Interaction of silylated superplasticizers with cementitious materials

Zichen Lu,[1] Xiangming Kong,[1] Hui Liu,[2] Ziming Wang,[2] Yanrong Zhang,[1] Biqin Dong,[3] Feng Xing[3]

[1]Department of Civil Engineering, Tsinghua University, Beijing 100084, People's Republic of China
[2]College of Materials Science and Engineering, Beijing University of Technology, Chaoyang District, Beijing 100124, People's Republic of China
[3]Department of Civil Engineering, Guangdong Provincial Key Laboratory of Durability for Marine Civil Engineering, Shenzhen University, Shenzhen 518060, People's Republic of China
Correspondence to: X. Kong (E-mail: kxm@mail.tsinghua.edu.cn)

ABSTRACT: Incorporation of silane groups into polycarboxylate superplasticizer (PCE) opens a new technical approach to improve properties of PCE, such as to enhance the adsorption of PCE on cement and hence the dispersing performance, to minimize the retardation effect, and potentially to increase mechanical strength of cement mortars. Silylated PCEs were synthesized using silane monomer via radical copolymerization. Dispersing effect, adsorption behaviors, and influences on mortar strength of these polymers were systematically investigated. Results show that increasing the incorporation of sliane groups in PCE promotes the adsorption of polymer on cement surface and hence leads to good fluidity retention capability. Furthermore, sulfate resistance ability of silylated PCE is superior due to stronger chemical adsorption of polymer on cement surface. The retardation effect of PCE is minimized by the introduction of silane groups. The addition of silylated PCE significantly increases 3 days compressive strength without notably affecting the long-term strength. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44161.

INTRODUCTION

Polycarboxylate superplasticizers (PCEs) are popularly used to improve the workability of concrete in practice.[1] The dispersing mechanism of these superplasticizers is generally accepted to be related to the electrostatic repulsive forces[2] provided by the adsorbed anionic polymers on surface of cement grains and the steric hindrance effect generated by the polyethylene oxide side chains.[3–7] It has been well accepted that the adsorption of PCE is caused by the electrostatic attraction between the anchoring groups, namely carboxyl functional groups ($-COO^-$) and the charged minerals surfaces, either the aluminate surface such as tricalcium aluminate (known as C_3A in cement notation) or ettringite displaying the opposite charge or the silicate surface including tricalcium silicates (known as C_3S in cement notation) and calcium silicate hydrate (so-called C—S—H) via bridging Ca^{2+} ions.[2,8,9] However, one common phenomenon caused by the adsorption of PCE is the retardation effect on cement hydration, which could lead to a delayed setting and a decrease of the early strength of cementitious materials.[10] It has been indicated that PCE retards the dissolution of the phase alite as a function of charge density.[11] Three possible mechanisms for the

retardation effect on cement hydration were proposed by Mollah,[12] namely: (1) the diffusion of water and calcium ions through the cement-solution interface was hindered by the adsorbed polymer molecules; (2) complexation of calcium ions with the polymer molecules was formed which prevents nucleation and precipitation of hydration products; and (3) the dispersive action of superplasticizers changes growth kinetics and morphology of hydrate phases. Based on the abovementioned conclusions, the adsorption of $-COO^-$ plays a very vital role on the effect of cement hydration. Low retarding PCE is often desired in some applications, such as prefabricated concrete, low temperature construction etc. In this particular context, we wonder whether the $-COO^-$ could be partially or completely replaced by some other anchoring group to reduce the retardation effect on cement hydration and to enhance the early strength of cementitious materials without affecting their workability.

On the other hand, organosilane acting as coupling agents, adhesion promoters, and surface primers has been commonly used in the field of advanced materials.[13] Organosilane contains both organic and inorganic reactivity due to the hydrolysis of

Table I. Chemical and Mineralogical Compositions of Cement (wt %)

		Chemical composition									Mineral composition		
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2Oeq	f-CaO	Others	C_3S	C_2S	C_3A	C_4AF	Others
22.10	4.04	3.38	61.91	2.66	2.87	0.56	0.79	1.69	57.34	18.90	6.47	11.25	6.04

wt %, mass fraction.

alkoxyl groups ($-OCH_3$ or $-OC_2H_5$) contained in the organo-silane monomer to hydroxyl groups ($-OH$) and a subsequent condensation with hydroxyl groups on the substrates to form siloxane chemical bonding which progressively takes place in acidic or alkaline conditions.[14–16]

Recently, Witt and Plank[17] and Fan et al.[18] introduced organosilane into the PCE molecule to obtain chemical bonds between the C−S−H surface and the superplasticizer polymer through the condensation reaction of silanol ($-Si-OH$) groups presented in both compounds. Both researchers found that such modified PCE polymers exhibit superior sulfate tolerance due to the formation of the chemical bonds between the cement surface and the adsorbed modified PCE molecules. Additionally, the N-maleic γ-amidopropyl triethoxy silane[17] modified PCE can disperse cement grains at substantially lower dosages than the nonmodified PCE.

However, to our best knowledge, the effect of organosilane functions incorporated polymers on cement hydration and then on the strength development of cementitious materials is still untouched so far. In the present study, a series of silylated PCE, namely 3-(trimethoxysilyl) propyl methacrylate (TMSPMA)-modified superplasticizers (silylated PCE), were synthesized through free radical copolymerization of acrylic acid (AA), methallylpolyoxethylene ether (HPEG), and TMSPMA. Their dispersing property and working mechanism of the silylated PCEs were investigated through flow table spread test and absorption measurement. More importantly, the effect of silylated PCEs on cement hydration and strength development of cementitious systems was elaborately discussed by means of isothermal calorimetry and mechanical strength measurement. It was found that the silylated PCEs proposed in this paper provide a promising technical approach to overcome the retardation drawback of the traditional PCEs.

EXPERIMENTAL

Materials

AA, ammonium persulfate (APS), and mercaptopropionic acid were used as received. TMSPMA was provided by Beijing North Fine Chemical Co., Ltd, Beijing, China. HPEG ($M_n \approx 2400$ g/mol) was provided by Liaoning Kelong Fine Chemical Co., Ltd, Liaoning Province, China. P.O.42.5 Ordinary Portland compliant with the Chinese National Standard GB8076-1997: Concrete Admixtures was used to prepare the cement pastes and mortars. The chemical and mineralogical compositions of the cement are presented in Table I. Sand according with ISO 679-2009: Cement-Test methods-Determination of strength was used as fine aggregates to prepared cement mortars for the mechanical strength tests. Deionized (DI) water was used in all experiments.

Synthesis of the Polymers

Both PCEs and silylated PCEs were synthesized via radical copolymerization of HPEG with AA and/or TMSPMA. The synthesis protocol has been well described in refs. 2,6, and 9. The polymers were synthesized in a 500 mL three-neck glass flask equipped with a mechanical stirrer and two dosing units for both the aqueous solution of monomers and initiator. A constant synthesis temperature of 70 °C was fixed through water bath during polymerization. A total of 0.395 g APS was dissolved in 40 g DI water to prepare the initiator solution. Monomer solution was prepared by mixing the defined amounts of HPEG, AA, TMSPMA, and 0.355 g mercaptopropionic acid into 252 g DI water. The total mass of monomers was kept constant at 71 g, and the mole ratios of the involved monomers are shown in Table II. First, 20% of the prepared monomer solution was charged into the flask as precharge. Then the temperature around the pre-charge was promptly increased to 70 °C under stirring and kept for 5 min. The rest monomer solution and the initiator solution were then separately dosed into the flask at constant dosing rates over 2 h. Later, another 2 h was kept to complete the

Table II. Molar Proportion and Molecular Weights of the Synthesized Polymers

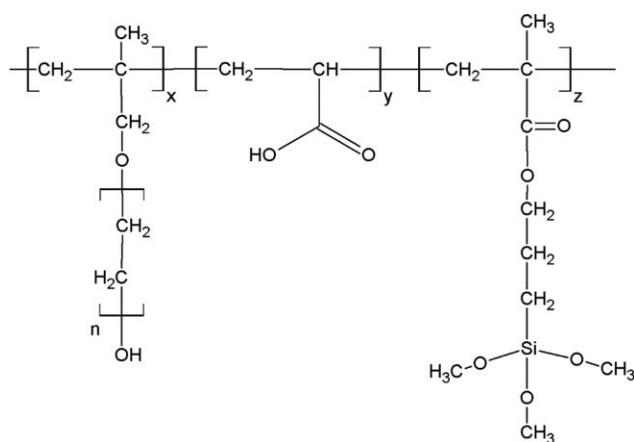|	Mole fraction (%)				Polydispersity
Polymers	HPEG	AA	TMSPMA	M_w (g/mol)	index (M_w/M_n)
P(H1S1)	50.0		50.0	10,520	1.354
P(H1S2)	33.3		66.7	31,280	1.948
P(H1S3)	25.0		75.0	468,900	1.830
P(H1A1)	50.0	50.0		7400	1.543
P(H1A2)	33.3	66.7		24,400	1.665
P(H1A3)	25.0	75.0		89,480	1.653
P(H1A1S1)	33.3	33.3	33.3	19,590	1.772

Figure 1. Chemical structure of the synthesized polymers.

polymerization at 70 °C. The obtained polymer solution was then allowed to cool down to the room temperature. Solid content of the prepared polymer solution was measured through drying a certain amount of the polymer solution at 80 °C until constant weight was reached. The measured solid content of the prepared polymer solution was about 20%. The corresponding chemical structure of polymer is given in Figure 1.

Characterization of the Synthesized Polymers

Size Exclusion Chromatography. Size exclusion chromatography (SEC) has been a standard method for the analysis of molecular weight and molecular weight distribution. In addition, SEC system equipped with a light scattering (LS) instrument allows obtain the absolute molecular weight that does not rely on calibration with standards of known molecular mass. In this study, SEC integrated with a multiangle laser LS detector (DAWN HELEOS II; Wyatt Technology, California, USA) and a refractive index detector (Optilab rEX; Wyatt Technology) was used to determine the molecular weight (M_w) and the polydispersity of the prepared polymers as listed in Table I. A total of 0.1 mol/L NaNO$_3$ solution at pH = 7 was used as the eluent during the measurement. All of the polymer solution concentrations were diluted to 5 mg/mL with DI water and directly injected into a 0.2 mL loop with an autosampler. Temperature during measurement was kept constant at 25 °C, and the flow rate was 0.5 mL/min. SEC columns of SB-804 HQ connected with SB-802.5 HQ (OHpak; Shodex, Tokyo, Japan.) were used for measurement of all polymers.

Fourier Transform Infrared Spectra. Fourier transform infrared (FTIR) was used to confirm the copolymerization of the involved monomers. As it is well understood that besides the desired polymer, the synthesis of sample usually contains a small fraction of oligomers, unreacted monomers, and so on. In this study, dialysis technique was adopted to remove un-reacted monomers and oligomers from the sample and thus a cleaned polymer solution was obtained. A cellulose ester semipermeable membrane MD44-7 with nominal molecular weight cut-off of 7000 Da was used in this paper. The membrane was provided by Beijing Ruida Henghui Science and Technology Development Co., Ltd., Beijing, China, and only globulin with a molecular

weight of 7000 and smaller molecules can pass through. First, the concentration of the synthesized product was diluted to 10.0 wt % and then 40 mL of the diluted polymer solution was poured into a dialysis bag which is made of the abovementioned semi-permeable membrane. Subsequently, the completely sealed dialysis bag was placed into a container filled with 5000 mL deionized water as dialysate. The conductivity of the dialysate was continuously measured to estimate the cleanness of the dialysate. The dialysate outside of the dialysis bag was renewed every 6 h. The dialysis ended when the conductivity of the dialysate dropped below 30 μS/cm. Thus, most of the residual monomers and oligomers that are able to pass across the semipermeable membrane were effectively removed from the sample. In this manner, the synthesized polymers were cleaned for FTIR spectra analysis. FTIR (Nicolet 6700 TIR; Thermo Fisher Scientific, Massachusetts, USA) instrument with a resolution of 4/cm was applied. The polymer film was prepared by drying a certain amount of the cleaned polymer solution at 60 °C for 24 h and then scanned by a FTIR apparatus in the absorption mode from 400 to 4000/cm at 25 °C.

Fluidity Test of the Fresh Cement Pastes with the Addition of Polymers

Fluidity test was conducted to evaluate the plasticizing efficiency of the synthesized polymers in cement pastes with water to cement (W/C) ratio of 0.35. The dosage of the polymers was in the range of 0–4% by weight of cement (bwoc). The tests were conducted according to the Chinese National Standard GB/T 8077-2000: Methods for testing uniformity of concrete admixture. A certain mass of PCE solution (mass concentration is about 20%), DI water, and cement were weighted according to the mix proportion. Then the required amount of water and PCE were added into a mixer and were homogeneously mixed. After that, cement was gradually introduced over a time span of 2 min into the mixer at 62 rpm. After a 10 s interval, mixing was resumed for an additional 2 min at 125 rpm. The freshly mixed cement pastes were instantly subjected to the fluidity measurement. The fluidity of fresh cement paste (fcp) with the addition of various polymers was characterized by spread diameter in a flow table spread test. After well mixed and vigorously stirred for 2 min, the fcp was poured into the cone with the dimension of top diameter of 36 mm, bottom diameter of 60 mm, and height of 60 mm. Then the fully filled cone was quickly lifted up. After 30 s, the spread diameter of fcp was recorded as the average of two perpendicularly crossing diameters.

In addition, the fluidity retention ability of the cement paste with the addition of the different polymers was determined by measuring the variation of fluidity of the fcp over time. It has been reported that the sulfate ions presents in fcp is an important factor affecting the fluidity of fcp as well as the dispersing efficiency of PCEs due to the competitive adsorption of SO_4^{2-} ions and PCE molecules on cement surface.[18] In order to evaluate the resistance ability of the polymers against sulfate, the fluidity retention ability of the cement paste with the addition of sodium sulfate was also tested with the same dosage of the polymers. The dosages of the polymers were fixed at 0.4 wt % bwoc and the addition amount of sodium sulfate was 0.745 wt

Figure 2. Images of the obtained polymer solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

% bwoc (about 150 mmol/L) in fcp. The polymer solutions were firstly prepared with deionized water according to the recipe, and then certain amount of Na_2SO_4 was added to the polymer aqueous solutions. After sufficient mixing of the fcp for 2 min, the bowl containing fcp was covered with a wet cloth and then was stored for 55 and 115 min. At a predetermined interval, the fcp was extracted from the bowl and then stirred at a speed of 125 rpm for 30 s to ensure homogeneity of cement paste. After that, the fluidity of the fcp was measured again by the flow table spread test. The fluidity at 5 min is regarded as the initial fluidity and the fluidity retention ability of the fcps with addition of the polymers can be compared by looking at the fluidity variation over time.

Adsorption on Cement

Depletion method was used to determine the adsorption amounts of the polymers on the cement grains with the assumption that the interaction between cement and polymers was solely contributed by adsorption. The nonadsorbed amount of polymers remaining in pore solution was determined by measuring the total organic content (TOC; TOC-VCPH; Shimadzu, Kyoto, Japan). Cement pastes (W/C = 1) with varied dosage of the polymer were filled into 50 mL centrifuge tubes and centrifuged

for 10 min at 10,000 rpm. The supernatant was then carefully collected using a syringe filter with a pore diameter of 0.22 μm. Subsequently, the supernatant solution was diluted with deionized water to a suitable concentration for TOC test.

Isothermal Calorimetry

Isothermal calorimetry was applied to investigate the influences of polymer on the kinetics of cement hydration. Eight-channel isothermal calorimeter (TAM-air; Thermometrics, New Castle, Sweden) was applied in this experiment. The W/C of cement pastes was fixed at 0.35. The measuring temperature was regulated constantly at $25 \pm 0.02\,°C$. The time range of the measurement is various due to the different effect of PCE on cement hydration at different dosage.

Mechanical Strength Measurement of Cement Mortars

Cement mortars with fixed W/C of 0.5 were prepared with and without the addition of polymers. The tests were conducted according to the Chinese National Standard GB/T 17671-1999: Method of testing cements -Determination of strength. The dosage of the polymers was fixed at 0.2% and 1.0% bwoc in the mortar formulation. The weight ratio of sand to cement is 3. Firstly, a certain mass of PCE solution (mass concentration is about 20%), DI water, cement and sand were weighted according to the mix proportion. Then the required amount of water and PCE were added into a mixer and were homogeneously mixed. After that, cement was introduced into the liquid mixture and stirring was immediately started at 62 rpm. After a 30 s mixing, sand was gradually introduced into the mixer within 30 s. Then the mixing was proceeded at 125 rpm for 30 s. After a 90 s interval, mixing was resumed for additional 60 s at 125 rpm and thus the homogenously mixed cement mortar was obtained. Cubic specimens with the dimension of 40 mm ×
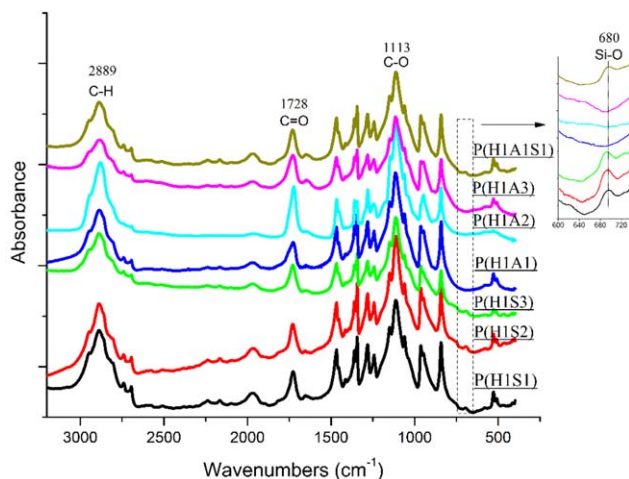

Figure 3. FTIR spectra of the synthesized polymers that were cleaned via dialysis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
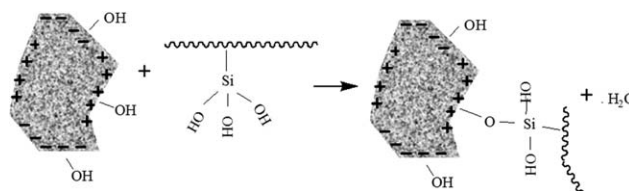

Figure 4. Schematic illustration of chemical adsorption of silylated PCE on the cement.
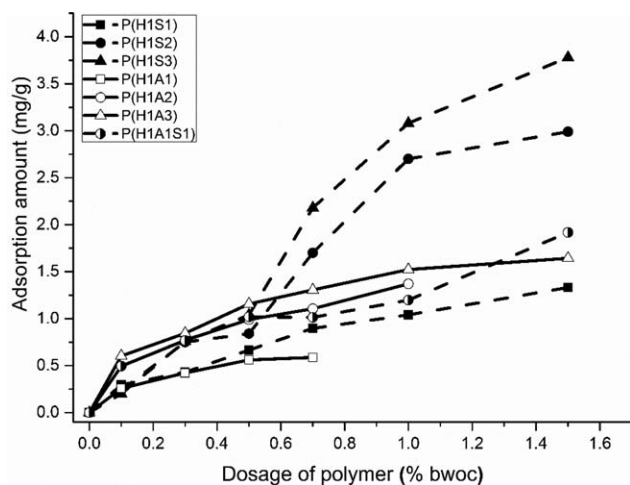
**Figure 5.** Adsorption amount of polymer in fresh cement pastes at different dosages.

40 mm × 160 mm were used for strength measurement. Mortar specimens were firstly cured in a humidified atmosphere at 20 ± 2°C and relative humidity of 95% for 24 h prior to demolding. After demolded, the specimens were placed in a standard curing chamber for 3, 7, and 28 days. The flexural and compressive strength was measured by using Toni Technik/Toni Norm Press (Zwick GmbH & Co. KG, Ulm, Germany) equipped with appropriate adapters.

RESULTS AND DISCUSSION

Characterization of the Obtained Polymers

As shown in Figure 2, with the increasing fraction of silane in the monomer combination during the synthesis [P(H1S1), P(H1S2), and P(H1S3)], the obtained polymer solutions change from transparent to milky white, which is believed to originate from the crosslinking of the polymer chains due to the known sequential hydrolyzation-condensation of the alkoxyl silane functional groups, as described in eqs. (1)−(3). As a consequence, the crosslinking of the polymers significantly increases the molecular weight as well as the molecular size and finally leads to the formation of polymer nanoparticles and thus changes the appearance of the obtained samples, form transparent solution to turbid dispersion. The reaction equations of the involved processes under alkaline condition are listed below. Equation (1) is the hydrolyzation of the silane modified polymer. Equations (2) and (3) are the condensation reaction of the silanol groups in polymers, which leads to crosslinking of polymers and/or formation of nanoparticles.
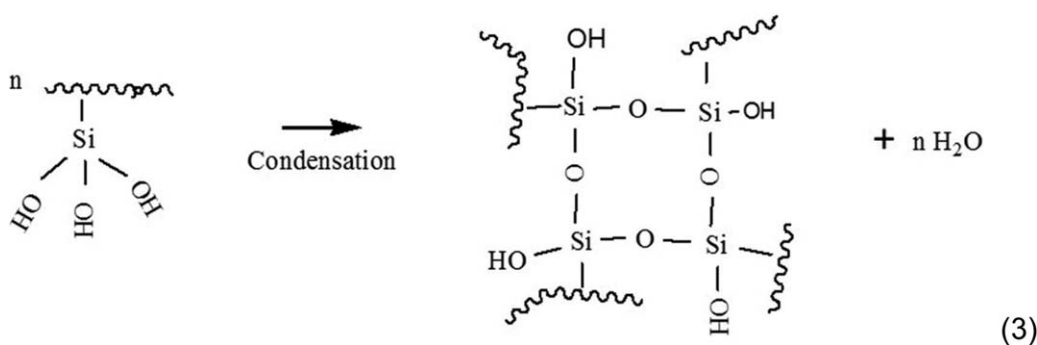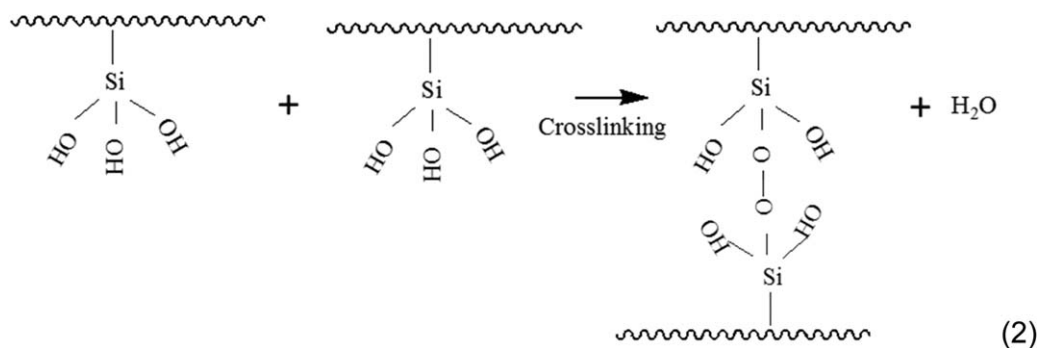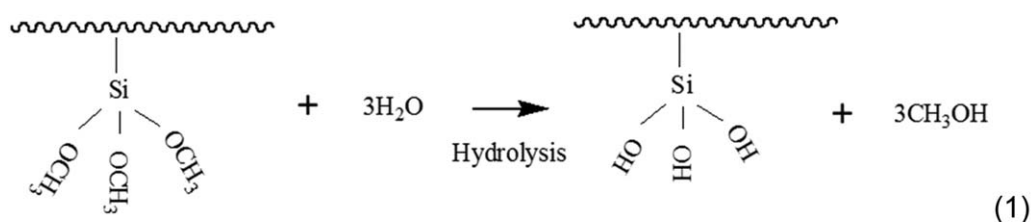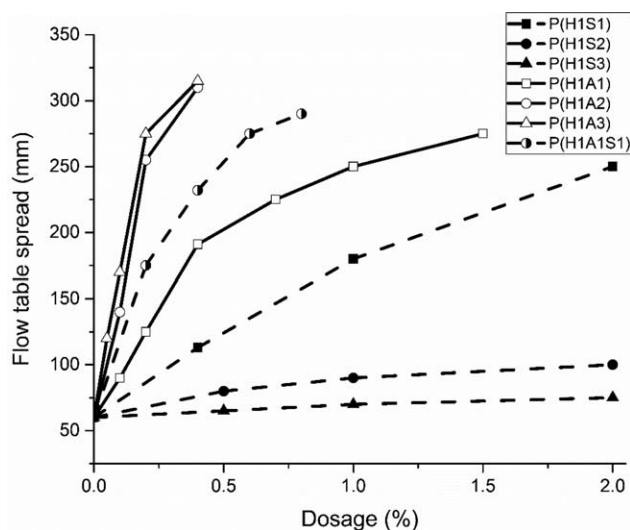
Figure 6. Influence of synthesized polymers on fluidity of cement pastes.

FTIR analysis was performed in order to confirm the co-polymerization of the involved monomers in the synthesized polymers. Polymer solutions were firstly cleaned via dialysis to remove the residual monomers and then polymer films were prepared by drying the cleaned polymer solutions. The FTIR spectra of the cleaned polymers are given in Figure 3. The sharp peak around 1113/cm is assigned to the stretching bands of C—O in HPEG repeating units. The peak at 1728/cm in samples P(H1S1), P(H1S2), and P(H1S3) are assigned to the stretching bands of C=O, which is contributed by the silane repeating units, while for the samples P(H1A1), P(H1A2), and P(H1A3), the peak at the same position is assigned to the stretching bands of C=O in carboxyl groups of AA monomer units. Since P(H1A1S1) has both AA and silane repeating units in the polymer chains, the peak at 1728/cm is also present. The peak at 2889/cm is assigned to the C–H stretching band of —CH$_2$. Moreover, the C=C absorption band in the region 1680–1620/cm does not appear in all spectra, which suggests that the measured samples do not contain any remaining monomers. Hence, the analysis on the FTIR spectra proves solidly that the related

monomer has been successfully copolymerized. In addition, the peak of Si–O usually appears around 920, 1080,[19] and 670/cm.[20] As the peak at 920 and 1080/cm overlaps with the peaks of HPEG, only a small peak at 680/cm could be observed for the samples containing silane units [P(H1A1), P(H1A2), P(H1A3), and P(H1A1S1)] in Figure 3, which proves the successful copolymerization of the silane monomer with HPEG and/or AA.

The molecular weight information of the synthesized polymers is presented in Table II. It can be found that with the increasing fraction of AA and silane in the monomer combination, the molecular weight of the obtained polymers increase correspondingly. P(H1S3) shows the highest molecular weight, which may be caused by the intensive crosslinking of the polymer chains due to the large amount of silane groups in the polymer chains as indicated in eq. (2).

Adsorption Isotherms

As mentioned before, the adsorption of PCE polymers on the surface of cement grains is the prerequisite for their dispersing effect.[2] It is also well accepted that the adsorption of the traditional PCE polymers is mainly driven by the electrostatic attraction between the charged surface of cement grains and the anchoring groups in the polymer chains, which is mostly the carboxyl groups.[2,8] In this article, as mentioned above, the condensation reaction between the —OH groups on cement surface and the ≡Si—OH groups in the silylated PCE chains may provide another driving force for the adsorption of the polymers on cement surface. The chemical bonds between cement surface and polymers can be stronger and more stable than the typical electrostatic bonds, as schematically indicated in Figure 4.

Figure 5 shows the adsorption isotherms of the synthesized polymers in cement pastes. For the HPEG–AA copolymers, it is clearly seen that the increasing incorporation of AA units in the PCE molecule leads to the larger saturated adsorption amount due to the higher charge density in the polymers, which is in good agreement with the literature.[21] On the other hand, in spite of the absence of charges in the polymer chains, HPEG–TMSPMA copolymers [P(H1S1), P(H1S2), and P(H1S3)] also exhibit significant adsorption on surface of cement grains. The saturated adsorption amounts of P(H1S2) and P(H1S3) are
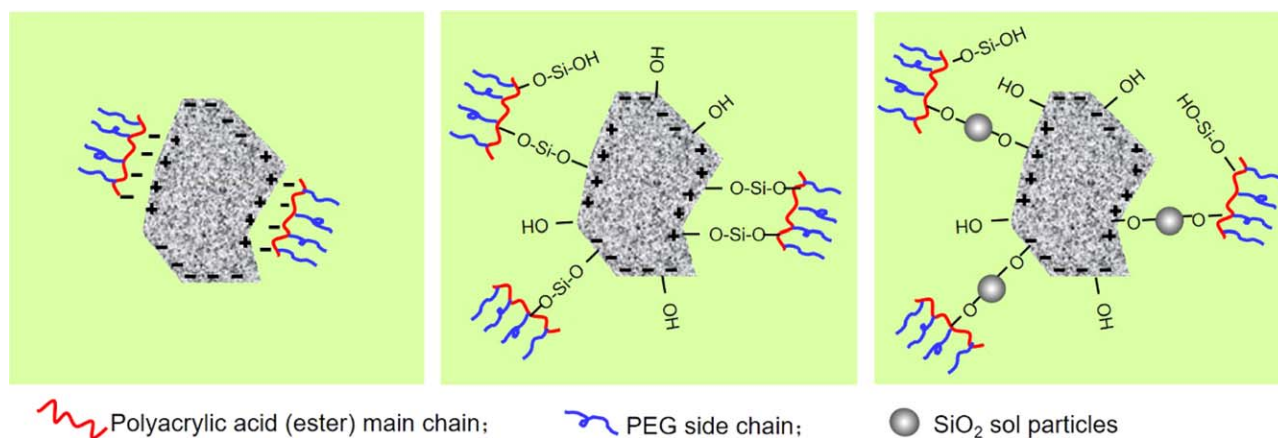

Figure 7. Schematic illustration of the adsorption of PCE and silylated PCE on cement particle: (a) PCE; (b) silylated PCE; and (c) silylated PCE with more TMSPMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
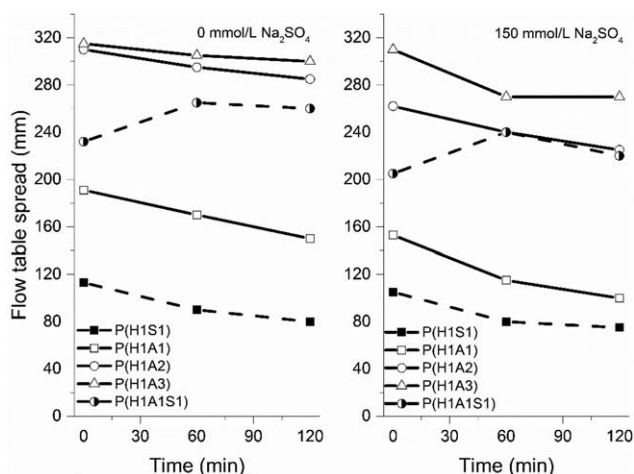
Figure 8. Time evolution of the fluidity for cement pastes incorporated with PCEs and silylated PCEs.

positively charge surface of cement grain upon the condensation reaction of silane groups in the polymers and electrostatic interaction of carboxyl groups.

Effect of Polymer on the Fluidity of fcps

The influence of synthesized polymers on the fluidity of cement pastes is studied by means of flow table spread test with fixed W/C of 0.35. As seen from Figure 6, the addition of HPEG–AA copolymers greatly increases the fluidity of fcps at low dosage (<0.5% bwoc) and the polymers containing more AA units show higher effectiveness at the same dosage, which is related to the higher adsorption amounts due to the more anchoring carboxyl groups in the polymer structure.[22] This result is in well agreement with the previous finding reported by Yamada et al.,[23] and the working mechanism is schematically shown in Figure 7(a).

On the other hand, as seen in Figure 6, the silylated PCE also show fluidizing capability as expected. However, the fluidizing effect of the silylated PCE is clearly lower than the HPEG–AA copolymers despite even higher adsorption amounts. It has been well accepted that the fluidizing effect of the traditional PCE originates from both the electrostatic repulsion and the steric hindrance provided by the adsorbed polymer as described in Figure 7(a). For the silylated PCE, only steric hindrance provided by the adsorbed polymers is thinkable for the fluidizing capability [Figure 7(b)], and we believe that the absence of
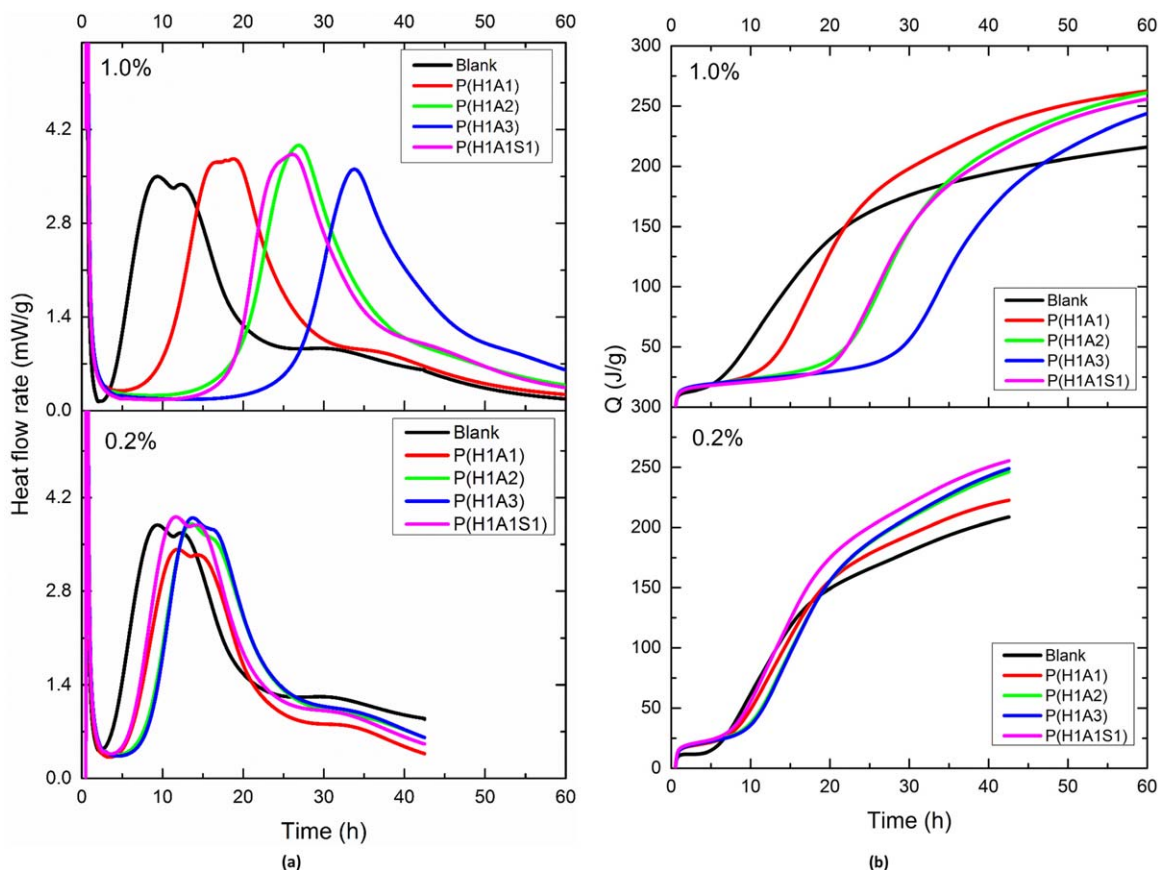
even notably higher than those of P(H1A2) and P(H1A3), respectively. These results certainly verify the fact that the silane groups in the polymer chains can be also working as the anchoring groups driving the adsorption of polymer on cement surface. The polymer P(H1A1S1) containing both silane and carboxyl groups shows more adsorption amount than P(H1A1) and P(H1S1) which can be adsorbed by both negatively and

Figure 9. Calorimetry curves of the cement pastes (W/C = 0.35) in the presence of PCE at different dosages (0.2, 1.0% bwoc) at 25 °C (a) differential heat flow and (b) cumulative heat flow. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 10. Calorimetry curves of the cement pastes (W/C = 0.35) in the presence of silylated PCEs at different dosages (0.2, 1.0% bwoc) at 25 °C (a) differential heat flow and (b) cumulative heat flow. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
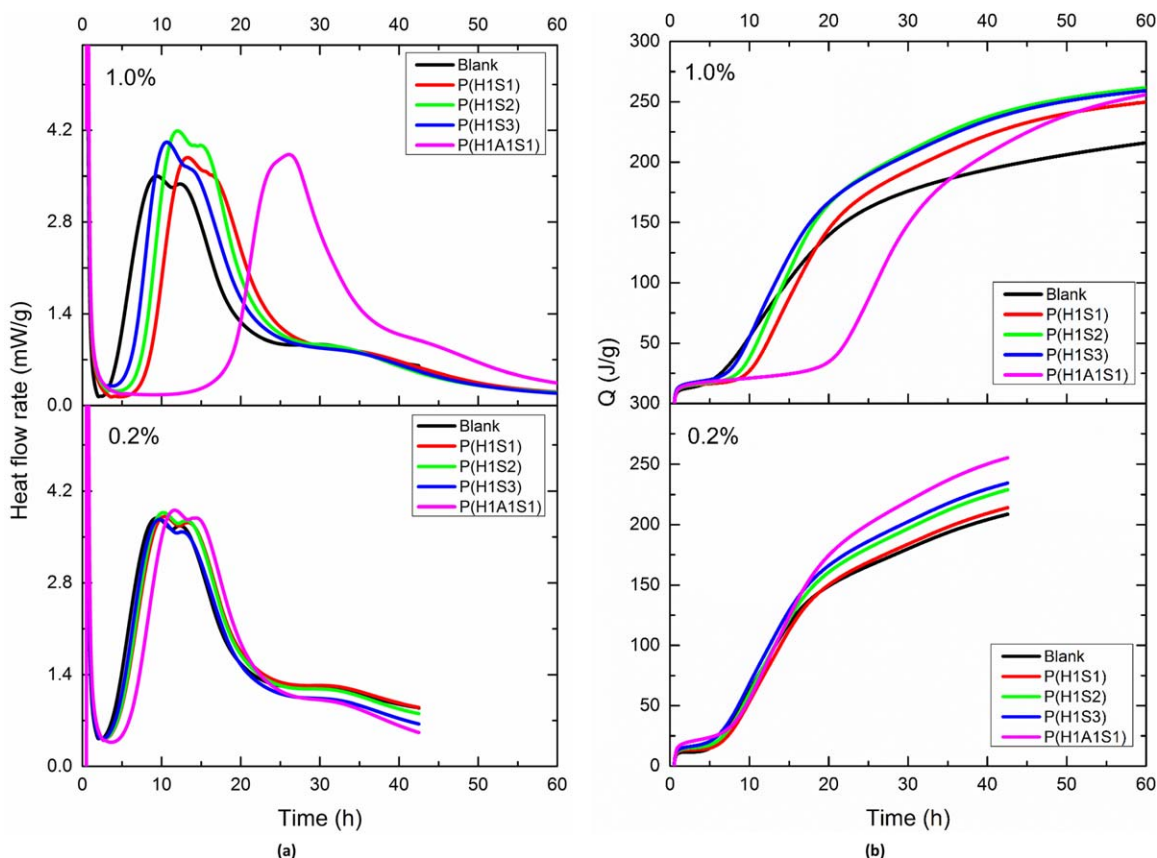
charging groups is responsible for the lower effectiveness. It is surprisingly noted that among the three silylated PCEs, P(H1S1) exhibits the highest effectiveness despite the lowest adsorption amount. It has been known that the condensation reaction may take place not only between the silane groups in silylated PCE and hydroxyl groups on the surface of cement grains under high alkaline condition (pH = 12–14), which leads to adsorption of polymer on cement surface, but also between the silane groups in silylated PCE polymer chains, which results in inter- as well as intra- polymer crosslinking and even formation of polymer particles separated from the homogenous aqueous solution.[24] The crosslinking of silylated PCEs may counteract the fluidizing effect of the silylated PCE and leads to lower fluidity of fcps. As described in Figure 7(c), a flocculate structure caused by the crosslinking reaction hinders the dispersion of cement grains in fcp.

As seen from Figure 6, the ternary copolymer of P(H1A1S1) shows significantly higher dispersing capability than P(H1A1), P(H1S1), and P(H1S2). It indicates that the silylated PCE with an appropriate amount of silane groups may also show excellent dispersing capability in cementitious materials.

Besides the good initial fluidity, the fluidity retention ability is another desired property for the fresh concrete in some applications, such as in the cases of long distance transportation, pumping concrete etc. The fluidity variations of the cement pastes with the addition of various polymers over elapsed time

are presented in Figure 8. Due to the low plasticizing efficiency, P(H1S2) and P(H1S3) were excluded in the tests. From Figure 8(a), it is seen that the fluidity of cement pastes generally decline over the elapsed time, while only the cement paste containing P(H1A1S1) presents an increasing fluidity, indicating an enhanced fluidity retention ability of the cement paste, compared to the HPEG–AA copolymer containing cement pastes.

It is commonly accepted that the dispersing mechanism of PCE is related to the adsorption of polymer on the surface of cement grains.[2,8] Hence it is reasonable to assume that the increasing fluidity retention ability of P(H1A1S1) may come from the slow adsorption of polymer on the cement surface caused by the chemical bond between the C–S–H and polymer.

As mentioned above, the sulfate ions present in fcps is usually harmful to the dispersing effect of PCE in fcps due to the competitive adsorption of SO_4^{2-} ions and PCE molecules on cement grains.[18,25] Therefore, resistance of PCE against sulfate ions is one of the important properties in terms of robustness. In this study, we measured the fluidity variation of cement pastes over time in the presence of different polymers and additional sodium sulfate to evaluate the sulfate resistance of the silylated PCEs. As shown in Figure 8(b), the addition of sodium sulfate in cement paste containing HPEG–AA polymers generally leads to a more drop of fluidity over the elapsed time of 2 h. However, for the cement paste containing P(H1A1S1), the fluidity is less affected by the addition of sodium sulfate, which indicates
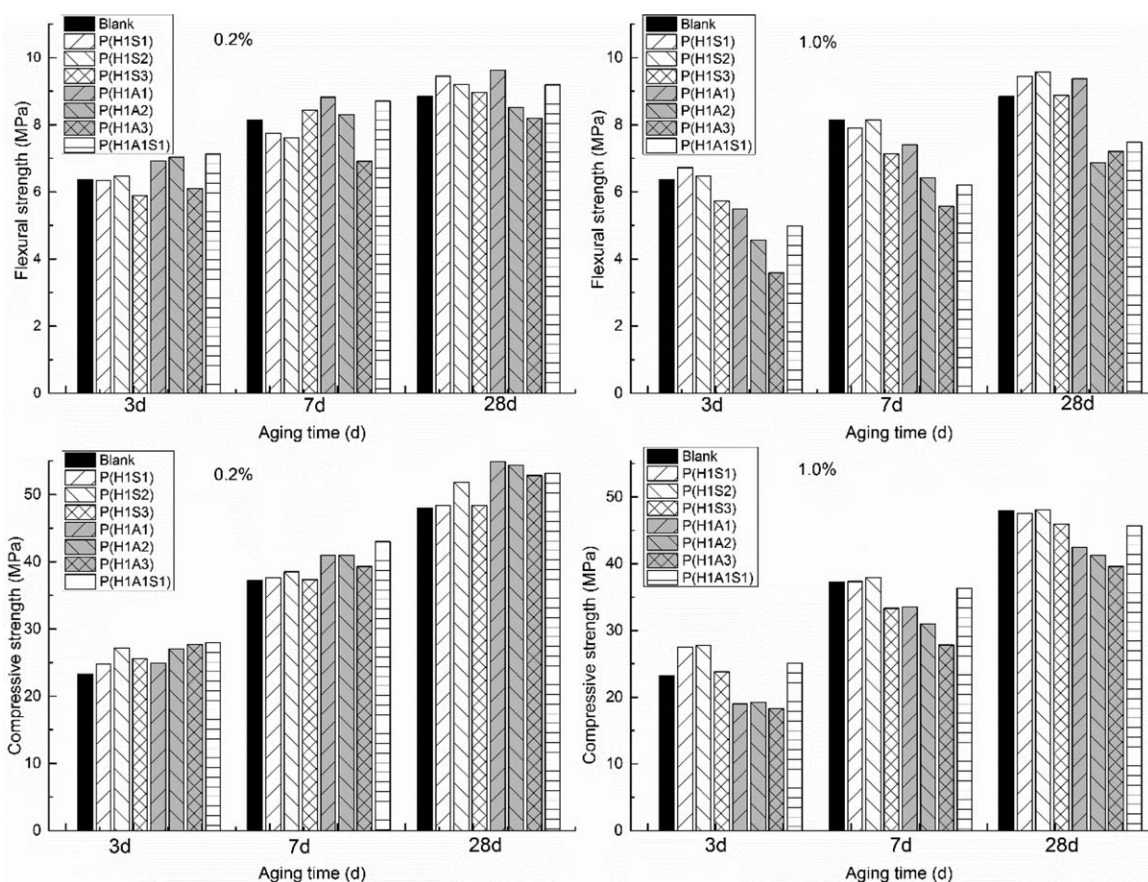
Figure 11. Influence of PCEs and silylated PCEs on the strength development of cement mortars at dosage of 0.2% and 1.0%, respectively.

the increasing sulfate resistance ability obtained for P(H1A1S1). All these results indicate that appropriate incorporation of TMSPMA into PCE molecule may lead to an improved performance of PCE by the introduction of the chemical bonding between the cement grains and the silylated PCEs.

Hydration Kinetics Measured by Calorimetry

It has been well documented that the addition of PCE usually retards cement hydration due to the complexation of carboxyl groups with Ca^{2+} ions and the adsorption of PCE polymers on the surface of cement grains.[12] Isothermal calorimetry was used to investigate the influences of the synthesized polymers on cement hydration as seen in Figures 9 and 10.

As seen in Figure 9(a), it is clearly shown that HPEG–AA polymers delay cement hydration by extending the induction period and the time of induction period is proportional to the mole content of AA unit in the molecular structure, which is well agreement with our previous findings.[26,27] In addition, the total hydration heat at 40 h (or 60 h) of the cement paste with the addition of PCE is always higher than that of the reference sample, which indicates the higher cement hydration degree can be achieved with the addition of PCE. For P(H1A1S1) polymer in which AA units were partially replaced by the silane units, the incorporation of silane groups benefits to the reduction of the induction period and to the increase of the total hydration heat. The same phenomenon can be observed at the two different dosages, which indicates the effectiveness of the silane

functional group to overcome the retardation effect caused by the carboxyl group.

The calorimetry results of the cement pastes with addition of HPEG–TMSPMA polymers are shown in Figure 10. It is clearly confirmed that the more incorporation of silane groups in the polymer leads to less retardation effect on cement hydration even though the adsorption amount is increased. This is exactly the opposite to the case of PCE, in which the more anchoring groups (e.g., carboxyl groups) usually leads to the more adsorption of the polymer on the surface of cement grains and at the same time the more retardation of cement hydration.[28] The retardation effects of the traditional PCE is known to be proportional to the amount of the carboxyl groups in PCE polymer. The results in Figures 9 and 10 clearly indicate that silane groups can perfectly work as the anchoring groups for the superplasticizer polymer, but with much less retardation of cement hydration, compared to the carboxyl groups in traditional PCE.

Strength Development of Hardened Cement Mortars

Due to the said retardation effect of traditional PCE on cement hydration, it has been well known that PCE strongly delays the setting of cementitious materials and depresses the growth of early strength, especially within the age of 24 h. Therefore, in this context, low retarding PCE is often desired in some applications, such as prefabricated concrete, low temperature construction etc. The commonly used method to improve the early

strength in engineer is to add early strength agent, sucn as TEA.[29,30] The silylated PCE, proposed in this article, provides a promising technical approach to overcome the retardation drawback of traditional PCE.

To confirm the benefits of the silylated PCE to mechanical properties, compressive and flexural strength of cement mortar with addition of various polymers were measured at ages of 3, 7, and 28 days, as presented in Figure 11. It can be found that PCE at low dosage (0.2% bwoc) exhibits positive influence on the compressive strength of mortars at the tested ages. However, the high dosage of 1% bwoc is harmful to the compressive strength development of cement mortars. The flexural strength shows the same trend as the compressive strength at the two different dosages. The mortar sample with P(H1A1) shows the highest flexural strength. The addition of silylated PCE, however, can significantly increase the 3 days compressive strength at the two different dosages and has little influence on the late compressive strength (28 days) compared to the reference sample. In addition, the flexural strength of the cement mortars with the addition of silylated PCE can be slightly increased after curing for 28 days compared to the reference sample at the two different dosages. Compared to the traditional PCE, the addition of silylated PCE significantly increases the mechanical property of cement mortar at the dosage of 1.0% bwoc, but this phenomenon is not notable at the dosage of 0.2% bwoc. For HPEG–TMSPMA–AA ternary copolymer, an admirable mechanical property can be observed in both compressive and flexural strength. In summary, an appropriate incorporation of silane groups into PCE can improve the performance of the traditional PCEs in different aspects, such as higher fluidity retention ability, enhanced sulfate resistance, less retardation effect on cement hydration and higher early strength of cement mortars.

CONCLUSIONS

In this study, a series of silylated PCE were synthesized, and their plasticizing effectiveness in fcps was evaluated. The working mechanism and the influence of synthetized polymers on cement hydration and strength development were discussed. Based on the results, the following conclusions can be drawn.

Unlike the physical adsorption of the traditional PCEs driven by the electrostatic interaction between PCE and cement grains, the silylated PCE can be adsorbed on cement grains through the chemical bonding between polymers and cement grains. Fluidity tests indicate that the silylated PCEs exhibit dispersing capability but not as strong as the traditional PCEs at a given dosage. An appropriate introduction of the silane groups in PCE molecules, such as HPEG–TMSPMA–AA ternary copolymer, may work effectively as a superplasticizer and the performance can be even better than the traditional PCE, for example, higher fluidity retention ability and enhanced sulfate resistance.

Compared to the traditional PCE, such as the HEPG–AA polymers, the silylated PCEs (HEPG–TMSPMA copolymers) exhibit much lower negative impacts on cement hydration. In addition, mechanical strength tests reveal that the addition of silylated PCE increase the 3 days compressive strength of mortar without negative influences on the long-term compressive strength. The

flexural strength of cement mortar with the addition of silylated PCE are also slightly increased after curing for 28 days compared to the reference sample. The silylated PCE shows stronger ability to improve the mechanical property of cement mortar at dosage of 1.0% bwoc compared to the traditional PCE, but this phenomenon is not notable at the dosage of 0.2% bwoc.

All results suggest that an appropriate incorporation of silane groups into PCE provides a promising technical approach to improve the performance of the traditional PCEs, such as higher fluidity retention ability, enhanced sulfate resistance, less retardation effect on cement hydration, and higher early strength of cement mortars.

AUTHORSHIP

Professor Kong put forward the research direction and participated in the experiment design. Zichen Lu and Hui Liu mainly conducted these experiments, and Zichen Lu finished the draft. Ziming Wang, Yanrong Zhang, Biqin Dong, and Feng Xing participated in the analysis of the experimental data and provided their valuable suggestions. All of the authors had made the substantial contribution to this article.

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