

A Water-Soluble Acrylate/Sulfonate Copolymer. I. Its Synthesis and Dispersing Ability on Cement

Yi-Shian Ye, Hung-Lung Huang, Kung-Chung Hsu

Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan 116, Republic of China

Received 3 February 2005; accepted 22 September 2005

DOI 10.1002/app.23606

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A new water-soluble methacrylate/2-acrylamido-2-methylpropane sulfonate copolymer (PMAMP) was synthesized and evaluated as a dispersion agent for cement particles. PMAMP was prepared from methacrylic acid and 2-acrylamido-2-methylpropane sulfonic acid (AMP). The structure of the prepared polymer was verified by its NMR and IR spectra. The dispersing properties of PMAMP were evaluated by a minislump test on cement pastes. The test results indicated that this copolymer could disperse the cement particles and improve the minislump of cement pastes. Compared with a commercial superplasticizer (sulfonated naphthalene formaldehyde condensates), PMAMP performed better in enhancing

the fluidity of the cement pastes. The polymer with about 40–50% AMP and a weight-average molecular weight of about 5×10^4 was most effective in dispersing cement particles and promoting the fluidity of cement pastes. Nevertheless, PMAMP with a higher AMP content or a higher molecular weight appeared to cause less slump loss. This was related to the interaction of this admixture with the cement particles and its adsorption behavior onto the cement particles. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2490–2496, 2006

Key words: water-soluble polymers; synthesis; dispersion

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 has been in the construction industry.^{4,5} These polymers are called *high-range water reducers* or *superplasticizers*. The addition of only a small amount of one of them can significantly improve the workability, mechanical strength, and other properties of concrete.^{4–6}

Sulfonated melamine formaldehyde condensates and sulfonated naphthalene formaldehyde (SNF) condensates are classified as superplasticizers of the first generation. These 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.^{4,5} Recently, a new generation of superplasticizer based on carboxylated acrylic ester have been developed. As these chemicals contain long, comb-type side chains, they can create not only electrostatic repulsions but also steric effects. Therefore, they exhibit better dis-

persing effects than the former sulfonate-based admixtures. More importantly, they offer less slump loss in the resulting fresh concrete. This has led to the development of high-performance concrete, self-compacting concrete, and reactive powder concrete.^{6–8}

Although superplasticizer based on carboxylated acrylic ester can maintain the workability of concrete for a long period of time, the uses of this chemical in the preparation of flowing concrete and high-performance concrete are limited because of economic reasons. In other words, SNF is still the main admixture used because of its relatively low cost. However, care must be taken to prevent the rapid slump loss of concrete when SNF is incorporated.

Recently, Lim et al.⁹ reported that a poly(carboxylic acid) polymer with a $-\text{COO}^-$ functional group caused a slump-releasing effect. The addition of 20 wt % of a copolymer of maleic anhydride and acrylic acid in SNF resulted in excellent control of the effect of slump loss on cement pastes and an increase in apparent viscosity. Therefore, it would be interesting to evaluate the performance of polymer containing both sulfonate and carboxylate groups in its molecular structure on the flow properties of cementitious materials. In this study, a simple sulfonate/carboxylate copolymer, methacrylate/2-acrylamido-2-methylpropane sulfonate copolymer (PMAMP), as a concrete admixture was synthesized. PMAMP was prepared from methacrylic acid (MA) and 2-acrylamido-2-methylpropane sulfonic acid (AMP) in basic conditions through free-radical polymerization. The structure of

Correspondence to: K.-C. Hsu (kchs@cc.ntnu.edu.tw).

Contract grant sponsor: National Science Council of the Republic of China; contract grant number: NSC-91-2622-E-003-002-CC3.

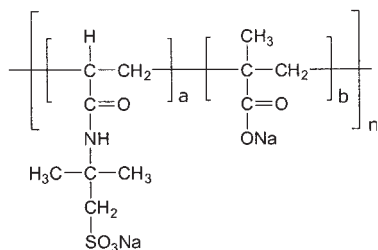


Figure 1 Chemical structure of PMAMP.

a prepared PMAMP was verified by its NMR and IR spectra. Several PMAMP samples with different reactant ratios and/or molecular weights were synthesized, and their effects on the fluidity of cement pastes were examined. In addition, the results were compared with those of a commercial SNF superplasticizer (HPC1000).

EXPERIMENTAL

Preparation of the PMAMP resins

MA, AMP, and ammonium persulfate were used without further purification. PMAMP was prepared from MA and AMP through free-radical polymerization. Ammonium persulfate was used as the initiator. PMAMP with 20 mol % AMP was prepared as follows. MA (9.6 g) and AMP (5.9 g) were dissolved in 60 mL of distilled water, and the pH value was adjusted to about 8 with 1N aqueous NaOH. The mixture was added to a 250-mL stirred reactor with refluxing. The reactor was purged with N_2 gas and heated. Ammonium persulfate aqueous solution (5.4 wt %, 10 mL) was added dropwise into the reactor, and the poly-

merization was carried out at 75°C for 2 h. After the reaction was completed, the mixture was precipitated and purified with a 1/1 acetone/water solution. The acetone solution was removed in a vacuum oven, and the dried precipitate was PMAMP (13.6 g). Figure 1 shows the chemical structure of the PMAMP resin.

In this study, polymers with different reactant ratios and molecular weights were prepared, purified, and tested. The AMP content of the samples ranged from 20 to 80 mol %, the weight-average molecular weight (M_w) ranged from 2.4×10^4 to 4.1×10^5 , and the number-average molecular weight (M_n) ranged from 1.2×10^4 to 7.2×10^4 . We prepared these polymer samples by varying the reactant ratios and initiator concentrations during polymerization. Table I lists the AMP content, M_w , and M_n of the prepared PMAMP samples. HPC1000, manufactured by Hi Con (Taichung, Taiwan), is an SNF superplasticizer with a M_w of about 2000; it was used for comparison.

Identification of the prepared resins

The dried PMAMP resins were further ground into powder before the determination of the structure and other procedures. In identifying the chemical structure, we mixed the proper amount of powder samples with predried KBr and pressed them into disks. Transmission IR spectra of the disks were recorded with a PerkinElmer Paragon 500 Fourier transform infrared spectrometer (Boston). Moreover, some powder samples were dissolved in D_2O and analyzed with a Varian Gemini 2000 NMR spectrometer (Palo Alto, CA).

Gel permeation chromatography measurements

The molecular weights of the PMAMP samples were determined with a gel permeation chromatograph,

TABLE I
AMP Content and Molecular Weights of the Prepared PMAMPs

Polymer	AMP (%)	M_w	M_n	Polymer	AMP (%)	M_w	M_n
P21	20	2.5×10^5	7.2×10^4	P61	60	2.5×10^5	2.6×10^4
P22		1.8×10^5	4.9×10^4	P62		1.3×10^5	2.3×10^4
P23		1.2×10^5	3.6×10^4	P63		1.1×10^5	2.0×10^4
P24		8.3×10^4	2.8×10^4	P64		9.9×10^4	1.9×10^4
P25		4.4×10^4	1.6×10^4	P65		5.8×10^4	1.5×10^4
P26		2.4×10^4	1.2×10^4				
P41	40	3.3×10^5	6.4×10^4	P81	80	4.1×10^5	2.6×10^4
P42		1.3×10^5	4.2×10^4	P82		2.2×10^5	2.6×10^4
P43		1.2×10^5	3.7×10^4	P83		1.7×10^5	2.5×10^4
P44		8.3×10^4	2.9×10^4	P84		1.5×10^5	2.0×10^4
P45		5.6×10^4	2.7×10^4	P85		1.1×10^5	1.9×10^4
P46		2.6×10^4	1.2×10^4				
P51	50	2.9×10^5	5.2×10^4				
P52		2.1×10^5	4.7×10^4				
P53		1.2×10^5	3.8×10^4				
P54		7.2×10^4	2.7×10^4				
P55		6.1×10^4	2.1×10^4				
P56		2.5×10^4	1.3×10^4				

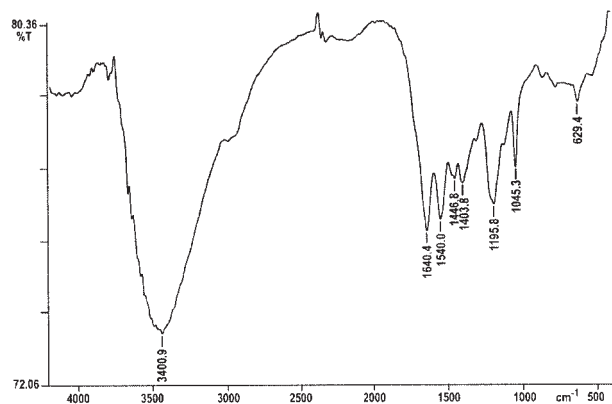


Figure 2 IR spectrum of PMAMP.

which consisted of a Jasco liquid chromatograph (Tokyo, Japan) equipped with three coupled columns (Shodex OHPak KB802.5, KB804, and KB806), a pump (Jasco PU-980), and a refractive index detector (Jasco RI-930). The samples were analyzed with a 0.1M KCl/methanol (80/20) aqueous solution as an eluent at a flow rate of 1 mL/min. Monodispersed polystyrene (PS) sulfonates of different molecular weights (1.8×10^3 , 8.0×10^3 , 3.5×10^4 , and 1.0×10^5) were used as calibration standards.

Preparation and fluidity tests of cement pastes

Aqueous solutions containing 20 wt % PMAMP resin were prepared. We made the cement pastes by mixing water and type I Portland cement with or without the addition of polymer solution. The water/cement ratios (W/C 's) were 0.3 and 0.6, and the resin/cement ratio (SP/C) ranged from 0 to 1 wt %.

The fluidity of the cement pastes ($W/C = 0.3$) was indicated by the measured minislump value. The minislump values of the cement pastes were 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 the base 4 cm in diameter, the top 2 cm in diameter, and a height of 6 cm. The minicone was set on a Plexiglas plate and filled with the cement pastes. Ten strokes were given on the top of the minicone before it was raised rapidly. The minislump value was indicated by the measured diameter of the spread pastes on the plate.

Adsorption and measurements

Cement pastes ($W/C = 0.6$) with PMAMP ($SP/C = 1.0\%$) were prepared. After the samples were mixed and centrifuged, the supernatants from the paste samples were taken. The residual dispersant concentration in the supernatants was analyzed and determined with gel permeation chromatography. The amount of dispersant adsorbed on cement particles was calcu-

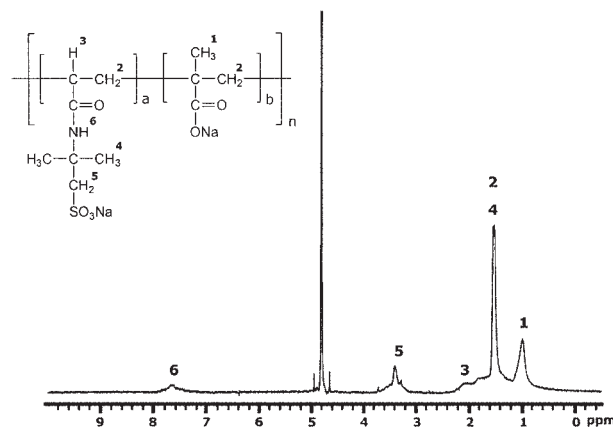


Figure 3 $^1\text{H-NMR}$ spectrum of PMAMP.

lated from the difference in the dispersant concentration before and after adsorption.

ζ potential measurements

Cement suspensions ($W/C = 400$) with PMAMP ($SP/C = 1.0\%$) were prepared. The ζ potential in the cement suspensions at 30 min was measured with a Malvern Zetasizer 3000HS. (Worcestershire, UK).

RESULTS AND DISCUSSION

Structure of the prepared resins

The structure of a typically prepared PMAMP sample was verified from their IR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectra, as shown in Figures 2–4, respectively. Figure 2 shows that the IR spectrum of this polymer displayed a O—H stretching band overlapped with a N—H stretching band at 3400 cm^{-1} , C=O stretching bands at 1640 cm^{-1} and 1404 cm^{-1} , an N—H bending band at about 1540 cm^{-1} , a S=O stretching band at 1196 cm^{-1} , and a S—O stretching band at 629 cm^{-1} . The $^1\text{H-NMR}$ spectrum in Figure 3 shows the signals

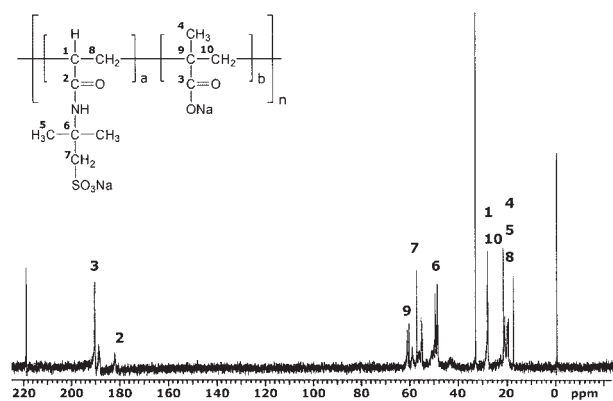


Figure 4 $^{13}\text{C-NMR}$ spectrum of PMAMP.

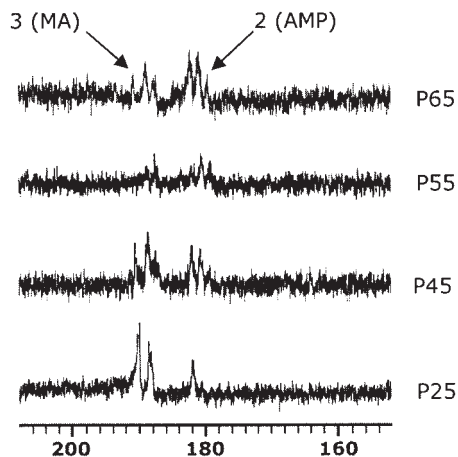


Figure 5 ^{13}C -NMR spectra of PMAMPs with different reactant ratios.

at $\delta = 1.0$ (1H), 1.5 (2H, 4H), 2.1 (3H), 3.3 (5H), and 7.7 ppm (6H). Figure 4 shows that the ^{13}C -NMR spectrum gave signals at $\delta = 28$ (1C, 10C), 19–21 (4C, 5C, 8C), 50 (6C), 58 (7C), 60 (9C), 182 (2C), and 190 ppm (3C).^{10–12} Furthermore, the peak intensity at 182 ppm to that at 190 ppm, corresponding to the carbonyl group on AMP to the carboxyl group on MA in the prepared PMAMP, increased for the polymer containing more AMP, as shown in Figure 5.

Minislump of the cement pastes with PMAMP

It is well known that the major function of superplasticizers is to disperse cement particles and improve the workability of cementitious materials. For cement pastes, the minislump test is appropriate for rapidly determining the effectiveness of these chemicals.⁶ Figure 6 shows the measured minislump value of cement pastes with PMAMP incorporated at various dosages. W/C was 0.3. Cement pastes without any chemical admixture present will not flow or spread in the minislump test under such a low W/C , and the slump

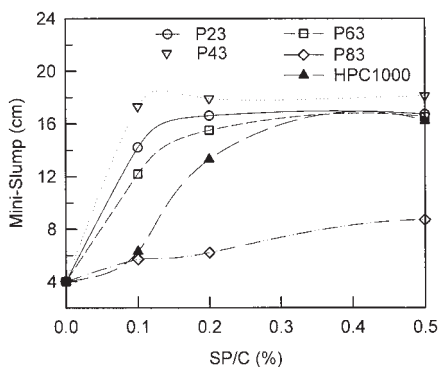


Figure 6 Minislump of the cement pastes with polymers at various dosages ($W/C = 0.3$).

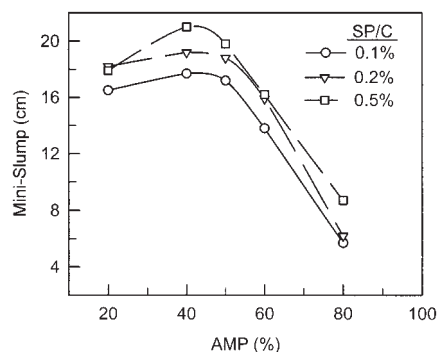


Figure 7 Effect of the AMP content of PMAMP on the minislump values of the cement pastes ($W/C = 0.3$).

value would be 4.0 cm. When PMAMP was added, the fluidity of the resulting paste increased. All of the tested polymers shown in Figure 6 were controlled with a close M_w , that is, about 1.2×10^5 . The slump value increased quickly with polymer dosage initially and then approaches a constant value gradually. The transition point, corresponding roughly to the saturation point,⁶ occurred at a polymer dosage of about 0.1–0.2% for samples P23, P43, and P63. The transition point occurred at a polymer dosage of about 0.35% for HPC1000. Except for P83, the other PMAMP samples shown in Figure 6 appeared to show better dispersion properties than the commercial one, as they required a lower dosage to achieve the same minislump value of the cement pastes. It was clear that polymer samples with different AMP contents exhibited different fluidity-enhancing capabilities. Figure 7 shows the effect of the AMP content of PMAMP with a M_w of about 5×10^4 on the minislump value of the cement pastes ($W/C = 0.3$). The minislump value first generally increased slightly with AMP content, approached a maximum value, and then decreased quickly afterwards. When the incorporated admixture contains about 40–50% AMP, the resulting cement pastes appeared to have the highest fluidity or slump value. Similar results and trends were also obtained for polymer samples with different molecular weights.

Ferrari et al.¹³ mentioned that both adsorption and steric stabilization were the main factors determining the performance of polycarboxylate superplasticizers. The dispersing efficiency of these polymers is a function of carboxylate groups/ester side chains, which affects a balance between adsorption and steric effects. PMAMP can be considered a polycarboxylate polymer with side chains linked with sulfonate groups. As the side chains of PMAMP molecules are much shorter than ester side chains, this polymer would only cause small steric effects at best when its molecules were adsorbed onto cement particles. That is, the dispersing effect generated by this polymer is caused mainly by electrostatic repulsion (due to carboxylate and sulfo-

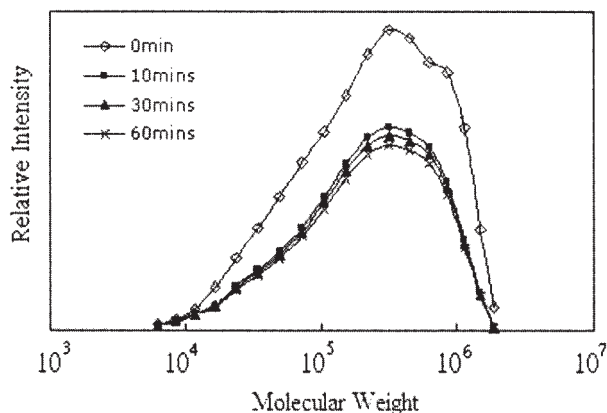


Figure 8 Change in the molecular weight distribution of free P41 molecules in cement pastes with adsorption time ($SP/C = 1.0\%$).

nate groups) and slightly by steric hindrance (due to short side chains). Furthermore, the adsorption of PMAMP is another factor to be considered. Figure 8 shows the change in the molecular weight distribution of free P41 (40% AMP, $M_w = 3.8 \times 10^5$) molecules in the pore solution of the cement pastes ($SP/C = 1.0\%$) with adsorption time. The peak area decreased with increasing time. The adsorption approached a constant value at a time of 10 min or more. On the basis of the difference in peak areas at different adsorption times, the amount of adsorbed polymer on the cement particles could be calculated. Table II lists the adsorption amounts of various PMAMP samples on the cement particles. The results indicate that the adsorbed amount of polymer with a M_w of about 5×10^4 was in the following order: P45 > P55 > P65 > P25; it increased with AMP initially, reached a maximum at 40–50% AMP, and then decreased subsequently. When the added polymer had a higher AMP content, it was adsorbed more on the cement particles and generated stronger electrostatic repulsion and steric effects. As a result, the fluidity of the cement pastes increased. However, if the incorporated PMAMP contained 50% AMP or more, the resulting cement pastes showed lower fluidity because the adsorption amount of the polymer decreased.

As shown in Figure 1, PMAMP molecules contained two functional groups, that is, the carboxylic acid

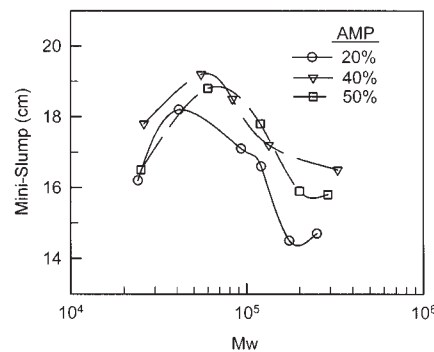


Figure 9 Effect of M_w of PMAMP on the minislump of the cement pastes ($SP/C = 0.2\%$).

group ($-\text{COOH}$) and sulfonic acid group ($-\text{SO}_3\text{H}$). These two groups had different characteristics. The acidity of the carboxylic acid group was less than that of the sulfonic acid group. Carboxylic acid groups are fully ionized only in alkaline environments, whereas sulfonic acid groups are highly ionized even in moderately acidic solutions. As the cement surface contained positive charges initially, the latter groups were more effective in enhancing the adsorption of PMAMP onto solid particles and promoting the fluidity of the cement pastes.^{5,9} Consequently, both the adsorbed amount of the polymer and the initial minislump of the resulting cement pastes were increased with AMP content of the polymer at first, approached a maximum value at 40–50% AMP, and then decreased afterward.

In addition to the AMP content, the molecular weight of the polymer was another influential factor on the flow properties of the cement materials. Figure 9 shows the effect of M_w on the minislump of the cement pastes ($SP/C = 0.2\%$). As expected, the paste fluidity first rose with increasing M_w of the polymer, reached a maximum value at a M_w of about 5×10^4 , and then decreased subsequently. The maximum of the curves seemed to occur at higher molecular weights for polymers with more AMP in their composition. Several studies have also indicated that there are optimal degrees of polymerization for best performance in concrete in terms of workability and other properties.^{14–16} Although the adsorption amount of PMAMP decreased with increasing M_w , the measured

TABLE II
Adsorption Amounts of PMAMP Samples and ζ Potentials of the Cement Particles ($SP/C = 1\%$)

Polymer	P25	P41	P43	P45	P46	P55	P65
Adsorption amount (mg/g of cement)	2.6	3.7	3.9	5.1	6.0	4.9	3.2
ζ potential (mV)	— ^a	−48.8	−29.7	−22.7	—	−20.6	−16.6

^a Not measured.

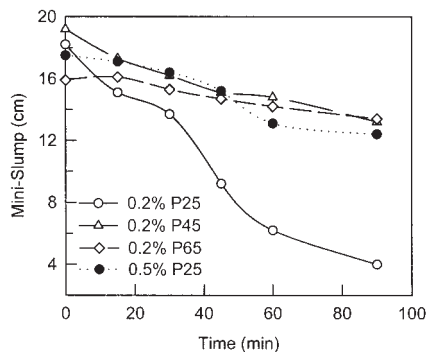


Figure 10 Slump retention of the cement pastes containing PMAMP with different AMP contents as a function of elapsed time.

ζ potential of the cement particles with adsorbed polymer at 30 min became more negative (Table II). Anderson et al.¹⁷ studied the effect of the molecular weight of sulfonated PS on adsorption on cement. They reported that the ζ potential depended not only on the amount of chemical adsorbed but also on the conformation of adsorbed polymer. PS with a higher molecular weight was more likely to show loop adsorption, whereas PS with a lower molecular weight was more likely to show train adsorption. Usually, a greater fluidity in cement pastes is produced for a higher ζ potential because of the stronger electrostatic repulsions generated. However, polymers such as poly(acrylic acid) with a molecular weight higher than 1×10^5 have been mentioned to act as flocculants; namely, the flocculation between adsorbed polymer molecules occurs, and the fluidity starts to decrease.¹⁷ As a result, the M_w for PMAMP for achieving the best plasticizing effects on the cement pastes was about 5×10^4 .

Finally, PMAMP with a proper M_w and AMP content appeared to be more effective than HPC1000, as indicated in Figure 6. The difference was attributed to the different chemical structures of these two admixtures. Also, the tested PMAMP was purified and had an optimum reactant ratio or molecular weight. In contrast, the commercial one contained some unreacted monomer, and its molecular weight might not have been optimized; these factors affected the performance of the commercial superplasticizer.^{5,18}

Minislump retention of the cement pastes with PMAMP

Aside from enhancing the fluidity of cementitious materials, ideal superplasticizers should prevent slump loss practically, especially in hot weather. A lower degree of slump loss will prolong the time available for the transport, handling, and placement of concrete. Figure 10 shows the slump retention of cement pastes

containing PMAMP with a M_w of about 5×10^4 and different AMP contents with time. The initial slump values of the tested cement pastes ranged from 15.9 to 18.2 cm. Generally, the slump retention decreased with increasing time, as cement particles became more hydrated. The slump-decreasing rate of the cement pastes ($SP/C = 0.2\%$) was in the following order: P25 > P45 > P65; it decreased with increasing AMP content. One possible reason was that sulfonate groups in PMAMP could have substituted for the sulfate groups (SO_4^{2-}) to be adsorbed and interacted with tricalcium aluminate, and retarded the cement hydration that contributed to a reduction in slump loss.⁵ Moreover, stronger steric effects were provided by more AMP in the polymer composition. Therefore, cement pastes also showed better slump retention when they contained PMAMP with higher AMP contents. Furthermore, cement pastes with 0.5% P25 were expectedly to show a lower slump-decreasing rate than those with 0.2% P25.

Figure 11 shows the slump retention of pastes ($SP/C = 0.2\%$) containing polymers with 40% AMP and different molecular weights as a function of elapsed time. The initial slump values of the tested cement pastes were about 17.2–19.2 cm. The slump-decreasing rates of the cement pastes were in the following order: P45 > P43 > P41; the rate decreased with increasing M_w . This was because bigger molecules move slower in pore solutions of cement pastes. They take longer to reach and be adsorbed onto solid particles. Moreover, the amount of adsorbed PMAMP increased with decreasing molecular weight, as mentioned before. The more polymer was adsorbed, the less the amount of free admixture molecules was left in the pore solution, and the faster the slump loss of the cement paste occurred. Also, PMAMP with a higher molecular weight caused stronger steric effects, which also favored the slump retention of cement materials.⁵ As a result, PMAMP with a higher molecular weight was more effective in preventing slump loss in cement pastes.

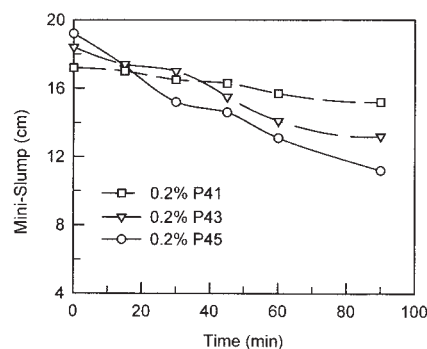


Figure 11 Slump retention of the cement pastes containing PMAMP with 40% AMP and different molecular weights as a function of elapsed time ($SP/C = 0.2\%$).

CONCLUSIONS

A new carboxylic acid-based copolymer (PMAMP) as superplasticizer was prepared, and its effect on the fluidity of cement pastes was examined. The test results indicate that cement pastes with this polymer exhibited greater minislump values. Compared with a commercial SNF superplasticizer, this admixture with a proper reactant ratio and molecular weight provided better dispersing effects and required a lower dosage to achieve the same slump value of cement pastes. PMAMP with about 50% AMP and a M_w of about 5×10^4 was the most effective in dispersing cement particles and promoting the fluidity of the cement pastes. Nevertheless, PMAMP with a higher AMP content or higher molecular weight appeared to produce better slump-retention effects. This was attributed to the interaction of this admixture with cement particles and the adsorption behavior of this admixture in the cement system.

References

1. Molyneux, P. *Water-Soluble Synthetic Polymers: Properties and Behavior*; CRC: Boca Raton, FL, 1984.
2. Piirma, I. *Polymeric Surfactants*; Marcel Dekker: New York, 1992.
3. Reed, J. S. *Introduction to the Principles of Ceramic Processing*, 2nd ed.; Wiley: New York, 1995.
4. Rixom, M. R.; Mailvaganam, N. P. *Chemical Admixtures for Concrete*, 2nd ed.; Spon: London, 1986.
5. Ramachandran, V. S.; Malhotra, V. M.; Jolicoeur, C.; Spirattos, N. *Superplasticizers: Properties and Applications in Concrete*; CANMET: Ottawa, Canada, 1998.
6. Aitcin, P. C. *High-Performance Concrete*; Spon: London, 1998.
7. Collepardi, M. in *Concrete Technology: Past, Present, and Future*; ACI SP 144-20; Mehta, P. K., Ed.; San Francisco, 1994, p 399.
8. Ohta, A.; Sugiyama, T.; Tanaka, Y. in *Proceedings of the Fifth International Conference on Superplasticizers and Other Chemical Admixtures in Concrete*; ACI SP 173-19; Malhotra, V. M., Ed.; Rome, Italy, 1997, p 359.
9. Lim, G. G.; Hong, S. S.; Kim, D. S.; Lee, B. J.; Rho, J. S. *Cem Concr Res* 1999, 29, 223.
10. Deguchi, S.; Lindman, B. *Polymer* 1999, 40, 7163.
11. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 5th ed.; Wiley: New York, 1991.
12. Pretsch, E.; Clerc, T. *Tables of Spectral Data for Structure Determination of Organic Compounds*, 2nd ed.; Springer-Verlag: Berlin, 1989.
13. Ferrari, G.; Cerulli, T.; Clemente, P.; Dragoni, M.; Gamba, M.; Surico, F. in *Proceedings of the Sixth International Conference on Superplasticizers and Other Chemical Admixtures in Concrete*; ACI SP195-31; Malhotra, V. M., Ed.; Nice, France, 2000, p 505.
14. Moukwa, M.; Youn, D.; Hassanali, M. *Cem Concr Res* 1993, 23, 122.
15. Chen, S. D.; Hwang, C. H.; Hsu, K. C. *Cem Concr Res* 1999, 29, 255.
16. Knaus, S.; Bauer-Heim, B. *Carbohydr Polym* 2003, 53, 383.
17. Anderson, P. J.; Roy, D. M.; Gaidis, J. M. *Cem Concr Res* 1988, 18, 980.
18. Basile, F.; Biagini, S.; Ferrari, G.; Collepardi, M. in *Proceedings of the Third International Conference on Superplasticizers and Other Chemical Admixtures in Concrete*; ACI SP 119-11; Malhotra, V. M., Ed.; Ottawa, Canada, 1989, p 209.