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Cement and Concrete Research 35 (2005) 867–873

Cement and Concrete Research

Effects of polyethlene oxide chains on the performance of polycarboxylate-type water-reducers

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Received 24 September 2002; accepted 30 April 2004

Abstract

A series of polycarboxylic acid-based copolymers with block and graft groups of polyethlene oxide (PEO) chains was synthesized; effects of the different PEO chains on the fluidity, Zeta potential and adsorption in cement paste and performances of the copolymer in concrete were discussed. It was proved that properties of the copolymer were affected by the length and density of PEO graft and block chains, and that copolymers with some block PEO chains at a certain length and moral percent had good performances in the water-reducing capability and fluid-retaining ability. Experimental results indicated that this kind of copolymers could be used as a high-range water-reducer because of the effects of electrostatic repulsive force and steric hindrance; one of its applications was to produce high-flowing concrete by incorporating with mineral admixtures, such as fly ash, etc.

Keywords: High-range water-reducers; Polycarboxylate type; Concrete; Mineral admixture

1. Introduction

Many new types of polycarboxylic water-reducers (called PCs) and methods of their application have been developed and studied [1–4]; they have drawn more and more attention in the construction industry recently because of their novel applications in concrete, such as high-volume fly ash concrete, superplasticized fiber-reinforced concrete and shotcrete, high-strength and high-performance concrete, etc. PCs can interact with cement particles physically and chemically, although some PCs have already been used to solve a variety of concrete problems because of their higher water-reduction ratio and their less slump loss; effects of PEO chains in the molecular structure on the performance are still not very clear [5–8]. Studies on this aspect may be useful in designing the molecular structure of this new and important class.

Observations have indicated that the absolute Zeta potential of ordinary Portland cement particles with NSF or MSF (naiphthylene- or melamin-type superplasticizers) must be more than 20 mV; in contrast, the PCs yield much smaller values for the Zeta potential, less than 10 mV [3,7,8]. Uchikawa et al. [2,7] considered that electrostatic forces play a major role in the dispersion mechanism for PNS water-reducer while steric hindrance is critical for a copolymer of acrylic acid with acrylic ester water-reducer. Yoshioka et al. [8,9] developed a model to describe the adsorption behavior of these water-reducers, calculated the total interparticle potential energy account for long-range Van der waals, electrostatic, and steric interactions, and concluded that the repulsive potential that resulted from electrostatic interactions was negligible; the steric hindrance plays a dominant role compared to electric repulsion in the deflocculating of cement pastes than previously believed.

PCs are copolymers of which chemical structures have the potential to be modified [5]. In our study, a polycarboxylic water-reducer (called MPC hereafter) containing block and graft groups of polyethlene oxide (PEO) was manufactured synthetically. The density of PEO block and graft chains in the molecular structure had been adjusted and a series of polycarboxylic acid-based copolymers, MPCs, were obtained. Effects of PEO chains on the results of fluidity, Zeta potential, and adsorption in cement pastes

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0008-8846/$ – see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.cemconres.2004.04.031

were discussed; one of the copolymers was then used to prepare high-flowing concrete.

2. Experimental

2.1. Synthesis of MPCs

The copolymers with the given PEO chains in length were synthesized; the synthetic process was carried out in four steps. The first step was esterifying the polyethylene glycol (PEG) of various molecule weights. In this study, chemicals of PEG1000, PEG2000, and PEG4000 were used, which contain a molecule weight of 1000, 2000, and 4000, at a length of $n=23$, 46, and 92 for PEO chains (the adding moles of ethylene oxide), respectively. The PEG1000 and PEG2000, which were esterified with (meth)acrylic acid into PEG mono (meth)acrylic acid esters, took the macromonomers as PEO1 and PEO2; the PEG4000 was esterified with maleic anhydride and changed into a PEG diester, the macromonomers as the PEO3. The harvest ratio of esterification might be controlled by changing the reaction conditions, such as reaction temperature, reaction time, quantity of acid and catalyzer, etc. The second step was to blend various compounds with the vinyl radical at a certain moral ratio, which included monomers containing carboxylic acid groups, sulfonic acid groups, and various PEO block and graft groups. The third step was to synthesize in aqueous system; the vinyl solution and initiator radical solution were dropped, respectively, for about 3 and 4 h, and the reaction temperature kept at a range from 70 to 75 °C. In the final step, the polymer solution was neutralized by alkali solution of 30% sodium hydroxide and ethylene diamine, so the alkali level could be lower and reduce the risk of alkali–silica reactivity.

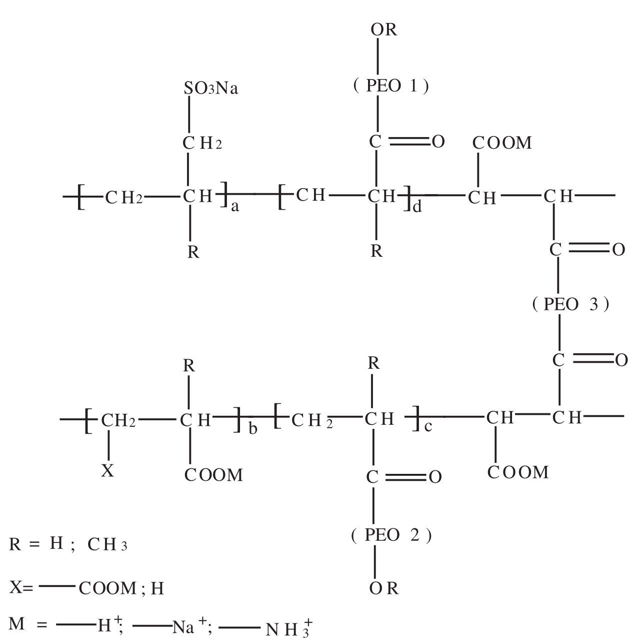

Fig. 1. The possible chemical structure of MPCs.

Table 1
Molar ratio of monomers with different groups and concentration

Series number	Monomer molar ratio (mol %)					Solid content (%)
	$-SO_3^-$	$-COO^-$	PEO1	PEO2	PEO3	
MPC-1	10	70	20	0	0	19.7
MPC-2	10	70	0	20	0	20.1
MPC-3	10	70	18	0	2	23.2
MPC-4	10	70	0	18	2	23.9
MPC-5	10	70	10	10	0	20.3
MPC-6	10	70	9	9	2	23.5
MPC-7	10	70	8.25	8.25	2.5	25.6
MPC-8	10	70	8	8	4	27.0
MPC-9	10	70	7	7	6	29.1

By adjusting the ratio of these PEOs as the copolymer was synthesized, a series of MPCs with different characteristics could be obtained. As the macromonomers of PEO3 were almost PEG diester of maleic acid, the PEO3 chains might be in the backbone of molecular structure; thus, macromonomers of PEO1, PEO2, and PEO3 were therefore grafted or blocked in the molecular structure. Because it is very difficult to estimate the actual structures, one of the possible chemical structures was shown in Fig. 1. In our study, MPCs were synthesized at different monomer moral ratios in Table 1. The total PEO chains was kept at about a monomer ratio of 15.5%, the moral percent of PEO3 chains in PEOs was from 0% to 30%; concentrations were also shown. More details about the synthetic process of the water-reducer could be seen in Ref. [10].

2.2. Property tests on cement paste

2.2.1. Flow test of cement paste (minislump)

The fresh cement paste with MPC was prepared at a water/binder ratio of 0.29 at 25 °C. The cement materials included an ordinary Portland cement and a fly ash; their chemical compositions were shown in Table 2. The admixture was added into the mixing water at a given content of 0.3% (weight percent of solid content to cement). The sample of cement paste was carefully sealed in a container during test intervals of 5, 30, 60, and 90 min after being mixed with water. The flow value was measured by using a minislump cone (60 mm high, top diameter 30 mm, and bottom diameter 60 mm), and the mixing and measurement procedure was carried out according to the Chinese standard GB/T 8077-2000: methods for testing uniformity of concrete admixture.

2.2.2. Zeta potential test

The Zeta potential of cement particle was tested within 3 min after the cement paste had been made. Pastes were prepared just as the test of minislump. The slurries were diluted with distilled water at a paste/solution ratio of 0.02, dispersed for about 30 s by an ultrasonic cell disruptor, took

Table 2
Chemical compositions of cement and fly ash (%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	MgO	K_2O	Na_2O	Ignition loss	Blaine value (cm^2/g)
Cement	22.25	4.81	3.30	63.2	2.20	1.93	1.03	0.25	2.5	3420
Fly ash	54.12	27.60	6.45	2.45	0.11	0.82	1.51	0.37	1.60	3610

some clearer paste solution from the topside, and fed into a measuring cell of electrophoresis meter. Zeta potential was measured by a Zeta potential analyzer (Zetaplus).

2.2.3. Adsorption evaluation

The ultraviolet absorption spectroscopy, which is performed on dilute aqueous solutions, provides a rapid and incisive method for the detection of the aromatic and conjugated bond groups in solution; it has been used to measure the adsorption behavior of water-reducers [11,12]. The adsorption of PCs was evaluated by measuring the reduction amount of PC in the aqueous phase before and after mixing using a total carbon analyzer in many cases [8,13]. However, in our studies, the method of UV spectroscopy was still used to evaluate the adsorption of PCs. It is a little weak for the conjugated bond groups of carboxyl or alkene to absorb the ultraviolet-visible light than that for the aromatic groups, and the light-absorbing strength should be controlled less than 1.0 and samples should dilute accordingly. To evaluate the adsorption of MPC, samples should be clear and the concentration of MPC in a dilute aqueous solution should be in the range of 10^{-5}–10^{-4} g/ml, while the concentration for naphthalene-type water-reducers was in the range of 10^{-6}–10^{-5} g/ml. The UV-2100S, a UV-visible recording spectrophotometer, was used in this study. The UV spectra position of the main peak for MPC was at approximately ë = 215 nm and the second peak at ë = 290 nm.

Samples should be clear and it could be done by diluting the cement paste with deionized water at 20 times of the mixing water in the paste. The slurries were filled into a centrifugal apparatus with a rotating radius of 200 mm, and rotated at 3500 rpm for 30 min; the sample solution was separated by a 0.22-um membrane filter using a suction pump. The concentration of MPC remaining in the resultant solution could be measured by UV spectra at the position of main peak, and the amount of MPC adsorbed on cement was calculated from the difference between the amount of MPC in liquid before and after mixing.

Table 3
Properties of MPC-7

Item	Test result	Item	Test result
Concentration (%)	25.5	Density (g/cm^3)	1.045
Alkali content (%)	1.0	pH	7.5
-NH_2 content (%)	1.0	Surface tension (dyn/cm)	58.6
Cl^- content (%)	Nothing	Appearance	Brown liquid

2.3. Application of MPCs for preparing high-flowing concretes

One of the advantages for the application of PCs was to prepare high-flowing concretes. In our study, some of the MPCs were used as high-range water-reducers in concrete test, and MPC-7 (shown in Table 1) was even used to prepare for high-flowing concretes with different strengths. The physical properties of MPC-7 can be seen in Table 3; the chemical compositions of cement and fly ash can be seen in Table 2; the fine aggregate was river sand and its fineness modulus was 2.83; the coarse aggregate was crushed gravel, with a maximum size of 20 mm. Design of the mixing proportion was mainly based on a Chinese standard of JGJ/T 55-1996: designing principles of normal concrete. The proportions of sand in these mixture proportions were a little higher than that in normal concretes. In Table 4, the No. 1 proportion of concrete mixture was designed to compare the effects of PEO3 on characteristics of MPC in dispersing capability and fluid-retaining ability, the dosage of MPC was regulated to control the fresh concretes at similar viscosity and flowing behavior; proportions which incorporate MPC-7 and fly ash from No. 2 to No. 7 were mainly designed to prepare high-flowing concretes with different strengths from C25 to C60.The slump was measured and the slump flow at a certain time after water was mixed, and the compressive strength of hardened concrete was measured after 7, 28, and 56 days of standard curing.

3. Results and discussion

3.1. Effects on dispersing and slump-retaining ability

The initial minislumps of cement pastes and the variation of minislumps with time were shown in Fig. 2a and b. The

Table 4
Proportions of concrete mixture

Test number	(C + FA)/ S/G	FA/ (C + FA)	W/ (C + FA)	C + FA [kg/m^3]	MPC-7 [*(C + FA)%]
No. 1	1:1.6:1.9	0	0.366	500	
No. 2	1:1.37:1.82	0.60	0.452	535	0.22
No. 3	1:1.45:1.81	0.50	0.405	540	0.26
No. 4	1:1.50:1.79	0.40	0.378	540	0.35
No. 5	1:1.55:1.78	0.30	0.370	550	0.45
No. 6	1:1.38:1.67	0.30	0.349	550	0.50
No. 7	1:1.45:1.78	0.20	0.321	560	0.60

W, water; C, cement; FA, fly ash; S, sand; and G, aggregate.

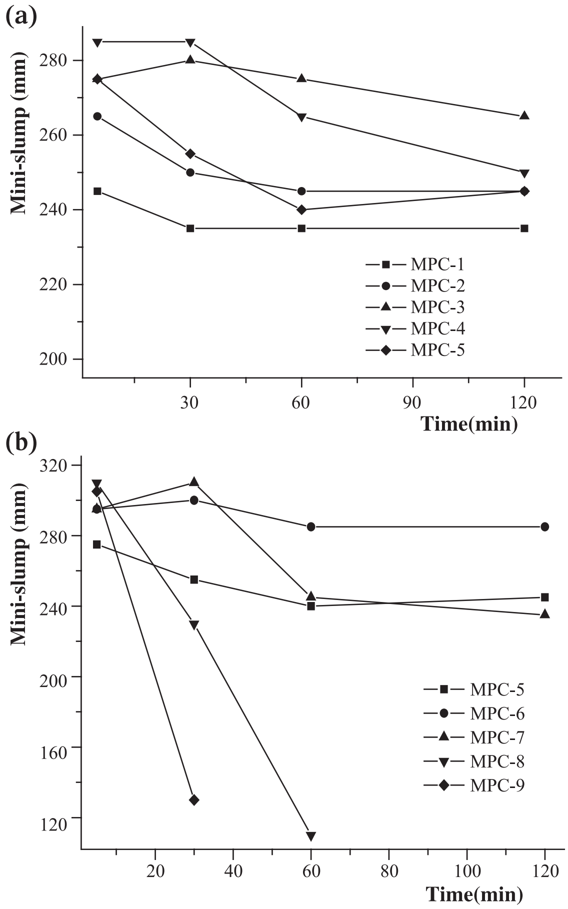

Fig. 2. (a) Variation of minislump flow of cement pastes with different MPCs. (b) Variation of minislump flow of cement pastes with different MPCs.

cement pastes were all prepared at the same water–cement ratio (W/C = 0.29) and solid content of MPC (0.3 * C%). The flow value of minislump showed a trend of increasing from MPC-1 to MPC-9; all pastes had enough long retention time except those with MPC-8 or MPC-9. The MPC-6 or MPC-7 exhibited a relatively strong dispersing ability and long slump-retention ability.

Combining the results with Table 1, the researchers considered that MPCs from MPC-5 to MPC-9 with PEO1 and PEO2, the two different lengths of PEO graft chains, contained a higher dispersing and retaining ability than those only with PEO1 or PEO2; if a suitable proportion of PEO3 chains blocked in the backbone of MPC molecular structure, a higher initial fluidity and a longer slump-retention time could be obtained, and the higher dispersion and retention ability would be quickly lost if the density of PEO3 chains was too high, as in the case of MPC-8 and MPC-9. For the PEO3, it was a PEG diester of maleic acid; if PEO3 macromonomers were excessive, they would be combined into the graft chain of copolymers, and destroyed the comb-like structures. Besides, many maleic acid monomers were accordingly copolymerized into the molecular structures and the copolymers came as higher ionic polymers, which might be adsorbed on the cement surface more easily and that would induce a multiplayer adsorption. Hence, the effective concentration of water-reducers in paste would decrease within a short time; thus, the slump lost relatively quickly.

3.2. Effects of PEOs on the Zeta potential of cement grout

In Fig. 3, the Zeta potential on cement particle surface in blank water solution was about +8.0 mV. The Zeta potential became negative as adsorbed by MPCs, those in the case of MPCs without PEO3, such as MPC-1 and MPC-5, did not reach −10 mV, but the Zeta potential value increased with the addition of PEO3 from MPC-1 to MPC-9, the highest one (MPC-9) exceeded to −30.0 mV. The steric hindrance was mainly caused by PEO side chains which added the thickness of slipping layers; the Zeta potentials of cement particle with MPCs were relatively lower because of the hindrance of PEO graft chains, but if the PEO3 chains blocked into the backbone and more maleic acid monomers were copolymerized, the adsorbing ability and electrostatic repulsive force would be increased.

The PEO block chains played an important role in the water-reducing capability and fluid-retaining ability. If the slipping layer could be more close to the stern layer in the case of MPC-8 and MPC-9, the Zeta potential might be higher. As illustrated in Fig. 4a, on a polar surface of cement particle, with few PEO3 block groups in the backbone of a comb-like structure, some anions of the carboxylic acid groups and the sulfonic acid groups were adsorbed; others pointed out to the solution as the graft PEO chains. The researchers considered that the dispersion ability would be improved if the electrostatic repulsive force and adsorbing ability were increased simultaneously. Hard layers over the surface of cement particles might be composed of the polar ionic groups and short nonpolar side chains, just like a crust over the cement particle, which were also advantageous to the water-reducing capability and fluid-retaining ability, as illustrated in Fig. 4b. Therefore, in the circumstances of MPCs, it was clarified that the electrostatic repulsive force and the steric hindrance contributed to the dispersion of large agglomerates of cement particles into smaller ones.

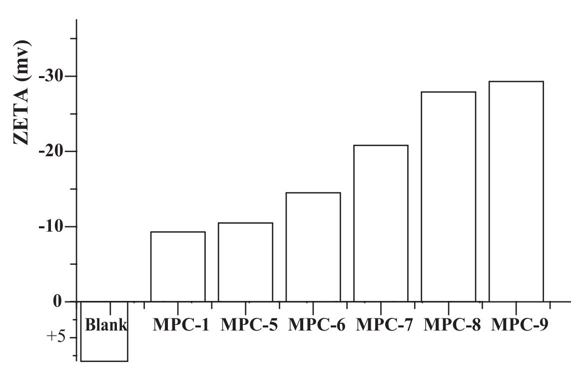

Fig. 3. Effects of MPC on the initial Zeta potential of cement particle surface.

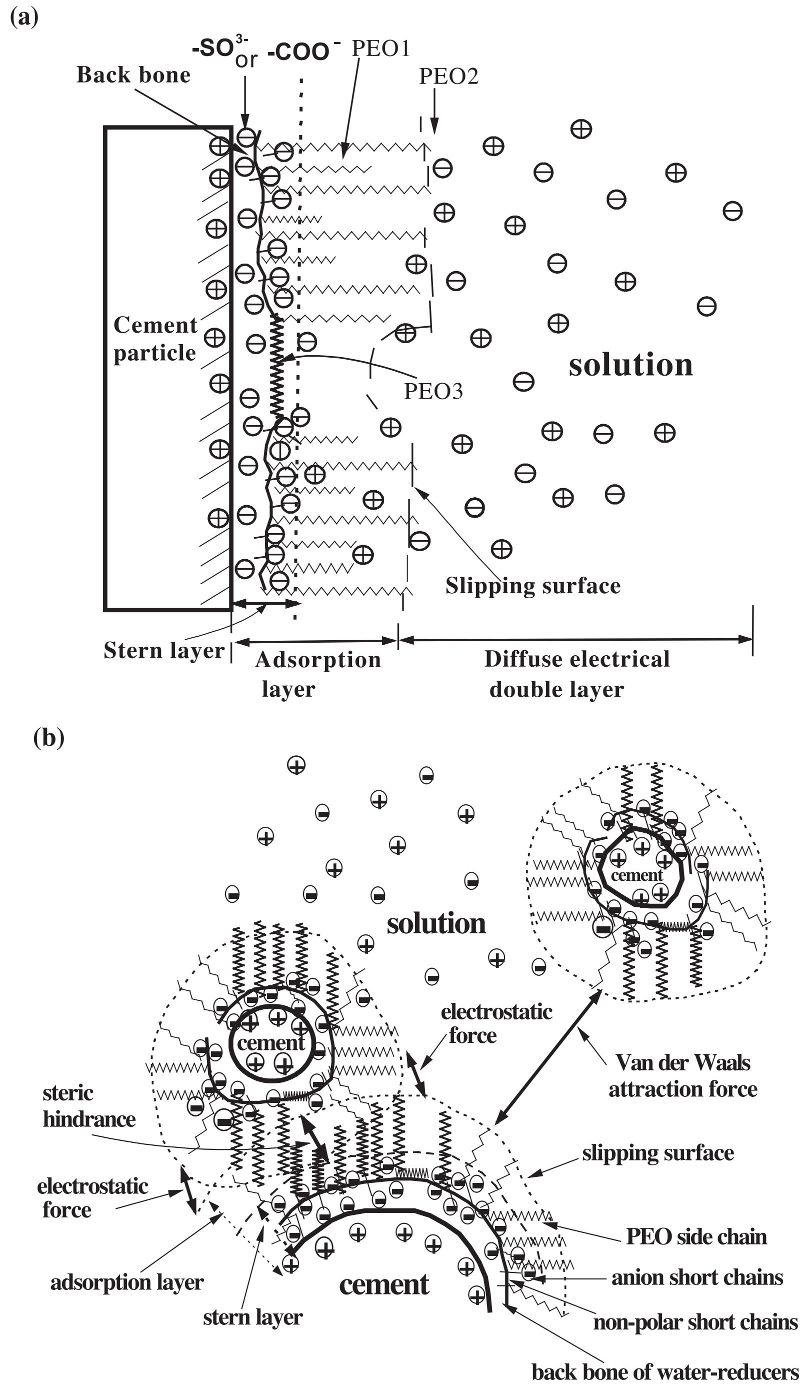

Fig. 4. (a) Schematic figure for electric double layer of MPCs on the cement particle. (b) Schematic figure of adsorption and repulsion for cement particles.

3.3. Effects of PEOs on the adsorption of cement particles

The adsorption results of MPCs were shown in Fig. 5. The MPC-5 without PEO3 was adsorbed less than 45%; MPC-6 and MPC-7 with 10–15% of PEO3 were adsorbed in a range of 45–65%, MPC-8 and MPC-9 with about 20–30% of PEO3, more than 85%. The adsorption percentage of MPC was increased with the enhancement of PEO3 in the structure; that is, the adsorption ability of MPCs was proportional to the density of PEO block chains. It was also illustrated that, if there are too many PEO3 and maleic acid units in the molecular structure, the adsorbing ability was improved greatly, which might induce multilayer adsorption on the surface of cement particle as analyzed above.

Although the adsorption quantity of MPC-7 was increased with the increment of concentration, the adsorption ratio was decreased after saturated adsorption. When a binder of 80% cement + 20% fly ash and 100% cement

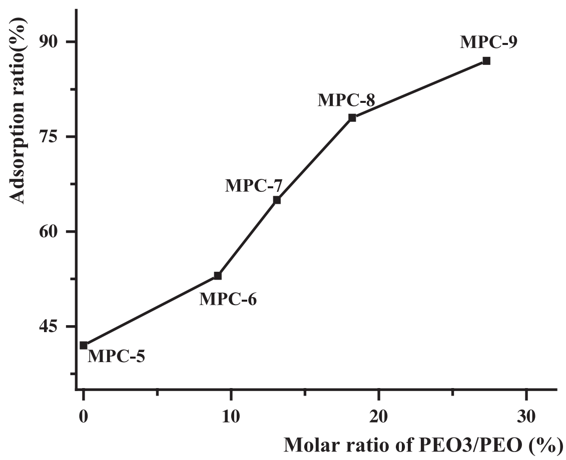

Fig. 5. Effect of different molar ratios of PEO3/PEO on the adsorption ratio.

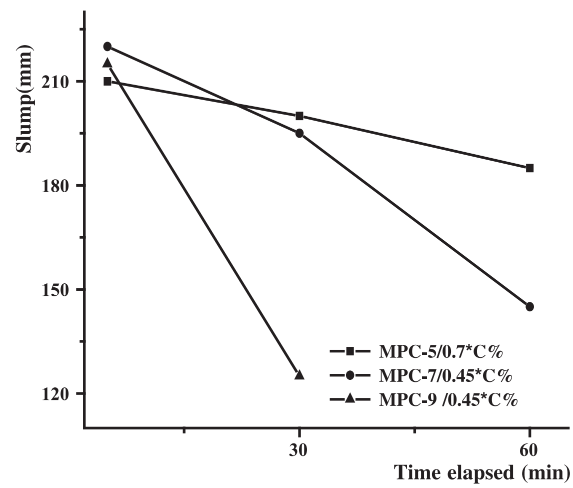

Fig. 7. Slump variation of concrete containing different MPCs.

were the adsorption agents in the paste, the adsorption ratios and their variations with time (quantities in the brackets) were shown in Fig. 6a and b. The saturated adsorption quantities of MPC-7 adsorbed by 80% cement + 20% fly ash, about 1.37 mg/g, was relatively lower than that by 100% cement, about 1.64 mg/g; the adsorption ratio and its variation with time adsorbed by 100% cement were apparently higher than those by 80% cement + 20% fly ash. It was considered that the adsorption on cement particles was

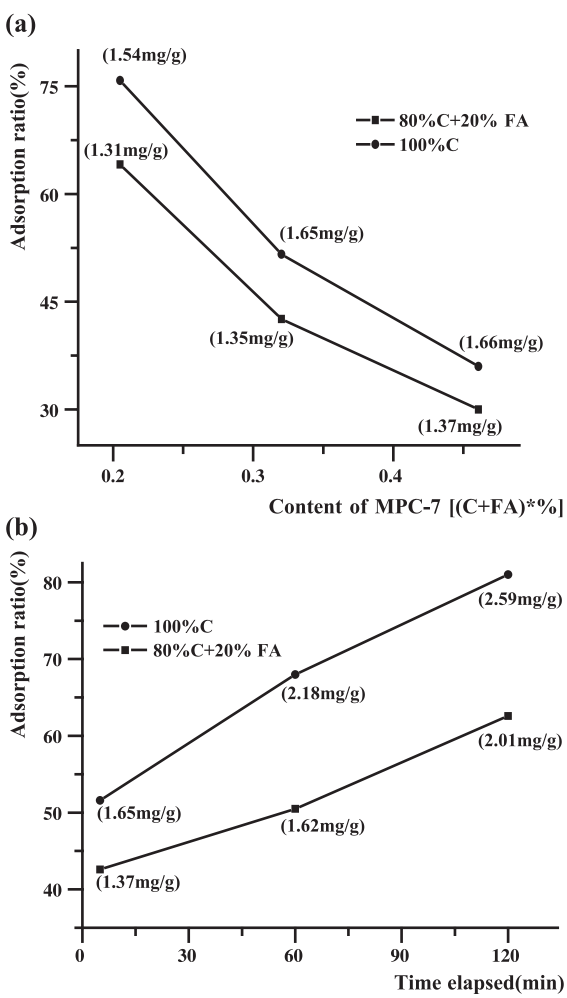

Fig. 6. (a) Effect of dosage on the adsorption of MPC-7. (b) Effect of time on the adsorption of MPC-7.

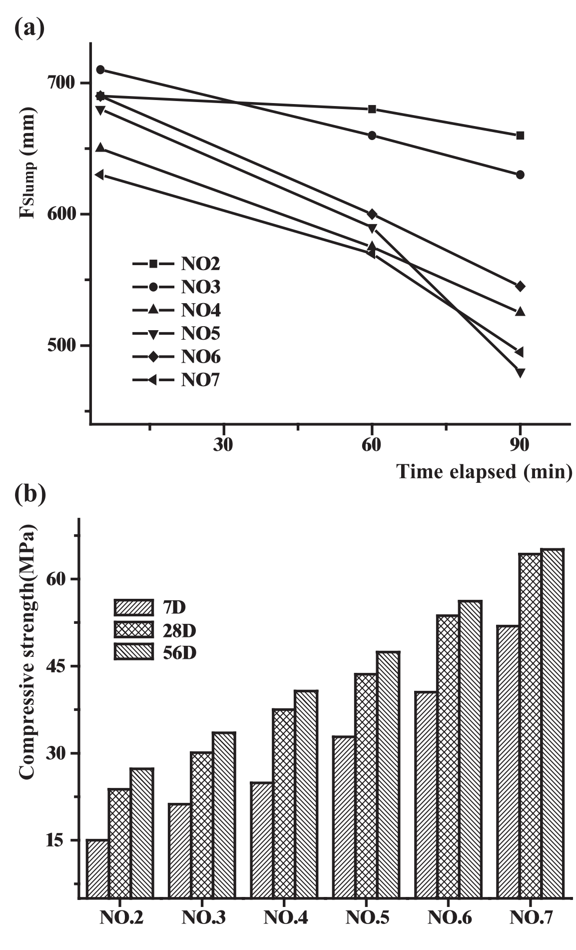

Fig. 8. (a) Slump flow of high-flowability concretes with MPC-7. (b) Compressive strength of high-flowability concretes with MPC-7.

higher than on the particles of fly ash because of the higher quantity of mineral C3A and alkalinity in cement [14,15]. The adsorption rate of MPCs in a range of 40–65% might be good to slump retention, and hydration of C3A on the surface of cement particle would generate positive charges and attract anion groups of MPCs easily, so that the saturated adsorption ratio in paste of 80% cement + 20% fly ash could be kept less than 65% for a little long time, and this would be good for retention slump.

3.4. Properties of high-flowability concrete with MPCs

Workabilities of concrete with the addition of MPC-5, MPC-7, and MPC-9 containing 0%, 12.5%, and 30% PEO3, respectively, were compared. The mix proportions were kept the same as No. 1 in Table 4; the dosage of different MPCs was adjusted to control the target slump of concretes at a range of 180–200 mm. The results are shown in Fig. 7. It was shown that MPC-7 and MPC-9 had higher dispersing ability than MPC-5 and the slump loss of concrete with MPC-9 was much quicker than others; MPC-5 and MPC-7 kept the slump of concrete over 200 mm during first 30 min after adding water at a solid dosage of 0.45%, but the content of MPC-5 was higher to get the similar fluidity.

It is possible to produce high-workable and high-strength concrete by using MPC-7 with other fine mineral materials, such as blast-furnace slag, lime stone, silica fume, and the like. More concrete tests were done with MPC-7; the mix proportions were shown in Table 4 and the experimental results in Fig. 8a and b. It was indicated by the results that, as the water–binder ratio of concrete was decreased from No. 2 to No. 7, the cement replacement of fly ash descended and the slump flow maintainability improved with the increase of mineral powders, because the content of C3A and alkaline in concrete was reduced and cohesiveness of mortar was increased; the compressive strength increased. The high amount of mineral powders reduced the early strength. The strength increased slightly after 28 days; the 56-day strength was higher than the 28-day strength for about 110%.

4. Conclusion

The copolymers MPCs contained with PEO graft and block chains possessed a high dispersing ability and a good retention ability; the Zeta potential was relatively low because of the hindrance of PEO graft chains and increased with the increment of PEO block chains. The polymer adsorption rate in the range of 40–65% would be good to slump retention. The electrostatic repulsive force and steric hindrance might be synchronously contributed to the dispersion ability, and the PEO block groups might induce multilayer adsorption on the surface of cement particle. The copolymer MPC-7 with PEO block chains at a moral percent of 12.5% to total PEOs had obvious characteristics of high water-reducing capability and good fluid-retaining ability, so it could be used as a high-range water-reducer for preparing high-flowability concrete.

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