

Influence of the Structural Modification of Polycarboxylate Copolymer with a Low Dispersing Ability on the Set-retarding of Portland Cement

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Abstract

Two structurally modified polycarboxylate (PC) copolymers were synthesized to explore the influence of structural modification with these polymers on the set-retarding of Portland cement. The dispersion ability of these polymers was eliminated by introducing very short graft side chains. The synthesized copolymer structures were verified by FTIR, GPC and ¹H NMR analyses. The initial and final setting times, polymer adsorption capability, strength development, paste fluidity, and XRD of hardened pastes were tested. The test results indicate that the PC copolymers do not increase the cement paste fluidity due to their short graft side chain length, while a significant set-retarding effect is observed when the polymer structure is highly anionic, with the set-retarding effect increasing linearly with polymer dosage up to 1%. The adsorption of copolymer on cement grains rapidly reaches saturation within 5 minutes after mixing for both polymers. Adding these PC copolymers does not noticeably change the early strength development, although the polymers selectively affect the hydration behavior of C₃S and C₂S at very early ages. Early hydration of groups, such as C₃S, C₂S, C₃A and C₄AF, is not likely to be significantly involved in the mechanism by which carboxylate copolymers with very short graft chains delay cement setting.

Keywords: *copolymers, plasticizer, surfactants, setting time, hydration*

1. Introduction

Polycarboxylate (PC) copolymers have been recognized in modern concrete technology as effective superplasticizers (Habbaba *et al.*, 2012; Lu *et al.*, 2010; Lv *et al.*, 2013; Lv *et al.*, 2012; Palacios *et al.*, 2009; Weng *et al.*, 2010). The term ‘superplasticizer’ refers to high-range water-reducing agents with high cement dispersal without resulting in a significant change in setting behavior (Cheung *et al.*, 2011; El-Hosiny and Gad, 1995; Taylor, 1997). Polycarboxylate (PC) superplasticizers have received more interest from industry than most water-reducing agents. PCs possess comb-shaped co-polymeric structures consisting of two separate parts: (a) anionic carboxylate groups, which allows the polymers to adsorb on the surfaces of

cement grains or hydrates; and (b) non-adsorbing graft side chains with no adsorption ability (Houst *et al.*, 2008; Janowska-Renkas, 2013; Lv *et al.*, 2013; Ran *et al.*, 2009; Yamada *et al.*, 2000; Yoshioka *et al.*, 1997; Zingg *et al.*, 2009). The structures of PC superplasticizers are highly flexible and amenable to modification (Houst *et al.*, 2008). Previous studies concluded that the major source of the high dispersion ability of PC superplasticizers in fresh cement paste systems is the steric hindrance effect due to the presence of long graft side chains rather than electrostatic repulsion (Han and Plank, 2013; Yoshioka *et al.*, 1997). Because the functional effectiveness and efficiencies of PC copolymers are generally affected by variations in the chemical structure (in particular, the number and length of graft side chains), many previous studies have discussed the

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influences of these structural changes on the mechanisms and effects of these polymers. However, most earlier studies of PC copolymers have focused on their cement dispersing effects without devoting much attention to their set-retarding effects, although the mechanism of dispersion induced by these copolymers occurs together with notable set-retarding of the cement concrete mixture (Habbaba *et al.*, 2012; Habbaba and Plank, 2012; Han and Plank, 2013; Houst *et al.*, 2008; Janowska-Renkas, 2013; Lu *et al.*, 2010; Lv *et al.*, 2013; Lv *et al.*, 2012; Palacios *et al.*, 2009; Ran *et al.*, 2009; Yamada *et al.*, 2000; Yoshioka *et al.*, 1997; Zingg *et al.*, 2009).

Setting of Portland cement concrete is defined as the onset of solidification of concrete in the plastic state (Dhinakaran *et al.*, 2012; Mehta and Monteiro, 2006; Taylor, 1997). ASTM (American Society for Testing and Materials) C403 defines the penetration resistance test used to measure setting time. Initial setting time is the time at which a flowable cement paste (or concrete mixture) begins to solidify, which indicates the approximate time limit of handling. The final setting time is roughly the time point at which the paste (or concrete) completes solidification and begins to increase in strength. After initial setting occurs, cement paste (or concrete) can no longer be appropriately handled at construction sites, and thus all concrete casting work must be completed prior to the initial setting time (Mehta and Monteiro 2006; Taylor 1997). Thus, the setting time of cement (or concrete) is an important engineering characteristic that must be controlled (Ozturk and Baradan, 2011; Uddin *et al.*, 2013).

Therefore, in the present study, two structurally modified PC copolymers were synthesized by varying the molar ratios between the Acrylic Acid (AA) and poly (ethylene glycol) methyl ether methacrylate (MPEG550) portions to better understand the set-retarding mechanism of PC copolymers. To remove the dispersing ability of these PC copolymers, the lengths of the graft side chains of the copolymers used in this study were designed to be much shorter than those used in previous studies (Han and Plank, 2013; Yamada *et al.*, 2000; Yoshioka *et al.*, 1997; Zingg *et al.*, 2009). The modified polymer structures were verified by FTIR, GPC and ^1H NMR analyses. The effects of these structural modifications were investigated by testing the initial and final setting times, polymer adsorption, development of the strength of the cement paste, paste fluidity, and X-ray powder diffraction of hardened cement pastes.

2. Experimental

2.1 Materials and Sample Preparations

Portland cement (type 1, KSL 5201) was purchased from Lafarge Halla Cement Co., Korea, and its chemical oxide composition was examined by an X-ray fluorescence (XRF)

spectrometer (Bruker S8 Tiger wavelength dispersive XRF spectrometer) as shown in Table 1.

Two PC copolymers (denoted AP75, AP25) were synthesized using Acrylic Acid (AA) (Samchun Chemical, Korea) and poly(ethylene glycol) methyl ether methacrylate (MPEG550) (GEO Specialty Chemicals, UK) with an average side chain length of 10.5 ethylene oxide units. Because the dispersion ability of PC dispersing agents is attributable to the steric hindrance effect resulting from the long graft side chains (Han and Plank, 2013; Yoshioka *et al.*, 1997), the PC used in this study has a much shorter graft side chain length than those of other similar studies (see the chain length of 10.5 in Fig. 1) (Han and Plank, 2013; Yamada *et al.*, 2000; Yoshioka *et al.*, 1997; Zingg *et al.*, 2009).

The molar ratios between the AA and MPEG550 units are 75:25 for AP75 and 25:75 for AP25. The general structure of the PC copolymers synthesized here is shown in Fig. 1, where '*m*' refers to the number of MPEG550 units and '*n*' indicates the number of AA units.

Figure 2 schematically illustrates the synthetic process used to generate the PC copolymers in this study. For the synthesis of AP75, 0.281 g of α, α' -azobis(isobutyronitrile) (AIBN) (Junsei Chemical, Japan) was added to the main ingredient chemicals (44.6 ml of AA and 108 ml of MPEG550) as a radical initiator for polymerization in 300 ml of Dimethylformamide (DMF) (Samchun Chemical, Korea). The solution mixture was reacted at 70°C for 30 minutes under an inert atmosphere with gentle stirring until a gel formed. The gel was mixed with ethyl ether (Fisher Scientific) and hexane (Samchun Chemical, Korea) to remove remaining monomers, AIBN, and DMF. The mixture was centrifuged at 5000 rpm for 3 minutes, and the resulting supernatant was discarded. These washing steps were repeated 2~3 times to obtain pure polymers. AP25 was synthesized by reacting 7.65 ml of AA and 144.48 ml of MPEG550 without any other changes to the method. Purified AP75 and AP25 were then

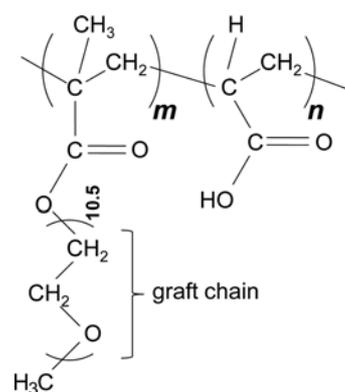


Fig. 1. General Chemical Structure of Synthesized PC Copolymers

Table 1. Oxide Composition (wt.%) of Portland Cement used in this Study

| CaO | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | MgO | SO ₃ | K ₂ O | Na ₂ O | MnO | TiO ₂ |
|------|------------------|--------------------------------|--------------------------------|-----|-----------------|------------------|-------------------|-----|------------------|
| 62.8 | 18.6 | 4.3 | 3.2 | 4.4 | 3.8 | 1.4 | 0.5 | 0.3 | 0.2 |

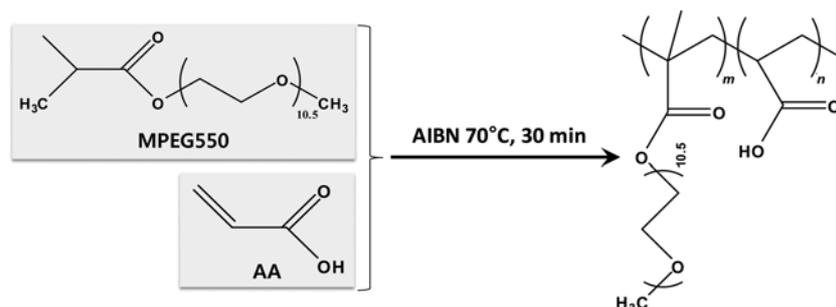


Fig. 2. Schematic Diagram of the Synthesis of PC Copolymers in this Study

characterized by Fourier-transform infrared spectroscopy (FT-IR), Nuclear Magnetic Resonance (NMR), and Gel Permeation Chromatograph (GPC).

Cement paste samples were prepared by mixing Portland cement with water containing copolymers in specified amounts. The pastes were mixed using a mechanical mixer following the steps specified in ASTM C305-11: (1) mixing for 30 seconds at a slow rotary speed of 140 ± 5 rpm; (2) mixing for another 30 seconds at an intermediate speed of 285 ± 10 rpm; (3) standing without mixing for 90 seconds; (4) mixing for 60 seconds at an intermediate speed of 285 ± 10 rpm. The water/cement (w/c) ratio was set to 0.28 for the flow test, setting time measurement, and compressive strength testing. The fresh cement pastes were cast into $5 \text{ cm} \times 5 \text{ cm}$ cubic molds for strength testing and cured under 99% relative humidity at $23 \pm 2^\circ\text{C}$ before testing. Compressive strength testing was carried out for four identical samples at 3 days and 14 days of curing.

2.2 Test Methods

FT-IR spectra of AP75 and AP25 were recorded using a 670-IR spectrometer (Agilent, USA). ^1H NMR spectra of AP75 and AP25 were obtained using a VNMRS 600 NMR spectrometer (Agilent, USA). The molecular weights (M_w , M_n) and Poly-Dispersity Index (PDI) for AP75 and AP25 were measured using a 1260 infinity Gel Permeation Chromatograph (GPC) (Agilent, USA) with a differential refraction detector to measure the polymer molecular weights. Tetrahydrofuran (THF) was used as an eluent with a flow rate of 1 ml/min at 23°C .

The adsorption abilities of the PC copolymers were evaluated by measuring adsorbed carbon contents using Flash 2000 element analyzer mass spectroscopy (Thermo Scientific, Netherlands). The samples for elemental analysis were prepared by reacting Portland cement with/without 10 wt% (to cement) polymers for 5 and 10 minutes. The amounts of carbon in the samples were measured as the relative wt % ratio three times within the error range of 0.005 wt%.

The initial and final setting times for cement pastes with/without the PC copolymers were measured according to ASTM C191-08 using a fully automatic Vicat needle apparatus (Vicatronic, Humboldt Mfg. Co., USA) in a driven mode.

The flow characteristic of each fresh cement paste was examined in accordance with ASTM C 1437-07, which was

originally designed for hydraulic cement mortar, using a flow table complying with ASTM C 230/C 230 M.

After strength testing, the fractured pieces of 3-day samples were collected and finely ground for powder X-Ray Diffraction (XRD). The 300-minute cured samples were also collected for XRD, but because these samples were still before the final setting, the pastes were dried using isopropanol and then finely ground. The samples were solvent-exchanged with isopropanol and vacuum dried for 24 hours to stop hydration and remove any remaining solvent (Zhang and Scherer, 2011).

Powder X-Ray Diffraction (XRD) measurements were performed for 300-minute and 3-day cured samples to determine whether the copolymers had any influence on the early hydration products of cement clinker compounds using a Rigaku high power X-ray diffractometer employing $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) with a 2θ scanning range of 5° – 60° at room temperature.

3. Results and Discussion

The peaks in the FTIR spectra for AP75 and AP25 are assigned (Workman, 2000) as shown in Fig. 3. The peaks from the acrylic acid components of the polymers are assigned to 3522 cm^{-1} and 1672 cm^{-1} , as designated by asterisks (*). The broad peaks at 3522 cm^{-1} arise from $-\text{OH}$ stretching vibrations. The peaks at 2872 cm^{-1} correspond to the $\text{O}-\text{CH}_3$ stretching of MPEGS50. The 1727 cm^{-1} and 1672 cm^{-1} peaks match the $\text{C}=\text{O}$

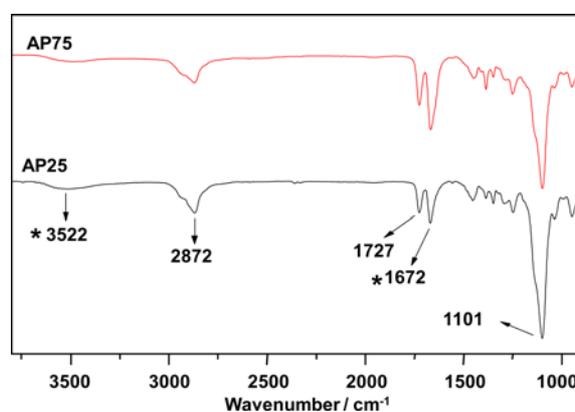


Fig. 3. FTIR Spectra of the PC Copolymers

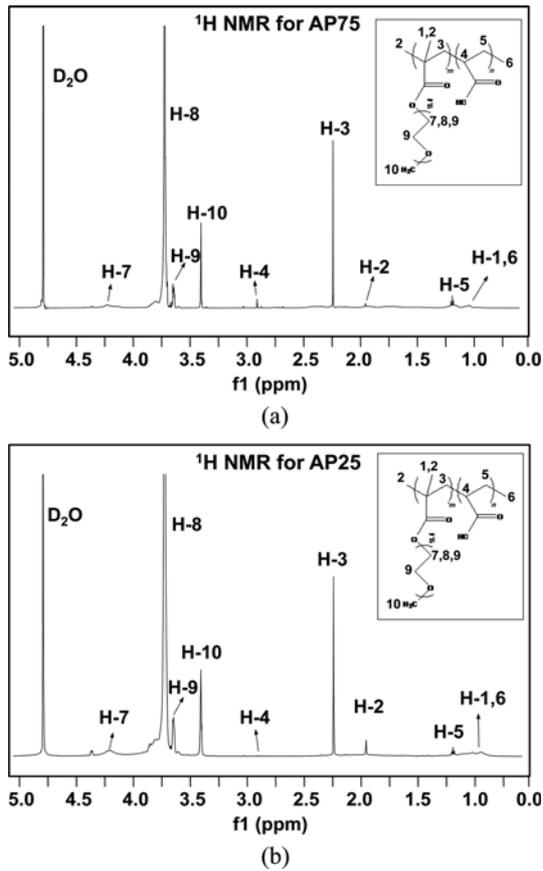


Fig. 4. ¹H NMR Spectra of: (a) AP75 Copolymers, (b) AP25 Copolymers

stretching vibrations in the aldehydes of MPEG550 and the carboxylic acid of AA, respectively. The peaks at 1101 cm⁻¹ are from asymmetric C-O-C stretching in MPEG550.

Figure 3 demonstrates that no monomers remain after synthesis, as no peak for C=C stretching is observed. A comparison of the peak intensity between AP25 and AP75 for the MPEG500 peaks at 1101 cm⁻¹ and 2872 cm⁻¹ verifies that AP25 has a higher ratio of PEG branches than AP75, as expected.

¹H NMR spectra of AP75 and AP25 are presented in Fig. 4,

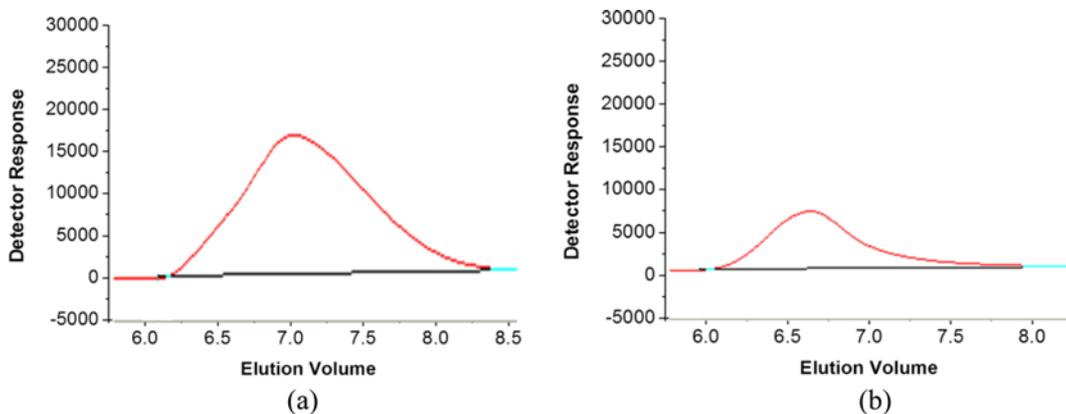


Fig. 5. GPC Data for: (a) AP75, (b) AP25

where each ¹H NMR peak is assigned to a structural component as numbered in the inset figure as follows (Sasaki and Center 1986): H-1, 6 (1.1-0.8 ppm), H-2 (2.0 ppm), H-3 (2.2 ppm), H-4 (2.9 ppm), H-5 (1.192 ppm), H-7 (4.2 ppm), H-8 (3.7 ppm), H-9 (3.6 ppm), H-10 (3.4 ppm).

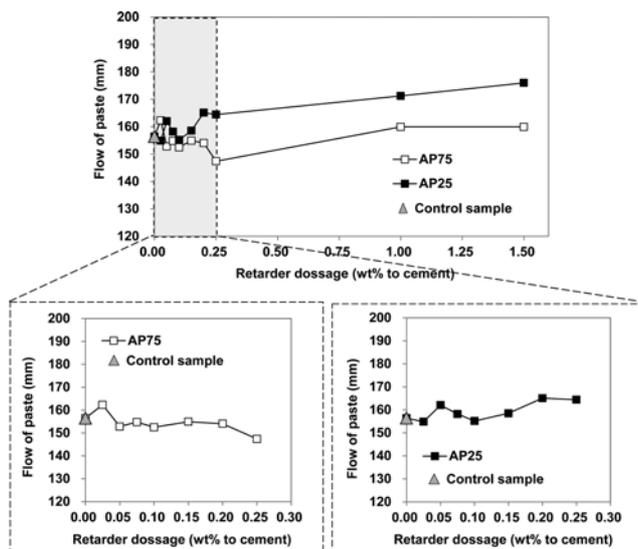
In the GPC result shown in Fig. 5, the number average molecular weight (M_n) and the weight average molecular weight (M_w) for AP75 are found to be 2.26×10^4 g/mol and 3.88×10^4 g/mol, respectively, with a PDI (polydispersity index) of 1.72, implying that the synthesized polymer has a narrow molecular weight distribution. The molecular weight distribution of AP25 is also found to narrow ($M_n = 3.64 \times 10^4$ g/mol, $M_w = 5.97 \times 10^4$ g/mol, and PDI = 1.64).

The elemental analysis results in Table 2 show that the total carbon contents of AP75 and AP25 do not change from 5 minutes after cement mixing begins, implying that the adsorption reaction rapidly reaches saturation. Note that the carbon content of the control cement sample is 0% because the amount of carbon in the sample was below the instrument detection limit. Note that there is no visible difference between the adsorption amounts of AP75 and AP25 as in Table 2, although these copolymers contain different amounts of AA units in their structures. If any observable adsorption difference does occur, it takes place before saturation, i.e., within 5 minutes after mixing begins.

The flow tests of the fresh cement pastes were carried out to evaluate any differences in dispersion effectiveness resulting from the structural differences between the two copolymers. Fig. 6 presents the flow test results for the cement pastes admixed with 0% to 1.5% of the copolymers. The results show no notable dispersion effect for either copolymer, confirming that a co-

Table 2. Polymer Adsorption of AP75 and AP25 (w/c = 0.28)

| Sample | Carbon adsorption weight (wt% to cement) | |
|---------|--|--------------|
| | After 5 min | After 10 min |
| Control | 0.00% | 0.00% |
| AP75 | 1.11% | 1.06% |
| AP25 | 1.17% | 1.19% |

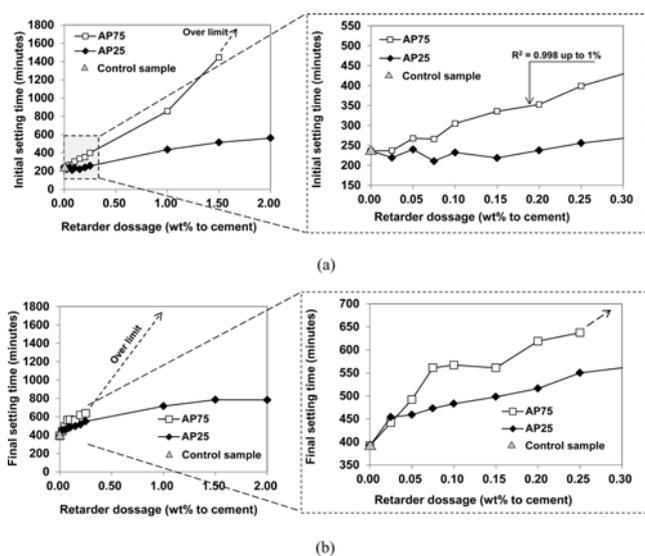


* Control sample does not contain any copolymers.

Fig. 6. Fluidity of Cement Pastes (w/c = 0.28) with/without Copolymers

polymer with a short graft chain length of 10.3 is not capable of increasing the fluidity of the cement paste (Yamada *et al.*, 2000) even when the copolymer contains a large number of side chain units or when a large amount is added. However, these results still show that a higher number of graft chains in the copolymer structure (i.e., AP25) improve the plasticizing performance for cement paste.

Figure 7 demonstrates the set-retarding effects of the copolymers up to 2.0% addition. Note that while all setting times for AP25 were measured for the entire dosage range, AP75 could not be measured over 1.0% for initial setting, nor above 0.25% for final setting because of the limits of the instrument, which has



* Control sample does not contain any copolymers.

Fig. 7. Retarding Effect of Copolymers on Cement Paste (w/c = 0.28) for: (a) Initial Setting Time, (b) Final Setting Time

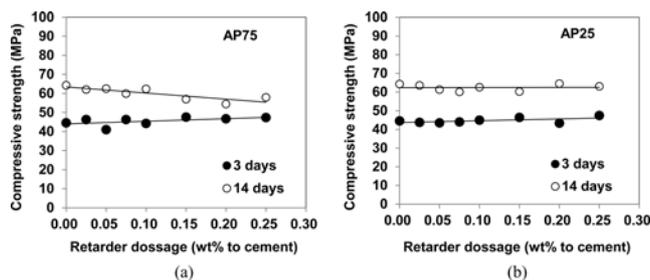
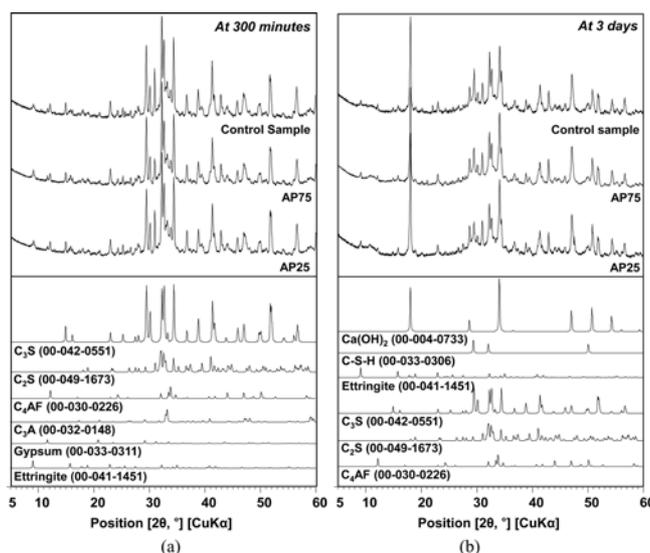


Fig. 8. Effects of Copolymers on Compressive Strength at 3 Days and 14 Days (w/c = 0.28) for: (a) AP75, (b) AP25



* Control sample does not contain any copolymers.

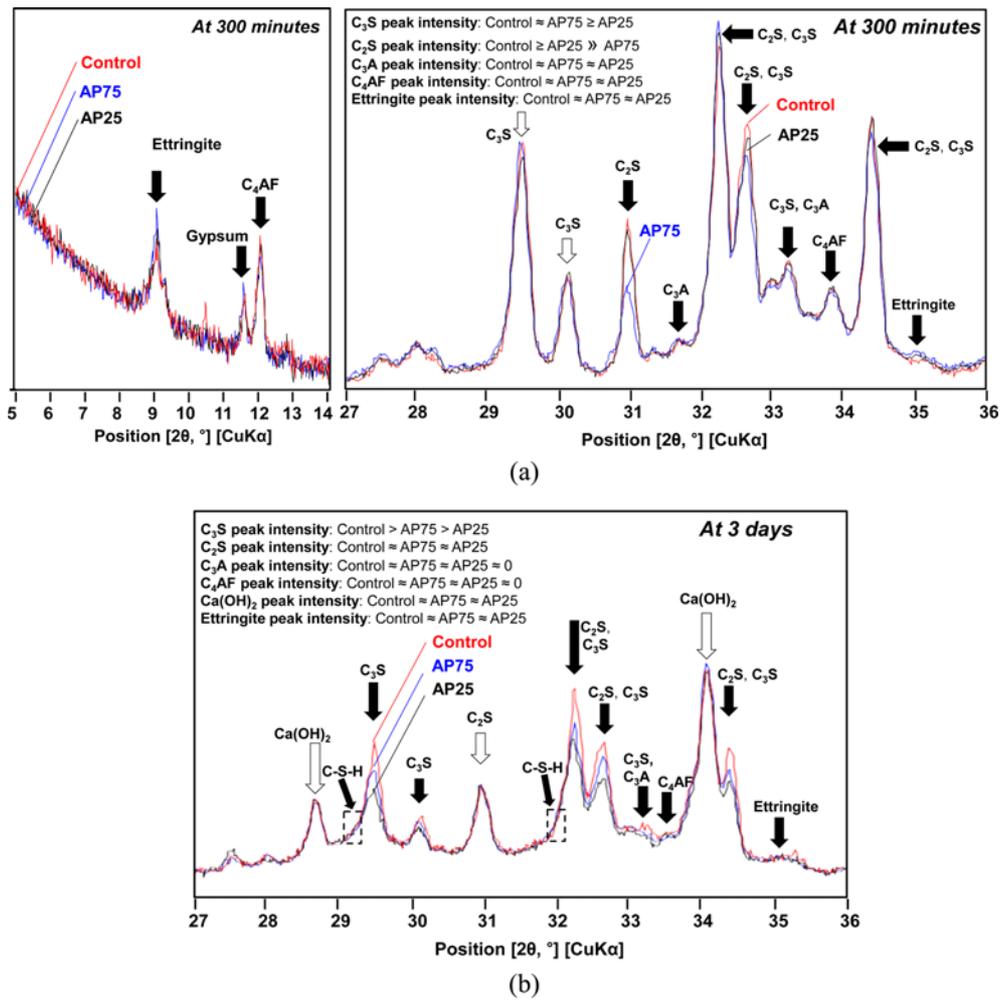
Fig. 9. XRD Patterns: (a) 300 Minutes, (b) 3 Days after Starting the Mixing of Cement Pastes (w/c = 0.28) with/without 0.25% Copolymer

a maximum measurement time of ~1,400 minutes.

Below 0.25%, AP25 shows almost no initial setting delay while AP75 displays relatively effective set-retarding performance. Note that the initial setting time for AP75 has a highly linear proportional relationship ($R^2 = 0.998$) to the polymer dosage up to 1.0% usage. The ability of AP75 to retard the initial setting is similar to the effects of sorbitol or xylitol when used in similar dosages (Zhang *et al.*, 2010). This result verifies that the set-retarding effect is mainly due to the presence of anionic groups in AA units as reported in earlier studies (Cheung *et al.*, 2011).

No early strength reduction is observed at 3 days for either copolymer, while a trivial reduction in 14-day strength is observed for increasing doses of AP75 (see Fig. 8(a)).

Figure 9 presents the XRD patterns of the cement pastes captured after 300 minutes and 3 days of curing for the samples with/without 0.25% copolymer. At 300 minutes, the AP75 sample has not gone through the initial setting, while the control and AP25 pastes have passed the initial setting time. Note that Portland cement mainly consists of four major clinker compounds: (1) tri-calcium silicate (Ca_3SiO_5 , i.e., C_3S); (2) di-calcium silicate (Ca_2SiO_4 ,



* Control sample does not contain any copolymers.

Fig. 10. Comparison of XRD Patterns between Samples (w/c = 0.28) for: (a) 300 Minutes, (b) 3 Days after Mixing of Cement Pastes with/without 0.25% Copolymer

i.e., C₂S); (3) tri-calcium aluminate (Ca₃Al₂O₆, i.e., C₃A); and (4) tetra-calcium aluminoferrite (Ca₄Al₂Fe₂O₁₀, i.e., C₄AF) (Taylor, 1997).

After 300 minutes of curing, all the cement clinker compounds are still observed, without significant reductions in peak intensities. The only cement hydration product formed by this time is ettringite. At 3 days, C₃A, C₄AF and gypsum peaks have almost disappeared along with the presence of C-S-H, Ca(OH)₂ and ettringite, but no apparent difference in peak intensity can be observed among the control, AP75 and AP25 samples for each hydration product.

Comparison of the detailed XRD patterns in Fig. 10 provides more useful information. At 300 minutes, no differences in peaks are observed between the control, AP75 and AP25 samples for the C₃S, C₃A, C₄AF and ettringite phases, but the use of AP75 leads to a greater reduction in the intensity of C₂S peaks (= a greater degree of hydration of C₂S). Given that the setting delay was only obvious in the case of AP75, the greater degree of C₂S hydration is interesting, but this greater degree of C₂S hydration

disappeared after 3 days of curing.

After 3 days, as shown in Fig. 10(b), the use of copolymer with more PEG branches (i.e., AP25) promotes a higher degree of C₃S hydration at 3 days while it makes no difference for C₂S hydration or for the formation of C-S-H, Ca(OH)₂ and ettringite. This result might appear to be inconsistent with earlier studies, which reported that similar polycarboxylate superplasticizers inhibited the formation of ettringite and Ca(OH)₂ (Lv *et al.*, 2013) or affected the initiation of C₃S hydration (Yamada *et al.*, 2000). However, note that because those studies focused on fluidity enhancement, those superplasticizers possessed much longer side chains, leading to high dispersing effects, possibly with different mechanisms of action. Note also that Fig. 8 demonstrates that the 3-day strengths are not influenced by the use of the copolymers despite the different degrees of hydration of cement compounds. Therefore, although the addition of copolymers may selectively affect the degrees of hydration of C₃S and C₂S to some extent, the early hydration of C₃S, C₂S, C₃A and C₄AF is not likely to be significantly involved in the setting-

delay mechanism in the case of carboxylate copolymers with short graft side chains.

4. Conclusions

This study explores the influence of the structural modification of polycarboxylate copolymer with little dispersing capability on the set-retarding of cement paste by examining two synthesized copolymers. The results lead to the following conclusions:

1. Two PC copolymers were successfully synthesized using acrylic acid and poly (ethylene glycol) methyl ether methacrylate with an average side chain length of 10.5 ethylene oxide units.
2. The FTIR analysis demonstrates that no monomers (i.e., the raw materials for the polymer synthesis) remain after synthesis. The ¹H NMR spectra and GPC results of AP75 and AP25 illustrate the successful synthesis of the expected AP75 and AP25 structures. Carbon elemental analysis of the polymer adsorption to cement grains demonstrates rapid adsorption saturation of the polymers.
3. The short graft chain length of 10.3 for both polymers is not capable of significantly increasing the fluidity of cement pastes, even when a polymer contains a large number of side chain units or when a large amount is added, confirming that the side chain length is a major factor in the dispersing capability of PC superplasticizers. However, increasing the number of graft chain units in the polymer structure tends to slightly improve dispersing performance in cement paste despite the short chain length.
4. The set-retarding effect is mainly due to the presence of the anionic groups of acrylic acid units. Below 0.25%, AP25 does not induce any visible initial setting delay, while AP75 is relatively more effective in set-retarding. The initial setting time for AP75 is linearly proportional ($R^2 = 0.998$) to the polymer dosage up to 1.0% usage.
5. No early reductions in strength at three days are observed for either polymer. The XRD analysis indicates that although the two different copolymers selectively affect the degrees of C₃S and C₂S hydration to some extent at early ages, the early hydrations of C₃S, C₂S, C₃A and C₄AF are not likely to be significantly involved in the setting-delay mechanism for the carboxylate copolymers with very short graft chains.

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