Available online at www.sciencedirect.com
SCIENCE DIRECT®
Cement and Concrete Research 36 (2006) 650 – 655
Cement and Concrete Research

Effects of a carboxylic acid/sulfonic acid copolymer on the material properties of cementitious materials

Tung-Sheng Liao [a], Chao-Lung Hwang [a], Yi-Shian Ye [b], Kung-Chung Hsu [b,*]

[a] Department of Construction Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan 106, ROC
[b] Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan 116, ROC

Received 3 October 2005; accepted 9 October 2005

Abstract

The effects of a carboxylic acid/sulfonic acid copolymer (PMAMP) on the properties of mortars or concrete made with Type I Portland cement were investigated. PMAMP was prepared from methacrylic acid and 2-acrylamido-2-methylpropane sulfonic acid (AMP) in a basic condition through a free radical polymerization. The results indicate that PMAMP with the AMP content of 20–60%, and a weight-average molecular weight (MW) of about 5×10^4, is effective in dispersing cement particles and the resulting mortars or concrete show good fluidity or workability. Besides, PMAMP with higher molecular weigh is more capable of maintaining the workability along with elapsed time. Compared with a commercial sulfonated naphthalene formaldehyde superplasticizer (SNF), PMAMP appears to be more effective in promoting concrete workability and preventing the slump loss. Finally, concrete incorporated with different PMAMPs at W/B = 0.28 shows similar compressive strength-developing behavior and meets the designed strength value.

Keywords: Carboxylic acid/sulfonic acid copolymer; Superplasticizer; Workability; Concrete

1. Introduction

Superplasticizer (SP) or high-range water reducer is an important chemical admixture commonly used in the construction industry. Only a small amount of the chemical could greatly improve the workability of concrete. Moreover, a good admixture should be able to maintain the workability of the resulting concrete during transportation, handling and placement. Sulfonated naphthalene formaldehyde condensates (SNF) and sulfonated melamine formaldehyde condensates are two typical examples. These admixtures, after being adsorbed on cement particles, create electrostatic repulsions and overcome attractive forces, and cause the dissociation of the cement agglomerates into primary particles. As a result, they provide good dispersing effect on cement and are able to reduce water demand of concrete up to 30%, while maintaining the flow characteristics [1–3]. Currently, a new generation of SPs based on polycarboxylate polymers with long, comb-type side chains (PC) has been developed. These chemicals are more effective for the water reducing capability and for preventing slump loss, for they can disperse cement particles not only by electrostatic repulsions aforementioned, but also by steric hindrance effects [4].

Although PC could maintain the workability of concrete for a long period of time, its applications in preparing flowing concrete and high performance concrete are limited due to economic reasons. In other words, SNF is still the main SP used instead because of the relatively low cost. However, care must be taken to prevent rapid slump loss of concrete when SNF was incorporated.

Recently, Lim et al. [5] mentioned that polycarboxylic acid polymer with $-COO^-$ functional group could cause a slump-releasing effect. They reported that addition of 20 wt.% of a copolymer of maleic anhydride and acrylic acid in SNF showed an excellent control of effect of slump loss of cement pastes and increasing apparent viscosity.

In this study, we have prepared a water-soluble carboxylic acid/sulfonic acid copolymer (PMAMP) as a chemical admixture. PMAMP was prepared from methacrylic acid and

* Corresponding author. Tel.: +886 2 2930 9088; fax: +86 886 2 29324249.
E-mail address: kchsu@ntnu.edu.tw (K.-C. Hsu).

0008-8846/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2005.10.005

2-acrylamido-2-methylpropane sulfonic acid (AMP) in a basic condition through a free radical polymerization. This chemical was found to be effective in improving the workability of the resulting cementitious materials [6]. In this article, PMAMP samples with different reactant ratios or molecular weights were prepared, and added into either mortars or concrete. The effects of this polymer on the fluidity or workability, and compressive strength of cementitious materials were examined and discussed.

2. Experimental

2.1. Materials

The materials used include Type I Portland cement, fine and coarse aggregate, fly ash and blast-furnace slag, and two chemical admixtures. Cement is from the Taiwan Cement and complies with ASTM C150. Fine aggregate is from the bank of Pearl River, China. The density is 2.59 g/cm^3, and the fineness modulus is 2.8. Coarse aggregate is from the bank of Da-An River. The density is 2.62 g/cm^3, and the largest diameter is 0.5 in. Both fine and coarse aggregate meet the standard of ASTM C33, and were washed and dried before use. Fly ash comes from the Hsin-Da Thermo-Power Plant, which is a subsidiary of Taiwan Electric Power, and the LOI value is 4%. Slag comes from China Steel, and the Blaine surface area is 4000 cm^2/g. Both fly ash and slag comply with ASTM C311. Table 1 lists the properties of cement, slag, and fly ash. Chemical admixtures used are PMAMP and a commercial SNF. PMAMP was prepared from methacrylic acid and AMP in a basic condition through a free radical polymerization. Details of the preparation procedure were described elsewhere [7]. Fig. 1 shows the chemical structure of PMAMP polymer. In this study, polymers with different reactant ratios and molecular weights were prepared, purified, and tested. Table 2 lists the AMP content and weight-average molecular weight (MW) of the prepared PMAMP samples. The AMP content (in molar ratio) of the samples was ranging from 20% to 60%, and the MW was ranging from 4×10^4 to 5×10^5. The commercial SNF, manufactured by Hi Con, has an MW of about 2000; it was used for comparison.

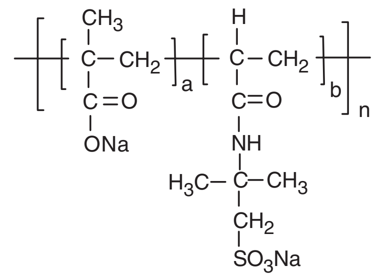

Fig. 1. The chemical structure of PMAMP polymer.

Table 1
The properties of cement, slag, and fly ash

Properties		Cement (type I)	Slag	Fly ash
Chemical compositions (%)	SiO_2(S)	22.01	34.86	52.66
	Al_2O_3	5.57	13.52	29.19
	Fe_2O_3(F)	3.44	0.52	3.98
	Ca0	62.80	41.77	4.14
	MgO	2.59	7.18	2.05
	SO_3	2.08	1.74	0.61
	f-CaO	1.05	–	–
	Na_2O	0.40	–	–
	K_2O	0.78	–	–
	Loss on ignition	0.51	0.31	4
	Insoluble residue	0.08	–	–
	C_3S	40.10	–	–
	C_2S	32.80	–	–
	C_3A	8.90	–	–
	C_4AF	10.50	–	–
Physical properties	Surface area (cm^2/g)	3460	4350	3110
	Density	3.15	2.87	2.21

2.2. Gel Permeation Chromatography (GPC) measurements

The molecular weight of either PMAMP or SNF was determined from GPC measurements which were carried out with a Jasco liquid chromatography equipped with three coupled columns Shodex OHpak KB802.5, KB804, and KB806, a pump (Jasco PU-980) and an RI detector (Jasco RI-930). The samples were analyzed using a 0.08 M KCl aqueous solution as eluant, at a flow rate of 1 mL/min. Monodispersed polystyrene sulfonates of different molecular weights were used as calibration standards.

2.3. Preparation of test of mortars

PMAMP was first dissolved in water to form an aqueous solution. Mortars were made by mixing water, cement, and fine aggregate, with or without addition of polymer solution. The water/cement (W/C) ratio was 0.42; cement/fine aggregate ratio was 1/2.75; and the polymer/cement (SP/C) ratio ranged from 0 to 1 wt.% (weight of SP solid relative to the weight of cement). The mixing procedure was as follows: (1) cement and fine aggregate were added in the bowl and mixed in a Hobart mixer at low speed for 3 min, (2) half amount of water was added to the mixture and mixed at low speed for 3 min, (3) the rest of water with or without the presence of polymer solution was added to the mixture and mixed for 3 min, and (4) stopping the mixer, quickly scraping down into the batch any mortar adhered on the side of the bowl, then starting the mixer and finishing by mixing for 1 min at medium speed.

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. Higher spread diameter value represents greater fluidity of materials.

Table 2
The AMP content and molecular weight of the prepared PMAMPs

PMAMP symbol	P15	P21	P23	P25	P35	P45
AMP (%)	20	40	40	40	50	60
MW	4.4×10^4	3.3×10^5	1.2×10^5	5.6×10^4	6.1×10^4	5.8×10^4

2.4. Preparation of tests of concrete

Concrete was made by mixing water, binder (cement + fly ash + slag), fine aggregate, and coarse aggregate, with or without the presence of polymer solution. Table 3 lists the mixture proportions of concrete with various PMAMPs and SNF. The water/binder (W/B) ratio was 0.28; and the polymer/binder ratio ranged from 1.7 to 2.8 wt.% (weight of SP solid relative to the weight of binder). The concrete was designed according to Hwang et al.'s densified mixture design algorithm [8]. The designed concrete should have the least initial slump of 25 cm and slump flow of 60 cm with 28-day compressive strength of 65 MPa. Besides, the designed concrete cannot have any bleeding or segregation occurred. The mixing procedure was as follows: (1) half amount of water with or without polymer solution present and binder were added in the mixing chamber and mixing in a concrete mixer for 1 min, (2) fine and coarse aggregate, and the rest of water were added and mixed for 2 min.

The workability of concrete was indicated by the slump and slump flow at 0 min, 1 h, and 2 h, in a slump cone test according to ASTM C143. The air content of fresh concrete was determined according to ASTM C403. Thereafter concrete specimens of 10ψ × 20 cm were prepared, cured, and their compressive strengths were measured according to ASTM C39 at the ages of 7, 28, 56, 90, and 150 days. Finally, the time of setting of concrete was determined by means of penetration resistance measurements on mortar sieved from the concrete mixture according to ASTM C231.

3. Results and discussion

3.1. Effect of PMAMP on mortar properties

It is well known that the major function of SPs is to disperse cement particles and improve the workability of concrete. As the effects of SP on the rheological properties of mortars are related to those of concrete, it is worthwhile to examine the fluidity of mortars in the beginning and determine the effectiveness of these chemical admixtures. Fig. 2 shows the measured spread diameter of mortars (W/C = 0.42) containing PMAMP with different molecular weights and SNF at various dosages. The tested polymers in Fig. 2 were controlled to have same AMP content, i.e., 40%. The mortar without any chemical admixture present will not flow or spread in the flow table, and the diameter value is 10.5 cm. When PMAMP was added, the fluidity of the resulting mortars increased. In general, the diameter value increases quickly with polymer dosage initially, and then approaches a constant value gradually. The transition point, corresponding roughly to the saturation point [9], occurs at a PMAMP dosage of about 0.25–0.6%, depending on the molecular weight of polymer. The mortar containing PMAMP with higher molecular weight has transition point at higher polymer dosage, and the achieved diameter value is smaller. Clearly, P25 (MW = 5.5×10^4), show the highest fluidity-enhancing capabilities, followed by P23 (MW = 1.2×10^5) and P21 (MW = 3.3×10^5). Moreover, the transition point of mortars containing SNF occurs at a polymer dosage of about 0.4%, which is higher than that containing either P23 or P25, and the achieved diameter value is lower. Finally, it is noted that bleeding and segregation occurred if the polymer dosage is far beyond the saturation point.

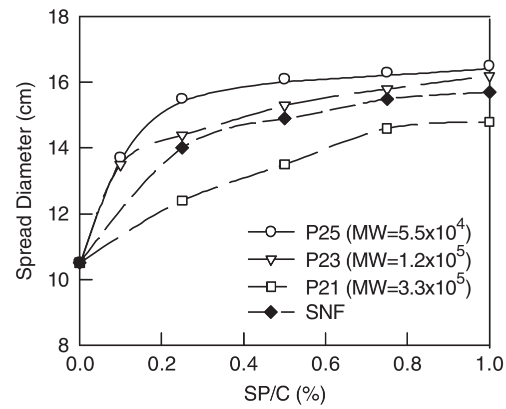

Fig. 2. The spread diameter of mortars containing PMAMP with different molecular weights and SNF at various dosages.

Table 3
The mixture proportions of concrete with different PMAMPs and SNF

Concrete symbol	SP symbol	W/B	Materials (kg/m^3)						
			Stone	Sand	Fly	Slag	Cement	Water	SP
C15	P15	0.28	816	856	111	23	437	144.2	15.8
C21	P21	0.28	816	856	111	23	437	148.8	11.2
C23	P23	0.28	816	856	111	23	437	149.6	10.4
C25	P25	0.28	816	856	111	23	437	150.4	9.6
C35	P35	0.28	816	856	111	23	437	150	10
C0	SNF	0.28	816	856	111	23	437	144.8	15.2

The fluidity of mortars is in general closely related to the effectiveness of SP in the system, which is determined by the degree of adsorption of the chemical admixture and the density of electric charges on the surface of particles. In turn, the degree of adsorption of SP is affected by the molecular weight of the chemical. Basile et al. [10] found that the fluidifying effect for cement pastes could be increased by reducing the content of monomer and increasing the molecular weight of the SNF condensates. Separately, Bonen and Sarkar [11] observed a shift of SNF UV-absorption peak during the adsorption experiment of SNF in different cements. They concluded that monomer, dimer, and probably other low molecular weight polymers were more likely to remain differentially in the pore solution, while higher molecular weight polymers were adsorbed on cement particles. Anderson et al. [12], Moukwa et al. [13] and Chen et al. [14] indicated that there were optimal degrees of polymerization of admixtures for best performance in concrete in terms of workability and other properties. The amount of adsorption and the optimal degrees of polymerization were different for admixtures with different chemical structures.

Fig. 3 is the change of molecular weight distribution of free P21 molecules in cement pastes along with elapsed time. (SP/C = 1.0%) The peak area was found to decrease with increasing time. It appears that the adsorption approaches the equilibrium

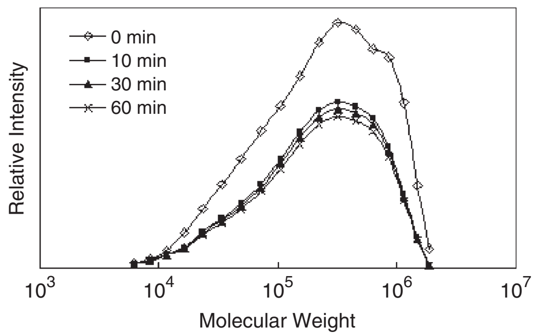

Fig. 3. The molecular weight distribution of free P21 molecules in cement pastes along with elapsed time (SP/C = 1.0%).

state at time of about 10 min. Based on the difference of peak area, the amount of adsorbed polymer on cement particles could be calculated. Table 4 lists the amount of adsorbed PMAMPs on cement particles. For those PMAMPs containing 40% AMP, the result indicates that the adsorbed amount of P25 is more than that of P23, which is more than that of P21. When the added polymer was adsorbed more on cement particles, it would generate stronger electrostatic repulsion. As a result, the fluidity of mortars with P25 is the highest, that with P23 is next, and that with P21 is the least.

Except for the molecular weight, the reactant ratio of PMAMP is another factor influencing the fluidity of mortars. Fig. 4 shows the measured spread diameter of mortars containing PMAMP with different AMP contents and SNF at various dosages. The tested polymers in Fig. 4 were controlled to have similar molecular weight, i.e., MW of about 5×10^4. When the incorporated admixture contains about 40% AMP, the resulting mortars appear to have the highest fluidity or diameter value. Nevertheless, the diameter values of mortars are close to each other when the incorporated PMAMP contains 20–50% AMP.

From Fig. 1, PMAMP contains two functional groups, i.e., the carboxylic group (–COOH) and sulfonic group ($-SO_3H$). The higher the AMP content of PMAMP, the more the sulfonic group and the less the carboxylic group of the polymer. The amount of adsorbed PMAMPs with different AMP contents (P15, P25, P35, and P45) on cement particles is listed in Table 4. The result indicates that the adsorbed amount of polymer is increased with AMP initially, reaches a maximum at 40% AMP, and then decreases subsequently. This trend agrees with that in Fig. 4, indicating that the fluidity of mortars would be higher if the adsorbed amount of polymer was greater.

Finally, PMAMP with MW of about 5×10^4 and 20–60% AMP appears to be more effective than SNF, as the saturation point of the former in Fig. 2 occurs at a smaller dosage and the achieved diameter value of the resulting mortar is higher than the latter. The difference is attributed to different chemical structures of these two chemical admixtures. Besides, the tested PMAMP was purified polymer, which has optimum reactant ratio or molecular weight. In contrast, the commercial one contains some unreacted monomer, and its molecular weight might not be optimized [10].

Table 4
The amount of adsorbed PMAMPs on cement particles

PMAMP Symbol	P15	P21	P23	P25	P35	P45
Adsorbed amount (mg/g cement)	2.6	3.7	3.9	5.1	4.9	3.2

(SP/C = 1%)

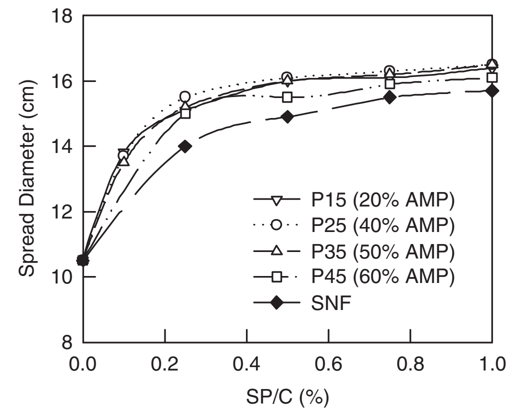

Fig. 4. The spread diameter of mortars containing PMAMP with different AMP contents and SNF at various dosages.

3.2. Effect of PMAMP on concrete properties

From above results, PMAMP with proper AMP content and molecular weight appears to be effective in improving the flow properties of mortars. In the following, the effect of this polymer on concrete properties was further examined and compared.

Table 3 lists the mixture proportions of concrete with different admixtures and Table 5 shows the properties of concretes with these admixtures. Generally all concrete mixes meet the designed requirements. However, the required dosage of each polymer was different. C25 has the least required amount of PMAMP (9.6 kg/m^3 P25). Followed by C35 (10 kg/m^3 P35), C23 (10.4 kg/m^3 P23), and C21 (11.2 kg/m^3 P21). C15 has the highest required amount of PMAMP (15.8 kg/m^3 P15). The required amount of SNF in C0 is the same as that of C15. The lower the required amount of SP, the better the fluidity-enhancing capability of this admixture. Therefore, P25 and P35 show the best fluidity-enhancing capability, followed by P23 and P21, and P15. The order is roughly consistent with that in the previous section.

Apart from promoting the workability of concrete, the addition of SP in concrete should be able to maintain the workability of the resulting concrete for at least 1–2 h. Fig. 5 shows the slump flow of concrete with different admixtures as a function of elapsed time. The initial slump flow of all tested concretes was about 68.5–74 cm, as shown in Table 5. The slump flow retention is defined as the percentage of the slump flow of concrete at certain time to the initial slump flow. As expected, the slump flow of each admixed concrete decreases with time. However, the rates of slump flow loss are different. C21 presents the lowest slump flow loss rate or best in slump retention, followed by C23, C15, and C35. C25 presents the worst performance in slump retention. From the order of tested

Table 5
The properties of concrete with different PMAMPs and SNF

Concrete symbol	Initial slump (cm)	Initial slump flow (cm)	28-day compressive strength (MPa)	Initial setting (h)	Final setting (h)	Air content
C15	27.5	69	63.4	5:30	7:10	1.6
C21	28	74	64.5	7:15	9:50	1.7
C23	28	70	67	7:10	8:55	1.8
C25	28	70	66.4	5:35	7:30	1.8
C35	28	70.5	62.9	8:20	9:55	1.9
C0	27.5	68.5	63	4:05	5:35	1.9

concrete in slump flow retention, it appears that PMAMP with greater molecular weight is more effective in controlling the slump loss of concrete. It is speculated that bigger molecules would move slower in pore solution, and take longer time to reach and be adsorbed onto solid particles. Moreover, the amount of adsorbed PMAMP is decreased with increasing molecular weight, or in the order of P25 > P23 > P21, as listed in Table 4. The more PMAMP was adsorbed, the less the amount of free admixture molecules left in the pore solution, and the faster the slump loss of the concrete. Besides, PMAMP with higher molecular weight would cause stronger steric hindrance effect which also favors the workability retention of concrete [2].

Fig. 5 also shows that the 2-h slump flow of concrete with PMAMPs is more than 69% of the initial value, which is higher than that of C0 which contains SNF. The difference in slump-retention performance is probably due to different MW of admixtures. The molecular weights of PMAMPs were listed in Table 2 to range from 4.4×10^4 to 3.3×10^5, which is 10 times higher than that of SNF (MW = 2×10^3). As SNF has lower MW, it would be adsorbed onto cement particles rapidly and promote the fluidity of mortars quickly. In contrast, high-MW PMAMPs would present slower adsorption, and provide better slump-releasing effect.

Separately, the time of setting of concrete with or without SP present was measured and listed in Table 5. The time of initial setting of control, i.e., concrete without any admixture present, is 4 h 10 min, and the time of final setting is 7 h 5 min. Addition of PMAMP into concrete prolongs the setting time. Apparently, concrete containing PMAMP with higher AMP content or greater MW shows longer setting time. In contrast, concrete with SNF has shorter setting than control. Accordingly, PMAMP will retard the setting time of fresh concrete, and SNF shows the opposite or accelerating effect. This is another reason why PMAMP shows better slump retention properties than the commercial SP.

Fig. 6 shows the compressive strength of concrete with different admixtures at various curing ages. In general, each admixed concrete exhibits similar strength developing behavior; the strength value increases with age initially, and then approaches a plateau. Among the tested concrete specimens, C23 appears to have the highest strength values at age of 7–150 days. However, the compressive strengths of all tested concrete are only slightly different from each other.

4. Conclusions

A new carboxylic acid/sulfonic acid copolymer (PMAMP) as an SP has been prepared and tested. The results indicate that this polymer with the AMP content of about 20–60%, and a weight-average molecular weight of about 5×10^4 is effective in dispersing cement particles and improving the fluidity of mortars and the workability of concrete made with Type I Portland cement. Moreover, PMAMP with higher molecular weight is more capable of preventing slump loss. Compared with SNF, PMAMP appears to be more effective in enhancing and maintaining concrete workability. This is because PMAMP molecules contain both carboxylic acid groups and sulfonic acid groups, and their molecular weights are higher. Finally, concrete incorporated with different PMAMPs at W/B = 0.28 shows similar strength-developing behavior and the achieved compressive strength is close to each other.

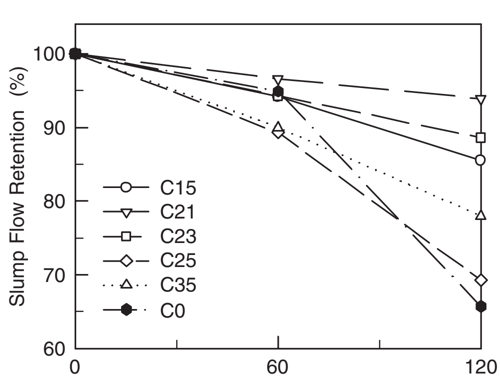

Fig. 5. The slump flow of concrete with different admixtures as a function of elapsed time.

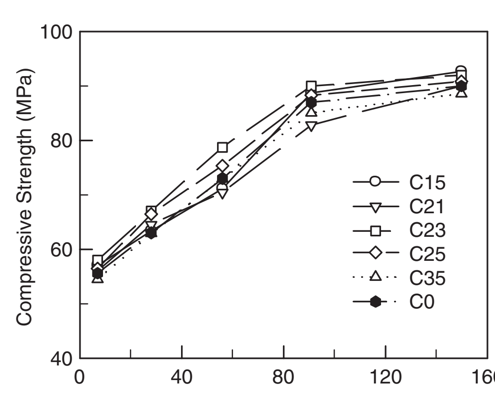

Fig. 6. The compressive strength of concrete with different admixtures as a function of curing age.

Acknowledgement

The authors are grateful for the support of this work by the National Science Council of the Republic of China (Contract # NSC-91-2622-E-003-002-CC3).

References

[1] M.R. Rixom, N.P. Mailvaganam, Chemical Admixtures for Concrete, 2nd edition, E and F. N. Spon, London, 1986.
[2] V.S. Ramachandran, V.M. Malhotra, C. Jolicoeur, N. Spirattos, Superplasticizers: Properties and Applications in Concrete, CANMET, Ottawa, Ontario, 1998.
[3] V.M. Malhotra, in: P.K. Mehta (Ed.), Mario Collepardi Symposium on Advances in Concrete Science and Technology, Rome, 1997, p. 271.
[4] R. Khurana, I. Torresan, in: V.M. Malhotra (Ed.), Proceedings of Fifth International Conference on Superplasticizers and other Chemical Admixtures in Concrete, Rome, 1997, p. 83.
[5] G.G. Lim, S.S. Hong, D.S. Kim, B.J. Lee, J.S. Rho, Cem. Concr. Res. 29 (1999) 223.
[6] Y.C. Tseng, W.L. Wu, H.L. Huang, C.T. Wang, K.C. Hsu, in: V.M. Malhotra (Ed.), Proceedings of Sixth International Conference on Superplasticizers and other Chemical Admixtures in Concrete, Nice, 2000, p. 401.
[7] Y.S. Ye, The synthesis and application of a new acrylate-based superplasticizers, MS Thesis, Department of Chemistry, National Taiwan Normal University, 2002.
[8] C.L. Hwang, J.J. Liu, L.S. Lee, F.Y. Lin, J. Chin. Inst. Civil Hydraul. Eng. 8 (2) (1996) 217.
[9] P.C. Aitcin, High-Performance Concrete, E and FN SPON, New York, 1998.
[10] F. Basile, S. Biagini, G. Ferrari, M. Collepardi, in: V.M. Malhotra (Ed.), Proceedings of Third International Conference on Superplasticizers and other Chemical Admixtures in Concrete, Ottawa, 1989, p. 209.
[11] D. Bonen, S.L. Sarkar, Cem. Concr. Res. 25 (7) (1995) 1423.
[12] P.J. Anderson, D.M. Roy, J.M. Gaidis, Cem. Concr. Res. 18 (6) (1988) 980.
[13] M. Moukwa, D. Youn, M. Hassanali, Cem. Concr. Res. 23 (1) (1993) 122.
[14] S.D. Chen, C.H. Hwang, K.C. Hsu, Cem. Concr. Res. 29 (2) (1999) 255.