Effects of β-Cyclodextrin Side Chains on the Dispersing and Retarding Properties of Polycarboxylate Superplasticizers

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ABSTRACT: A modified polycarboxylate (MPC) superplasticizer was synthesized by the copolymerization of acrylic acid, methallyl sulfonic acid, allyl poly(ethylene glycol)s, and β-cyclodextrin (β-CD) grafted maleic anhydride. The molecular structure of the MPC was characterized by Fourier transform infrared spectroscopy and gel permeation chromatography. The effects of the content of β-CD on the application performance of MPC were investigated with measurements of the cement paste fluidity, setting time, amount of adsorption of MPC on the cement particles, and ζ potentials of the cement particles and differential scanning calorimetry–thermogravimetric analysis of different hydration ages of the cement pastes. The results indicate that the initial fluidities and setting times of the cement pastes increased with increasing number of β-CD side chains. The dispersion capacity of MPC on the cement particles mainly came from a steric hindrance effect and an air-entraining effect of the β-CD side chains. The better retarding performance of MPC was attributed to the solvation water film formed by the polyoxyethylene side chains and chelates formed by —OH groups on the β-CD structure combined with Ca^{2+} ions on the surface of the cement particles. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 396–404, 2012

Key words: copolymerization; dispersions; retardation time; synthesis

INTRODUCTION

Polycarboxylate (PC) superplasticizers are recognized as one type of important admixture used in modern concrete engineering. As soon as the superplasticizers are in contact with cement particles, some of them are adsorbed on the cement particles and create negatively charged particles, repulsing each other so that the cement particles no longer flocculate.[1,2] In recent decades, to improve the fluidity and setting time of superplasticizers and the compatibility between PC and cement, more and more research on the relationship among the molecular structures, microscopic mechanisms, and macroscopic performances has been conducted. Yamada et al.[3] analyzed the chemical structure of the dispersing properties of PC superplasticizers and found that the fluidity of cement paste increased with increasing length of the polyoxyethylene (PEO) side chains and the contents of the sulfonic groups. Grabiec and Piasta[4] studied the compatibility of cements and superplasticizers using multicriteria statistical optimization and found that different cement pastes modified with superplasticizers appeared helpful in analyzing the effects of some factors, such as the water-to-cement ratio (W/C), the amount of admixture, and the type of cement, on the characteristics of the pastes. Felekoğlu and Sarıkahya[5] investigated the compatibility of a PC-based superplasticizer with different set-controlling admixtures and the influence of the admixtures on the properties of the cement pastes. The results show that improvement in the properties of admixtures varied with the type and amount of set-controlling admixtures. In addition, other studies have been conducted on the relationship of PC superplasticizers and the mechanical properties of cement paste or concrete.[6–9]

However, problems regarding the poor workability retention performance of PC and the shortage of raw materials have not received enough attention. Therefore, the question of how to maintain the dispersion stability and flow retention of concrete and its sustainability has become a hot topic in research.

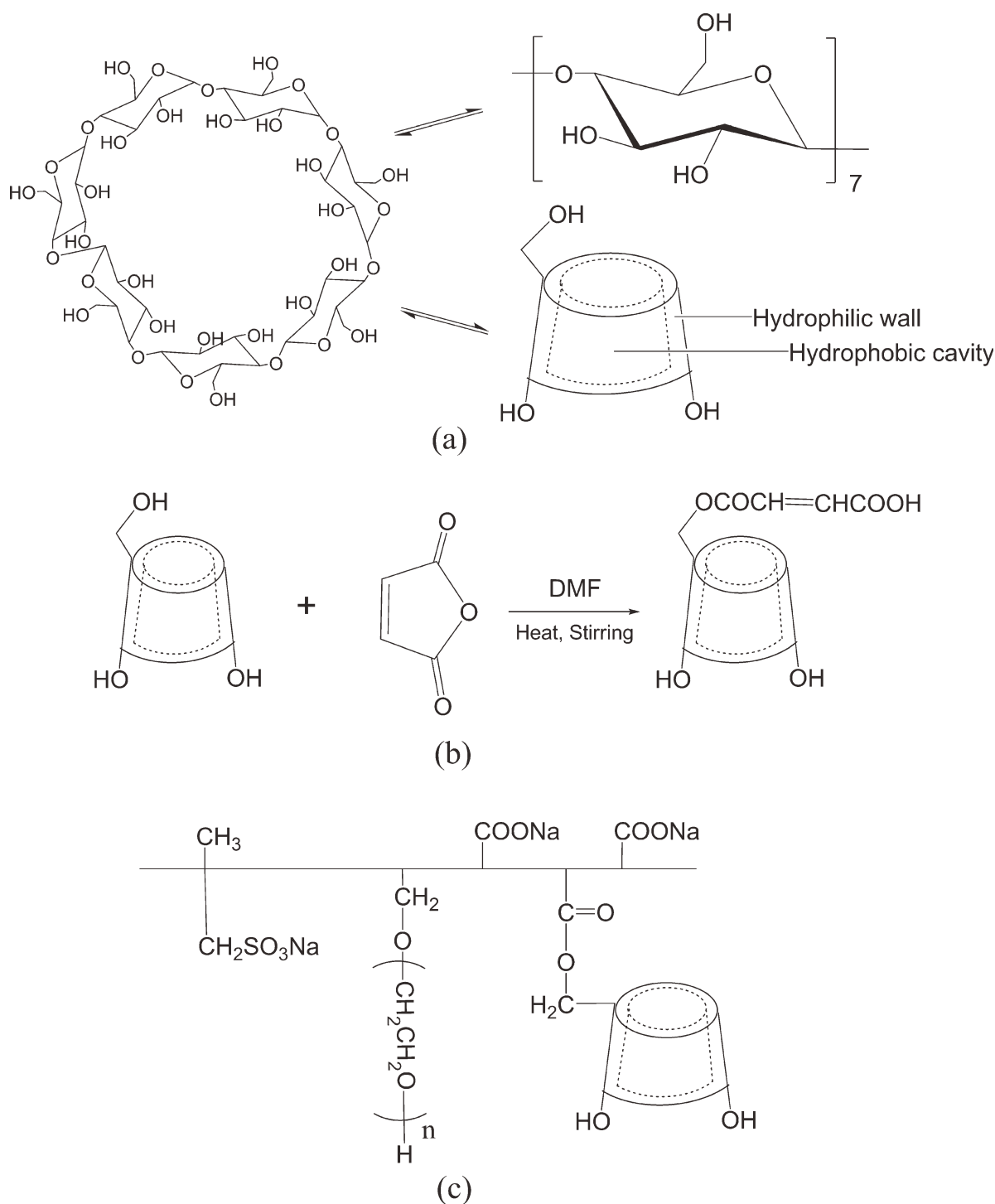β-Cyclodextrin [β-CD; Fig. 1(a)], a degradation of starch, is known to have a hollow, truncated cone

Figure 1 Molecular structure of (a) β-CD and (c) MPC and scheme diagram of synthesis of (b) MAH-β-CD.

with a hydrophobic cavity and a hydrophilic wall; it possesses good stability and solubility when it is modified. Because of this unique behavior, β-CD and its derivatives, including β-CD containing polymers, have been studied extensively in many research fields such as in drug-delivery systems,[10] the separation and absorption of materials,[11–13] and emulsifiers.[14] Therefore, a modified superplasticizer

with water-reducing and set-retarding properties was synthesized by the introduction of β-CDs onto the main chain of a polymer. Experimental research on the effect of β-CD side chains on the ζ potential of the surface of cement particles and the amount of adsorption, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) of cement pastes was conducted to elucidate the action

TABLE I
Monomer Composition of the PC Superplasticizers

Copolymer	APEG/AA/MAS/ MAH-β-CD (molar ratio)	Amount of raw material					M_n (Da)
		AA (g)	MAS (g)	APEG (g)	MAH-β-CD (g)	H₂O (g)	
PC	1/5.00/0.50/0	7.20	1.58	46.00	—	220	45,830
MPC1	1/4.99/0.50/0.01	7.18	1.58	46.00	0.24	220	42,260
MPC2	1/4.95/0.50/0.05	7.13	1.58	46.00	1.22	220	44,750
MPC3	1/4.90/0.50/0.10	7.05	1.58	46.00	2.43	220	46,200
MPC4	1/4.80/0.50/0.20	6.91	1.58	46.00	4.86	220	49,370

mechanism. The content of β-CD was found to be critical to either the dispersing action or the set-retarding action.

EXPERIMENTAL

Materials

Ordinary Portland cement (Qinling 42.5) was obtained from Qinling Cement Co., Ltd. (Shaanxi Province, China). Maleic anhydride (MAH), the initiator ammonium persulfate (APS), acrylic acid (AA), and methallyl sulfonic acid (MAS) were purchased from Hongyan Reagent Factory (China). Allyl poly(ethylene glycol) (APEG) was supplied by Liaoning Oxiranchem Co., Ltd. (China). β-CD was purified two times by recrystallization from distilled water before use. Naphthalene sulfonated formaldehyde condensates and general domestic PC superplasticizer were from Huaxi concrete admixture Co., Ltd. (Sichuan province, China).

Synthesis of MAH-β-CD

β-CD (5.68 g, 5 mmol) and MAH (4.90 g, 50 mmol) were dissolved in 25 mL of purified *N,N*-dimethylformamide (DMF) in a 250 mL, four-necked, round-bottom flask with a stirrer. The flask was heated to 80°C for 10 h under vigorous stirring and then cooled to room temperature. The resulting product was MAH-β-CD. The product was purified by precipitation with trichloromethane and washed with anhydrous ethanol. The purified product was vacuum-dried at 60°C. The product yield was 71.5%. The reaction schematic is described in Figure 1(b).

Synthesis of the modified polycarboxylate (MPC)

A suitable amount of APEG, MAS, and MAH-β-CD (according to Table I) were placed in 60 mL of distilled water in a clear, 250 mL, four-necked, round-bottom flask with a stirrer, a condenser, and a thermometer. AA and 80 mL of distilled water were placed in a 250 mL dropping funnel and APS (the weight was 1 wt % of total mass of vinyl monomers), and 80 mL of distilled water was placed in another 250 mL dropping

funnel. As the solution in the flask was heated to 90°C, the AA aqueous solution and the APS aqueous solution were slowly dripped into the flask at the same time for about 1 h. After the drop feeding ended, the thermal insulation reaction was conducted for 3 h at the design temperature. Then, the product was cooled to room temperature, and the pH was adjusted to 7.0 with 30 wt % NaOH solution. The specimens used for testing by Fourier transform infrared (FTIR) spectroscopy (Bruker company, Verte-70, US) and gel permeation chromatography (Waters company, 1525/2414, US) were further purified by precipitation with anhydrous ethanol. The scheme of the molecular structure of MPC is shown in Figure 1(c).

FTIR analysis

We purified MAH-β-CD via precipitation in trichloromethane and by washing at least three times in acetone. We purified MPC via dissolution in alcohol and by washing at least three times. Then, all of the products were dried in a vacuum at 80°C for 5 h, and the FTIR spectra were determined with a Verte-70 FTIR spectrometer (Bruker Co., US).

Fluidity and setting time of the cement paste

Cement (300 g) was added to 87 mL of distilled water containing 0.6 g of MPC (solid content) and stirred at low speed (140 rpm) for 1 min and at high speed (290 rpm) for 3 min. The fluidity of the cement paste was measured with a truncated cone with upper and lower diameters of 65 and 75 mm, respectively, and a height of 40 mm (Wuxi Jianyi NJ-160A, Jiangsu province, China) with the People's Republic of China National Standard method GB/T 8077-2000. The fluidity of the cement paste was the average of two perpendicularly crossing diameters. The setting time of the cement paste was measured with the People's Republic of China National standard method GB/T 1346-2001.

Measurement of the ζ potential

The ζ potential of the cement particles was determined with a microscopic electrophoresis instrument

JS94H (Zhongchen digital Co., Ltd, Shanghai, China). The specimen was prepared by the addition of 0.25 g of the superplasticizer and 1 g of the cement to 100 mL of distilled water in a volumetric flask. The samples were examined five times. The average of 10 experimental potential tests was regarded as the ζ potential of the cement particles.

Measurement of the amount of adsorption

The amount of adsorption of MPC on the surface of the cement particles was investigated with a sedimentation test with a W/C of 5. MPCs were added at concentrations of 0 - 10 g/L to the cement suspension. After it was stirred for 5 min, the mixture was separated by centrifugation at 16,000 rpm for 20 min. The concentration of nonadsorbed MPC remaining in the supernatant fluid was measured with an ultraviolet–visible adsorption spectrophotometer (HACH Co., Ltd, DR5000, Colorado-CO state, US). The amount of absorption on the cement particles was calculated as the difference in the concentration of MPC in the solution before and after the adsorption with eq. (1):[15]

$$n^s = V(C_0 - C)\big/ m \qquad (1)$$

where n^s is the adsorption capacity (mg/g); C_0 and C are the concentrations of MPC before and after adsorption (mg/mL), respectively; V is the volume of solution (mL); and m is the weight of cement (g).

Measurement of the DSC–TGA curve

The exothermic peaks and loss of weight at different hydration ages of the cement pastes were determined with DSC–TGA (NETZSCH-Geratebau GmbH, STA409PC, Selb, Germany). DSC–TGA measurements were done in an N_2 atmosphere at a heating rate of 10°C/min up to 900°C. The exothermic peaks for the DSC and TGA data were used to characterize the degree of hydration and to calculate the content of portlandite, calcite ($CaCO_3$), and ettringite (Aft) in the hydrated samples. Hydration was halted at 2 h and 1 day by immersion in anhydrous ethanol for 30 min. Then, the samples were ground adequately and dried in a vacuum at 50°C for 1 h.

RESULTS AND DISCUSSION

Chemical structures of β-CD, MAH-β-CD, and MPC

The molecular structures of β-CD, MAH-β-CD, and MPC were characterized with FTIR spectra (Fig. 2). We found that three clear changes in the characteris-
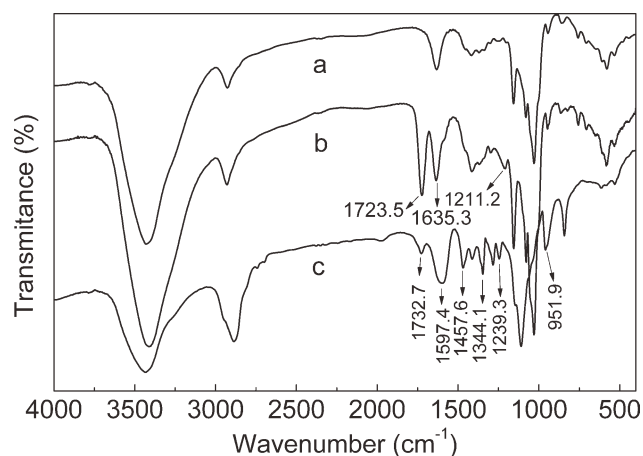

Figure 2 FTIR spectra of (a) β-CD, (b) MAH-β-CD, and (c) MPC.

tics of the absorption peaks appeared in the structure of MAH–β-CD in comparison with purified β-CD: $\sigma_{C=C}$ peak at 1635.3 cm^{-1}, $\sigma_{C=O}$ peak at 1723.5 cm^{-1}, and $\sigma_{C-O-C=}$ peak at 1211.2 cm^{-1}. This indicated that MAH was introduced to the β-CD molecule. As for the molecular structure of MPC, peaks were obtained at 2881.6, 1457.6, and 951.9 cm^{-1}, corresponding to the ─C─C─OH group of PEO, and at 1344.1–1239.3 and 1732.7 cm^{-1}, corresponding to S─O and C═O, respectively. In addition, characteristic peaks for β-CD were found at 3431.9 and 1597.4 cm^{-1}; this indicated that the cavity structure of β-CD was well maintained.

The number-average molecular weight (M_n) of MPC was determined with gel permeation chromatography (eluent: 0.1 mol/L NaNO$_3$ solution, flow rate = 0.42 mL/min). The results are shown in Table I.

Effects of the β-CD content on the fluidity of the cement pastes

For all of the superplasticizers, minislump tests were carried out over a period of 4 h to study the effect of the β-CD content on the fluidity of the cement pastes (Fig. 3). For PC, the fluidity decreased relatively slowly, from 265 to 258 mm, within the first 2 h, and the loss rate of fluidity was 2.6%. This behavior is known for PC made with longer PEO side chains, which form a solvation water film to maintain better the fluidity. However, the loss rate of the cement pastes doped with PC decreased dramatically within 4 h and was about 23.8%. Except for MPC1, the superplasticizers with β-CD side chains did not lose their effective fluidity as fast as PC did. This provided better slump retention, particularly within the first 2 h. Moreover, during the hydration process, the fluidities of the cement pastes with MPC2 and MPC3 first increased slightly from 270 and 288 mm, respectively, to their maximal fluidities of 278 and
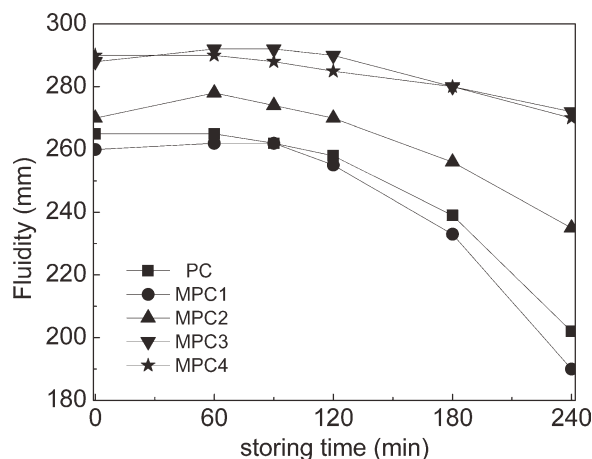
Figure 3 Effects of the content of β-CD side chains on the fluidity of the cement pastes.

Figure 5 ζ potential of cement particles with different water reducers (temperature = 20°C).

292 mm, respectively, and then decreased to 235 and 272 mm, respectively, after 4 h. The fluidity loss rates were just 12.9 and 5.6%, respectively, within 4 h; this indicated that the dispersion stability of the superplasticizers with β-CD side chains was superior to that of PC when the content of β-CD was kept constant. These results are closely correlated to the adsorption characteristics of the superplasticizers on the cement particles.

Figure 4 shows the adsorption isotherm for superplasticizers on the surface of the cement particles. For each adsorption isotherm, the adsorption amount increased dramatically with increases in the concentration of superplasticizers and then reached a saturation point. Meanwhile, the adsorption amount increased as the content of β-CD in the MPC increased. In addition, the saturation concentration of the amount adsorbed decreased with an increase in the content of β-CD. This indicated that
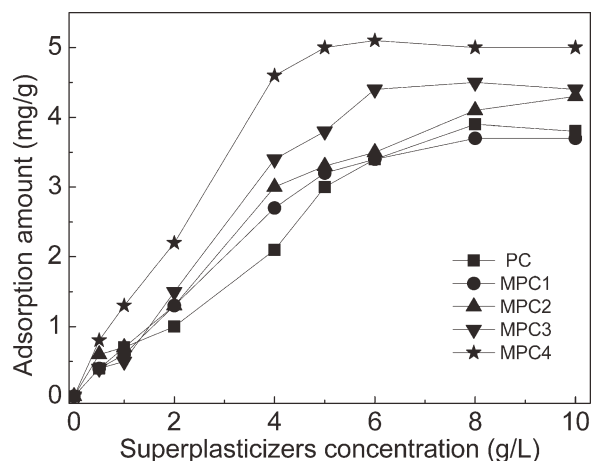
the β-CD side chain increased the adsorption capacity of superplasticizers and improved its rheological behavior. The —OH groups and the special structure of β-CD explained these behaviors. With the —COO^- to —SO_3^- ratio maintained and the side chain length kept constant, the anion concentration would increase when —OH groups were ionized under alkaline conditions. Meanwhile, the hollow truncated cone structure that provided the steric hindrance effect resulted in an increase in the adsorption amount.[12,13]

On the other hand, the adsorption behavior of the superplasticizers on the surface of the cement particles was confirmed by ζ-potential measurements (W/C = 400) after hydration for 20 min (Fig. 5). As shown in Figure 5, the ζ potential of the cement particles changed in PC from −7.08 to −2.48 mV with the concentration of PC increasing from 0 to 10 g/L. Similar trends were obtained when the particles

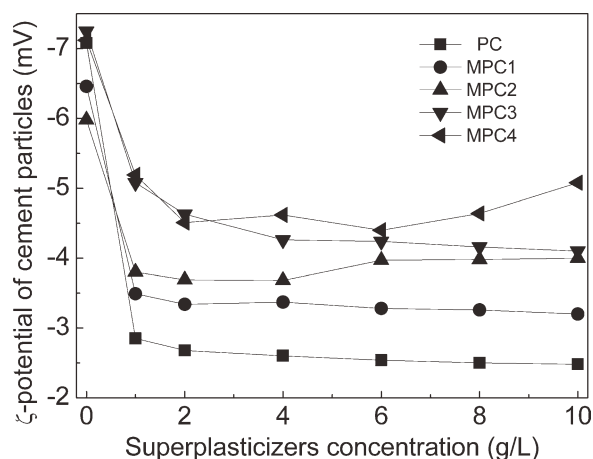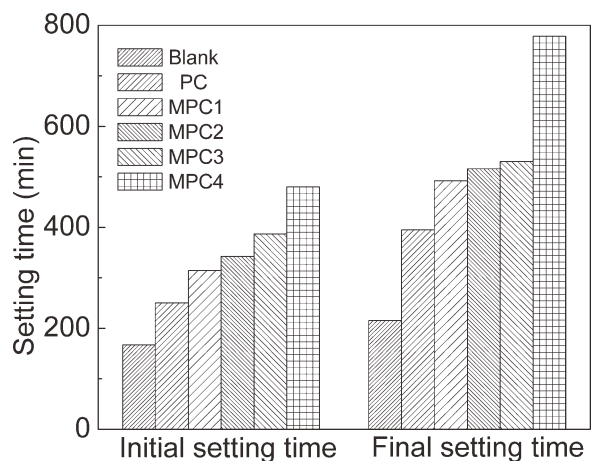**Figure 4** Adsorption amount of the water reducers on the surface of the cement particles (temperature = 20°C).

Figure 6 Effects of the content of β-CD side chains on the setting time of the cement pastes.
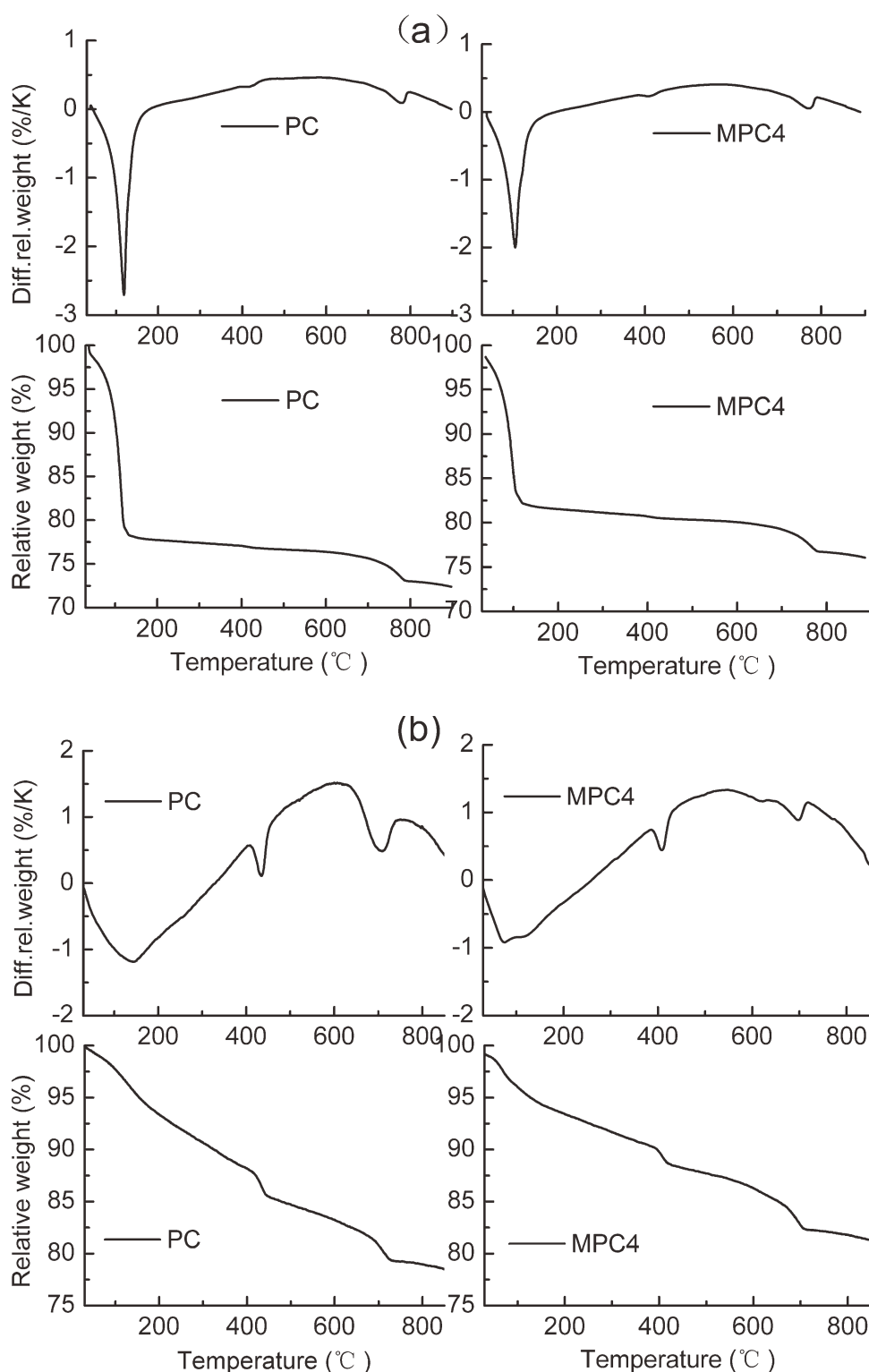
Figure 7 DSC–TGA data of cement paste doped with MPC with a W/C of 0.35 after (a) 2 h and (b) 1 day of hydration time.

were doped with other superplasticizers containing β-CD side chains. The relatively low ζ potential was due to the steric hindrance effect of the PEO side chain.[16,17] As the hydroxyl groups of the β-CD molecules were ionized at the alkaline pH of the cement

pastes, Ca^{2+} on the surface of the cement particles were easily absorbed by hydroxyl groups; this shifted the ζ potential toward more negative results. In addition, we found that the ζ potential increased with increasing content of β-CD in the

TABLE II
Properties of Concrete Doped with Superplasticizers

Test item		Naphthalene sulfonated formaldehyde condensates	Domestic PC	MPC
Dosage (wt %)		0.80	0.20	0.20
Water-reducing ratio (wt %)		13.8	19.8	31.2
Bleeding water radio (wt %)		8	3	0
Setting time (min)	Initial	232	254	390
	Final	380	400	520
Compressive strength (MPa)	3 days	18.8	22.2	23.4
	7 days	27.5	29.1	32.2
	28 days	38.2	44.7	51.8

superplasticizers when the concentration of super-plasticizers was held constant. This suggested that the adsorption behavior of β-CD took place. This behavior could be explained by the ─OH groups in the structure of β-CD, which absorbed on the surface of the cement particles and provided electrostatic repulsion.

Effects of the β-CD content on the setting time of the cement pastes

The effects of superplasticizers on the setting times of the cement pastes were studied at a superplasticizer dosage of 0.2 wt % and a W/C of 0.29. Figure 6 shows the effects of MPC on the setting times of the cement pastes. The initial setting times for all of the cement pastes were greater than 2 h, the final setting times were less than 13 h, and the setting time increased with an increase in the content of β-CD side chains. The results suggest that the introduction of the β-CD side chains in the structure of PC improved its retarding effects. However, excessive β-CD content caused serious retardation (an initial setting time of more than 8 h), such as in the cement paste doped with MPC4, which was not expected in engineering applications.

Generally, the process of hydrating cement pastes has been investigated with the heat of hydration, DSC–TGA, XRD, and electrical resistivity and conductivity measurements; this has been reported in many research articles.[18–21] In this study, the retarding effects were confirmed with thermal analysis curves [Fig. 7(a,b)], where the formation of Aft or C─S─H, portlandite (CH) and $CaCO_3$ peaks started at 105, 412, and 770°C, respectively. Figure 7(a) indicates that greater amounts of Aft and C─S─H in the cement pastes were formed when they were doped with PC after being hydrated 2 h in comparison with MPC4, whereas the amounts of CH and $CaCO_3$ were very low, whether with PC or MPC4. Meanwhile, the cement paste with MPC4 showed a lower total loss of weight compared to the cement paste with PC

throughout all of hydration times. This indicated that MPC4 showed a better retarding effect.

The formation of CH and $CaCO_3$ in the paste with PC and MPC4 began after 1 day [Fig. 7(b)]. However, the intensities of the CH and $CaCO_3$ endothermic peaks for the cement paste with MPC4 were weaker than that of PC. In addition, the total loss of weight of dosage with PC or MPC4 cement pastes was similar after longer hydration times. The DSC–TGA results indicated that the introduction of β-CD side chains on the PC superplasticizers main chain inhibited the initial hydration of the cement pastes and prolonged the setting times.

Application properties of MPC

Table II summarizes the application results of MPC. The results showed that MPC had a higher water-reducing ratio and a longer setting time; this improved the compressive strength of concrete. Furthermore, the mortar doped with MPC had a good cohesive quality, and it did not display bleeding and segregation.

Discussion of the action mechanism of MPC

The dispersing action of superplasticizers is largely dependent on the adsorption of the polymer on cement particles; this results in changes in the ionic charge on the surface of cement particles and leads to electrostatic repulsion between the cement particles.[22–24] However, the adsorption capability and dispersion mechanisms vary with the molecular structure of the superplasticizers. As shown in Figure 8(a), when MPC was absorbed onto the surface of the cement particles, it could form a heterogeneous charge distribution on the surface of the hydrating cement particles. Thus, the hydrating cement particles provided adsorption sites for positively and negatively charged ions (e.g., ─COO^-, ─SO_3^-). Therefore, the electrostatic repulsion force among the cement particles was strengthened [Fig. 8(b)].
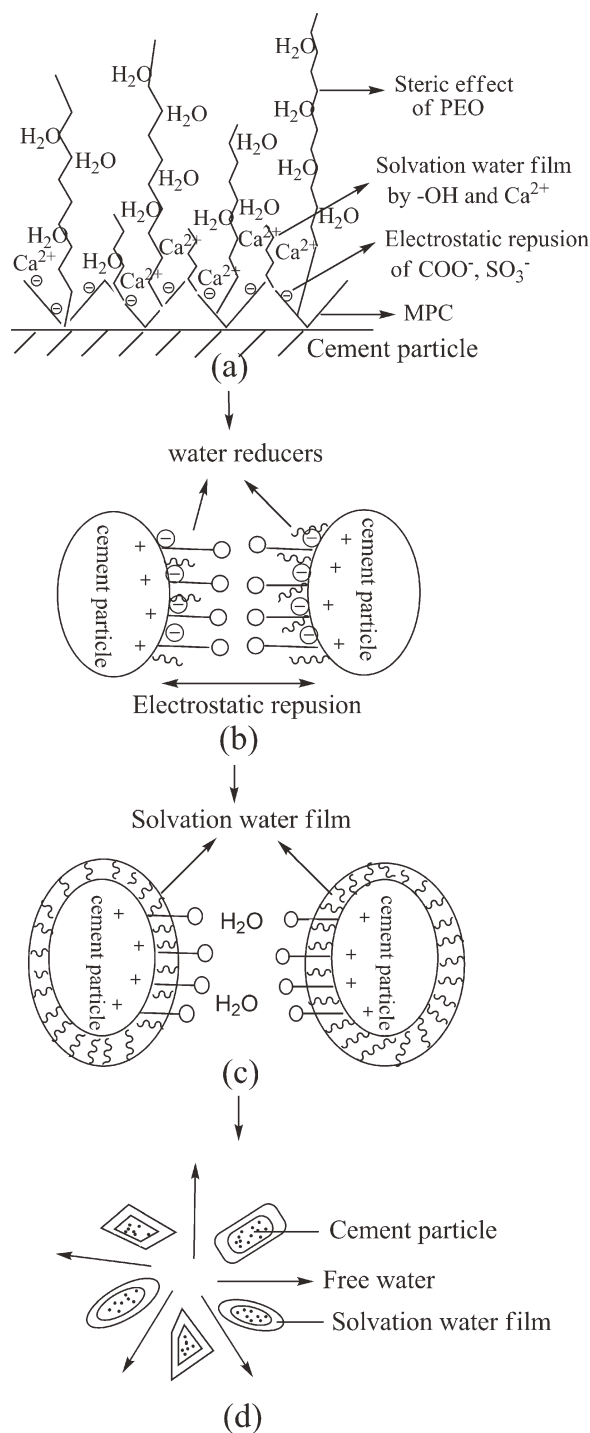
Figure 8 Scheme illustration of the dispersing and retarding effects of the water reducer.

Consequently, during the progress of hydration, the β-CD side chains and the PEO side chains displayed different actions. Chelates formed in the cement pastes because the interaction between Ca^{2+} ions and —OH of β-CD lowered the Ca^{2+} concentration in the system; this hindered the solid-phase nucleation and growth of the hydration products and retarded cement hydration. However, the new hydration products could not completely shelter the adsorption layer of the superplasticizers formed by the steric hindrance effect of the β-CD and PEO side chains. The uncovered polar side chains also displayed a dispersing effect, as shown in Figure 8(c). Meanwhile, the thickening of the adsorption layer by β-CD side chains could also hinder the growth of the hydration products. Therefore, steric hindrance was less affected by cement hydration and could retain the dispersion and retardation capacities for a relatively long time [Fig. 8(d)].

CONCLUSIONS

A PC superplasticizer with β-CD side chains was synthesized by the radical copolymerization of APEG, AA, MAS, and MAH–β-CD with APS as the initiator. The dispersion and retarding performance of MPCs was closely related to the number of β-CD side chains. An increase in the number of β-CD side chains led to increases in the initial fluidity and prolonged the setting times of the cement pastes, whereas excessive numbers of β-CD side chains led to serious retardation. The super dispersing and retarding performance of MPC was attributed to the introduction of β-CD side chains. Under alkaline conditions, the anions of β-CD were released slowly, and a solvation water film was formed by the β-CD molecular structure by adsorption on the surface of the cement particles. This resulted in better dispersing and retarding performances. The FTIR spectra indicated that the hydroxyl group of β-CD had crosslinked with the carboxyl group of MAH, and at the same time, the structural characteristics of β-CD were maintained well in MPC.

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