units show less retardation effect on cement hydration and hence higher early strength of cementitious materials may be achieved by using amphoteric PCs with appropriated content of cationic units without losing their plasticizing efficiency. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41348.

INTRODUCTION

With the development of modern concrete, higher early strength and faster strength growth are becoming more and more important for saving production and construction time, especially in the industry of prefabricated concrete. Fast setting and quick early strength growth of concrete can be obtained through the use of chemical admixtures such as setting accelerators or hardening accelerators, which are usually chemicals such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), triisopropanolamine, and calcium salts.[1–4] During the last decades, superpalsticizers have become one of the indispensable ingredients in concrete formulations, among which polycarboxylate superplasticizers (PCs) are getting dominant thanks to their higher water reducing efficiency and lower dosage, compared to other types of superplasticizer such as naphthalene formaldehyde polycondensate type and lignin sulfate type.[5] However, it has been known for long that the addition of superplasticizers in concrete has significant influences on cement

hydration, usually by retarding cement hydration.[6] The retardation effect of PCs is often stronger than other types of superplasticizer and thus lead to slower growth of early strength of concrete.[7] Generally, superplasticizer works as a dispersing agent for cement grains and increases the flowability of cementitious mixtures without additional water demand,[8] which is called plasticizing effect. It has been well understood that the dispersing effect of superplasticizers is closely related to their adsorption on cement surface.[9] The adsorbed PC molecules on cement surface, which are usually anionic charged polymers, create both electrostatic repulsive forces and steric hindrance due to the long poly (ethylene oxide) (PEO) side chains. On the other hand, it has been understood that the retardation effect of PCs originates from the two facts[10]: (1) the adsorbed PC layers hinder the diffusion of water and ions at the cement-solution interface; (2) the COO^- groups in PCs molecules may form complexes with Ca^{2+} in aqueous phase and thus inhibit the nucleation and growth of Ca-containing hydration products. It

Table I. Chemical 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_2S	C_3A	C_4AF
22.10	4.04	3.38	61.91	2.66	2.87	0.56	0.79	57.34	18.9	6.47	11.25

Note: The composition was obtained according to EN 196-2:2005 and Chinese Standard GB/T176–2008 "Chemical Analysis of Cement". The abbreviations of C_3S, C_2S, C_3A and C_4AF respectively represent the four major mineral phases of Portland cement, Ca_3SiO_5, Ca_2SiO_4, $Ca_3Al_2O_6$, $Ca_4Al_2Fe_2O_{10}$.

has widely accepted that the surfaces of silicate phases (C_3S, C_2S) and calcium silicate hydrates (C—S—H) are negatively charged, whereas the surfaces of the aluminate phases (C_3A, C_4AF) are positively charged.[11,12] It is reasonable to deduce that adsorption behavior of PC molecules on cement surface and the retardation effect can be modified by partly replacing the COO^- groups in PC molecules with other functional groups, such as cationic groups. Hsu et al.[13,14] prepared a water-soluble amphoteric copolymer with acrylamide and 2-(3-carboxy-acryloyloxy)-N-(carboxymethyl)-N,N-dimethylethanaminium (CAC) through free radical polymerization. The result indicated that this copolymer could work as an effective cement dispersant due to its adsorption on cement surface. Miao et al.[15,16] reported a new type of amphoteric comb-like copolymer synthesized by using acrylic acid (AA), ω-methoxypolyoxyethylene methacrylate ester (MPEGMA) and methacryloxyethyltrimethyl ammonium chloride (DMC). The water reducing ratio of such amphoteric polymer could reach up to 45% and it showed no retardation effect on cement hydration at dosage lower than 0.15 wt % of the mass of cement. Guo et al.[17] synthesized an amphoteric polycarboxylate superplasticizer by copolymerizing monomers of maleic anhydride (MA), allyl polyethylene glycol (APEG), and methacryloxyethyltrimethyl ammonium chloride (DMC) and applied it in sulfoaluminate cement mixtures. Under such circumstance, on the one hand, it become a hot topic to develop an amphoteric superplasticizer with combined properties of high water reducing ratio and low retardation effect on cement hydration, namely fast early strength growth of concrete. On the other hand, it is also in urgent need of understanding the influences of such amphoteric polymers on cement hydration.

In this study, a quaternary ammonium salt [3-(methacryloylamino) propyl] trimethylammonium chloride (MAPTAC) was used to copolymerize with the typical monomers for synthesis of PCs, namely acrylic acid (AA) and ω-methoxypolyoxyethylene methacrylate ester (MPEGMA), with the intention of introducing cationic groups into PC molecules to reduce the retardation effect on cement hydration caused by the addition of PCs and thus to obtain higher early strength of hardened cementitious materials, compared to the case of the traditional anionic PC superplasticizers. Because MAPTAC is positively charged in aqueous phase, the copolymierized PC molecules with MAPTAC repeating units become amphoteric due to the presence of both —COO^- groups from monomer AA and $\equiv N^+$— groups from monomer MAPTAC. The performance of the amphoteric polymers with varied AA to MAPTAC ratios were evaluated by measurements of flowability of fresh cement pastes, adsorption

amount of PC molecules on cement particles and zeta-potential of cement pastes. Impacts of the synthesized PC polymers on cement hydration were studied by isothermal calorimetry. The compressive strength of cement mortar at curing ages of 3 and 7 days were measured to determine the influences of the PC polymers on strength development of mortar.

EXPERIMENTAL

Raw Materials
Analytical grade of chemicals, acrylic acid (AA) (Tianjin Fuchen Chemical) [3-(methacryloylamino)propyl] trimethylammonium chloride (MAPTAC) (Jiangsu Feixiang Chemical), and sodium methyl acryl sulfonate (SMAS), ammonium persulfate (APS) 3-mercaptopropionic acid (MPA) (all of the three from Beijing Chemical Works), were used as received (all >98% purity). Deionized water was used in all experiments in this study including synthesis of polymers and preparation of cementitious mixtures. ω-methoxy polyethylene glycol methacrylate (MPEGMA, 85%) used as macro-monomer for preparation of PC superplasticizers, was prepared at 130°C via esterification reaction of methacrylic acid and methyl polyethylene glycol whose M_w was about 1300 and the average polymerization degree of the poly(ethylene glycol) was about 28.

Portland cement 42.5R complying with the Chinese standard GB175–2007 was used, whose composition is listed in Table I. The composition of cement was obtained according to the European standard EN 196-2:2005 and the Chinese Standard GB/T176–2008 "Chemical Analysis of Cement." The fineness of cement is 2.3 and the density is 3.10 g cm^{-3}.

Synthesis of the Amphoteric Polycarboxylate Superplasticizers
The monomer combinations for synthesis of the amphoteric PC superplasticizers are listed in Table II. PAMM1-0, which is a copolymer of AA and MPEGMA with molar ratio of 1.0 to 0.25, represents the typical anionic PC superplasticizer. It was used as reference in this study for comparison of various amphoteric polymers. Cationic monomer MAPTAC was introduced into the PC molecules by simply replacing the monomer AA with MAPTAC in a certain ratio and the synthesized PC molecules became amphoteric. Complete replacement of AA with MAPTAC made the produced PC sample turn to cationic one (PAMM0–1). The synthesis formula of the amphoteric PC is presented in Figure 1.

Detailed description of the preparation procedure of the above mentioned PAMM polymers is summarized as following. Monomers with mix proportion as described in Table II, together with the chain transfer agent (MPA), were dissolved in

Table II. Monomer Combinations in the Synthesis of the PAMM Polymers

| PC samples	Molar ratio of AA:MPEGMA:MAPTAC	AA:MAPTAC	M_w	Polydispersity
PAMM1-0	1.00:0.25:0.00	1 : 0	24860	1.297
PAMM7-1	0.88:0.25:0.12	7 : 1	43920	1.680
PAMM3-1	0.75:0.25:0.25	3 : 1	40490	1.643
PAMM1-1	0.50:0.25:0.50	1 : 1	45910	1.541
PAMM0-1	0.00:0.25:1.00	0 : 1	43950	1.253

deionized water and an aqueous solution with mass concentration of 55.0% was prepared. Initiator solution with mass concentration of 2.0% was prepared by dissolving APS in deionized water. In the polymerization process, 350.0 g monomer solution was used and the molar ratio of initiator to total monomers was fixed at 1.0%. A flask vessel filled with 35.0 g water and 35.0 g monomer solution as pre-charge and equipped with two feeding pipes, was first washed by nitrogen gas for three times and heated up to 80°C in oil bath. Then the initiator solution and the rest of the monomer solution were separately fed into the vessel dropwise over 2.5 and 2.0 h, respectively. The inside temperature was kept constant at 80°C ± 2°C during polymerization. After complete dosing, the whole reactant mixture was kept at 80°C for additional post-polymerization time of 30 min

Figure 1. The synthesis formula of the amphoteric PC molecules containing the cationic groups of $\equiv N^+-$.

under stirring to complete the polymerization and then was allowed to cool down to room temperature of 25°C. NaOH solution with mass concentration of 40.0% was used to adjust the pH value of the product to about 8–9.

Characterization of the Prepared PC Samples
The synthesized products appeared yellowish transparent solutions with solid contents in a range of 36.0–39.0 wt %, which indicated a successful polymerization with high conversion (>90%). Gel permeation chromatography (GPC) and Fourier transform infrared spectroscopy (FTIR) were applied to characterize the synthesized PC samples. GPC equipped with a multiangle laser light scattering (LS) detector (DAWN HELEOS II, Wyatt Technology, USA) and a refractive index (RI) detector (Optilab rEX, Wyatt Technology, USA) was used to determine the weight average molecular weight (M_w) as well as the number average molecular weight (M_n), and the polydispersity (PDI) of the prepared polymers. 0.1 mol L^{-1} NaNO$_3$ aqueous solution was used as the eluent. All polymer samples were diluted to concentration of 5 mg mL^{-1} and directly injected into a 0.2 mL loop with a spectra system autosampler. Temperature during measurement was kept constant at 25°C and the flow rate was adjusted to 0.5 mL min^{-1}. Connected GPC columns of SB-804 HQ and SB-802.5 HQ (OHpak, Shodex, USA) were employed.

FTIR measurement was performed to identify the composition of the prepared PC samples. Because the synthesized PC samples contained a small amount of residual monomers and a tiny amount of salts from decomposition of initiator, a purification process was carried out prior to FTIR analysis. The synthesized PC sample was firstly diluted to about 10% and dialyzed by deionized water by using a cellulose ester semipermeable membrane MD44-7 with nominal molecular weight cut-off of 7000 Da provided by Beijing Ruida Henghui Science and Technology Development was used, which allows globulin with molecular weight of 7000 and smaller molecules to pass through. The electrical conductivity of the dialysate was measured by using a conductivity meter (FE30, Mettler Toledo, Switzerland) every 3 h before the dialysate was renewed. Knowing that the electrical conductivity of deionized water was about 10 μs cm^{-1}, we ended the dialysis process when the electrical conductivity of dialysate dropped below 30 μs cm^{-1}. Thus, most of salts, residual monomers were effectively removed from the sample. Afterward, a proper amount of the purified PC solution was homogeneously mixed with KBr salt by a grinding mixer and then completely dried in a vacuum oven at 80°C. The KBr salt
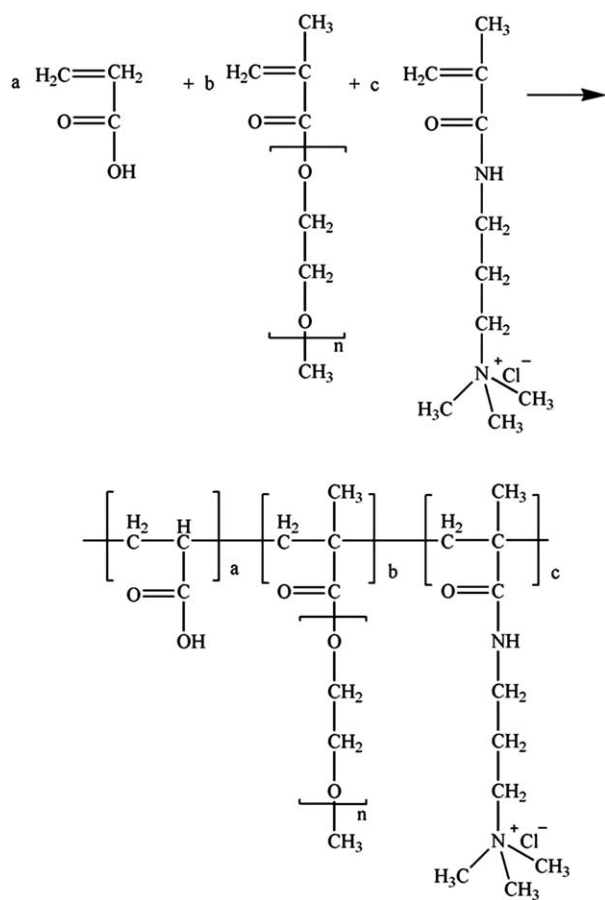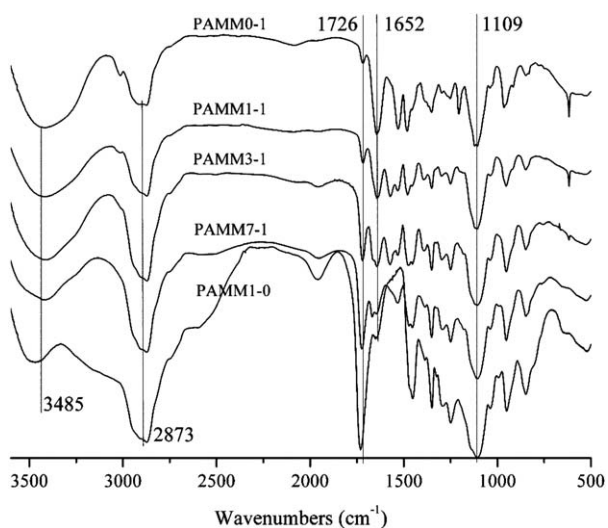
Figure 2. FTIR spectra of the prepared PCs.

was pressed into a tablet and then scanned by FTIR instrument (Nicolet 6700 FTIR, Thermo Fisher Scientific, USA) in the transmission mode from 400 to 4000 cm^{-1} at room temperature of 25°C.

Flowability of Cement Pastes

Cement pastes were prepared at 25°C with water-cement ratio (W/C) of 0.29. The amount of PCs added into the cement pastes was fixed at 0.2% by weight of cement (bwoc). The flowability of the cement paste was measured by using a mini-slump cone (60 mm high with a top diameter of 36 mm and a bottom diameter of 60 mm), following the procedure described in the standard GB/T 8077–2000, "methods for testing the uniformity of a concrete admixture." The cement paste was sealed in a container during testing intervals at 0, 30, 60, 90, and 120 min after being mixed with water.

Adsorption Amount of PCs on Cement Particles

The dispersing function of PCs in cement pastes is facilitated by the adsorption of PCs on the surface of cement particles. The adsorption amount of PCs on cement particles was measured by using a TOC Analyzer (Shimadzu, TOC-VCPH, Japan). The freshly mixed cement pastes were centrifuged at 4000 rpm for 10 min, and the clear supernatant solutions were collected through a membrane filter with a pore diameter of 0.45 μm. TOC tests were conducted to determine the concentration of PCs in the aqueous solution. Thus, the adsorbed amount of PCs on cement particles was then calculated by deducting the amount of PCs that is remaining in the aqueous phase from the initially added PCs amount in the cement pastes.

Zeta-Potential

Cement pastes were mixed at W/C of 0.5. The amount of PCs added into cement paste was fixed at 0.2% bwoc to investigate the impacts of various PC polymers on zeta-potential of fresh cement pastes. Zeta potential of cement pastes containing different PCs was measured by using Acoustic and Electroacoustic Spectrometer (Dispersion Technology, DT1201, USA), with the measuring range of −3000 mV to +3000 mV. Prior to the measurements, zeta probe were calibrated by using the

supernatant solution of the cement paste as ionic background for the zeta potential measurements of the corresponding cement paste. After mixing time of 4 min, 40 mL fresh paste was immediately transferred into a 50 mL sample cell equipped in DT1201. The probe was dipped into the well mixed fresh cement paste and the zeta potential was then measured. During the measurement, the cement paste was kept stirring by using a magnetic mixer at 200 rpm in order to keep the suspension homogeneous. The measurement of zeta-potential was repeated seven times over 10 min for each sample and then an average of these measured values was recorded.

Isothermal Calorimetry

Isothermal calorimetry tests were conducted on the cement pastes by TAM Air calorimeter (Thermometric AB, Sweden). Cement pastes were mixed at 25°C with W/C of 0.29. The addition of PCs in cement pastes was fixed at 0.2% bwoc. Prior to the calorimetry tests, the calorimeter was regulated at constant temperature of 25°C ± 0.02°C and then equilibrated for 24 h. Thereafter, 6 g cement was placed into a 20 mL ampoule bottle and then introduced into the channel of the micro-calorimeter. After the channel was sealed and the baseline reached the equilibrium, the water together with the PCs were injected into the ampoule bottle and then stirred for 10 min. The heat evolution was recorded for 3 days.

Compressive Strength of Mortar

The compressive strength of mortar was measured at ages of 3 and 7 days to investigate the effects of the amphoteric PC superplasticizers on the strength development of cementitious materials. The testing procedure follows the standard GB/T 8077–2000, "methods for testing the mortar (ISO method)." The cubic specimens of the pastes with dimensions of 40 mm × 40 mm × 160 mm were used for the strength measurement. Mortar was mixed with W/C of 0.35 and sand-cement ratio of 1.33. The amount of PCs in the formulation of the mortar was 0.12% bwoc. The standard testing procedure was followed according to EN 196.

RESULTS AND DISCUSSION

Characterization of the Prepared PCs

As seen from Table II, the M_w of the prepared PCs lies in a range of 20,000–50,000 with relatively narrow distribution. To confirm the co-polymerization of the various monomers during synthesis of the PC co-polymers as designed in Table II, FTIR analysis was performed on the purified PC samples and the spectra are given in Figure 2.

As seen in Figure 2, the broad peak around 3485 cm^{-1} and the sharp peak at 2873 cm^{-1} are respectively assigned to the O—H and C—H stretching bands. The absorption band at 1652 cm^{-1} corresponds to the C=O of carboxamide, which derives from the monomer MAPTAC. The peak at 1726 cm^{-1} is assigned to the overlapping of C=O in AA and macro-monomer MPEGMA. Moreover, the characteristic band of MPEGMA also appears at 1109 cm^{-1} for C—O—C asymmetric stretching. The presence of these characteristic peaks in the FTIR spectra demonstrates the occurrence of copolymerization of the involved monomers. On the other hand, with increasing proportion of
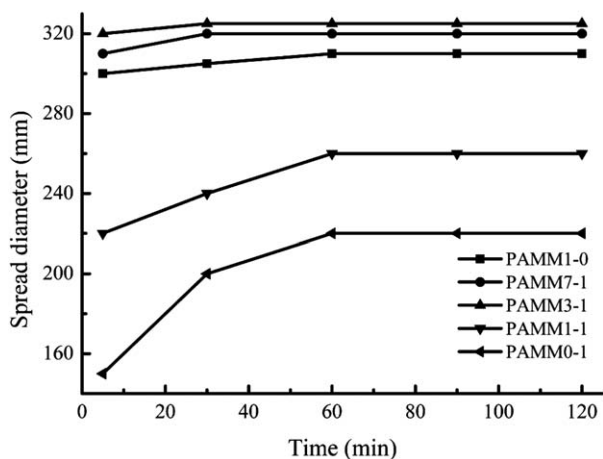
Figure 3. Flowability of cement pastes with addition of the synthesized amphoteric PC superplasticizers at dosage of 0.2% bwoc (W/C = 0.29).

MAPTAC in the synthesis recipe, the peak of C=O of carboxamide at 1652 cm^{-1} in the polymers become more intense, while that of C=O at 1726 cm^{-1} gets lower when the height of the peak at 1109 cm^{-1} for C—O—C is fixed constant, as seen in Figure 2. This indicates that the molar ratio of the repeating units of AA to MAPTAC in the PCs molecules decreases as expected.

### Flowability of Cement Pastes with Addition of Various Superplasticizers

The dispersing capability or the plasticizing efficiency of superplasticizers is usually evaluated by the flowability measurement of cement pastes with addition of superplasticizers. The flowability of cement pastes in presence of various amphoteric PCs at dosage of 0.2% bwoc is presented in Figure 3. It should be mentioned that the neat cement paste with W/C of 0.29 does not show any flowability, indicated by the small spread diameter (<60 mm). From Figure 3, it is clearly seen that the reference sample PAMM1-0, which is a copolymer of AA and MPEGMA, presents good fluidizing effect and also good flowability retention capability over elapsed time. Meanwhile, it is found that the amphoteric PCs with a certain amount of cationic monomer units, such as PAMM7-1 and PAMM3-1, exhibit even higher fluidizing capability than the reference sample PAMM1-0. More incorporation of the cationic monomer MAPTAC into PC molecules leads to decreases in the dispersing capability such as in cases of PAMM1-1 and PAMM0–1. These results are in good agreement with the literatures.[13] It is interesting to note that the sample PAMM0–1, which is a completely cationic polymer, still shows a fair fluidizing effect, but with a postponed acting power.

The Adsorption Isotherms of the Amphoteric PCs on Cement Surface and Their Influences on Zeta-Potential of Cement Pastes

As well accepted that the superplasticizers provide the dispersing effect through adsorption on cement surface and create the electrostatic repulsion and/or the steric hindrance between cement grains,[18] it is necessary to investigate the adsorption of the PCs and their influences on zeta potential of cement pastes. The

adsorption isotherms for the synthesized PCs on cement surface are presented in Figure 4. It is seen that from the completely anionic PC (PAMM0–1) to the completely cationic PC (PAMM1-0), each synthesized PC shows a certain capability to adsorb onto cement surface. As well understood, in a hydrating cement paste, a heterogeneous charge distribution is developed on surface of cement grains. Usually surface of silicate phases (C$_3$S and C—S—H) is negatively charged, while surface of aluminates such as C$_3$A and AFt possesses positive charges.[12] Such heterogeneous distribution of surface charges is responsible for the flocculation of cement particles, and at the same time provides adsorptive sites for both cationic and anionic species.

On the other hand, it should be noted that the saturated adsorption amount seems to decrease with the increasing incorporation of cationic monomer units (MAPTAC) in PC molecules, as seen in Figure 4. The anionic PC (PAMM1-0) shows the maximum saturated adsorption amount, whilst the cationic one (PAMM0–1) exhibits the minimum. Similar phenomenon have been reported when adsorption of polymer latexes and asphalt emulsions on cement surface are concerned.[19,20] It has been well documented that anionic polymer latexes and asphalt emulsions respectively exhibit higher adsorption capability on cement surface than their cationic counterparts. In case of that anionic species are added into a hydrating cement paste, such as anionic PC molecules (PAMM1-0) in this article, they can be adsorbed onto both the positively charged due to the electrostatic attraction and negatively charged cement surface thanks to the bridging effect of Ca^{2+} ions. The Ca^{2+} ions that are rich in the aqueous phase of a hydrating cement paste, may form stable complexes with the carboxyl groups —COO$^-$ in the PC molecules and thus play a role of bridging-linker between the PCs molecules and the negatively charged cement surface. However, when the cationic polymers are added into cement paste, they can be only adsorbed onto the negatively charged cement surface because those anionic ions presenting in a hydrating cement paste, OH$^-$ and SO$_4^{2-}$ do not have such bridging effect. This way, the saturated adsorption amount of the anionic PC molecules is much higher than the cationic ones, as observed in Figure 4. Figure 5 shows the adsorption amount of
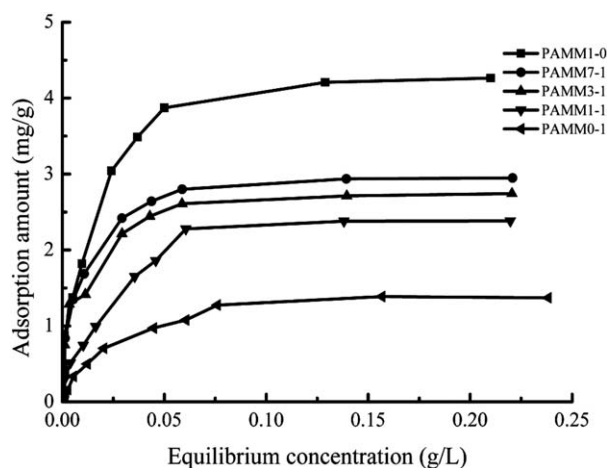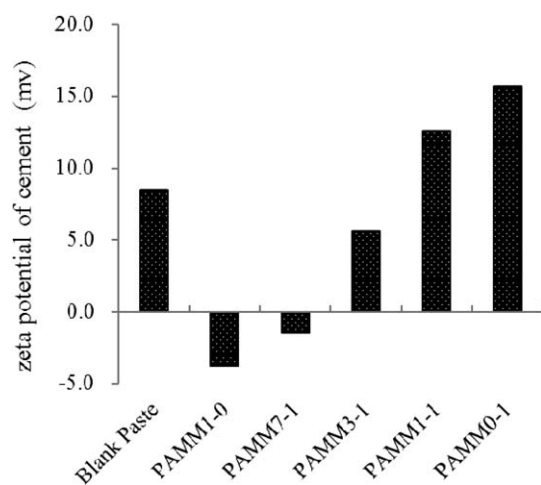

Figure 4. The adsorption isotherms of the synthesized amphoteric PCs on cement surface (W/C = 0.29).
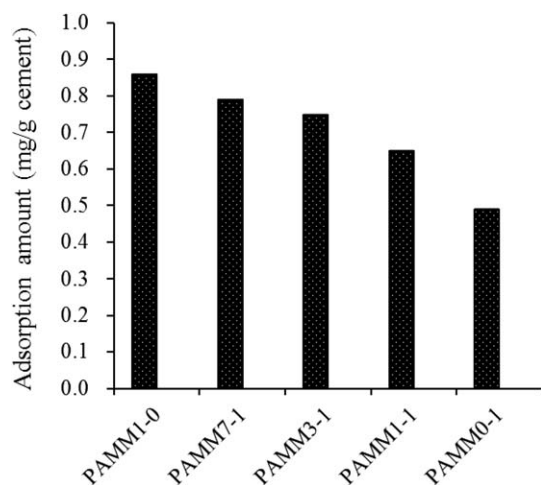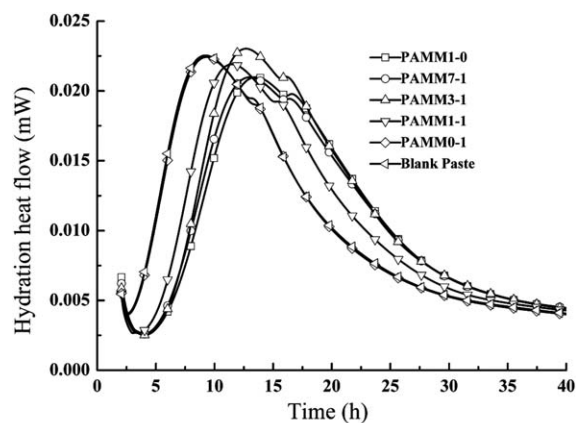
Figure 5. The adsorption amount of various PCs on cement surface at dosage of 0.2% by weight of cement (W/C = 0.29).

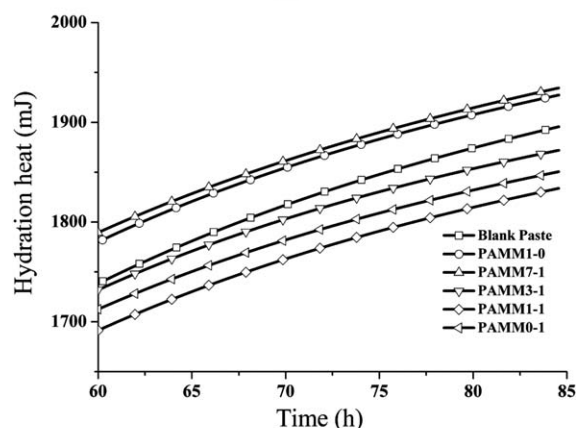various PCs on cement surface at fixed dosage of 0.2%, which indicates the same trend as discussed above.

Zeta potential of cement pastes is another index for indirect indicating the adsorption of PCs on cement surface and for understanding the influences of PCs on the flowability of cement pastes.[19] Figure 6 presents the zeta-potentials of the blank cement paste as well as those cement pastes with incorporation of various PCs. It is seen that the blank cement paste exhibits a positive zeta potential value of 8.4 mV. The addition of the completely anionic PC polymer PAMM1-0 turns the zeta potential of cement paste to a negative value of −3.7 mV. A clear trend can be found that for those amphoteric PCs with increasing incorporation of cationic monomer MAPTAC units, the zeta potentials of cement pastes in presence of amphoteric PCs increase with increasing ratio of the cationic units in PC molecules. The addition of the completely cationic PC, PAMM0–1 leads the zeta potential of cement paste to a higher value than the blank cement paste. All these results of zeta potential measurement indicate effective adsorption of the PCs on cement surface.

Figure 7. Isothermal calorimetry curves of the cement pastes with various PCs at dosage of 0.2% (W/C = 0.29) (a) differential heat flow; (b) accumulative heat flow.

It is interesting to note that two amphoteric PCs with a small fraction of incorporated cationic units in the polymers, PAMM7-1 and PAMM3-1 perform even more powerful fluidizing capability than the reference PC, PAMM1-0 (as seen in Figure 3), although they are adsorbed on cement surface in a less

Figure 6. Influences of the synthesized PCs on the zeta-potential of cement paste at dosage of 0.2% by weight of cement (W/C = 0.5).

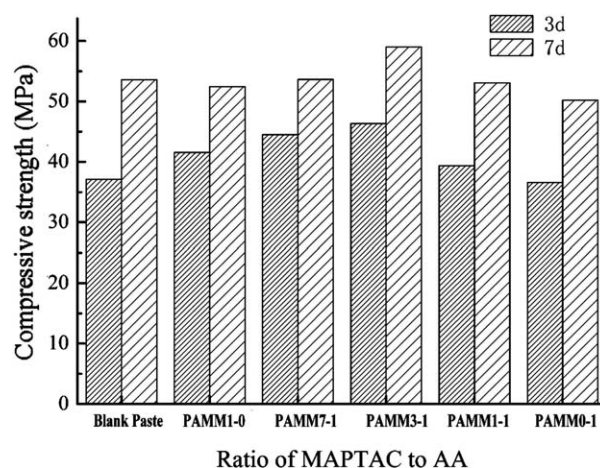**Figure 8.** Compressive strength of hardened cement mortars with addition of various PC polymers at dosage of 0.2% and at curing ages of 3 and 7 days (W/C = 0.35).

quantity and less change the zeta potential of cement pastes. This result clearly suggests that an amphoteric PC polymer with a proper content of cationic units may perform more powerful in fluidizing cement pastes than the completely anionic PC polymers, which are the most traditional type of PC superplasticizers in practical application. This result is consistent with the previous finding.[13]

Impacts of the Amphoteric PCs on Cement Hydration

Isothermal calorimetry was carried out on cement pastes to investigate the influences of various PCs on cement hydration as seen in Figure 7. It has been well known that the traditional polycarboxylate superplasticizers usually have a retardation effect on cement hydration due to the adsorption of superplasticizer molecules on the surface of hydrating cement particles, indicated by prolonged induction period and lowered maximum exothermic rate in the acceleration period of cement hydration.[21] As seen in Figure 7, this is again confirmed by the reference PC sample PAMM1-0, which is a typical anionic PC superplasticizer. With increasing incorporation of the cationic units in PC molecules, it is clearly seen from Figure 7(a) that the retardation effect becomes less significant. The completely cationic PC, PAMM0–1 shows minimized retardation effect, indicated by the mostly overlapped heat flow curve of the cement paste in presence of PAMM0–1 with that of the blank cement paste.

The retardation mechanism of PC superplasticizers has been understood from the two aspects as follows. Firstly, the adsorbed superplasticizer molecule layers hinder the diffusion of water and ions at the cement-solution interfaces, which can be defined as physical retardation. And secondly, the carboxyl groups ($-COO^-$) richly contained in the PC molecules may form complexes with Ca^{2+} ions, which leads to either reduction of Ca^{2+} ion concentration in solution, or inhibition of nucleation and growth of Ca-containing hydration products. The latter one can be called as chemical retardation.[22] From this point of view, the retardation effect of the amphoteric PCs can be explained as follows. On the one hand, the adsorption amount of the amphoteric PCs on the surface of cement particle is visibly lower than the reference PC sample, PAMM1-0 and thus the amphoteric PCs less affect the diffusion process of ions and water across the interface of hydrating cement particles and water phase. On the other hand, with increasing incorporation of the cationic units in PC molecules, the content of $-COO^-$ in PC molecules is decreasing. Therefore the chemical retardation is getting lower. For the completely cationic PC, PAMM0–1, there is no chemical retardation observed due to the absence of $-COO^-$ in the molecules and its adsorption on cement surface is minimized.

The cumulative heat amount generated by cement hydration can be an indicator of hydration degree. From Figure 7(b), one can clearly see that at age of 3 days, the hydration degree of cement pastes with various PCs is lower than the blank cement paste to different extent. The anionic PC (PAMM1-0) leads to the lowest hydration degree, whilst the cationic one exhibits almost no reduction on hydration degree. All these results suggest a possibility for reducing the retardation effect of PC superplasticizers by incorporating cationic units into the conventional anionic PC molecules.

Effect on Compressive Strength of Mortar

From the results above, it has been shown that the amphoteric PCs with a proper content of cationic units in polymer may have reduced retardation effect on cement hydration without losing the fluidizing performance on fresh cement pastes at the same time. Thus, higher early strength of the hardened cement pastes can be expected. Figure 8 shows the compressive strength of hardened cement mortars with addition of various PCs at ages of 3 and 7 days. It is clearly found that the mortar with addition of the amphoteric PC, PAMM3-1, shows the highest compressive strength at both ages of 3 and 7 days. This must be a result of its balanced fluidizing effect on fresh cement paste (Figure 3) and the retardation effect on cement hydration (Figure 7).

CONCLUSIONS

A series of amphoteric PC polymers are synthesized with varied content of cationic groups in molecules, which are expected to provide less retardation effect on cement hydration for higher early strength, compared to the traditional anionic PC superplasticizers. The performances of the amphoteric superplasticizers are evaluated by measurements of flowability of cement pastes, adsorption amount of PCs in cement pastes, zeta-potential of cement pastes and isothermal calorimetry. Based on the abovementioned results, it could be concluded that both anionic and cationic PC polymers can be effectively adsorbed onto the surface of cement particles and thus change the zeta potential of cement pastes. The adsorption amounts of the amphoteric PCs polymers decrease with increasing content of cationic units. A proper incorporation of cationic units into PC polymers may lead to a higher fluidizing performance in fresh cement pastes compared to the traditional anionic PC superplasticizers. The amphoteric PC polymers with higher content of cationic units show less retardation effect on cement hydration and the complete cationic PC polymers exhibits nearly no influence on cement hydration. Compared with the traditional PC superplasticizer, higher early strength of cement mortar can be achieved by using the amphoteric PC polymers with appropriated content of cationic units. This study opens up a new possibility for reducing the retardation effect of PC superplasticizers by incorporating cationic units into the conventional anionic PC molecules without compromise of losing their plasticizing efficiency.

AUTHOR CONTRIBUTION

Professor Kong put forward the original idea of this study and designed the frame of the this research; Lingfei Jiang and Shanshan Hou mainly conducted the experimental work and finished the draft; Zichen Lu analyzed the experimental data and revised the draft under the direction of Professor Kong. All of the authors had made the substantial contributions to this article.

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