

Effects of an Amphoteric Copolymer on the Properties of Cementitious Materials

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ABSTRACT: The effects of an amphoteric copolymer, poly(acrylamide-co-(2-(3-carboxyacryloyloxy)-N-(carboxymethyl)-N,N-dimethyl-ethanaminium) (PAC) on the properties of cement pastes or mortars were investigated. PAC was prepared from acrylamide and 2-(3-carboxy-acryloyloxy)-N-(carboxymethyl)-N,N-dimethylethanaminium (CAC) through free radical polymerization. The results indicate that the presence of the polymer delayed the setting of cement pastes; it also reduced the water demand

so that the resulting mortars showed improved compressive strength and reduced length change. PAC with about 16.7% CAC and a weight-average molecular weight of about 5×10^4 was effective in promoting the material properties of mortars. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2318–2324, 2012

Key words: amphoteric copolymer; setting; cement; water reduction; compressive strength; length change

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. Addition of only a small amount of polymers can significantly improve the workability, mechanical strength, and other properties of concrete.^{4–6}

Sulfonated naphthalene formaldehyde condensates (SNF), 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 polycarboxylate polymers with long, comb-type side chains (CAE)

were developed. These chemicals can create not only electrostatic repulsions, but also steric effects. In fact, the steric effects plays a dominant role compared to electrostatic repulsions in the deflocculating of cement particles.^{7,8} Therefore, they exhibit better dispersing property than the former sulfonate-based admixtures. More importantly, they offer less slump loss in the resulting of fresh concrete.^{4,5} Except the admixtures aforementioned, several novel water-soluble polymers containing different structural units or functional groups have also been reported.^{9–14}

To date, most chemical admixtures, including SNF and CAE, belonged to anionic polymers. Others, such as amphoteric or cationic admixtures have seldom been reported. Recently, Miao et al.¹⁵ have prepared a new amphoteric comb-like copolymer and reported that this polymer could reduce the amount of mixing water up to 45% and significantly increased the compressive strength of hardened concrete. An amphoteric copolymer, i.e., poly(acrylamide-co-(2-(3-carboxyacryloyloxy)-N-(carboxymethyl)-N,N-dimethylethanaminium) (PAC), was also prepared in our laboratory. PAC with a proper monomer ratio and molecular weight was found to be effective in dispersing cement particles and enhancing the fluidity of either cement pastes or mortars.^{16,17} Except the dispersion property, the effects of PAC on other properties of cementitious materials were further investigated in this study. Three PAC samples with different reactant ratio or molecular weight were synthesized and their effects on the setting times of cement pastes, and on the water-reduction ratio,

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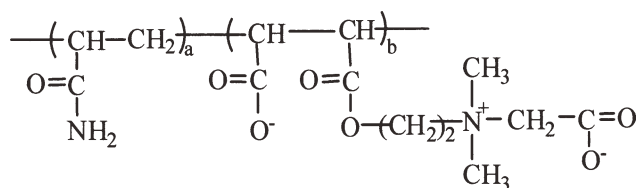


Figure 1 The chemical structure of PAC polymer.

compressive strength, rebound number, and length change of mortars were examined and discussed.

EXPERIMENTAL

Materials

The materials used include Type I Portland cement, river sand, and a chemical admixture. The cement was supplied by Asia Cement (Taipei, Taiwan) and complies with ASTM C150. The sand was from the bank of Kaoping River, Taiwan. The density was 2.61 g/cm³, and the fineness modulus was 2.87. It meets the standard of ASTM C778, and was washed and dried before use. The chemical admixture used was PAC, which was prepared from acrylamide (AM) and 2-(3-carboxyacryloyloxy)-*N*-(carboxymethyl)-*N,N*-dimethyl ethanaminium (CAC) in a basic condition through a free radical polymerization. Details of the preparation procedure were described elsewhere.¹⁶ Figure 1 shows the chemical structure of PAC polymer. Previously PAC with about 16.7% CAC and a weight-average molecular weight (MW) of about 1×10^5 , was shown to be most effective in dispersing cement particles and enhancing the fluidity of either cement pastes or mortars.^{16,17} In this study, the influence of this polymer on other properties of cement pastes and mortars with various water/cement (W/C) ratios were examined further. Three PAC samples with the reactant ratio and molecular weight close to the optimum values

TABLE I
The Properties of PAC Polymers

Polymer symbol	CAC (%)	MW ^a
PAC5b	16.7	4.7×10^4
PAC5c	16.7	1.1×10^5
PAC10	9.1	5.5×10^4

^a Weight-average molecular weight.

mentioned above were prepared. Table I lists the properties of the polymer samples. PAC5b and PAC5c have same CAC content but different molecular weight; PAC5b and PAC10 have different CAC content but close molecular weight.

Preparations of tests of cement pastes

Aqueous solutions containing 28.5 wt % PAC resin were prepared. Cement pastes were made by the mixture of cement and water with or without addition of the polymer solution. The W/C ratio ranged from 0.25 to 0.4, and the polymer/cement (SP/C) ratio ranged from 0 to 1.6 wt %.

The setting times of cement pastes were determined using the Vicat needle according to ASTM C191. The initial setting time refers to the time when the penetration depth of the needle into the cement pasts is 25 mm. The final setting time is the time when the needle does not penetrate visibly into the paste.

Preparations of tests of mortars

Aqueous solutions containing 28.5 wt % PAC resin were prepared. Mortars were made by the mixture of cement, sand, and water with or without addition of 28.5 wt % PAC solutions. Mixing of mortar was made following ASTM C305. Table II lists the mixture proportions of mortars. W/C ranged from 0.367

TABLE II
The Composition and Properties of Mortars^a

Mortar symbol	W/C	SP/C (wt %)	Water (g)	SP ^b			ΔW^c (%)	Unit weight (kg/m ³)
				PAC10 (g)	PAC5b (g)	PAC5c (g)		
Control	0.522	0.0	386.0	0.0			0.00	2225
M1	0.459	0.5	335.8	3.7			12.1	2242
M2	0.428	1.0	309.3	7.4			18.0	2296
M3	0.392	1.5	279.3	11.1			24.8	2315
M4	0.472	0.5	345.8		3.7		9.46	2233
M5	0.441	1.0	319.3		7.4		15.4	2288
M6	0.367	1.5	260.4		11.1		29.7	2320
M7	0.493	0.5	361.3			3.7	5.44	2224
M8	0.458	1.0	331.7			7.4	12.2	2280
M9	0.376	1.5	267.0			11.1	28.0	2333

^a Mortars contained 740 g cement and 2035 g sand.

^b 28.5 wt % PAC.

^c Water-reducing ratio.

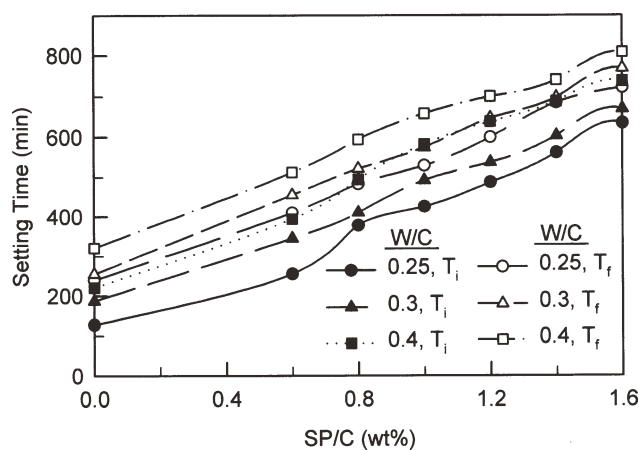


Figure 2 Effect of W/C on the relationship between the setting times of cement pastes and PAC5b dosage.

to 0.522; the cement/sand ratio was fixed at 1/2.75; SP/C ranged from 0 to 1.5 wt %.

The fluidity of mortars is defined as the consistency of mixtures indicated by the spread diameter of tested samples on a flow table according to ASTM C230. Besides, the unit weight of mortars was determined following ASTM C138. Mortar specimens of $50 \times 50 \times 50 \text{ mm}^3$ were prepared, cured, and the compressive strength at the ages of 3–91 days was measured according to ASTM C109; the rebound number was also determined according to ASTM C805 using a PROCEQ Type N Rebound Hammer (Zurich, Switzerland). The Hammer, consisting of a spring-loaded steel hammer which when released struck a steel plunger in contact with the mortar surface. The rebound number was the rebound distance of the steel hammer from the steel plunger which was measured on a linear scale attached to the frame of the instrument. The rebound number was calculated based on the average readings of two measurements on each of the six faces of mortar cubes. Finally, the length change of mortar samples of $25 \times 25 \times 285 \text{ mm}^3$ at the ages of 3–91 days was measured according to ASTM C157.

RESULTS AND DISCUSSION

Effect of PAC on the setting time of cement pastes

Cementitious materials such as cement pastes and concrete are plastic in the freshly mixed state and gradually become hard, stiff, and strong. The change in their physical properties is due to the hydration between cement and water. The reaction is gradual, first causing hardening of the material, and then development of strength.

Setting of the material is a gradual transition process from a liquid state to a solid state. Initial setting refers to the beginning of solidification. Final setting

corresponds to the point where the solidification is complete, hardening begins, and stress starts to develop.¹⁸ Determination of the setting times of cementitious materials is clearly important in the practical applications. It is clear that both W/C and incorporation with polymer affect the setting of mortars. Figure 2 shows the effect of W/C on the relationship between the setting times of cement pastes and PAC5b dosage. The initial and final setting times of cement pastes were measured using a Vicat needle at 25°C. When W/C was 0.25, the measured initial setting time (T_i) and final setting time (T_f) of the cement paste without any polymer present were 128 and 240 min, respectively. When W/C was 0.3, T_i and T_f were 187 and 255 min, respectively. When W/C was 0.4, T_i and T_f were 221 and 321 min, respectively. As expected, the setting times increased with increasing W/C. The presence of PAC5b increased both T_i and T_f , indicating the polymer had a retarding effect and delayed the setting of pastes. Furthermore, the setting times extended with increasing polymer dosage. At a fixed polymer dosage, both T_i and T_f also extended with increasing W/C.

Figure 3 shows the effect of PAC type on the relationship between the setting times of cement pastes (W/C = 0.3) and polymer dosage. The paste incorporated with any PAC was found to show higher T_i and T_f than that without any polymer, indicating all the three tested polymers retarded the cement hydration. More the polymer was added, the longer the setting times became. As the setting times of pastes with PAC5b were close to those with PAC5c, the retarding effect of the polymer on cement pastes increased in the order: PAC5b ~ PAC5c > PAC10. When superplasticizer or polymeric molecules were adsorbed onto the surface of hydrating cement particles, they usually inhibited the nucleation and growth of hydration products; that retarded the

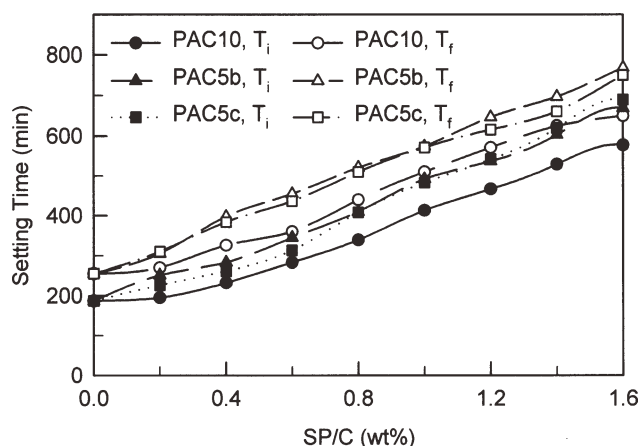


Figure 3 Effect of PAC type on the relationship between the setting times of cement pastes and polymer dosage (W/C = 0.3).

hydration of cement and delayed the setting times.¹⁹ Retarding the cement hydration is usually required when mixing and placing concrete in hot weather or in tropical area.

It is indicated in Figure 1 that PAC contained an AM moiety and a CAC moiety, which contained carboxylate anions and quaternary ammonium cations. The adsorbed PAC molecules on cement particles would cause not only electrostatic repulsions, but also some steric effects due to the existence of CAC moieties. As shown in Table I, PAC10 contained lower CAC content and PAC5c had higher molecular weight when compared to PAC5b. Therefore, the adsorption rate of PAC5b was found to be faster than other two polymers.¹⁶ As a result, PAC5b caused stronger retarding effect than either PAC5c or PAC10.⁵

Effect of PAC on the properties of fresh mortars

Water reducer or superplasticizer is used to disperse cement particles and reduces the amount of mixing water at a given mortar fluidity. The degree of water reduction depends on the effectiveness of the chemical. Figure 4 shows the effect of PAC type and dosage on the water-reducing ratio (ΔW) of mortars. ΔW was calculated as follows:

$$\Delta W(\%) = (W_0 - W_1)/W_0 * 100$$

where W_0 was the weight of the water added in the control mortar without any polymer present and W_1 was the weight of the water added in the mortar with polymer incorporated; both mortars achieved the original fluidity of 105–115 mm.

As shown in Figure 4, addition of PAC indeed reduced the water demand of mortars; the more PAC was incorporated, the more water reduction was

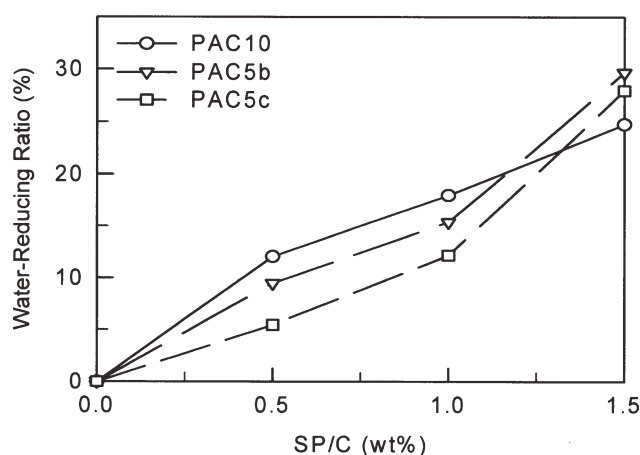


Figure 4 Effect of PAC type and dosage on the water-reducing ratio of mortars.

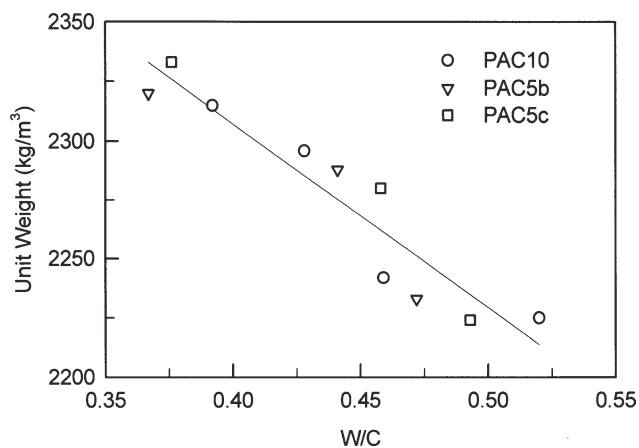


Figure 5 Effect of W/C on the unit weight of mortars.

observed. For mortars with polymer dosage less than 1 wt %, the degree of water reduction increased in the following order: PAC10 > PAC5b > PAC5c. For mortars with polymer dosage greater than 1 wt %, the degree of water reduction increased in the following order: PAC5b > PAC5c > PAC10. The trend agreed roughly with our previous result¹⁶; that is, PAC10 showed better fluidity-enhancing effect in cement pastes with low polymer dosage than PAC5b. The trend was reversed with high polymer dosage. However, PAC5c was found to show slightly better plasticizing effect than PAC5b in cement pastes, but the opposite effect was observed in mortars. When compared with PAC5b, the molecular weight of PAC5c was higher and the polymeric molecules had higher tendency to flocculate with each other. It is clear that the distance among solid particles in the mortar was lower than that in the cement paste when both materials had same W/C, because the mortar contained sand in addition to cement and water. The probability of flocculation of the polymeric molecules

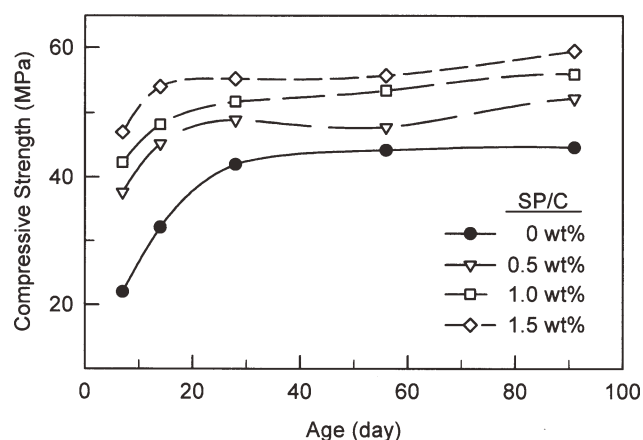


Figure 6 Effect of PAC5b dosage on the compressive strength of mortars at different ages.

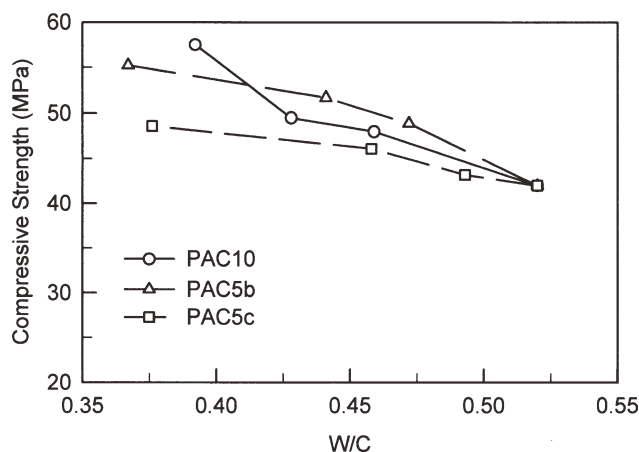


Figure 7 Effect of PAC type on the compressive strength of mortars at 28 days.

would be greater in mortars than in cement pastes. When compared with PAC5b, PAC5c became relatively less effective in mortars than in pastes.

The unit weight of mortars with PAC present was measured right after mixed. The results were summarized in Table II. In general, the mortar with more PAC incorporated contained less water and the unit weight was higher because the solid particles had higher density than water. Figure 5 shows the relationship between the unit weight of mortars and W/C. Regardless of which PAC was incorporated, the unit weight decreased almost linearly with W/C, suggesting that the density of mortars was mainly determined by W/C and little dependent on polymer type.

Effect of PAC on the properties of hardened mortars

Figure 6 shows the compressive strength of mortars with PAC5b at different ages. In general, each

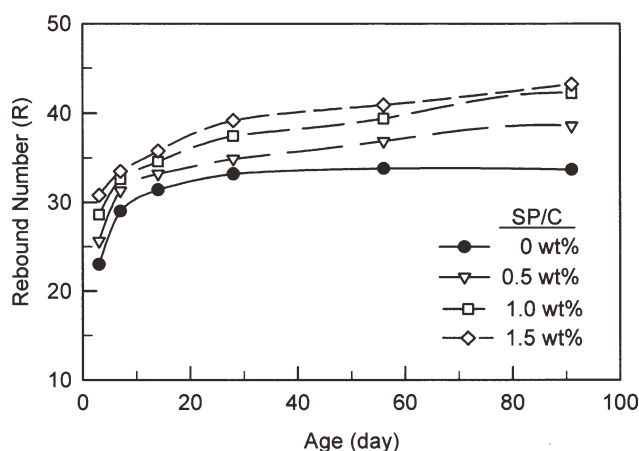


Figure 8 Effect of PAC5b dosage on the rebound number of mortars at different ages.

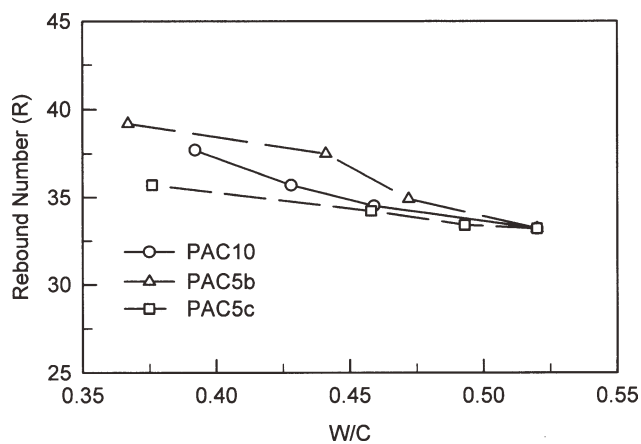


Figure 9 Effect of PAC type on the rebound number of mortars at 28 days.

admixed mortar exhibits a similar strength developing behavior; the strength value increased with age initially, and then approached a plateau. The transition point occurred at about 28 days. As it contained less water, the mortar with PAC5b showed greater strength than the control one. Incorporation of more PAC5b and the consequent lower water demand improved the strength of mortars. Similar results were also found for mortars with other two PACs.

Figure 7 shows the effect of W/C on the compressive strength of mortars with PAC at 28 days. As expected, the strength decreased with increasing W/C. Except when W/C was less than 0.4, the effect of polymer in improving the compressive strength increased in the order: PAC5b > PAC10 > PAC5c. Although, PAC5b caused strongest retarding effect from the previous setting time measurements, the mortar with this polymer showed highest strength. This verified the viewpoint of Collepardi that there was no relationship between the setting time and the gain strength of cement.⁵

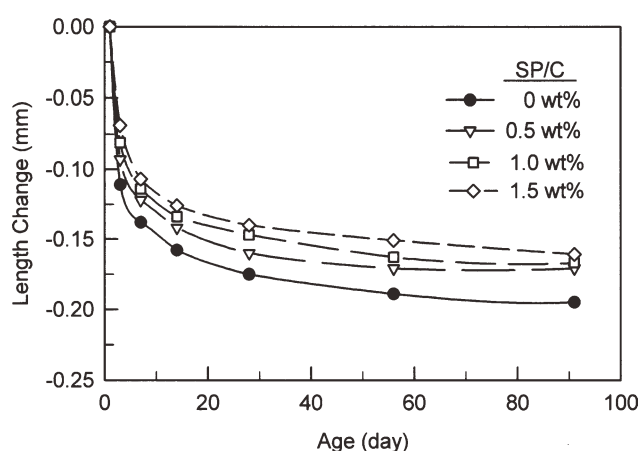


Figure 10 Effect of PAC5b dosage on the length change of mortars at different ages.

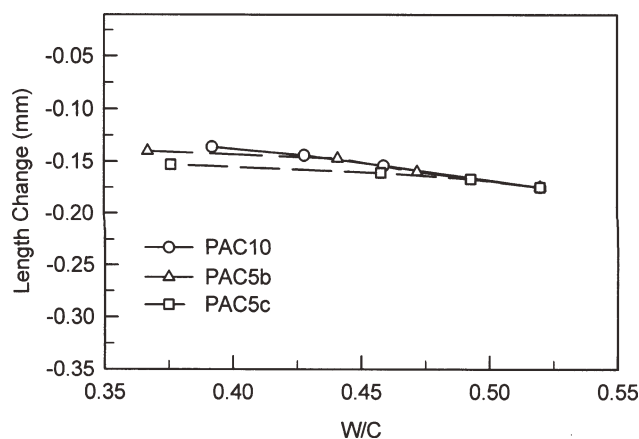


Figure 11 Effect of PAC type on the length change of mortars at 28 days.

Figure 8 shows the rebound number of mortars with PAC5b at 7–91 days. The test method for rebound number of hardened mortars is nondestructive; it could be used to assess the in-place uniformity of the materials and to indicate the relative strength at different locations in a structure. In general, the rebound number of each admixed mortar was found to increase with age initially, and then approach a plateau. The transition point also occurred at about 28 days. When the polymer was present and the water demand decreased, the rebound number of resulting mortar increased. The presence of more PAC5b caused the resulting mortar to show higher rebound number. Similar results were also observed for mortars with other two PACs.

Figure 9 shows the effect of W/C on the rebound number of mortars with PAC at 28 days. The rebound number was expectedly to decrease with increasing W/C. Besides, the polymer in improving the rebound number was in the order: PAC5b > PAC10 > PAC5c. The trends in Figures 8 and 9 are similar to those in Figures 6 and 7, indicating a relationship exists between the rebound number and the compressive strength of mortars.^{20,21}

Normally, the volume of mortars after mixing decreased gradually because of the hydration of cement and dry shrinkage. Shrinkage will induce cracks and affect the durability of the material. Incorporation of chemical admixture affects the degree of volume change. Measurement of length change of the mortar permits assessment of the potential for its volumetric variation. Figure 10 shows the length change of mortars with PAC5b at 7–91 days. In general, each admixed mortar exhibited a similar shrinkage behavior; the length change increased with elapsed time initially, and then approached a plateau. The transition point occurred

at about 28 days. As it contained less water, the mortar with PAC5b showed smaller change in length than the control one. Incorporation of more polymers and the consequent lower water demand resulted in lower shrinkage. Similar results were observed for mortars with other two PACs.

Figure 11 shows the effect of PAC type on the length change of mortars at 28 days. The length change was generally found to increase with increasing W/C. The mortar with PAC contained lower amount of water and showed less shrinkage than the control one. Regardless of which PAC was incorporated, the length change of mortars at a fixed W/C was close to each other. This indicates that all three tested PACs played a similar role in reducing the shrinkage of mortars.

CONCLUSIONS

A new carboxylic acid-based amphoteric copolymer (PAC) as a chemical admixture has been prepared and tested. Incorporation of PAC delayed the setting of cement pastes; it also reduced the water requirement, improved the compressive strength and rebound number, and reduced the length change of mortars. PAC with CAC content of about 16.7% and an MW of about 5×10^4 is effective in lowering the water demand and promoting the mechanical properties and reducing the length change of mortars.

References

- Molyneux, P. *Water-Soluble Synthetic Polymers: Properties and Behavior*; CRC: Boca Raton, FL, 1984.
- Piirma, I. *Polymeric Surfactants*; Marcel Dekker: New York, 1992.
- Reed, J. S. *Introduction to the Principles of Ceramic Processing*, 2nd ed.; Wiley: New York, 1995.
- Ramachandran, V. S.; Malhotra, V. M.; Jolicoeur, C.; Spiratos, N. *Superplasticizers: Properties and Applications in Concrete*; CANMET: Ottawa, Canada, 1998.
- Collepari, M. *The New Concrete*; Grafiche Tintoretto: Italy, 2006.
- Aitcin, P. C. *High-Performance Concrete*; E&F. N. Spon: London, 1998.
- Zingg, A.; Winnefeld, F.; Holzer, L.; Pakusch, J.; Becker, S.; Figi, R.; Gauckler, L. *Cem Concr Compos* 2009, 31, 153.
- Felekoglu, B.; Tosun, K.; Baradan, B. *Constr Build Mater* 2011, 5, 1466.
- Lim, G. G.; Hong, S. S.; Kim, D. S.; Lee, B. J.; Rho, J. S. *Cem Concr Res* 1999, 29, 223.
- Ye, Y. S.; Huang, H. L.; Hsu, K. C. *J Appl Polym Sci* 2006, 100, 2490.
- Pei, M. S.; Yang, Y. Q.; Zhang, X. Z.; Zhang, J.; Dong, J. *J Cem Concr Res* 2004, 34, 1417.
- Ouyang, X.; Jiang, X.; Qiu, X.; Yang, D.; Pang, Y. *Cem Concr Res* 2009, 39, 283.
- Mahmoud, A. A. M.; Shehab, M. S. H.; El-Dieb, A. S. *Cem Concr Compos* 2010, 32, 392.

14. Vieira, M. C.; Klemm, D.; Einfeldt, L.; Albrecht, G. *Cem Concr Res* 2005, 35, 883.
15. Miao, C. W.; Ran, Q. P.; Liu, J. P.; Mao, Y. L.; Shang, Y.; Sha, J. F. *Polym Polym Compos* 2011, 19, 1.
16. Weng, W. H.; Hsu, K. C.; Sheen, Y. N. *J Appl Polym Sci* 2010, 118, 1313.
17. Weng, W. H.; Hsu, K. C. In *Proceedings of the 2nd International Symposium on Design, Performance and Use of Self-Consolidating Concrete*; Shi, C.; Yu, Z.; Khayat, K. H.; Yan, P., Eds.; Beijing, China, 2009, p 270.
18. Mehta, P. K. *Concrete: Structure, Properties, and Materials*; Prentice-Hall: New Jersey, 1986.
19. Spirotos, N.; Page, M.; Mailvaganam, N. P.; Malhotra, V. M.; Jolicoeur, C. *Superplasticizers for Concrete; Supplementary Cementing Materials for Sustainable Development* Ottawa, Canada, 2003.
20. Rao, M. C.; Bhattacharyya, S. K.; Barai, S. V. *Mater Struc* 2011, 44, 205.
21. Mohammed, B. S.; Azmi, N. J.; Abdullahi, M. *Constr Build Mater* 2011, 25, 1388.