

A Water-Soluble Amphoteric Copolymer: Synthesis and Its Dispersion Properties on Cement Particles

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ABSTRACT: A new water-soluble amphoteric copolymer (PAC) was synthesized and evaluated as a dispersion agent for cement particles. PAC was prepared from acrylamide and 2-(3-carboxyacryloyloxy)-*N*-(carboxymethyl)-*N,N*-dimethyl ethanaminium (CAC) through free-radical polymerization. The structure of the prepared polymer was verified by the IR spectra. The dispersion properties of PAC were evaluated by the minislump test on cement pastes. The test results indicate that this copolymer could disperse the cement particles and improve the fluidity of the cement pastes. Compared with a commercial superplasticizer, sul-

fonated naphthalene formaldehyde condensate, PAC showed better dispersion properties. This polymer, with about 16.7% CAC and a weight-average molecular weight of about 1×10^5 , was most effective in dispersing cement particles and enhancing the fluidity of the cement pastes. This was attributed to the interaction and adsorption behavior of this admixture with cement particles. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1313–1319, 2010

Key words: adsorption; dispersions; synthesis; water-soluble polymers

INTRODUCTION

Water-soluble polymers have been applied in many areas, including mineral and ceramic processing, water treatment, and coatings.^{1–3} Another important area of application is in the construction industry.^{4,5} The polymers are called *high-range water reducers* or *superplasticizers*. The addition of only a small amount of them can significantly improve the workability, mechanical strength, and other properties of concrete.^{4–6}

Sulfonated naphthalene formaldehyde (SNF) condensates and sulfonated melamine formaldehyde condensates are classified as superplasticizers of the first generation. These chemical admixtures, after being adsorbed on cement particles, create electrostatic repulsions and overcome attractive forces. This results in the dissociation of the cement agglomerates into primary particles with a significant decrease in the viscosity of the mixes and a great improvement in the workability of fresh concrete without segregation or bleeding. Lately, a new generation of superplasticizers based on polycarboxylic acids (PCA) with long, comb-type side chains were developed. These chemicals can create not only electrostatic repulsions but also steric effects.

Therefore, they exhibit better dispersion properties than the former sulfonate-based admixtures. More importantly, they offer less slump loss in the resulting fresh concrete.^{4,5} Also, several novel water-soluble polymers have been reported. For example, Lim et al.⁷ prepared a copolymer of maleic anhydride and acrylic acid, which caused a slump-releasing effect on cement pastes. Ye et al.⁸ prepared an acrylate/sulfonate copolymer and found that this polymer, with a proper reactant ratio and molecular weight, was effective in dispersing cement particles and promoting the fluidity of cement pastes. Pei et al.⁹ revealed a sulfonated acetone formaldehyde resin and discussed the effect of the molecular weight of the polymer on the concrete properties in terms of workability, slump loss control, and compressive strength. Ouyang et al.¹⁰ prepared sulfanilic acid–phenol–formaldehyde (SPF) condensate and discussed the effect of the molecular weight of SPF on the properties of the cementitious system. Vieira et al.¹¹ reported that starch and cellulose anionic derivatives could be used as biodegradable dispersing agents for mortar and concrete mixtures.

To date, most chemical admixtures, including SNF, PCA, and SPF, have belonged to anionic polymers. Others, such as amphoteric or cationic admixtures, have seldom been reported. Recently, some amphoteric copolymers (PACs) have been revealed to be effective in dispersing barium titanate or zinc oxide powder in aqueous solutions.^{12–14} Therefore, it would be interesting to determine the performance of such polymers on the flow properties of cementitious materials. In this study, a PAC was prepared and evaluated

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as a concrete admixture. The PAC was prepared from acrylamide (AM) and 2-(3-carboxyacryloyloxy)-*N*-(carboxymethyl)-*N,N*-dimethyl ethanaminium (CAC) under basic conditions through free-radical polymerization. The structure of the prepared PAC was verified by the IR spectrum of the polymer. Various PAC samples were synthesized, and their effects on the fluidity of cement pastes were examined.

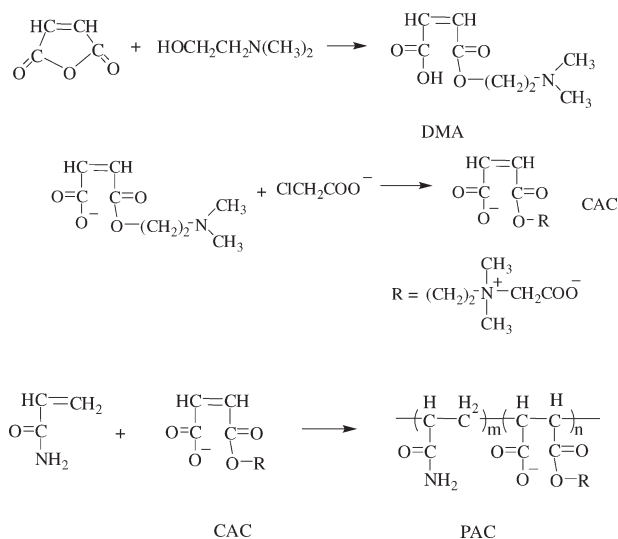
EXPERIMENTAL

Materials

AM (98.5%), maleic anhydride (99%), dimethyl ethanolamine (99%), sodium chloroacetate (98%), and ammonium persulfate (98%) from Acros Organics (Morris Plains, NJ) and sodium 2-methyl-2-propene-1-sulfonate (>98%) from Tokyo Chemical Industry (Tokyo, Japan) were used without further purification. PAC was prepared from the chemicals mentioned previously. The preparation details are described later. As shown in Table I, the prepared PAC samples had different monomer ratios and molecular weights. In addition, a commercial SNF superplasticizer from Hi Con (Taichung, Taiwan) was also used for comparison. SNF had a weight-average molecular weight (M_w) of about 4×10^3 . The molecular weight of the PAC and SNF samples were measured by a gel permeation chromatography method reported elsewhere.¹⁵

Preparation of the PAC resins

PAC was prepared from AM and CAC through free-radical polymerization. In turn, CAC was prepared from 4-[2-(dimethylamino)ethoxy]-4-oxobut-2-enoic acid (DMA) and sodium chloroacetate. DMA was prepared from maleic anhydride and dimethyl ethanolamine. The reaction equations for the preparation of DMA, CAC, and PAC were



For example, DMA, CAC, and PAC were prepared as follows. Maleic anhydride (49 g) was dissolved in

TABLE I
Properties of the PAC Samples

Polymer symbol	CAC (%)	M_w
PAC1	50	3.9×10^4
PAC5a	16.7	2.0×10^4
PAC5b	16.7	4.7×10^4
PAC5c	16.7	1.1×10^5
PAC5d	16.7	3.3×10^5
PAC10	9.1	5.5×10^4

200 g of acetone, and then, we added dimethyl ethanolamine (44.5 g) drop by drop into a 500-mL stirred reactor over 10 min. Thereafter, the reaction proceeded at 5°C for 8 h. After the reaction, the mixture was vacuum-filtered and washed with acetone, and the filtered solid powder was dried in a vacuum oven at room temperature for 24 h to collect DMA (80 g).

After we obtained DMA, CAC was prepared. That is, DMA (74.8 g) was dissolved in 240 mL of deionized water. The pH of the solution was adjusted to 9 with a 1N NaOH solution; we then added sodium chloroacetate (46.6 g). Thereafter, the solution was mixed at 30°C for 7 h. A majority of the solvent was removed in a vacuum condenser; then, the solution was washed with acetone. After the acetone was removed, the sample was dried in a vacuum oven at room temperature for 24 h to collect the sodium salt of CAC (108 g).

After we obtained CAC, PAC with an AM/CAC molar ratio of 5 : 1 in the feed was synthesized. Namely, AM (59.2 g) and sodium salt of CAC (48.3 g) were dissolved in 240 mL of deionized water; we then added an aqueous solution containing ammonium persulfate (4.6 g) and sodium 2-methyl-2-propene-1-sulfonate (1.6 g). Ammonium persulfate was used as the initiator, and sodium 2-methyl-2-propene-1-sulfonate was used as a chain-transfer agent. The reactor was purged with N₂ gas, and the polymerization was carried out at 40°C for 2 h. The product was precipitated thereafter and purified with methanol. The methanol was removed in a vacuum oven at room temperature for 24 h to collect PAC (74.2 g), which had a M_w of 1.1×10^5 . PAC samples with different molecular weights, shown in Table I, were obtained by the variation of either the initiator or chain-transfer concentration in this polymerization step.

Identification of the prepared resin

The dried DMA, CAC, and PAC resins were further ground into powder before structural determination or other uses. In identifying the chemical structure, we mixed proper amounts of the powder samples with predried KBr and pressed them into disks.

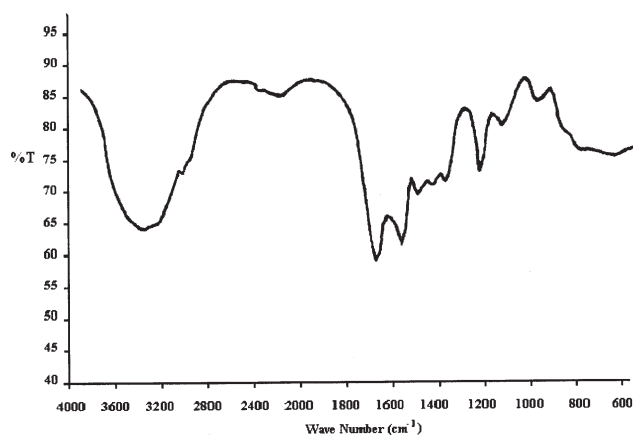


Figure 1 IR spectrum of DMA.

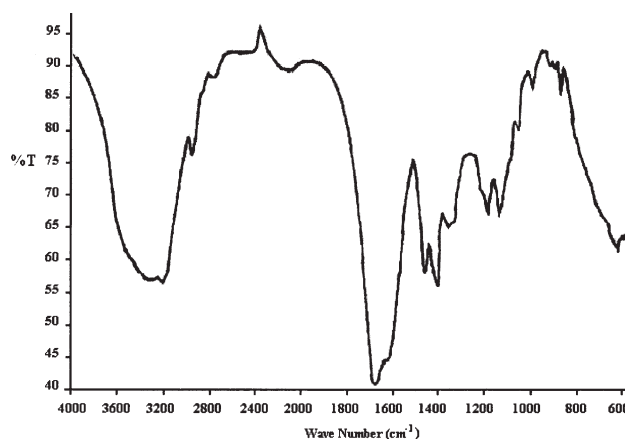


Figure 2 IR spectrum of CAC.

Transmission IR spectra of the disks were recorded with a PerkinElmer Paragon 500 Fourier transform infrared spectrometer (Boston, MA).

Preparations and fluidity tests of the cement pastes

Aqueous solutions containing 20 wt % PAC resin were prepared. Cement pastes were made by the mixture of water and type I Portland cement with or without the addition of the polymer solution. The cement was supplied by Taiwan Cement Co. (Taipei, Taiwan). The water/cement (W/C) ratio was either 0.3 or 0.6, and the polymer/cement (SP/C) ratio ranged from 0 to 1 wt %.

The fluidity of the cement pastes (W/C = 0.3) was determined from a minislump test.⁶ The apparatus for this test consisted primarily of a hollow mold in the form of a frustrum of a minicone with a base 4 cm in diameter, a top 2 cm in diameter, and a height of 6 cm. The minicone sat on a Plexiglas plate and was filled with cement pastes. Ten strokes were given on the top of the minicone before it was raised rapidly. The fluidity was indicated by the measured spread diameter or the minislump of the pastes on the plate.

Adsorption and measurements

Cement pastes with PAC were prepared. The W/C ratio was fixed at 0.6, and the SP/C ratio was fixed at 0.5 wt %. After it was mixed and centrifuged, the supernatant from the paste samples was taken. The molecular weight distribution of the polymer and the residual polymer concentration in the supernatant at various adsorption times were determined by a gel permeation chromatography method reported elsewhere.¹⁵ The amount of dispersant adsorbed on the cement particles was calculated from the difference in the dispersant concentration before and after adsorption.

ζ potential measurements

Cement suspensions with PAC were prepared. The W/C ratio was fixed at 4000, and the SP/C ratio ranged from 0 to 1 wt %. The ζ potential in the cement suspensions at 30 min was measured with a Malvern Zetasizer 3000HS. (Worcestershire, United Kingdom).

RESULTS AND DISCUSSION

Structure of the prepared resins

The structures of typically prepared DMA, CAC, and PAC were verified from their IR spectra, as shown in Figures 1–3, respectively. Figure 1 shows the IR spectrum of DMA, which displays an OH stretching band at 3600–3200 cm^{-1} . The peak at 1667 cm^{-1} was due to the C=O stretching band of the carboxylate group. The peak at 1549 cm^{-1} represented the C=C stretching band. The peak at 1205 cm^{-1} occurred because of C–N stretching. Figure 2 shows the IR spectrum of CAC. The peaks in the region 3600–3200 cm^{-1} were caused by the OH stretching band. The peak at 1675 cm^{-1} was due to

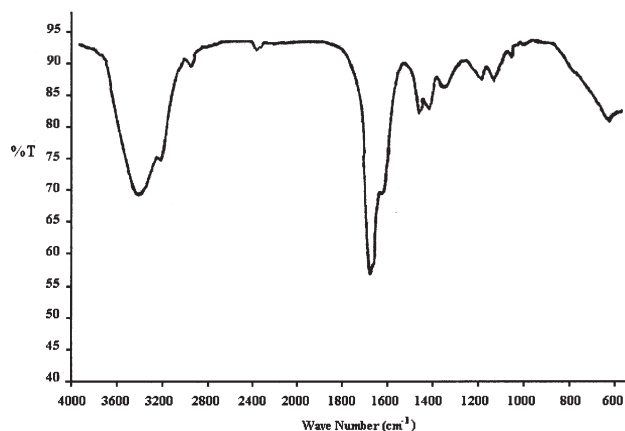


Figure 3 IR spectrum of PAC.

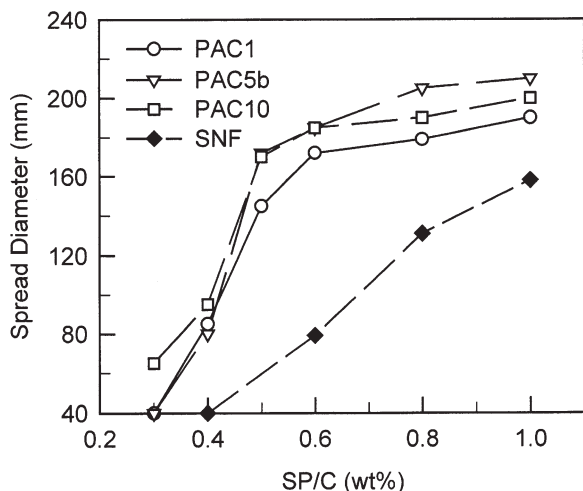


Figure 4 Minislump of the cement pastes with the chemical admixture at 0 min.

the C=O stretching band of the carboxylate group. The presence of the peak at about 1610 cm^{-1} represented the C=C stretching band. The band at 1177 cm^{-1} occurred because of C—N stretching. Compared with Figure 1, the C=O peak at about 1670 cm^{-1} shown in Figure 2 became sharper; this indicated that a CAC molecule contained more carboxylate groups than a DMA molecule.

Figure 3 shows the IR spectrum of PAC, which displayed an OH stretching band at 3394 cm^{-1} , an NH stretching band at 3210 cm^{-1} , a C=O stretching band at 1667 cm^{-1} , and a C—N stretching band at 1127 cm^{-1} . Compared to Figure 2, the C=C absorption band at about 1610 cm^{-1} became smaller in Figure 3; this suggested that the polymerization of AM and CAC occurred. Also, the IR spectrum in Figure 3 showed a distinct N—H stretching band at 3210 cm^{-1} ; this indicated that PAC contained the primary amide group.^{16,17}

Minislump of the cement pastes with PAC

A superplasticizer or chemical admixture is usually added in cementitious materials to disperse the cement particles and promote the workability of concrete. The minislump test on cement pastes is a screening test to determine the effectiveness of these chemicals on concrete workability.⁶ Figure 4 shows the measured spread diameter or minislump of cement pastes ($W/C = 0.3$) incorporated with either PAC or SNF after the end of mixing (0 min). The cement paste without any chemical admixture present did not flow, and the diameter was 40 mm. When PAC was added, the fluidity of the resulting paste increased. All of the tested PAC samples shown in Figure 4 were controlled to have a close M_w of about 5×10^4 . The diameter value was found to increase quickly with polymer dosage and then

gradually approached a constant value. The transition point or saturation point⁶ occurred at a polymer dosage of about 0.6–0.8 wt % for all three tested PAC samples. The transition point occurred at a polymer dosage greater than 1.0 wt % for SNF. All three PAC samples appeared to show better dispersion properties than the commercial one, as they required a lower dosage to achieve the same minislump value of cement pastes. It was clear that the fluidity-enhancing effect of the polymer on the cement pastes was in the following order: PAC5b > PAC10 > PAC1 > SNF.

Aside from enhancing the fluidity of cementitious materials, ideal chemical admixtures should practically prevent slump loss; a lower degree of slump loss will prolong the time available for the transport, handling, and placement of concrete. Figure 5 shows the spread diameter of the cement pastes with chemical admixture 60 min after the end of mixing. The trend agreed roughly with that in Figure 4, except that SNF became more effective than PAC1 instead. Regardless of which admixture was tested, the diameter value of the pastes at 60 min was generally lower than that at 0 min; this indicated that some fluidity loss occurred. Figure 6 shows the effect of the CAC content of PAC with an M_w of about 5×10^4 on the fluidity of the cement pastes. As expected, cement pastes with 0.8 wt % polymer showed greater diameter values than those with 0.6 wt % polymer. The minislump was increased with CAC content first, reached a maximum value, and then decreased thereafter. The optimal CAC content appeared to be about 16.7%, which made the pastes with the highest fluidity. When the CAC content was different from the optimal value, the polymer became less effective. Again, there was some fluidity loss with time, as the fluidity of the pastes at 0 min

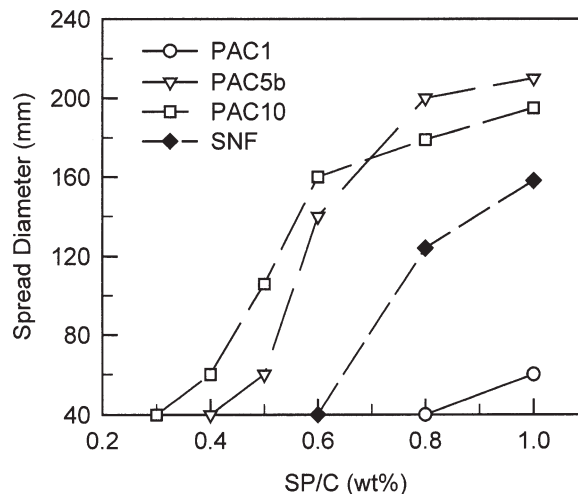


Figure 5 Minislump of the cement pastes with the chemical admixture at 60 min.

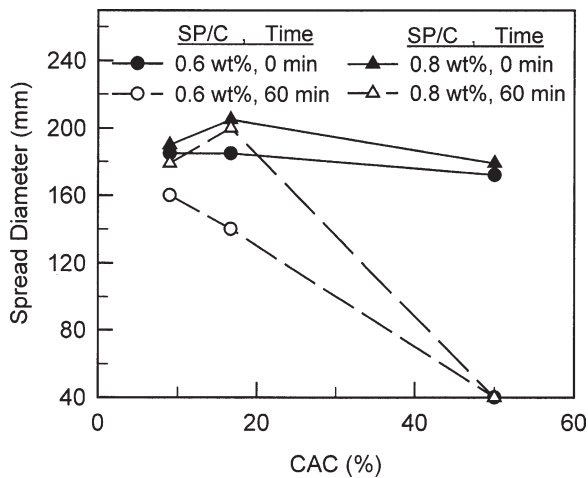


Figure 6 Effect of the CAC content of PAC on the fluidity of the cement pastes.

was higher than that of the pastes at 60 min. The degree of fluidity loss was found to depend on the CAC content and added polymer dosage.

Clearly, the adsorption behavior of the polymer onto cement particles is one factor affecting the performance of chemical admixture. Figure 7 shows the molecular weight distribution of free PAC5b molecules in the pore solution of the cement pastes (W/C = 0.6, SP/C = 0.5 wt %) at various adsorption times from 0 to 60 min. The peak area was found to decrease with increasing time. It appeared that the adsorption approached a constant value at times greater than 30 min. On the basis of the difference in the peak areas at different adsorption times, the amount of adsorbed polymer onto the cement particles could be calculated. Figure 8 shows the adsorbed amount of the PAC samples onto cement particles at different adsorption times. The results

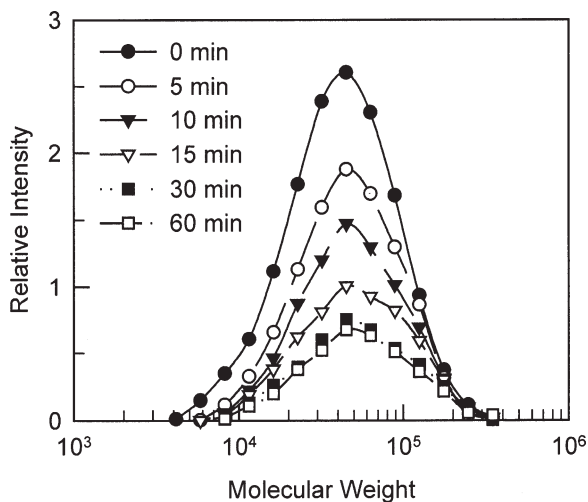


Figure 7 Molecular weight distribution of the PAC5b molecules in the pore solution of the cement pastes at various adsorption times.

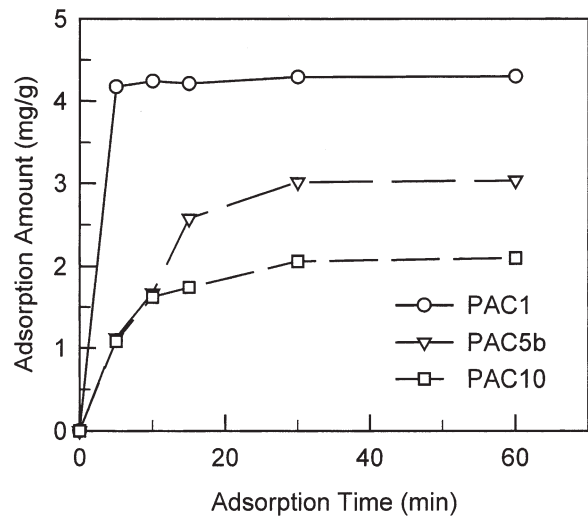


Figure 8 Adsorbed amount of the PAC samples onto the cement particles at different adsorption times.

indicate that the adsorbed amount of the polymer was in the following order: PAC1 > PAC5b > PAC10. It decreased with CAC content monotonically. It is known that C₃S, C₂S, C₃A, and C₄AF are four major mineral phases of cement. The C₃S and C₂S phases show negative ζ potentials, whereas the C₃A and C₄AF phases show positive ζ potentials. When cement contacts water, it becomes hydrated. Ettringite and monosulfate are hydrated products that show positive ζ potentials, whereas portlandite shows negative ζ potentials.^{18,19} PAC contained an AM moiety and a CAC moiety, which contained carboxylate anions and quaternary ammonium cations. Cement adsorbed PAC through the ionic interactions with the CAC moiety of the polymer. Among the three tested PAC samples, PAC1 contained the highest CAC content and charge density, so the adsorbed amount was the greatest, followed by PAC5b and PAC10. The greater the amount of polymer was adsorbed, the lower the amount of free admixture molecules was left in the pore solution and the faster the fluidity loss of the cement paste occurred. This explained why the cement pastes with 0.8 wt % PAC1, shown in Figure 1, showed good fluidity initially and had a diameter value of about 170 mm; it eventually had no flow 60 min after mixing, as shown in Figure 2.

Figure 9 shows the ζ potential of the cement particles with adsorbed PAC with different CAC contents. The result indicates that the ζ potential became more negative in the following order: PAC5b > PAC10 > PAC1. The trend agreed with that in Figure 4; a greater fluidity of cement pastes was produced with higher absolute ζ potential because stronger electrostatic repulsions were generated.

Except for the effect of CAC content, the molecular weight of PAC is another factor influencing the

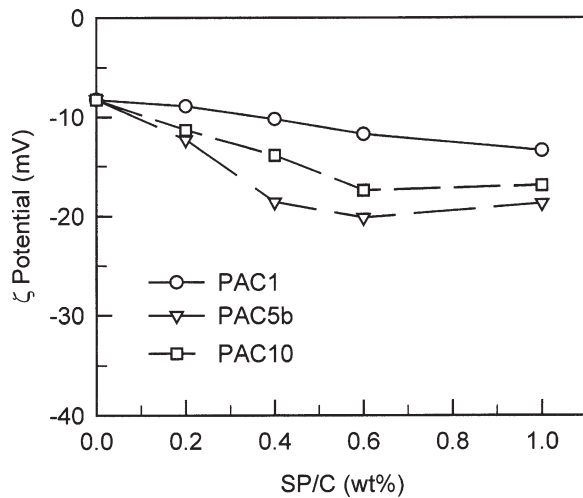


Figure 9 ζ potential of the cement particles with adsorbed PAC of different CAC contents.

flow properties of cementitious materials. Several works have indicated that there are optimal degrees of polymerization for the best performance in concrete in terms of workability and other properties.^{8-10,19-21} Figure 10 shows the effect of M_w of PAC on the fluidity of the cement pastes (W/C = 0.3) containing 0.6 or 0.8 wt % polymer at 0 or 60 min after the end of mixing. All of the tested polymers had a fixed 16.7% CAC content. Generally, the diameter value increased quickly with M_w initially, reached a maximum, and then decreased subsequently. The optimal molecular weight of PAC appeared to be about 1×10^5 , which made the resulting pastes exhibit the highest fluidity. Also, cement pastes with 0.8 wt % polymer suffered less fluidity loss than those with 0.6 wt % polymer. Figure 11 shows the ζ potential of cement particles with

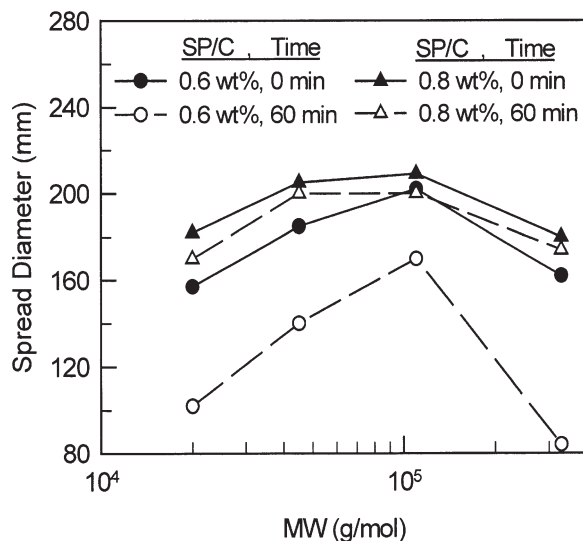


Figure 10 Effect of M_w of PAC on the fluidity of the cement pastes.

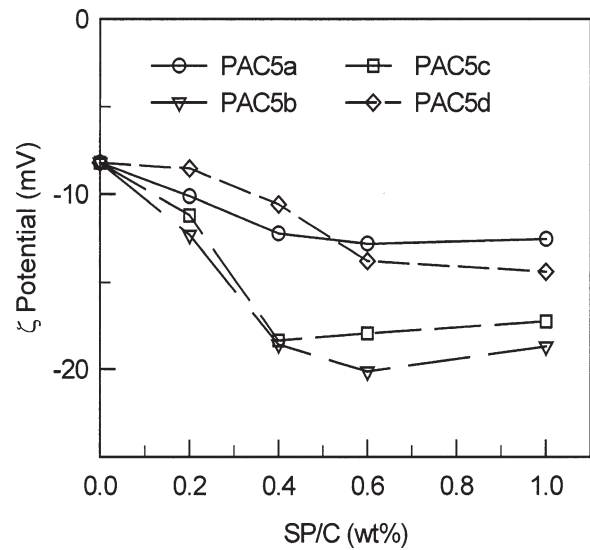


Figure 11 ζ potential of the cement particles with adsorbed PAC of different M_w 's.

adsorbed PAC of different M_w values. When the polymer dosage was more than 0.5 wt %, the ζ potential became more negative in the following order: PAC5b > PAC5c > PAC5d > PAC5a. This suggested that the adsorbed PAC5b caused more electrostatic repulsions than the adsorbed PAC5c on the cement particles. Separately, polymers with different molecular weights tended to show different conformations after adsorption onto solid particles. Polymers, such as PAC5c, with higher molecular weights were more likely to be adsorbed in a loop conformation, whereas PAC5b, with a lower molecular weight, was more likely to be adsorbed in a train conformation; the former caused more steric effects than the latter. As a result, PAC5c showed better dispersion properties than PAC5b. Nevertheless, the difference in the performance between these two polymers was only slight. Finally, polymer molecules with a molecular weight higher than 1×10^5 tended to flocculate with each other;²² this decreased the performance in promoting the fluidity of the resulting cement pastes. This was the reason PAC5d showed less plasticizing effects on the cement pastes than PAC5c.

CONCLUSIONS

A new carboxylic acid based PAC as a chemical admixture was prepared and verified by the IR spectra. The incorporation of PAC improved the minislump of the cement pastes. Compared with a commercial SNF superplasticizer, this polymer provided better dispersion effects on the cement pastes. PAC with a CAC content of about 16.7% and an M_w of about 1×10^5 was most effective in promoting the fluidity of the cement pastes. This was related to the

interaction and adsorption behavior of this admixture with cement particles.

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