

Effects of Connection Mode Between Carboxyl Groups and Main Chains on Polycarboxylate Superplasticizer Properties

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ABSTRACT: Preparation and characterization of polycarboxylate superplasticizers of IPCs (copolymer of itaconic acid and allyl polyoxyethylene ether) and MPCs (copolymer of maleic anhydride and allyl polyoxyethylene ether) are shown. The difference between IPCs and MPCs is that half of the carboxyl groups of IPCs indirectly connect to the main chains through methylene. The effects of the carboxyl group-main chain connection mode on the properties of IPCs and MPCs were investigated by assessing the paste fluidity and the pore diameters and compressive strength. The interaction between IPCs (MPCs) and cement were revealed by zeta-potential and the adsorption amount. The results indicated that the indirect connection mode favorably improved paste fluidity, decreased pore diameters, and increased the compressive strength compared with the direct connection mode. This is likely because that when carboxyl groups are connected to the main chains indirectly, more moving space allows easier adsorption on cement particles. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 3925–3932, 2013

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INTRODUCTION

In modern concrete technology, concrete admixtures have become a prerequisite component of high-performance concrete and have been widely used in various concrete. The principal role of concrete admixtures is to improve working performance and mechanical properties and extend the useful life of concrete.^{1–3} A superplasticizer or water reducer is one of the leading concrete admixtures, and polycarboxylate superplasticizers (PCs) are the primary superplasticizer because of a high water-reducing ratio, lower dosage, and obvious increase in the mechanical properties of concrete. Therefore, PCs have gained considerable attention and have been broadly applied in concrete. Generally, PCs are synthesized by the free-radical polymerization of acrylic acid, methacrylic acid, and polyethylene glycol (PEG) methacrylate using persulfate as an initiator. Non-ionic polyethylene glycol side chains mixed with anionic carboxyl pendant groups can form the comb structure, which is the most striking characteristic of PC molecules. Carboxyl groups with a negative charge favor adsorption on cement particle surfaces with a positive charge, form an electric double layer, and exhibit electrostatic repulsion. Polyethylene glycol side chains wrap around cement particles and display steric hindrance.^{4–6} The properties of PCs are determined by their molecular structure, and differential molecular structures of PCs may be synthesized using suitable monomers with PEG side chains through free-

radical copolymerization.^{7–10} A clear relationship appears to exist among structure, properties and monomers, and a ideal superplasticizer seem may be presumed to be synthesized by using suitable monomers; however, this is not the case.

Although PCs have more advantages than traditional superplasticizers, they also some limitations, such as easily bleeding and segregating, being incompatible with these traditional superplasticizers of naphthalene sulfonate (NPS) and sulfamate series (SFS), and being sensitive to muddy aggregate. These problems are currently difficult to solve by the synthesis process. The fundamental reason for this is that the relationship between the chemical structure and properties of PCs is not yet fully understood. Therefore, many studies have been conducted to discover this mysterious relationship. Yamashita¹¹ showed that PCs constituted by long and short side chains of alkoxy polyoxyethylene ester and unsaturated anhydride have lower slump loss. Nawa¹² found that anhydride hydrolysis in PCs can produce strong anionic groups that make the cement particle surface have a negative charge and improve dispersion and slump loss. Yamada¹³ investigated the effects of carboxyl groups, sulfonic groups, the length of polyoxyethylene side chains, and the polymerization degree of the main chain on PC performance. They found that PCs have better dispersity when they have long side chains, a short main chain, and a high density of carboxyl and sulfonic groups. The effects of functional groups on the fluidity and

Table I. Composition and Properties of Portland Cement

Cement	Chemical compositions (wt %)								Particle size (μm)	Density (g/cm^3)	Blaine value (cm^2/g)
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O			
Shengwei42.5	22.25	4.43	2.92	64.58	1.89	1.76	0.95	0.23	13.6	3.12	3269

hydration of concrete have been investigated by regulating the ratios of the hydroxyl, carboxyl, and sulfuric groups^{14,15}. The effects of PEG branch chain linkage mode, hydroxyl termination, and methoxyl termination on the properties of PCs have also been studied.^{16–19}

All of these studies help us understand the relationships between properties and structure and improved PC properties. However, the effects of the connection mode between the carboxyl groups and main chains on the applied performance of PCs are not well understood. Therefore, in the present study, IPCs and MPCs were synthesized by the separate copolymerization of allyl polyoxyethylene ether (APE) with itaconic acid (IA) and maleic anhydride (MAH). The major difference was that half of the carboxyl groups in IPCs connected to the main chains through methylene, whereas all the carboxyl groups of MPCs connected to the main chains by direct linkage. The effects of the carboxyl connection mode on the properties of PCs were investigated by assessing the paste fluidity, adsorption, setting times and zeta-potential of cement particles.

EXPERIMENTAL

Materials

Allyl polyoxyethylene ether, with an average molecular weight of 2200, was supplied by Liaoning Oxiranchem (Liaoyang, China). Maleic anhydride, ammonium persulfate (APS), sodium hydroxide (NaOH), and IA were all chemically pure and purchased from Aladdin Chemistry (Shanghai, China). The commercial Portland cement Shengwei 42.5 was obtained from Shenwei Cement (Xi'an, China). The properties of the cement material, including chemical composition, average particle size (d_{50} value), density, and Blaine value, are shown in Table I.

Synthesis of IPCs and MPCs

Approximately 20 mL of deionized water was added to a 250 mL three-neck, round-bottom flask, and heated to 80°C. The monomer mixture and initiator solution were added dropwise into the flask at the same time using a dropping funnel. The monomer mixture was prepared by mixing APE and MAH (IA) in deionized water at a molar ratio of 1:2.5. The initiator solution was obtained by dissolving 0.8 wt % APS (by total mass of the monomers) in deionized water. The dropping time were controlled for ~ 1.5 h. The reaction was then performed for 2 h at 80°. The copolymer was cooled to room temperature and neutralized to pH 7 with 20 wt % NaOH solution. The copolymer of MAH and APE is referred to as MPCs, and the copolymer of IA and APE is referred to as IPCs. The monomer conversions of MPCs and IPCs are 99.36% and 99.54%, respectively. The solid content of MPCs and IPCs is 38.64% and 40.26%, respectively. The MPCs and IPCs were purified by precipitation, washed with methanol, and then tested by Fourier

transform infrared (FTIR) spectroscopy, ¹H-nuclear magnetic resonance (NMR), and gel permeation chromatography (GPC). The structures of IPCs and MPCs are shown in Figure 1.

Test Methods

GPC, FTIR, and NMR. The molecular weight (M_n , M_w) and polydispersity index (PDI) were determined at 40°C on a Waters 575-2414 GPC (Massachusetts, USA) equipped with a differential refraction detector. The FTIR spectra were obtained using a Bruker EQUINOX-55 spectrometer (Bremen, Germany) by coating purified anhydrous IPCs and MPCs on KBr pellets. The ¹H-NMR spectra were obtained by a Varian INOVA-400 MHz spectrometer (Palo Alto, CA, USA) at room temperature.

Surface Tension of IPCs and MPCs Solutions. Surface tension was tested using a Zhongchen JK99B automatic surface tension apparatus (Shanghai, China). The solutions of MPCs and IPCs were prepared by controlling their solid content (1, 2, 3, 4, 5, 6, 7, 8, and 9 mg/mL).

Fluidity and Setting Time of Cement Paste. The fluidity of cement paste was determined using a mini-slump cone (60 mm height, 36 mm top diameter, 60 mm bottom diameter) according to GB/T 8077-2000 (the People's Republic of China National Standard methods). The water-to-cement (w/c) ratio was 0.29. The fluidity of the cement paste was measured twice, with the second measurement at a 90° angle to the first measurement, and averaged to provide the fluidity value. The cement paste was returned to the casserole and covered with a wet towel to prevent drying. Fluidity was then tested 30, 60, 90, 120, 150, 180, and 210 min after the first test.

After measuring fluidity, the cement paste was transferred to a Vicat cone (40 mm height, 65 mm top diameter, 75 mm bottom diameter) on a glass plate to test the initial and final setting times according to GB/T 1346-2001. Initial setting occurred when the Vicat needle could be inserted into cement paste 4 ± 1 mm from the floor, and the final setting occurred when the Vicat needle only penetrated 0.5 mm into the cement paste.

Zeta-Potential of Cement Particles. To gain additional insights into the interaction between MPCs and IPCs with cement particles, the zeta-potential of the cement particles in the presence

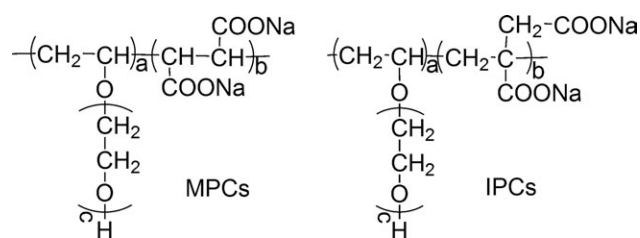


Figure 1. Schematic diagram of chemical structure of MPCs and IPCs.

Table II. Mixture Proportions of Cement Mortar

Superplasticizers	Dosage (g) (by cement weight)	Cement (Shengwei42.5) (kg/m ⁻³)	Standard sand (kg/m ⁻³)	Water (kg/m ⁻³)
PCE*/MPCs/IPCs	0.9	450	688	225

*Commercial polycarboxylate superplasticizer produced by Xi'an Daliang Concrete Admixture (Xian, China). The functional groups are -COOH, -SO₃H and -(OCH₂CH₂)_n-OH. The solid content is 40.5%, pH 7.3.

of MPCs and IPCs separately was measured immediately after fluidity was measured.²⁰ The zeta-potential was measured on a Zhongcheng JS94H microscopic electrophoresis instrument (Shanghai, China). The apparatus was designed based on the theory of a diffuse electric double layer, and it is suitable for measuring a dilute solid suspension, provided the solid particles size range between 0.5 μm and 20 μm. To perform the measurement, 1 g of above cement paste was promptly placed into 100 g of deionized water after fluidity was measured. The mixture was then stirred for 2 min and left standing for awhile. The supernatant was used for zeta-potential test. Considering the accuracy of the measurement, choosing several different cement particles and using repeated measurements within a short time should be adopted to reduce errors and increase zeta-potential reliability.

Adsorption Amount. Five grams of cement were accurately weighed in a 50 mL volumetric flask and brought to a final volume with deionized water in the presence of PCs. A stopper was then placed on the flask, and the flask was repeatedly shaken upside down for 1 min. The cement particles were deposited by centrifugation, and the residual PCs in the upper supernatant were measured using a Waters 575-2414 GPC.²¹ The residual PC concentration was obtained by contrasting the GPC curve of the residual PCs with the known PCs concentration GPC curve. The adsorption amount was calculated according to the concentration differences of PCs in the solution before and after adsorption. The adsorption amount were calculated using eq. (1):

$$\text{Adsorption amount (mg/g-cement)} = \frac{V(C_0 - C)}{m} \quad (1)$$

where C_0 is the initial concentration (mg/mL) of PCs before adsorption, and C is the residual concentration after adsorption;

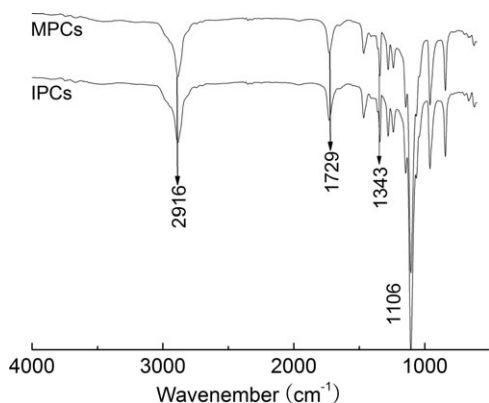


Figure 2. FTIR spectra of IPCs and MPCs.

V is volume of the solutions (mL), and m is the weight of the cement (g).²²

XRD and SEM of Hardened Cement Paste. The XRD spectra of the hardened cement paste was measured at 3, 7, and 28 days on a D/max2200PC X-ray spectrometer (Rigaku, Japan). The cement paste was prepared at a w/c ratio of 0.29, with a PC dosage of 0.2 wt % (solid cement weight). The fresh cement paste was then poured into cubic molds (50 mm × 50 mm × 50 mm). The molds were then removed after 24 h, and the cement paste was hardened at a standard temperature and humidity for 3, 7, and 28 days according to GB/T 8077-2000. The hardened cement paste samples were immersed in anhydrous ethanol for 30 min to terminate the hydration reaction prior to the test.²³

SEM of the fractured sections of the hardened cement paste were obtained using a HITACHI S4800 Scanning Electron Microscope (Japan). The samples were fixed on an aluminum stub using a conductive adhesive and coated with gold using a

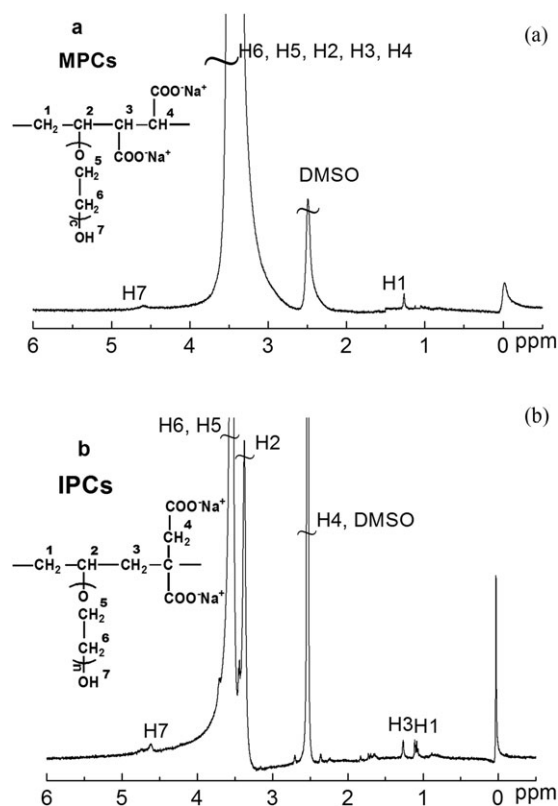


Figure 3. ¹H-NMR spectra of (a) MPCs and (b) IPCs.

Table III. Structure and Properties of MPCs and IPCs

PCs	Solid content (wt%)	pH	Dosage ^a (wt %)-w/c ^b	Fluidity ^c (cm)	M_w	M_n	PDI (M_w/M_n)	PEG:carboxyl (molar ratio)
MPCs	40.26	7.13	0.20-0.29	29.6	138,622	107,463	1.29	1:5
IPCs	38.64	7.51	0.20-0.29	31.2	130,183	105,705	1.23	1:5

^aBy weight percent cement powder.^bWater/cement ratio.^cPaste flow was tested at a w/c ratio of 0.29 using Shengwei 42.5 cement according to standard method GB/T 8077-2000.

sputter process. The results can be used to indicate the surface morphology of the hardened cement samples.

Pore Structure of Hardened Cement Paste. The pore structure of concrete significantly influences the mechanical properties and durability of the concrete structure. The effects of IPCs and MPCs on the pore structure of concrete may be investigated by measuring changes in the pore structure of hardened cement paste doped with IPCs and MPCs, respectively. The hardened cement paste (2.0 g) at 28 days was used to test the pore structure using an Autopore III9420 automatic mercury pressure meter (Micromeritics instruments, Indianapolis, USA). The test pressure was 300 MPa, and the pore diameters ranged from 3 to 11,000 nm.

Compressive Strength of Hardened Cement Mortar. The mixture proportions of the cement mortar are shown in Table II. The viscosity of the fresh cement mortar was determined using a digital rotational viscometer NDJ-5 S (Shanghai, China) to evaluate the dispersion ability of PCs.

The compressive strength of hardened cement mortar was tested according to GB/T 17617-1999. The sizes of the specimens were 40 mm × 40 mm × 160 mm, which were cured for 3, 7, and 28 days at standard temperature and humidity.

RESULTS AND DISCUSSION

Chemical Structure of IPCs and MPCs

The FTIR and ¹H-NMR spectra of MPCs and IPCs are shown in Figure 2 and 3, respectively. The results were analyzed as the following: FTIR (KBr, coating, $\nu_{\max}/\text{cm}^{-1}$): 2916 (CH₃, CH₂), 1729 (CO), 1471, 1343 (CH), 1323 (COC), 1106 (CO);

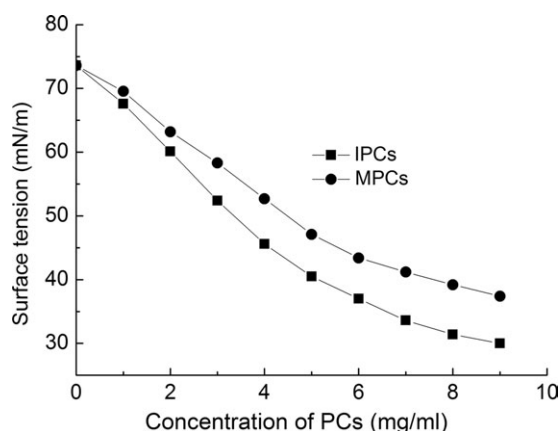
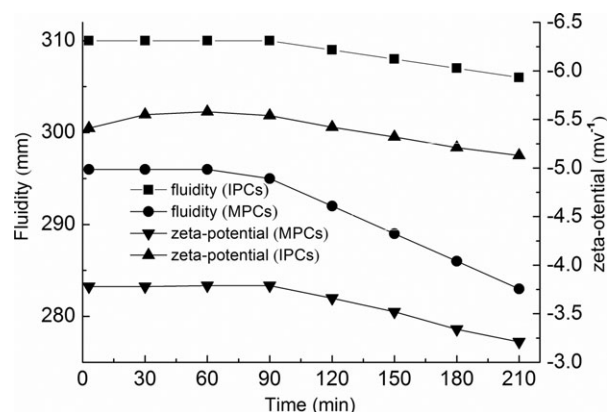
¹H-NMR of MPCs: δ (400 MHz, DMSO-*d*₆, Me₄Si, ppm), 4.601 (7 H, s), 3.542 (6 H, d), 3.516 (5 H, d), 3.429 (2 H, s), 3.365 (3 H, s), 3.230 (4 H), 1.279 (1H, d); ¹H-NMR of IPCs: δ (400 MHz, DMSO-*d*₆, Me₄Si, ppm), 4.622 (7 H, s),

The results showed that the chemical structures of IPCs and MPCs have a difference in the connection mode of half of the carboxyl groups in the main chains (Figure 1). All of the carboxyl groups in the MPCs directly connected to the main chains, whereas half of the carboxyl groups in the IPCs connected to the main chains directly, and another half connected to the main chains through methylene. The number of carboxyl groups in the IPCs is identical to MPCs.

The solid content, pH, molar mass (M_w , M_n), and polydispersity index (PDI) of MPCs and IPCs are shown in Table III. The results showed that molar mass (M_w and M_n) and PDI were similar for IPCs and MPCs. The PDI describes the uniformity of a polymer with respect to molecular mass distribution. IPCs and MPCs possess the same PEG side chains, showing a narrow and similar mass distribution (PDI = 1.23 and 1.29, respectively). The ratio of the side chain PEG and carboxyl groups was 1:5.

Surface Tension of IPCs and MPCs Solutions

The relationships between the surface tensions and concentrations of IPCs and MPCs were assessed, and the results are shown in Figure 4. The results showed that both of the surface tensions decreased with an increase in their concentrations, reaching a maximum at a concentration of 9 mg/ml. The degree of the surface tension reduction of IPCs was slightly lower than MPCs at the same concentration. The results also indicated that

**Figure 4.** Surface tension of IPCs and MPCs.**Figure 5.** Fluidity and zeta-potential of cement paste doped with IPCs and MPCs.

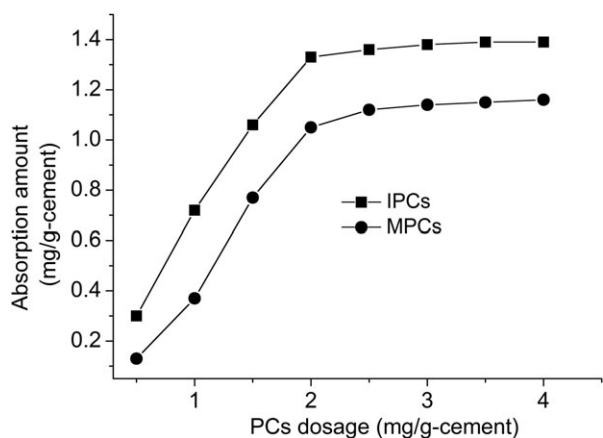


Figure 6. Relation between adsorption amount on cement particle surface and PCs dosages.

the surface activity of IPCs was slightly stronger than MPCs. The critical surface tension and critical micelle concentration (CMC) of IPCs and MPCs were 29.3 mN/m and 9 mg/ml and 33.6 mN/m and 9 mg/mL, respectively. An explanation for this result may be that half of the carboxyl groups of IPCs connected to the main chains through methylene (-CH₂-), the lower surface tension with IPCs may be due to an extra methylene group as supposed to indirect COOH, resulting in change in hydrophobicity that improved surface activity compared with MPCs.

Effects of IPCs and MPCs on Fluidity of Cement Paste

The effects of IPCs and MPCs on the fluidity and fluidity loss of cement paste over time are shown in Figure 5. The results showed that the fluidity of cement paste doped with IPCs was larger and the corresponding fluidity loss was smaller compared with MPCs. The results also showed that the fluidity of cement paste doped with IPCs was nearly unchanged until 90 min and then decreased slightly. The fluidity of cement paste doped with MPCs remained constant until 60 min and then obviously decreased. The results suggest that the half of the carboxyl groups that were indirectly connected to the main chains exhibited stronger dispersion than that of direct connection mode. The indirect connection mode may have more moving space than that indirect connection mode, leading to easier adsorption and wrapping around cement particles. An alternative explanation may be that the indirect connection carboxyl groups could not be embedded easily in twisting PEG branch chains and may be more free to move around, leading to easier adsorption on the cement particle surface compared with the direct connection carboxyl groups. The longer polymer molecule chain wrapped around the cement particle surface may more easily express steric hindrance, contributing to the fluidity of cement paste.

Consequently, the degree of flexibility of half of the carboxyl groups in PCs may be important for dispersion capacity.

Zeta-Potential of Cement Paste with IPCs and MPCs

Zeta-potential was measured to probe the interaction between PCs and cement particles. The changes in the zeta-potential of the cement particles over time are shown in Figure 5. The results indicated that the zeta-potential of cement particles without PCs had a less negative value during the initial stage and then remained almost level over time. The zeta-potential of cement particles doped with IPCs was lower compared with MPCs. The logical explanation is that half of the carboxyl groups in IPCs had more moving space and more easily formed a linkage with cement compared with the carboxyl groups of MPCs that were easily enclosed by PEG side chains. This may be the reason for the better fluidity of cement paste doped with IPCs compared with MPCs. Therefore, the carboxyl groups likely connected indirectly to the main chains could provide more electrostatic repulsion compared with direct connection to the main chain.

Adsorption Amount of PCs on Cement Particle Surface

The relationships between the adsorption amounts of IPCs and MPCs on the cement particle surface and their dosages are shown in Figure 6. The adsorption amount of IPCs and MPCs on cement increased with an increase in their dosage, and the adsorption amount remained nearly level after the PCs dosage was > 2 mg/g-cement. The optimum dosage of IPCs and MPCs was 2 mg/g cement, and this optimum dosage was equated with an optimum dosage of paste fluidity. The results also indicated that the adsorption capacity of IPCs was stronger than MPCs. Therefore, IPCs were easily adsorbed on cement particles compared with MPCs.

The molecular weight and distribution of residual IPCs and MPCs are shown in Table IV. The results showed that the molecular weight of residual IPCs and MPCs markedly decreased compared with the original IPCs and MPCs. The PDI also become more narrow and approached 1. These results suggest that the larger PCs molecules tended to be preferentially adsorbed on the cement particles and clearly indicate the importance of molecular size when attempting to control the action of PCs.

A schematic diagram of the presumed adsorption mechanism of IPCs and MPCs on the cement particle surface is shown in Figure 7. The adsorption process may consist of adsorption via electrostatic interactions, the coordination between carboxyl groups and Ca²⁺ (Ma²⁺), and the wrapping of PCs main chains and PEG side chains around the cement. The half of the carboxyl groups that connected indirectly to IPC main chains were more flexible and more easily formed bonds and electrostatic interactions with Ca²⁺ and Mg²⁺ on the cement particle surface.

Table IV. Adsorption Behavior of MPCs and IPCs on Cement Particles

PCs	Dosage (mg/g-cement)	Adsorption amount (mg/g cement)	Adsorption ratio (%)	M _w	M _n	PDI (M _w /M _n)
IPCs	2	1.33	66.5	32231	35454	1.11
MPCs	2	1.05	52.5	35238	39819	1.13

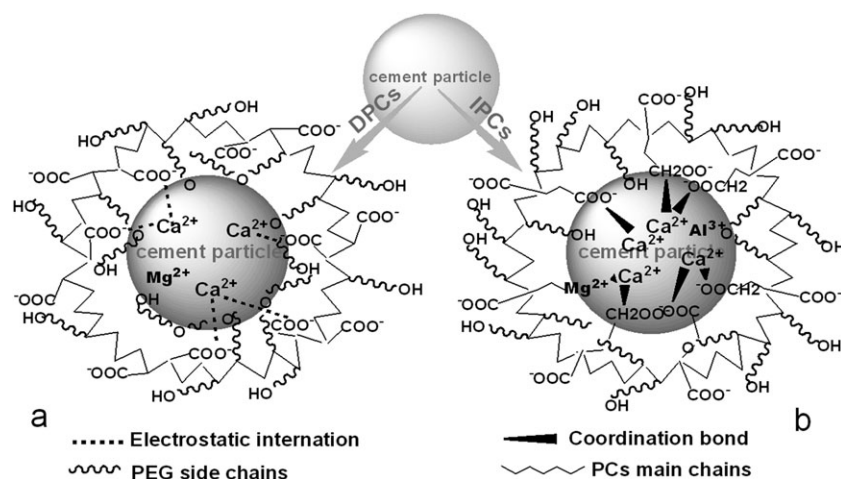


Figure 7. Schematic diagram of adsorption of (a) MPCs and (b) IPCs on cement particles.

The wrapping of PEG side chains resulted in a more robust combination layer on the cement particle surface. The other half of the carboxyl groups that connected directly to IPC main chains may have tended to be wrapped by PEG side chains and were distributed in the combination layer and principally provided electrostatic repulsion. The carboxyl groups in the MPCs rely mainly on the electrostatic interaction with cement particles to form a wrapped layer in the cement particles surface, which the adhesion is poorer than that of IPCs. The hypothesized adsorption mechanism is consistent with the results of the fluidity, fluidity loss, and zeta-potential of cement paste.

Effects of IPCs and MPCs on Cement Hydration Products

The major components of cement are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF). During hydration, a sophisticated chemical reaction occurs among these components and CaO , SiO_2 , Al_2O_3 , and Fe_2O_3 to create complex crystal ettringite (AFt) and portlandite (CH) structures and C-S-H gel. Decreasing the crystal product content and increasing the C-S-H gel content improves the mechanical properties and durability of the concrete structure.^{24,25} The XRD patterns of hardened cement paste at 3, 7, and 28 d are shown in Figure 8(a–c), respectively. The results showed that IPCs and MPCs exerted an inhibitory effect on AFt and CH crystal products. Figure 8(a–c) show that the height of the diffraction peaks of AFt and CH of hardened cement paste mixed with IPCs were small and lower than the control samples. The results suggest that IPCs have greater inhibitory effect on forming AFt than MPCs. The reason could be that some flexible carboxyl groups of IPCs may form a coordinated bond with Ca^{2+} , resulting in a decrease in CH and AFt. The results also showed that IPCs can control CH crystal products during cement hydration. The decrease in crystal products results in an inevitable increase in the C-S-H gel and the mechanical properties of concrete.

Effect of IPCs and MPCs on Microstructure of Hardened Cement Pastes

SEM of fractured surfaces of hardened cement paste doped with IPCs and MPCs at 7 and 28 days are shown in Figure 9. The

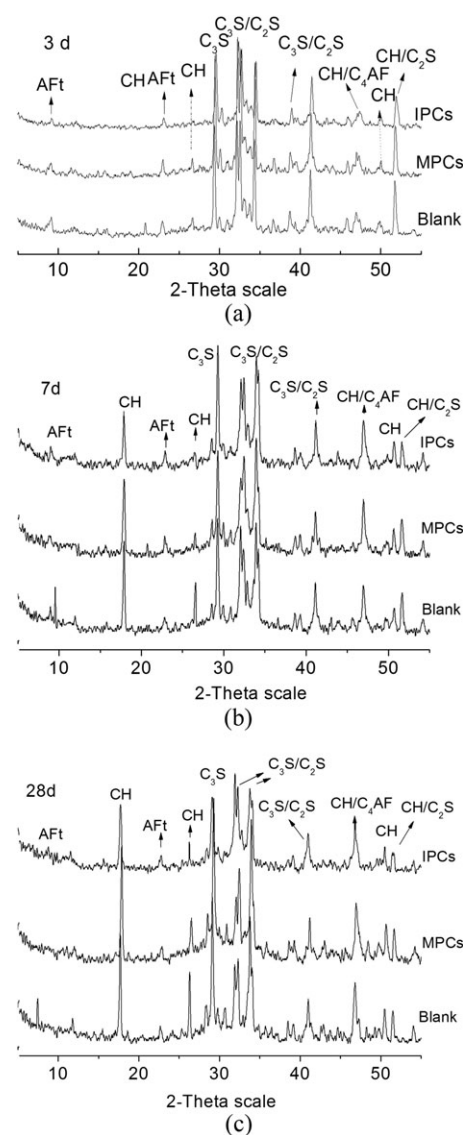


Figure 8. XRD of hardened cement paste at (a) 3 d, (b) 7 d, and (c) 28 d.

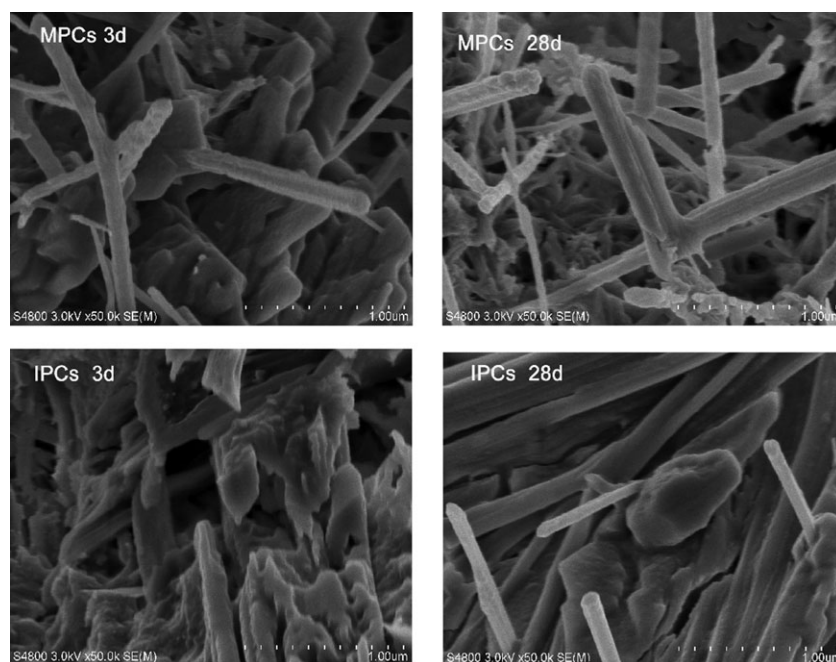


Figure 9. SEM of fractured surfaces of hardened cement paste.

results indicated that fewer rod-hydrated crystal products were found in the hardened cement paste doped with IPCs compared with MPCs. The IPCs may contribute to improving the degree of density of hardened cement paste. These SEM results are also consistent with the XRD analysis and compressive strength of hardened cement paste (Table IV).

Effect of IPCs on Pore Diameters of Hardened Cement Paste

The pore diameters of hardened cement paste are closely related to the mechanical strength and durability of concrete. The pores in concrete were compartmentalized into four types according to their pore diameters.^{26,27} A pore diameter <20 nm is referred to as a harmless pore. A pore diameter between 20 and 50 nm is referred to as a less harmful pore. A pore diameter between 50 and 200 nm is referred to as a harmful pore. A pore diameter >200 nm is referred to as a more harmful pore. The pore diameter distributions of hardened cement paste cured for 3 d, 28 d were tested, the results of which are shown in Table V. The results showed that pore diameters of less 20 nm in hardened cement paste doped with IPCs were the smallest compared with that of MPCs and PCE, and the pore diameters of larger than 50 nm decreased remarkable in the hardened cement paste

doped with IPCs. These results indicate that IPCs can decrease harmful porosity resulting in improving the mechanical properties of cement base materials.

Effects of IPCs and MPCs on Application Performance

The application results of MPCs and IPCs were investigated and shown in Table VI. The results indicated that the water-reducing ratio of IPCs was larger than MPCs and reached 32.4%. The setting time of hydraulic cement mortar with IPCs was also longer than MPCs, with an initial setting time of 330 min and final setting time of 410 min. The problems of bleeding and segregation no longer existed. The appearance viscosity of cement mortar doped with IPC is greater than that of MPCs and PCE, and the fresh cement mortar has not bleeding and segregation. A properly large paste viscosity is certainly needed for without segregation and larger fluidity. IPCs is one way to get it done, which benefited from contributions of excellent interaction of IPCs functional groups and cement. The compressive strength of hydraulic cement mortar mixed with IPCs was larger than MPCs at 28 days, indicating that IPCs can improve the compressive strength of hydraulic cement mortar. The compressive

Table V. Pore Diameters (d) of Hardened Cement Paste Cured for 3d and 28d

Pore diameter distribution	Porosity(%)					
	IPCs		MPCs		PCE	
	3d	28d	3d	28d	3d	28d
<20 nm	0.086	0.075	0.078	0.064	0.076	0.068
20~50 nm	0.052	0.712	0.067	0.532	0.086	0.675
50~200 nm	2.541	0.316	3.436	2.134	2.153	1.561
>200 nm	2.236	0.352	3.562	0.723	3.562	0.854

Table VI. Properties of Hydraulic Cement Mortar Doped with MPCs and IPCs

	PCE	MPCs	IPCs
PCs dosage (wt % by cement weight)	0.2	0.2	0.2
Water-reducing ratio (%)	30.6	29.2	32.4
Appearance viscosity (mPa.s)	2134	1826	2351
Bleeding /Segregation	A little	A little	no
Setting time (min)			
Initial setting	276	310	330
Final setting	332	385	410
Compressive strength (MPa)			
3 d	37.4	37.5	39.3
7 d	46.6	46.8	49.3
28 d	53.3	50.7	58.1

strength of hydraulic cement mortar is intimately associated with dispersion capacity.

CONCLUSIONS

The connection mode of carboxyl groups, either direct or indirect, in the PCs main chains affects the fluidity of fresh cement paste and the setting time of hardened cement. IPCs with half of the carboxyl groups connected indirectly to the main chains and the other half connected directly to the main chains have the advantages of better dispersion capacity, larger paste fluidity, smaller fluidity loss, and smaller pore diameters compared with PCs with only direct connections. The carboxyl groups of IPCs connected indirectly to the main chains likely have more moving space, facilitating the surrounded of side chains to be adsorbed on cement particles, and therefore IPCs exhibited stronger dispersion capacity than MPCs. The synthesis of PCs with carboxyl groups with an indirect connection mode may improve dispersion capacity and mechanical properties.

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