



## Synthesis of A Novel Polycarboxylate Superplasticizer with High Performance†

KELI ZHOU<sup>1</sup>, JIN LIU<sup>1,2,\*</sup> and ZHEN LI<sup>1</sup>

<sup>1</sup>School of Materials Science & Chemical Engineering, Anhui University of Architecture, Hefei 230022, Anhui, P.R. China

<sup>2</sup>Anhui Key Laboratory of Advanced Building Materials, Hefei 230022, Anhui, P.R. China

\*Corresponding author: E-mail: liujin@aiai.edu.cn

AJC-9548

The novel polycarboxylate superplasticizers (NPCS) were prepared by copolymerizing of novel maleic anhydride citric acid ester (MACA), methoxyl polyethylene glycol ether methyl acrylate (MPEGMAA), acrylic acid (AA),  $\alpha$ -methylacrylic acid (MAA), sodium alkyl sulfonate (SAS). The structure and properties of novel polycarboxylate superplasticizers were characterized by FTIR, intrinsic viscosity and surface tension. Moreover, the application properties of the fluidity, zeta potential and drying shrinkage of adding novel polycarboxylate superplasticizers into cement paste were also investigated. The results showed that the fluidity of cement grout reached as high as 360 mm at the copolymer usage of 0.25 wt %, water-cement ratio of 0.29. No obvious loss of fluidity occurred within 2 h and the cement paste without bleeding and segregation was homogeneous. In addition, the novel polycarboxylate superplasticizer is good for reducing the drying shrinking, improving the mesoporous volume and making cement hardenite more compact by proved from N<sub>2</sub> adsorption and desorption measurement.

**Key Words:** Polycarboxylate superplasticizer, Fluidity, Zeta potential, Drying shrinkage, Pore structure, Citrate acid.

### INTRODUCTION

Polycarboxylate superplasticizer (PCS) has drawn more and more attention in modern construction industry because of its superior dispersibility and retention effects<sup>1-4</sup>. Moreover, its molecular structure has the potential to be modified because it can be synthesized by copolymerization from different monomers<sup>5-7</sup>. But some deficiencies, such as limited water-reducing property and retention ability, excessive sensitivity, certain early-age cracking of the concrete, *etc.*, are still critical problems needing to be solved. In this research, based on the analysis of the chemical structure of polycarboxylate superplasticizer, a novel superplasticizer with short side chains of multiple -COO- groups and long side chains of polyoxyethylene (PEO) groups was designed and synthesized in order to improve the comprehensive performance of polycarboxylate superplasticizer.

### EXPERIMENTAL

**Synthesis of novel polycarboxylate superplasticizer (NPCS) and analysis of its chemical structure:** Firstly,  $\alpha$ -methylacrylic acid (MAA) was reacted with methoxyl polyethylene glycol methyl ether (MPEG) in solvent to synthesize methoxyl polyethylene glycol methyl ether methyl acrylate

(MPEGMAA). Maleic anhydride (MA) was reacted with citrate acid (CA) in solvent to synthesize maleic anhydride citric acid ester (MACA). Secondly, some polymers were synthesized through free radical polymerization from MPEGMAA, MACA, MAA, acrylic acid (AA) and sodium alkyl sulfonate in water solution. In this step, the mixed monomer solution and initiator solution were dropped in the vessel for 3.5-4.0 h at 75-80 °C, respectively. The reaction system was left for 1 h at 90 °C to copolymerize completely. Then, the polymer solution was neutralized by 20 wt % sodium hydroxide solution until the pH value reached to 7.0.

At a constant temperature of 30 °C, the intrinsic viscosities of the NPCS (1) and the monomer mixture before reaction (2) were determined respectively by Ubbelohde viscosity method with the solvent of 1mol/L aqueous sodium chloride. The physical properties of the NPCS synthesized are shown in Table-1.

### RESULTS AND DISCUSSION

FTIR spectra of the copolymers were shown in Fig. 1. It can be found that the absorption peak of 1727 cm<sup>-1</sup> with relatively high intensity belonging to the characteristic of C=O stretching vibration. The C=C stretching vibration absorption

†Presented to the 4th Korea-China International Conference on Multi-Functional Materials and Application.

TABLE-1  
PHYSICAL PROPERTIES OF THE NOVEL POLYCARBOXYLATE SUPERPLASTICIZERS (NPCS)

Item	Appearance	Solid content (%)	Density (g/cm <sup>3</sup> )	pH	Cl <sup>-</sup> content (%)	Intrinsic viscosity of 1 (mL/g)	Intrinsic viscosity of 2 (mL/g)
Test result	Umber, liquid	25.34	1.041	7	0	8.60	3.15

TABLE-2  
CHEMICAL COMPOSITIONS OF CEMENT

Cement	SO <sub>2</sub>	AL <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	Loss	f-CaO	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF
Fly ash (%)	21.4	4.46	2.65	62.4	1.9	2.91	0.65	2.89	0.65	54.3	21.4	6.44	7.75

(1650-1640 cm<sup>-1</sup>) cannot be found, which indicates that the monomers had completely polymerized<sup>8</sup>. The adsorption bands of 1587 and 1238 cm<sup>-1</sup> were caused by the stretching vibrations of the -COO<sup>-</sup> group and the -SO<sub>3</sub><sup>-</sup> group, respectively. Novel polycarboxylate superplasticizers contained carbon-oxygen single bond (C-O-C) with the signal at 1115 cm<sup>-1</sup>, which proves that it contained the side chain of polyethylene glycol methyl ether in the molecular structure. And, the signals at 1454 and 1353 cm<sup>-1</sup> are the characteristic absorptions of PEO group<sup>9</sup>, too. The analyses show that the valuable and effective groups mentioned above were grafted into the molecular structure of NPCS and the structure of NPCS is shown in Fig. 2.

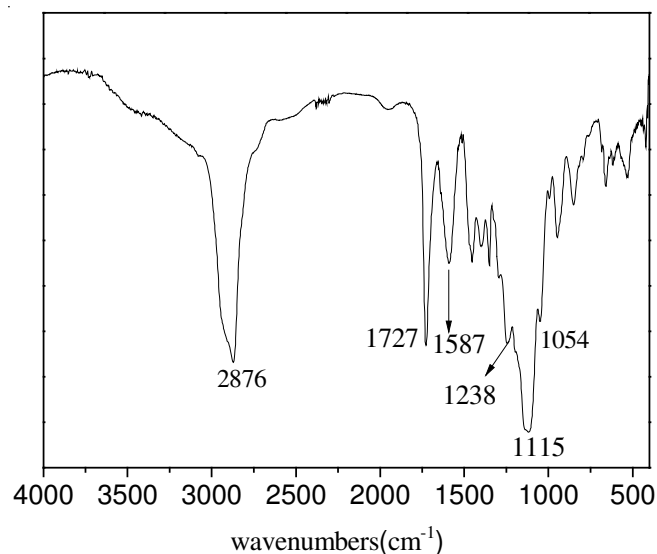


Fig. 1. FTIR spectrum of novel polycarboxylate superplasticizers (NPCS)

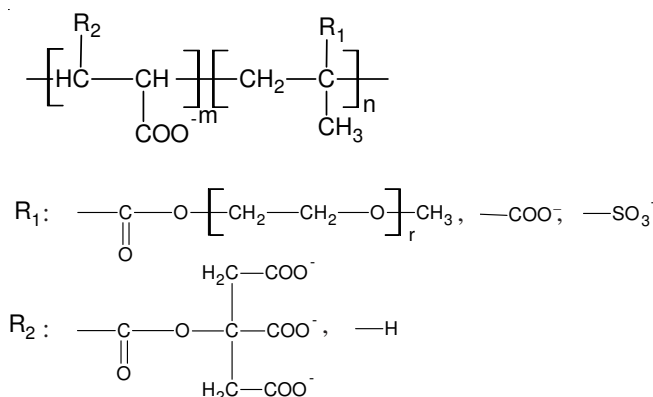


Fig. 2. Estimated chemical structure of NPCS

**Fluidity of the cement paste:** Determination of the cement paste fluidity was carried out according to Chinese standard GB/T8077-2000: Methods for Testing Uniformity of Concrete Admixture. And, the chemical compositions of Grade 42.5 Portland cement (reference cement of China) were shown in Table-2. In these experiments, it can be found that the NPCS had superior dispersibility and dispersion retention stability. And, the cement pastes with NPCS were homogeneous, bleeding and segregation was not found. The results are shown in Fig. 3.

The compatibility of PCS with the cement is closely related to the molecular structure of superplasticizer. Fig. 3 shows that the dispersibility and dispersion retention stability of NPCS were better than those of the naphthalene superplasticizer and the conventional PCS. The fluidity of cement paste reached as high as 360 mm at the copolymer usage of 0.25 wt %. In addition, the fluidity did not decrease and it increased slightly in 2 h. It may be because the new monomer MACA can not only increase the content of carboxyl, but also regulate the distribution of functional groups in the backbone of molecular structure. At the same time, MPEGMAA and MACA improved the dispersion ability and dispersion retention ability of the NPCS by enhancing the steric hindrance. However, it is still a complicated process needing a further research.

The novel superplasticizer molecules containing more -COO<sup>-</sup> groups were adsorbed more easily on the polar surface of cement particles and the adsorption layers were more compact.

So, the layers cannot be crushed to form flocculation when the particle collided with another<sup>10</sup>. For NPCS, it was similar to traditional PCS, the higher the content was, the higher the fluidity was, the smaller the rate of increase became. Even if the mixing amount of the NPCS was reduced to 0.15 wt %, the fluidity of the cement paste still reached as high as 320 mm. Moreover, when the content was more than 0.35 wt %, the cement paste with NPCS remained homogeneous and the fluidity of the fresh cement paste did not decrease with time elapsing. This may be explained as follows: the ester bond on the side chain broke in alkaline aqueous phase and then the micromolecule adsorbed on cement particle again<sup>10</sup>. In this case, the secondary dispersion was caused by the adsorption, which not only was helpful for the cement particles to keep dispersive, but also made the cement pastes homogeneous. In contrast, varying degrees of bleeding and segregation can be found in the cement pastes with conventional PCS and naphthalene superplasticizer, respectively.

The effect of water content on the fluidity of cement pastes with the same NPCS dosage is shown in Fig. 3(c). It is quite

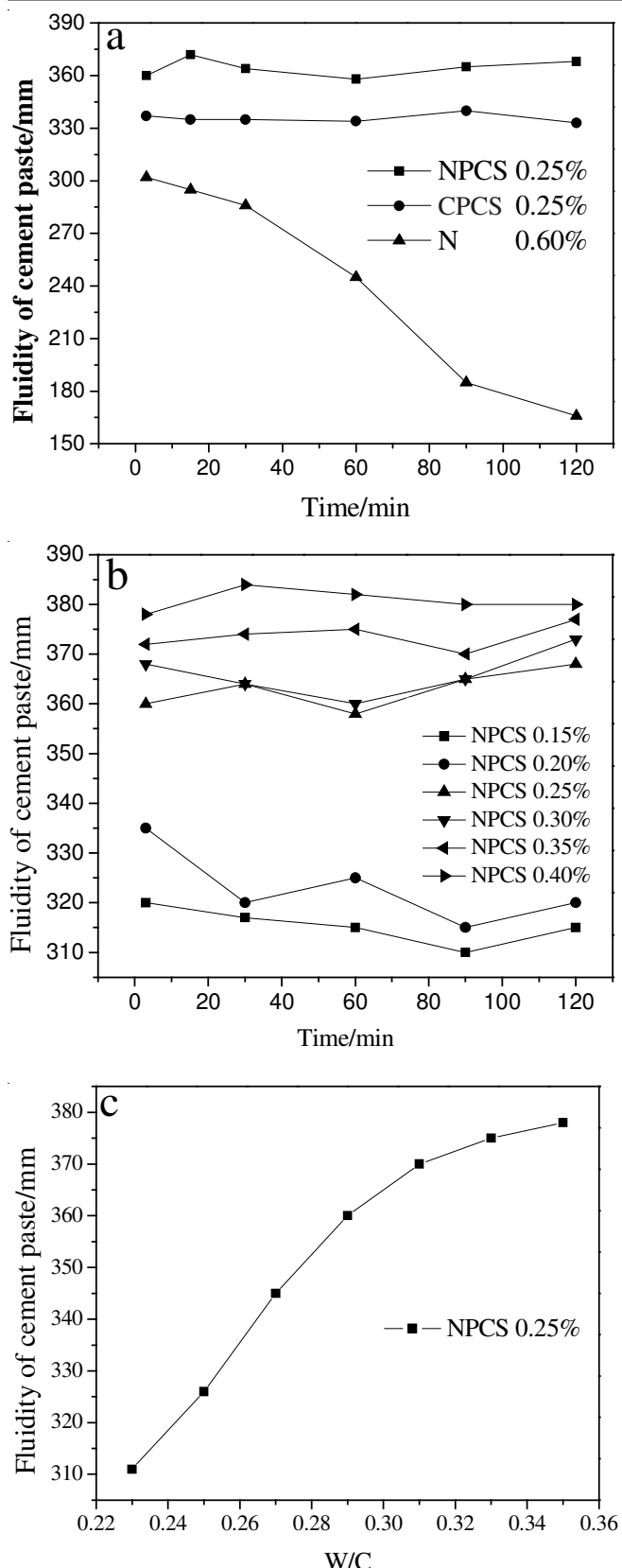


Fig. 3. (a) Fluidity variation of cement pastes containing different superplasticizers, water/cement: 0.29; (b) Fluidity variation of cement pastes containing different contents of NPCS, water/cement: 0.29; (c) Fluidity variation of cement pastes containing different contents of water

NPCS = the novel polycarboxylate superplasticizer; CPCS = the conventional polycarboxylate superplasticizer; N = naphthalene superplasticizer

noticeable that the fluidity of cement paste with the NPCS increased with the enlargement of water content, but the rate of the increase became smaller. One thing to be mentioned is that, at lower water-cement ratio, the fluidity changed significantly when the water content fluctuated slightly. And, the fluidity of cement grout can still reach as high as 310 mm at the copolymer usage of 0.25 wt %, water-cement ratio of 0.23. Therefore, it can be used to cast stronger concrete in modern construction industry. In conclusion, the NPCS is a high-performance superplasticizer with even higher dispersing ability and better compatibility with cement.

**Zeta potential of cement particle surface:** Different kinds of superplasticizers were added in the cement pastes which were prepared with a high water-cement ratio, respectively. Then, a Zeta Potential Analyzer was used to analyse the Zeta potential of cement particle surface by taking the suspension of the cement paste at 25 °C. Fig. 4 shows that the absolute value of Zeta potential of the cement particle with the NPCS was slightly higher than that of the cement particle with no superplasticizer. And, compared with the Zeta potential of the cement particle with naphthalene superplasticizer, its Zeta potential had little change over time. It was relatively lower because of the hindrance of PEO graft chains<sup>11</sup>. This rule was similar to variation of Zeta potential of the cement particle with conventional PCS. It can be inferred that the action mechanism of the novel superplasticizer is the interaction of electrostatic repulsive force and steric hindrance<sup>9,11</sup> and steric hindrance effect plays a dominant role in its dispersion retention stability. This action mechanism is more sustained and effective than the action only depending on the electrostatic repulsive force which is the major action mechanism of naphthalene superplasticizer<sup>12</sup>.

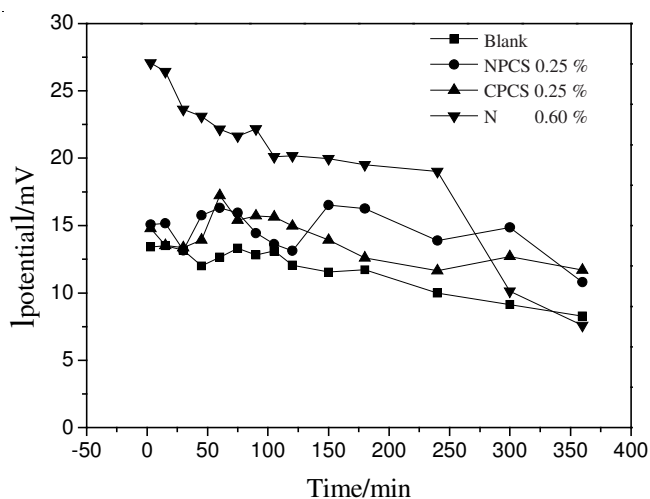


Fig. 4. Effects of different superplasticizers on the Zeta potential of cement particle surface; NPCS = the novel polycarboxylate superplasticizer; CPCS = the conventional polycarboxylate superplasticizer; N = naphthalene superplasticizer

**Drying shrinkage of cement paste and surface tension of novel polycarboxylate superplasticizers:** Drying shrinkage will lead to concrete cracking, which affects the use and durability of concrete. So, the drying shrinkage of cement paste was tested according to Chinese standard JC/T603-2004: Standard test method for drying shrinkage of mortar. And, the surface

tensions of different superplasticizer solution were measured by method of maximum bubble pressure method at 30 °C. The results are shown in Fig. 5 and Table-3, respectively. From the data in Fig. 5, it can be observed that the cement test blocks with the same water-cement ratio, which were placed in the identical curing box with the temperature of  $20 \pm 2$  °C, relative humidity of  $50 \pm 3$  % and constant wind speed, had varying degrees of drying shrinkages. And, compared with the cement pastes added with the other superplasticizers, the cement paste with NPCS had less drying shrinkage. As the molecule of NPCS had the structure with more  $-\text{COO}^-$  groups because of MACA, the surface tension of NPCS solution was reduced significantly<sup>12</sup>. That is, the surface tension of the NPCS solution was lower than the surface tensions of the others. According to capillary tension theory<sup>13</sup>, the reduction of surface tension was advantageous to reduce the drying shrinkage of cement. So, the shrinkage rates of cement pastes with NPCS were lower than the shrinkage rates of cement pastes with naphthalene superplasticizer for about  $80 (\times 10^{-6})$  and  $410 (\times 10^{-6})$ , respectively, when the curing age was 3 and 28 days. And similarly, the shrinkage of cement paste with conventional PCS was larger significantly than the shrinkage of the cement paste with NPCS.

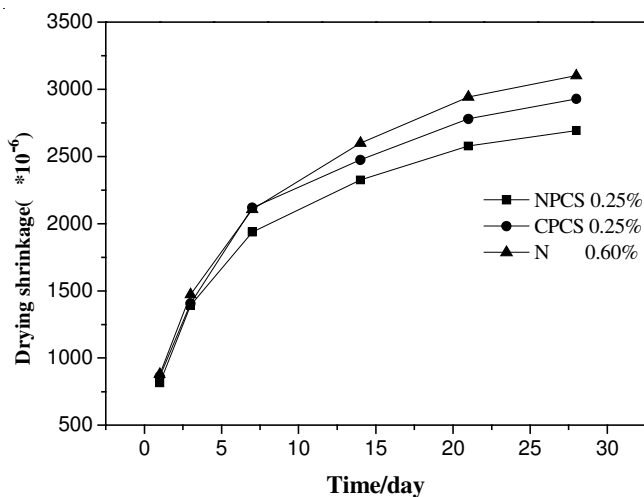


Fig. 5. Influence of different kinds of superplasticizers on drying shrinkage of cement pastes.

Sample	wt %	Surface tension (dyn/cm)
Water	0.0	71
NPCS solution	1.0	46
CPCS solution	1.0	54
N solution	1.0	69
N solution	2.4	64

**Pore structure of cement paste:** Pore structure of cement pastes containing different superplasticizers was determined by  $\text{N}_2$  adsorption. The results are shown in Table-4 and Fig. 6. The data shows that the intruded mesoporous volume for the paste containing superplasticizers was higher than the paste without superplasticizer and cement paste with NPCS had the highest mesoporous volume which was harmless to

TABLE-4  
NITROGEN SORPTION DATA OF THE CEMENT PASTE WITH DIFFERENT SUPERPLASTICIZERS, CURING AGE: 28 DAYS

Item	NPCS	CPCS	N	Blank
$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	8.345	9.915	10.901	7.559
BJH desorption cumulative volume of pores ( $\text{cm}^3/\text{g}$ )	0.059335	0.048879	0.050744	0.041083
BJH Adsorption average pore semi-diameter (nm)	12.42	8.60	8.34	9.76
Low-pressure absorption step ( $P_i/P < 0.03$ )	1.212	1.464	1.556	1.072

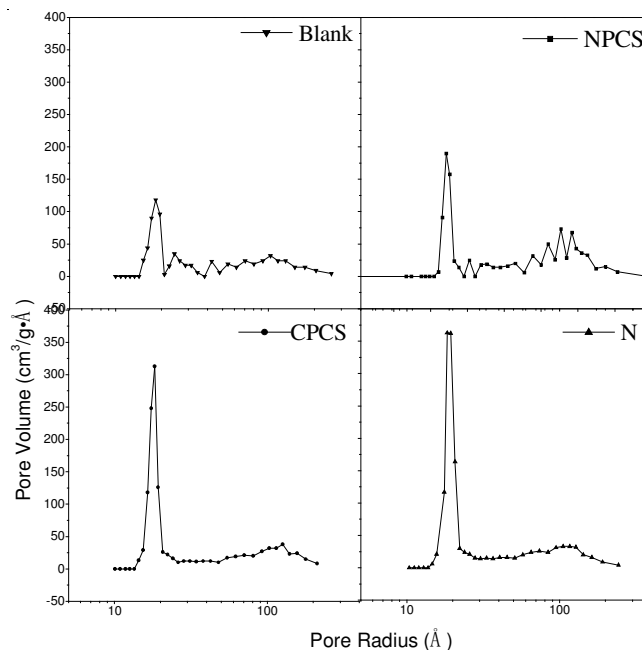


Fig. 6.  $dV/dD$  pore volume of the cement hardenites with different superplasticizers

the strength of concrete. The mesoporous volume of paste with NPCS increased by *ca.* 45 % compared with that of paste without superplasticizer. Cement paste with NPCS exhibited a lower mesoporous volume in the range of 3-5 nm and a higher mesoporous volume in the range of 20-40 nm, so its average pore size was higher than that of the other samples. In the cement paste, the water surface in the capillary will form capillary meniscus with the decline of surface when the ambient humidity was 40-90 %. Then, the surface tension of water will lead to the shrinkage stress to the pipe wall, which increased fast with the reduction of capillary diameter. That is, the appropriate enlargement of pore size led to the reduction of shrinkage stress. It is generally believed that the large drying shrinkage and cracking of paste occurred when the pore shrinkage stress exceeded the tensile strength<sup>12</sup>. In addition, the NPCS with excellent dispersibility had the short side chains of multiple  $-\text{COO}^-$  groups and long side chains of PEO groups, thus, hydration process of paste containing NPCS became more orderly. And, the paste with more orderly hydration produced more hydration products, which were helpful for the paste to offset the shrinkage stress caused by the pores. Moreover, in preliminary hydration stage, the relatively larger pores in the range of mesoporous can not only fill the gap between particles with the other smaller bubbles, but also support and bond

cement particles more effectively to make the paste more compact. So, the shrinkage rate of paste with NPCS was lower than that of pastes with the other superplasticizers. But, the variation of macropores (diameter > 50 nm) volume will be studied in the next step.

### Conclusion

Finally, the various results collected in this work show that the NPCS with the molecular structure containing multiple  $\text{-COO}^-$  groups had better dispersibility and excellent dispersion retention ability in cement paste. Furthermore, the NPCS, which had good compatibility with the cement, can reduce the surface tension and improve the mesoporous volume to obviously reduce the drying shrinkage of cement paste.

### ACKNOWLEDGEMENTS

This work was supported in part by the Natural Science Foundation of Anhui Province (070414183), the Natural Science Foundation of Anhui Province Education Department (KJ2007A057, 2003kj015zd) and the fund of Top-Notch Talents of Anhui Province Universities.

### REFERENCES

1. C.Z. Li, N.Q. Feng and D.M. Wang, *J. Chin. Ceramic Soc.*, **33**, 87 (2005).
2. K. Yamada, S. Ogawa and S. Hanehara, *Cement Concrete Res.*, **31**, 375 (2001).
3. G.G. Lim, S.S. Hong, D.S. Kim, B.J. Lee and J.S. Rho, *Cement Concrete Res.*, **29**, 223 (1999).
4. J.Y. Shin, J.S. Hong, J.K. Suh and Y.S. Lee, *Korean J. Chem. Eng.*, **25**, 1553 (2008).
5. J. Plank, K. Pöllmann, N. Zouaoui, P.R. Andres and C. Schaefer, *Cement Concrete Res.*, **38**, 1210 (2008).
6. E. Sakai, K. Yamada and A. Ohta, *J. Concrete Technol.*, **1**, 16 (2003).
7. R.G. Zhang, Q. Li, A.F. Zhang, Y. Liu and J.H. Lei, *J. Wuhan Univ. Technol.-Mater. Sci. Ed.*, **23**, 830 (2008).
8. M.H. Zhu, *Instrumental Analysis*, Higher Education Press, Beijing, China, edn. 3 (2000).
9. S. Li, Z.Y. Wen and H.C. Wang, *J. Chin. Ceramic Soc.*, **36**, 886 (2008).
10. Y.F. Zuo, D.M. Wang and W.F. Xiong, *J. Wuhan Univ. Technol.-Mater. Sci. Ed.*, **21**, 132 (2006).
11. C.Z. Li, N.Q. Feng, Y.D. Li and R.J. Chen, *Cement Concrete Res.*, **35**, 867 (2005).
12. D.Y. Xiong and X.H. Wang, *Concrete Admixtures*, Chemical Industry Press, Beijing, China (2002).
13. Y.B. Yang, *Study of the Influence of Chemical Admixtures and Mineral Additions on Cement Mortar Drying Shrinkage and Cracking*, South China University of Technology, Guangzhou, China (2002).