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Evaluating the operational properties of concrete admixtures containing molecularly modified polycarboxylate superplasticizers

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The objective of this study focused on the design and preparation of a molecularly modified polycarboxylate superplasticizer to develop concretes with enhanced engineering features. For this purpose, polyethylene glycol was chemically modified with maleic anhydride to give the mono polyethylene glycol maleate (MPEGM). Then, polycarboxylate superplasticizer comprising of isoprenyl oxy polyethylene glycol (TPEG) and acrylic acid (AA, PCE-1), and the synthesized MPEGM with TPEG and AA (PCE-2) were prepared through solution radical polymerization. Subsequently, concrete mixtures with different dosages (0, 0.1, 0.15, 0.2, 0.25, 0.3 wt%) of PCE-1 and PCE-2 were prepared. Chemical structure of the synthesized MPEGM and superplasticizers together with their copolymer composition were identified by FTIR and ¹HNMR analyses. The molecular weights (M_w) and molecular weight distributions (PDI) of PCE-1 (8.74 × 10⁴, 1.36) and PCE-2 (8.74 × 10⁴, 2.19) were studied by GPC analysis, respectively. The zeta potential of cement particles (2.8 mV) becomes negative in the presence of 0.6 g/L of PCE-1 (−7.8) and PCE-2 (−9.5). This implies that electrostatic and steric hindrance forces of adsorbed superplasticizers synergistically provide a situation for appropriate dispersion of cement particles. The results of water-reducing percentage, fluidity, air content, bleeding water rate, initial and final setting times, wet density, flexural and compressive properties, and ultrasonic pulse velocity analyses exhibit significant enhancement on the features of concrete mixtures made of polycarboxylate superplasticizer. The superiority of PCE-2 to PCE-1 was connected to its adsorption-dispersibility potent induced by stronger electrostatic and steric repulsion forces, which result in quality and continuity enhancement in concretes.

Keywords Polycarboxylate, Superplasticizer, Concrete mixtures, Water reducer admixtures, Electrostatic and steric repulsion forces

Superplasticizers as high-grade water reducer admixtures are made of synthetic water-soluble macromolecules which are largely utilized in concrete mixtures^{1–4}. Chemical functional groups and molecular architecture of superplasticizers such as anchoring groups, polymer backbone, and length and density of side chains beside water quality show a significant effect on the performance of cement mixtures^{5–9}. These functional groups generate ionic interactions (electrostatic repulsive forces) and steric hindrance with cement particles, respectively^{10–12}. The repulsive interactions between cement particles result in concrete with special features like lower water consumption to achieve equal slump, enhanced workability, and improved strength of the cement-based materials^{10,13–15}.

Superplasticizers are categorized into three generations; (I) modified lignosulfonates (MLS), (II) sulfonated naphthalene formaldehyde (SNF) or sulfonated melamine formaldehyde (SMF), and (III) polycarboxylate superplasticizers (PCEs)¹⁶. Some drawbacks of lignosulfonates such as high dosage consumption and postponed setting time (especially in cold weather) together with the declining workability of SNF/SMF over time, especially in high-temperature environments, have limited their extended applications. However, the advantages of polycarboxylate superplasticizers such as prolonged concrete slump retention with reliable setting time at low dosages and well dispersing of cement particles have led to their wide development for achieving high-performance concrete¹⁷. Water-reducing and dispersion effects of polycarboxylate superplasticizers can be varied by controlling molecular weight and tuning the balance of lipophilic and hydrophilic moieties¹⁸. The structural modifications of PCEs including adjusting side chain lengths, polyether- or polyester-based side chains, creating functional

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groups, and modifying molecular topology have been extensively studied^{19–21}. For instance, the high density of negatively charged carboxylate groups on the polymer backbone makes reasonable initial dispersion, while exhibiting poor slump retention²². This was attributed to their quick adsorption on the surface of positively charged cement particles. On the other hand, short side-chain length and high grafting density are responsible for the dispersion of cement particles and making retardation effect on the hydration of cement particles^{23–25}. Polyester-based macromonomers such as ω -methoxy polyethylene glycol (MPEG) and polyether-based macromonomers like isoprenyl oxy polyethylene glycol (TPEG) are widely used as the common macromonomer in superplasticizers^{26–29}. He et al.³⁰ studied the influence of PCEs with various densities of carboxylic and functional groups on the adsorption, dispersing, and hydration behavior of cement particles. It was found that the increase in carboxylic density resulted in enhanced adsorption and initial dispersing ability and maximized the hydration degree during the acceleration period. The preparation of PCE superplasticizer comprising acrylic acid (AA), maleic anhydride (MA), and TPEG (as macromonomer) was reported by Li et al.²⁶. The prepared MA-modified PCE indicated remarkable fluidity and flow retention capabilities with high-range water reducers, which is suitable for practical concrete applications.

Major efforts have been devoted to developing new types of compatible PCEs with raw materials with higher dispersing capability and stability for the preparation of high-performance concrete mixtures. To develop the performance of the previously prepared PCE, MA will be reacted with PEG to construct a polyester-based mono-polyethylene glycol maleate (MPEGM) macromonomer in a new approach, firstly, and then copolymerized with AA and TPEG to fabricate the corresponding high-performance superplasticizer (PCE-2). In addition, AA and TPEG was copolymerized via solution radical polymerization to generate PCE-1 superplasticizer. After fully characterization of the prepared PCE-1 and PCE-2, their influence on the operational properties of concretes such as water-reducing percentage, fluidity, air content, bleeding water rate, slump retention, setting times, mechanical properties, and ultrasonic pulse velocity were studied and discussed.

Experimental Materials

Acrylic acid (AA) and ammonium persulfate (as the initiator, APS) were analytical grade and purchased from Merck Chemical Co. Isoprenyl oxy polyethylene glycol (98% purity, TPEG, with Mw of 2400) was supplied by China Liaoning Kelong Fine Chemical Co. Thioglycolic acid (as chain transfer agent, TGA), p-toluenesulfonic acid (PTSA), polyethylene glycol (PEG, with Mw of 1500), maleic anhydride (MA), and acetone were provided by Sigma-Aldrich. Deionized (DI) water was utilized in all recipes and formulations. All solvents and reagents were used without further purifications. Moreover, ASTM Type II Portland cement (PC), which meets ASTM C 150-07, with a strength class of 52.5 was used in this project. Cement's oxide composition, phase composition, and physical properties are shown in Table 1.

Synthesis of mono-polyethylene glycol maleate (MPEGM)

The mono-polyethylene glycol maleate (MPEGM) was synthesized through chemical modification of PEG1500 with MA according to the modified route reported before²⁷. For this reason, 9.12 g MA (93 mmol) and 0.16 g PTSA (0.93 mmol) were dissolved in 400 mL acetone in a round-bottom reactor equipped with a reflux condenser and mechanical stirrer and purged with N₂ gas. After complete dissolving, 139.5 g PEG (93 mmol) was added to the above mixture together with gentle mixing, while the temperature reached 80 °C. The esterification reaction continued for 2 h and then cooled down to room temperature. Finally, the acetone was eliminated by vacuum distillation and subsequently dried in an oven at 50 overnight to give the yellow MPEGM product (Fig. 1a).

Preparation of P(AA-co-TPEG) superplasticizer (PCE-1)

P(AA-co-TPEG) superplasticizer (PCE-1) was synthesized through water-based radical polymerization (Fig. 1b). For this reason, 40 gr TPEG (16.67 mmol) was dissolved in 100 mL DI water and transferred into a 250 mL three-necked round bottom reactor equipped with a mechanical stirrer (constant stirring at 400 rpm), condenser, and an inlet of inert N₂ gas. After raising the temperature to 65 °C, APS (1 part per hundred monomers) as the initiator was added to the reactor mixture to start the polymerization reaction. Then, 7.2 g AA (100 mmol) and TGA (1 part per hundred monomers) were fed into the reaction within 3 h dropwise using a dropping funnel, while the temperature was kept constant at 65 °C during the polymerization reaction. After 3 h, the polymerization reaction continued for 2 h at 65 °C for completion of the reaction (reaching conversions of above 97%). At the end of the reaction, the reaction mixture was dried using an oven (with air condition) at 70 °C within 48 h, grounded, and purified (triplicate washing with acetone) to remove unreacted components and give P(AA-co-TPEG) superplasticizer (PCE-1)³¹. The monomer conversion and progress of polymerization were monitored and measured by gravimetric technique. It should be noted that the total solid content was kept constant at 32–33 wt% with a pH of 5 ± 1.

Oxide compositions (%)			Phase compositions (%)				Physical properties		
SiO ₂	CaO	TiO ₂ , K ₂ O, Na ₂ O, SO ₃ , MgO, Fe ₂ O ₃ , Al ₂ O ₃	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Specific gravity (g/cm ³)	Particle size (d ₅₀) (lm)	Fineness cm ² /g
22.5	65.8	0.275, 0.3, 0.4, 0.8, 1.8, 3.1, 4.6	61.5	18.1	6.9	9.43	3.11	15.23	3800

Table 1. The oxide compositions, phase compositions, and the physical properties of cement.

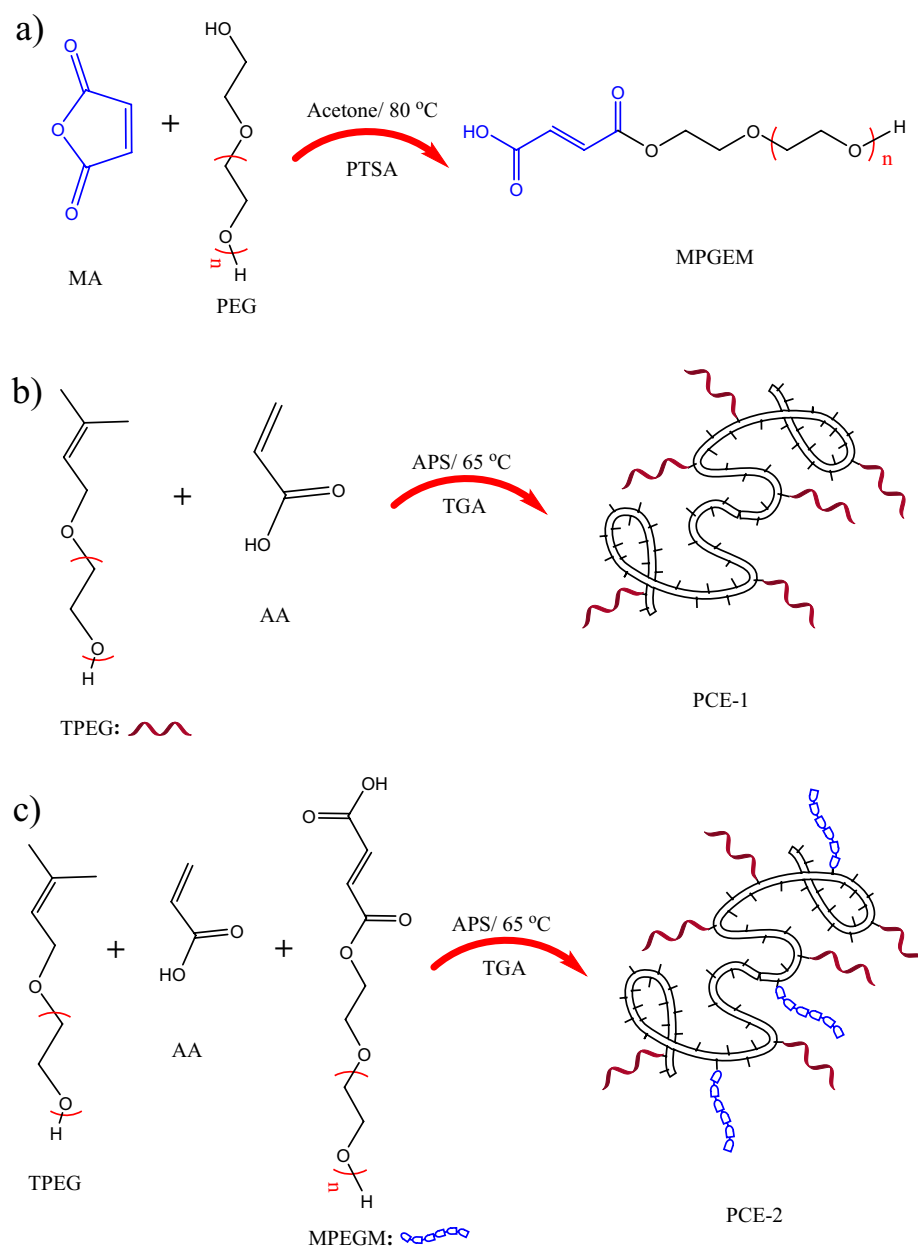


Fig. 1. Schematic representation of the synthesis of MPEGM (a), and preparation of PCE-1 (b) and PCE-2 (c) by water-based solution radical copolymerization.

Preparation of P(AA-co-TPEG-co-MPEGM) superplasticizer (PCE-2)

P(AA-co-TPEG-co-MPEGM) superplasticizer (PCE-2) was prepared in a procedure similar to PCE-1 (Fig. 1c). In general, a 182 mL aqueous solution containing 40 g TPEG (16.67 mmol) and 13.32 g MPEGM (8.33 mmol) was poured into a 400 mL three-necked round-bottom reactor with a mechanical stirrer (operating at 400 rpm), reflux condenser, and purged under a flow of N_2 gas. The reactor temperature was set at 65 °C, and then APS (1 part per hundred monomers) was fed into the reaction to start the reaction. Afterward, 7.2 g AA (100 mmol) and TGA (1 part per hundred monomers) were added to the reactor within 3 h dropwise using a dropping funnel. After the addition of monomers, the polymerization continued for 2 h at 65 °C until reaching conversions greater than 97%. It should be noted that the produced PCE-2 copolymer was purified similar to PCE-1 and monomer conversion was obtained by the gravimetric method.

Production of concrete mixtures

A fixed weight ratio of cement/fine aggregate/total coarse aggregates mixtures of 1/1.75/2.95 was used to prepare concrete mixtures (the cement content in each concrete mixture was kept constant at 340 kg/m³). The weight ratio (wt%) of each PCE-1 and PCE-2 superplasticizer to cement was considered 0, 0.1, 0.15, 0.2, 0.25, and 0.3 wt% in the process of concrete mixture fabrication. The prepared concrete mixture without superplasticizers was

considered as the control sample. The amount of mixing DI water for each dosage of PCE-1 and PCE-2 superplasticizers was manipulated until the initial slump value of 200 ± 15 mm was achieved.

In general, solid materials (cement and fine aggregate) are dry mixed for 1 min, and then the determined amount of freshly premixed water and PCE-1 or PCE-2 superplasticizers is added to the solid materials. The mixing process continued for 5 min to give a homogeneous concrete mixture. The freshly prepared concrete mixture was instantly subjected to various analyses such as; water reduction, initial fluidity, slump retention, bleeding water rate, air content, wet density, and initial and final setting times, which have been described in the following.

In addition and to investigate the compressive strength of the cured concrete mixture, the fresh concrete mixtures were transferred into the molds and subjected to 2–3 min of vibration to create a homogeneous and compact concrete mixture. Under GOST 10180³², the produced molds were kept in an environment with a temperature of 20 °C for 24 h. Finally, the concrete samples were removed from the molds and placed in water at a temperature of 20 °C for 3, 7, and 28 days.

Characterization

Functional groups and chemical structure of the synthesized MPEGM and the fabricated PCE-1 and PCE-2 superplasticizers were investigated by Fourier-transform infrared spectroscopy (FTIR, BRUKER-IFS48 spectrophotometer, Germany). Chemical composition of the prepared PCE-1 and PCE-2 were investigated using ¹HNMR spectroscopy (AVANCE 400 MHz spectrometer, Germany) in D₂O as the solvent and tetramethylsilane as the internal reference. The average molecular weight and polydispersity index (PDI) of the prepared PCE-1 and PCE-2 copolymers were measured using an Agilent 1100 chromatographic apparatus (Santa Clara, CA/USA). Polyethylene glycol and chromatographic grade water were used as the calibration standard and solvent, respectively. An aqueous solution of Na₂SO₄ (0.1 M, as the eluent) at a flow rate 0.5 mL/min was used during analysis.

The interaction between PCE-1 and PCE-2 superplasticizers and the cement particles were investigated by Zeta potential analyzer. For this purpose, 200 mg of cements was dispersed in 100 mL DI water. Then, different concentrations (0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, and 1g/L) of PCE-1 and PCE-2 was added to the above-prepared cement slurry. Zeta potential measurements were done on a Brookhaven Instruments Corporation (US) at a temperature of 22 ± 1 °C. Before analysis, cement suspensions were shaken for 10–15 min. The evaluation of the wet density of freshly mixed concrete was carried out using the methodology outlined in BS EN 12350-6³³. In this procedure, a container with defined dimensions was filled with fresh concrete, compacted, and weighed. By dividing the weight of the concrete in the container to the volume of the container the wet density (D) of the concrete (kg/m^3) was obtained.

Mechanical strength of the prepared concrete mixtures were studied by Tensile analysis using an STM-50 universal machine (Santam, Tehran, Iran). To measure the compressive strength of the prepared concrete mixtures, Cube-shaped specimens (100 mm × 100 mm × 100 mm) of the concretes were prepared according to BS EN 12390-3 method and analyzed at a constant loading rate (0.3 N/mm²)³⁴. Before analysis, the prepared cube specimens were stored in water at a temperature of 37 ± 1 °C for 3, 7, and 28 days to ensure proper hydration and strength development. Then, the hydrated concrete samples at different times were separated from the water and immediately analyzed in 3 replicates to survey their mechanical properties. To study the flexural strength of the prepared concrete mixtures, rectangular cube specimens with the dimensions of 100 mm × 100 mm × 400 mm were prepared and then a three-point flexural test was done according to BS EN 12390-5 standard³⁵. The condition of flexural testing was similar to compressive test and rectangular concrete specimens were stored in water for 3, 7, and 28 days. The prepared concrete specimens were analyzed at a constant loading rate of 0.05 N/mm². Statistical Analysis was performed by Originlab software package (2022 version) at the significance level of $p < 0.05$, using Tukey's test³⁶. The ultrasonic pulse velocity (UPV) test was conducted after surface preparation and transducer placement following the guidelines of ASTM C597-16b³⁷. For this purpose, three cubic concrete mixture specimens with dimensions of 100 mm × 100 mm × 100 mm were prepared and after 3, 7, and 28 days of water curing analyzed.

Water reduction percentage

The water reduction percentages of the prepared PCE-1 and PCE-2 superplasticizers at various dosages in the concrete mixture have been measured based on ASTM C494³⁸. The values of slump for all concrete mixtures were controlled within the range of 200 ± 15 mm. The difference between the water consumption of the reference sample (concrete mixture without superplasticizer) and concrete mixtures containing superplasticizers was used to estimate the amounts of water reduction percentage of the prepared superplasticizer in concrete.

Fluidity and fluidity preservation

The fluidity of the freshly produced concrete was investigated by pouring the fresh concrete into the slump cone and compacting and then the slump cone was lifted vertically. The initial slump of the concrete (representative of fluidity) was estimated as the difference between the height of the cone and the highest point of the sample. This analysis was carried out according to the BS EN 12350-2 standard test method³⁹. The ability to retain fluidity was evaluated by measuring the variation of slump of the concrete with 30, 60, 90, and 120-min intervals. It is noteworthy that, each concrete sample was remixed for 20 s before analysis.

Air content and bleeding water rate

The air content of the freshly prepared concrete mixture was measured using the pressure gauge method based on BS EN 12350-7⁴⁰. For this reason, the concrete mixture was transferred into a sealed container and then it was charged with a specific volume of air under a defined pressure. The percentage of air content in the concrete mixture can be estimated based on the applied pressure. The bleeding water rate of the prepared concrete mixture

was investigated by the described methodology outlined in BS EN 480-4 standard test method⁴¹. For this purpose, the freshly prepared concrete mixture was transferred into a cylindrical mold and remained undisturbed for 60 min. Afterward, the collected water on the surface of the concrete mixture was separated and accumulated in a container at 10 (for 4 times) and 30 min (until the bleeding water was seasoned) intervals, respectively. Finally, by dividing the total weight of collected water from the surface of the concrete by the initial weight of the mixing water, the bleeding water rate (BWR) of each concrete mixture was determined.

Setting times

The setting times of the concrete mixture were conducted using the penetration resistance technique in accordance with the guidelines specified in BS EN 480-2⁴². The fresh mortar was obtained by passing the concrete mixture through a sieve (5 mm) and then poured into a mold for testing. In general, the depth of penetration of a standard Vicat needle into the mortar is recorded at regular intervals. The initial and final setting times of the mortar were measured as the times when the Vicat needle reached the height of 4.0 mm from the bottom of the sample and when the needle failed to penetrate the mortar more than 2.5 mm, respectively. It is necessary to say that the setting times for each concrete formulation were measured and averaged over three replicates.

Results and discussion

Characterization of the synthesized PCE-1 and PCE-2

FTIR spectroscopy was used to investigate the chemical structure of the synthesized MPEGM and the prepared PCE-1 and PCE-2 copolymers as superplasticizers (Fig. 2). The characteristic stretching vibration peaks of MPEGM including carbonyl (C=O), symmetric and asymmetric C-O, aliphatic C-H, and out-of-plane hydroxyl group (-OH and -COOH) have appeared at 1724, 1000–1200, 2879, and 3460 cm^{-1} , respectively, approves progress of esterification reaction between PEG and MA. The absence of the C=O stretching vibration peak of the anhydride group at 1780–1830 cm^{-1} indicates that MA has been thoroughly consumed in the related reaction with PEG^{26,27}. In addition, the bending signals of the aliphatic -C-H (symmetric and asymmetric) are located at 1346, and 1462 cm^{-1} . Another evidence for the reaction of PEG and MA is attributed to the appearance of a stretching vibration peak of the vinyl group (C=C, in MA) at 1636 cm^{-1} ^{127,43}. The FTIR spectra of the prepared PCE-1 and PCE-2 superplasticizers are shown in Fig. 2. The absence of stretching vibration peak of the vinyl group (C=C, available in the AA, TPEG, and MPEGM) in the FTIR spectra of PCE-1 and PCE-2 copolymers refers to the successful participation of the related comonomers in the copolymerization reaction. The broad band at 3100–3500 cm^{-1} is related to the stretching vibration peaks of the hydroxyl group (-COOH) of AA in the prepared copolymers. Moreover, displacement of the stretching vibration peak of the C=O group in the PCE-1 (1740) and PCE-2 (1736) relative to MPEGM (1724) refers to the precise copolymerization of MPEGM with other monomers. Actually, the carbonyl bonds in MPEGM are in resonance and conjugate with the vinyl group (delocalized) which results in their vibration peaks shifted to lower wavenumbers. However, the absence of the aforementioned resonance for the carbonyl bond in AA and TPEG is the reason for the observed shift to higher wavenumbers. Therefore, the observed vibration signals from FTIR spectra confirm that MPEGM, PCE-1, and PCE-2 have successfully been synthesized.

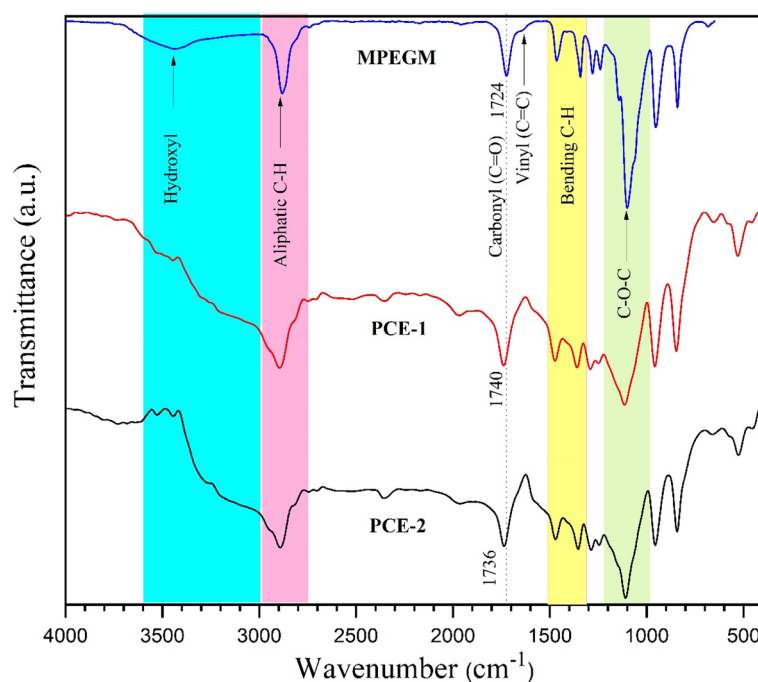


Fig. 2. FTIR spectra of the synthesized MPEGM, PCE-1, and PCE-2.

^1H NMR spectra of PCE-1 and PCE-2 copolymers are shown in Fig. 3. It is obvious that the signal of the $-\text{CH}_2-\text{CH}_2-\text{O}-$ group is dominant due to its highly repetitive unit, while other peaks are so small. Good evidence for the progress of copolymerization of monomers is related to the elimination of vinyl group ($\text{C}=\text{C}$) protons signals at the region of 5–6 ppm (Fig. 3). The characteristic peak at 0.6–0.9 ppm is assigned to the hydrogens of methyl group on the TPEG segment of the both superplasticizers. Protons of the methylene (H_b) groups of AA in the backbone of PCE-1 and PCE-2 copolymers could be seen at 1.5–1.9 ppm. In addition, the appeared peaks at 2.2–2.7 ppm is correspond to C-H signals in the backbone of copolymers. The presence of H_c in PCE-2 spectrum at 4.1–4.3 ppm confirmed the participation of MPEGM in the copolymerization with AA and TPEG too. Mole fraction or chemical composition of the prepared PCE-1 and PCE-2 copolymer chains were measured by dividing the integral of distinct peaks of each monomer to the total integrals of all protons (Eqs. 1–3).

$$\text{Mole fraction of TPEG in PCE} - 1 = \frac{\frac{A_{\text{Ha}}}{6}}{\frac{A_{\text{Ha}}}{6} + \frac{A_{\text{Hb}}}{2}} \quad (1)$$

$$\text{Mole fraction of TPEG in PCE} - 2 = \frac{\frac{A_{\text{Ha}}}{6}}{\frac{A_{\text{Ha}}}{6} + \frac{A_{\text{Hb}}}{2} + \frac{A_{\text{Hc}}}{2}} \quad (2)$$

$$\text{Mole fraction of MPEGM in PCE} - 2 = \frac{\frac{A_{\text{Hc}}}{2}}{\frac{A_{\text{Ha}}}{6} + \frac{A_{\text{Hb}}}{2} + \frac{A_{\text{Hc}}}{2}} \quad (3)$$

The calculated compositions (molar ratios of reactants) of PCE-1 and PCE-2 has been summarized in Table 2. It is noteworthy that the incorporation efficiency of monomers to the corresponding copolymer chains for both samples is in a reasonable range. These finding is in accordance with the FTIR results and confirms the progress of copolymerization reaction.

GPC analysis was used to determine the molecular weights and molecular weight distributions of the prepared PCEs (Fig. 4a). Table 2 shows the molar ratio of the reactants (AA: TPEG: MPEG) in copolymerization process

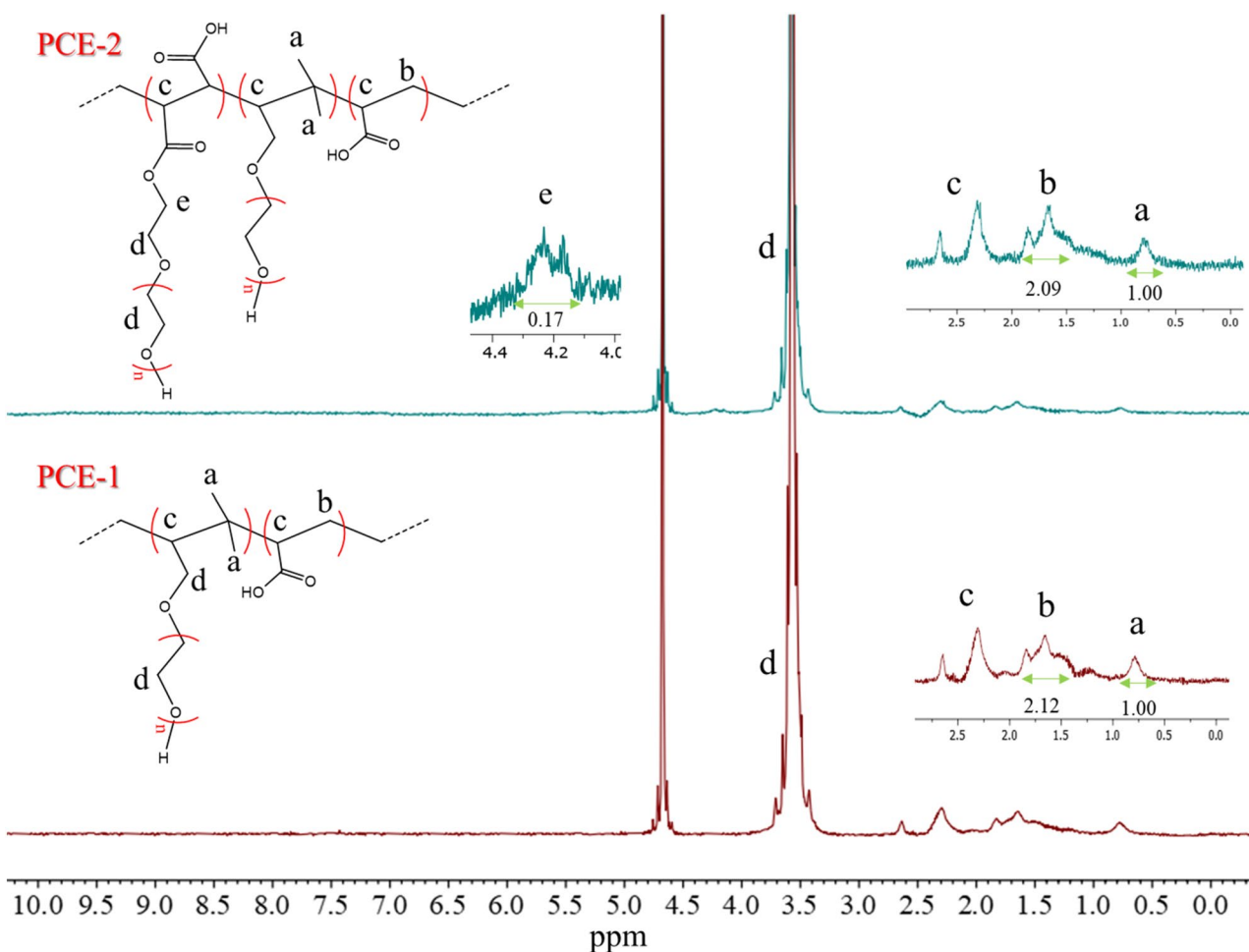


Fig. 3. ^1H NMR spectra of the prepared PCE-1 and PCE-2.

Sample	Molar ratio of AA: TPEG: MPEG		Mw (Da)	Mn (Da)	PDI (Mw/Mn)
	Theoretical	Experimental			
PCE-1	6: 1: 0	6.05:0.95:0	8.74×10^4	6.41×10^4	1.36
PCE-2	6: 1: 0.5	6.05:0.96:0.49	7.37×10^4	3.36×10^4	2.19

Table 2. The molar ratios of reactants and molecular weight and polydispersity index (PDI) of the prepared PCE-1 and PCE-2.

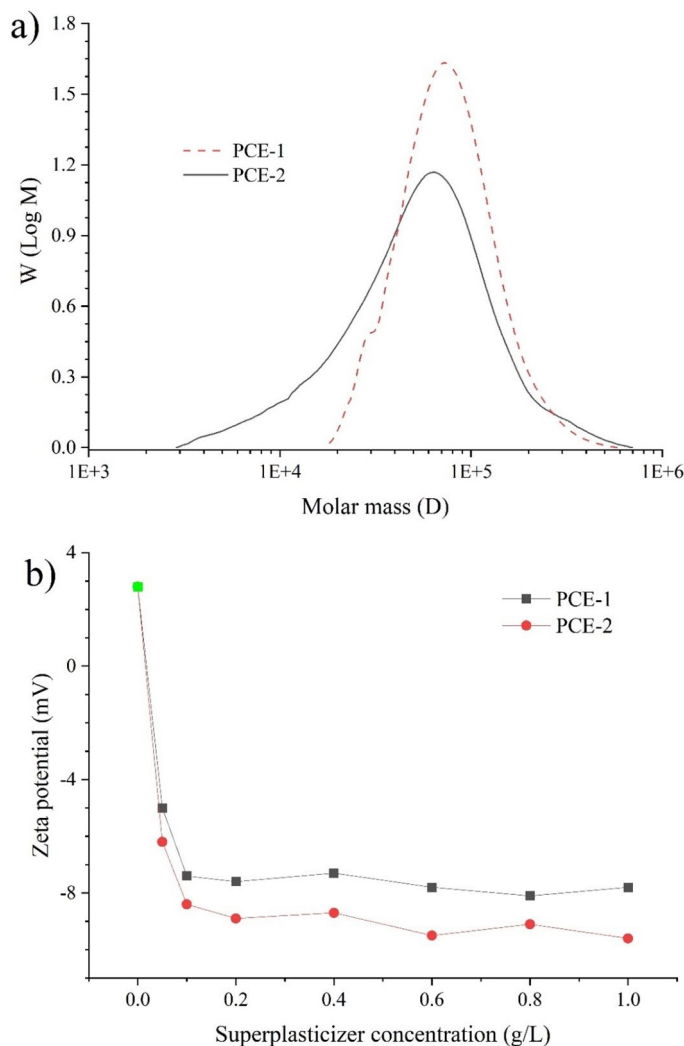


Fig. 4. GPC curves of the prepared PCE-1 and PCE-2 (a) and changes in zeta potential of cement particles incorporated with different concentrations of PCE-1 and PCE-2 (b).

and Mw (weight average molecular weight), Mn (number average molecular weight), and polydispersity index (PDI) of the prepared PCE-1 and PCE-2 copolymers. It is obvious that by introducing MPEG to PCE-1 structure, molecular weight and polydispersity index (PDI) of its copolymer changed from 8.74×10^4 g/mol (PDI of 1.36) to 7.37×10^4 g/mol (PDI of 2.19). Both of PCE-1 and PCE-2 copolymers revealed a single peak, but distribution of PCE-2 is broader than PCE-1. The results of GPC suggest that AA, TPEG, and MPEG monomers had been completely participated in copolymerization process.

Zeta potential

Zeta potential measurement was carried out to illustrate the adsorption behavior of PCE-1 and PCE-2 on cement particles. The zeta potential of cement particles without superplasticizer is positive (2.8 mV) and become negative by the introduction of both PCE-1 and PCE-2 (Fig. 4b). This is attributed to the adsorption of carboxylate groups

of superplasticizers on the surface of cement particles which made double diffuse layer and changes their zeta potential into negative. It has been stated that the side chains of PCEs are the main source of steric hindrance that makes the shear plane (slipping layer) on cement particles thicker and their zeta potential are relatively declined (more positive)^{26,44}. If the slipping layer approaches the stern layer the zeta potential can be more negative. Polar ionic (i.e. carboxylate) functional groups and short side chains cover the surface of cement particle and composed the stern layers. The results of zeta potential measurements illustrate a more negative amount for PCE-2 compared to PCE-1. This denotes to better dispersibility of cement particles induced by PCE-2. The introduction of MPEG to copolymer chains of PCE-2 results in higher short side-chains and carboxylic group density and subsequently decreasing the adsorption layer thickness. In addition, side chains of MPEG have a shorter length (lower molecular weight) compared to TPEG, which affects the thickness of adsorption layer. Accordingly, by decreasing the thickness of adsorption layer the relative zeta potential has become more negative, as showed in Fig. 4b. The obtained result implies that electrostatic and steric hindrance forces synergistically provide a situation for appropriate dispersion of cement particles.

Water-reducing percentage

Figure 5 illustrates the influence of PCE-1 and PCE-2 dosages on the percentages of water reduction in the corresponding concrete mixtures. The results indicated that the concretes made of 0.1 wt% of PCE-1 and PCE-2 show a 16 and 26.5% reduction in the water demand compared to concrete without superplasticizers. By increasing the dosage of PCE-1 and PCE-2 from 0.1 to 0.3 in the prepared concrete mixture the percentage of water reduction remarkably reaches 37.3 and 40%, respectively. The water reduction percentage of concretes made of PCE-1 and PCE-2, even at the lowest dosages, is higher than the specified value of Type F water-reducing admixtures in ASTM C494 (at least 12 to 40%)³⁸. Based on the previous study⁴⁵, the addition of a superplasticizer increases the initial zeta potential on the surface of cement particles and lowers their inter-particle friction which results in the release of trapped water on the flocculated cement particles together with a decrement in the water demand of concretes. As can be seen in Fig. 5, the amounts of water-reducing percentage raise sharply by increasing the PCE-1 and PCE-2 dosages from 0.1 to 0.25 wt% and then become relatively plateau at higher dosages (0.3 wt%). This certifies that the saturation dosage of PCE-1 and PCE-2 superplasticizers is 0.25 wt%. A comparison between PCE-1 and PCE-2 superplasticizers depicts that at similar dosages, PCE-2 results in a more water-reducing percentage. The reason for the higher water-reducing percentage of PCE-2 compared to PCE-1 can be attributed to more negative charge on their polymer backbone and also higher short side-chain density, which provide stronger electrostatic and steric repulsion between cement particles as observed in previous section (zeta potential). The aforementioned interactions result in quick adsorption of PCE-2 on positively charged cement particles and retard the hydration of cement particles^{22–24}.

Fluidity

The influence of PCE-1 and PCE-2 dosages with different carboxylic densities on the time-dependent fluidity of the relative concrete mixtures was investigated and the results of slump change (with the initial slump of 200 ± 15 mm) versus elapsed time are shown in Fig. 6. It can be seen that the initial slump value (200 ± 15 mm) of all concretes incorporated with different dosages of PCE-1 and PCE-2 and without superplasticizer (control)

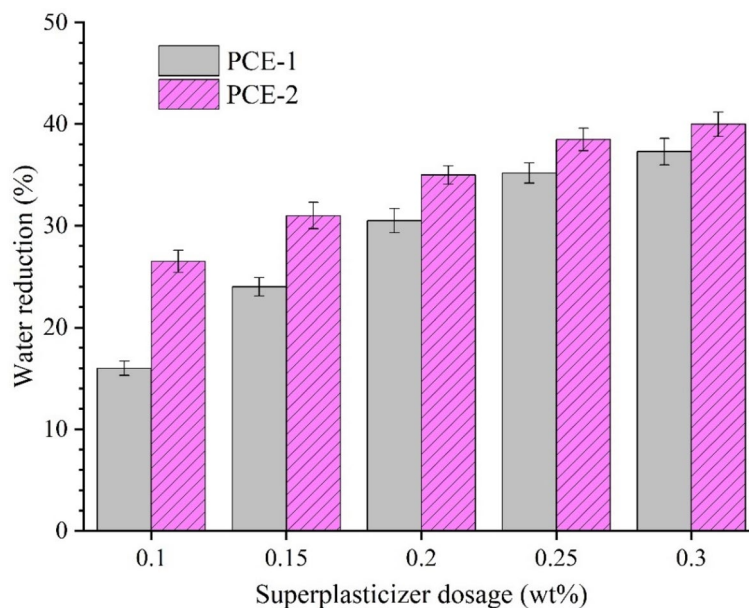


Fig. 5. The percentages of water reduction of concrete mixtures in the presence of different dosages of PCE-1 and PCE-2 superplasticizers.

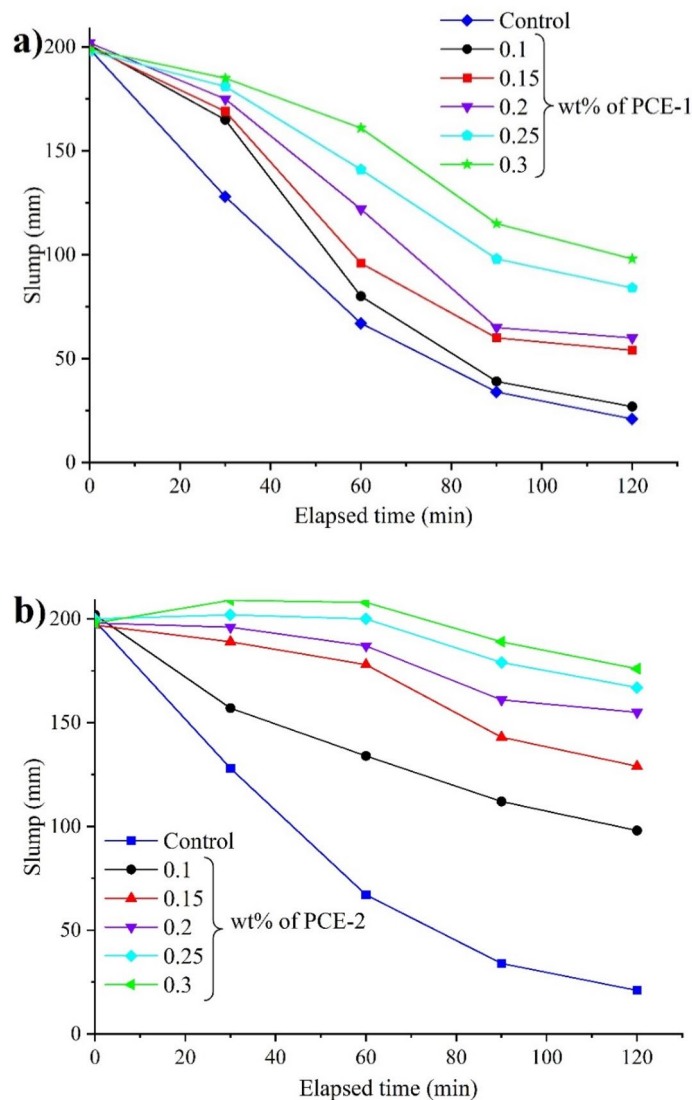


Fig. 6. The changes in the slump of the concrete mixture incorporated with different dosages of PCE-1 (a) and PCE-2 (b) toward elapsed time.

sample) exhibit a decrement during time. After 2h, the initial slump of the concrete sample without superplasticizer reached 21 mm and depicted a slump loss rate of 89.5%. However, the slump flow loss rates of concrete mixtures made of 0.1, 0.15, 0.2, 0.25, and 0.3 wt% PCE-1 are 86.6, 73, 70.3, 57.6, and 50.8% after 2h, respectively (Fig. 6a). The observed results show a significant enhancement in the decline of the slump flow rate of concretes (after 2h) by incorporation of PCE-1. For instance, the loss in slump flow rates of the control sample reduced from 89.5 to 50.8%, after 2h, by incorporation of 0.3 wt% PCE-1. On the other side, the concrete mixtures prepared by 0.1, 0.15, 0.2, 0.25, and 0.3 wt% PCE-2 reveal significant fluidity preservation with slump loss rates of 51.5, 34.5, 21.7, 16.5, and 11.2% after 2h (Fig. 6b). This implies that the introduction of a comonomer with different functional groups (MPEGM) has led to a change in the fluidity of concretes. As a result, the incorporation of both PCE-1 and PCE-2 into the concrete mixture enhances the fluidity preservation of the relative concretes. The dispersing stability of polycarboxylate superplasticizers in the concretes is strongly related to the content of carboxylic groups in their polymeric backbone, which adsorbed on the surface of cement particles (possessing Ca^{2+} ions) and provides electrostatic repulsive force between them during the elapsed time^{46,47}. Therefore, the incorporation of PCE-series superplasticizers into the concrete will improve their dispersing ability at prolonged times. It is obvious that the slump retention of PCE-2 follow an increasing trend from 30 to 60 min and moderately decreased over 2h. This is related to the presence of ester groups of MPEGM in the copolymer composition which are prone to hydrolysis in alkaline condition^{27,48}. In continuum, the newly formed carboxylic groups adsorbed on the surface of cement particles and contributing in the adsorption of the PCE-2 onto the cement particles. Therefore, hydrolysable ester groups in the PCE-2 composition improved its potential for good initial fluidity and flow retention over time. Besides, this phenomenon may be attributed to the higher short-chain density and relatively more carboxylic group in the structure of PCE-2 superplasticizer compared to PCE-1.

Air content (%) and bleeding water rate

The results of air contents (%) of the incorporated concrete mixture with different dosages of PCE-1 and PCE-2 superplasticizers are summarized in Table 3. It can be seen that the air contents (%) of the prepared concrete mixture without superplasticizer is 0.93%. By increasing the dosages of PCE-1 and PCE-2 from 0.1 to 0.3 wt% in the prepared concretes, the air content reached 1.18–1.93 and 1.04–1.81%, respectively. The air content sharply raised by increasing the dosage of PCE-1 and PCE-2 from 0.1 to 0.25 wt%, while the further increase to 0.3 wt% shows a slow increment in the air content. The reason for increasing the air content in fresh concrete made of superplasticizer is ascribed to the easy movement of air bubbles in fresh concrete⁴⁹. In fact, the employed superplasticizer enhances the cement particle dispersion by adsorption on their surface in the fresh concrete and facilitates air bubble moving. As a result, there is no significant difference between the air content values of the fresh concrete made of PCE-1 and PCE-2 at the same dosages.

The results of bleeding water rates of the prepared concrete mixtures with different dosages of PCE-1 and PCE-2 are given in Table 3. It is evident that the bleeding water rate of concretes made of 0–0.3 wt% PCE-1 and PCE-2 changes from 1.8–7.5 to 1.8–9%, respectively. This implies that the incorporation of 0.1–0.3 wt% of PCE-1 or PCE-2 to the concretes induced 16.7–316.7 and 38.9–400% higher bleeding water rates than the concrete mixtures without superplasticizers (control sample). Therefore, by increasing the PCE-1 or PCE-2 dosages the bleeding water rate of the concrete shows an excessive increment. The reason for the upward trend in the bleeding water rates of concretes with superplasticizer dosages is described by the adsorption of superplasticizer on cement particles together with repulsive forces between side chains, which make the distance between cement particles and their good dispersion. Accordingly, the dispersed cement particles facilitate the migration of water molecules to the surface of concretes⁵⁰. Moreover, the higher impact of PCE-2 compared to PCE-1 at the same dosages on the bleeding water rate of the concrete depends on the molecular structure of PCE-2 which contains more negatively charged carboxylate groups and higher short side-chain density on the polymer backbone. The higher negatively charged carboxylate groups and higher side-chain density create stronger electrostatic and steric repulsive forces between cement particles with higher bleeding water rates.

Setting time analyses

The influence of PCE-1 and PCE-2 superplasticizers dosages on the initial and final setting times of the concrete mixtures were investigated and the obtained results are presented in Fig. 7. The initial and final setting times of all concrete incorporated with different dosages of PCE-1 and PCE-2 demonstrate an enhancement compared to the control sample. The initial and final setting times of concrete mixture incorporated with 0.1, 0.15, 0.2, 0.25, and 0.3 wt% of PCE-1 were 360, 410, 475, 502, and 518 min and 475, 521, 555, 588, and 605 min which were significantly longer than control sample (without superplasticizer) with 290 and 460 min, respectively. In addition, the concrete prepared by PCE-2 has longer initial (425, 440, 500, 530, and 555 min) and final (510, 568, 627, 655, and 690 min) setting time than that made of PCE-1 at the same adding amount. These results revealed that retarding effect on the setting times of concretes is dependent on the superplasticizer content and PCE-2 has a remarkable retardation effect on setting times compared to PCE-1 and control samples. Moreover, water–cement ratio influences the connectivity of cement particles and consequent retardation. It has been stated that the negatively charged carboxylate groups react with Ca^{2+} and make calcium chelate complexes associated with a layer of water on the surface of the cement particle, which hinders the solid phase nucleation and cement hydration progress^{51–53}. Accordingly, the retardation mechanism of PCE-1 and PCE-2 is ascribed to the steric hindrance of side chains and electrostatic repulsion of carboxyl groups which restrict the further cement hydration process. The higher retardation effect of PCE-2 relative to PCE-1 owed to the presence of MPEGM possessing both carboxyl and side chain functional groups to the backbone structure. A comparative study between the initial (500 min) and final (627 min) setting times of the PCE-2 superplasticizer in this research and those reported in literature (made of AA, MA, and TPEG)²⁶, with 420 (initial) and 530 (final) min for the best sample, denotes its superiority for practical applications.

Wet density evaluation

The results of the wet density of the concrete mixtures prepared by different dosages (0, 0.1, 0.15, 0.2, 0.25, and 0.3 wt%) of PCE-1 and PCE-2 superplasticizers are given in Fig. 8. It can be seen that the wet density of the concrete mixtures follows an increasing trend by elevating the dosages of each of the PCE-1 and PCE-2

Dosage (wt%)	Air content (%)		Bleeding water rate (%)	
	PCE-1	PCE-2	PCE-1	PCE-2
0 (Control)	0.93	0.93	1.8	1.8
0.1	1.18	1.04	2.1	2.5
0.15	1.31	1.14	3.2	3.9
0.2	1.58	1.33	5.5	7.3
0.25	1.82	1.69	7	8.4
0.3	1.93	1.81	7.5	9

Table 3. Air contents (%) and bleeding water rate (%) of the incorporated concrete mixture with different dosages of PCE-1 and PCE-2 superplasticizer.

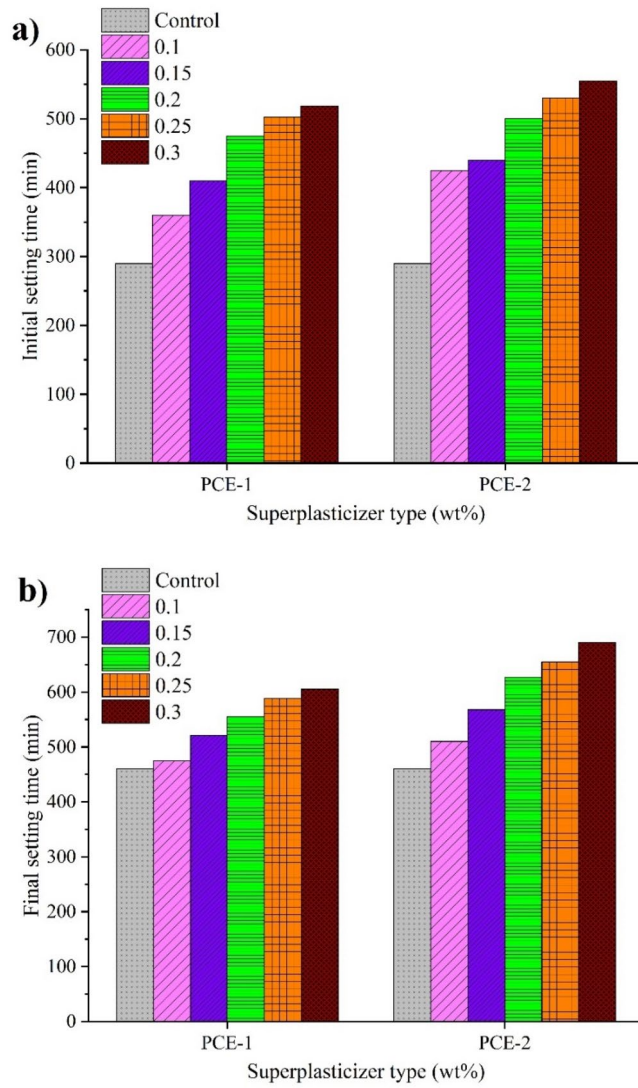


Fig. 7. Initial (a) and final (b) setting times of the prepared concrete mixture with different dosages of PCE-1 and PCE-2 superplasticizers.

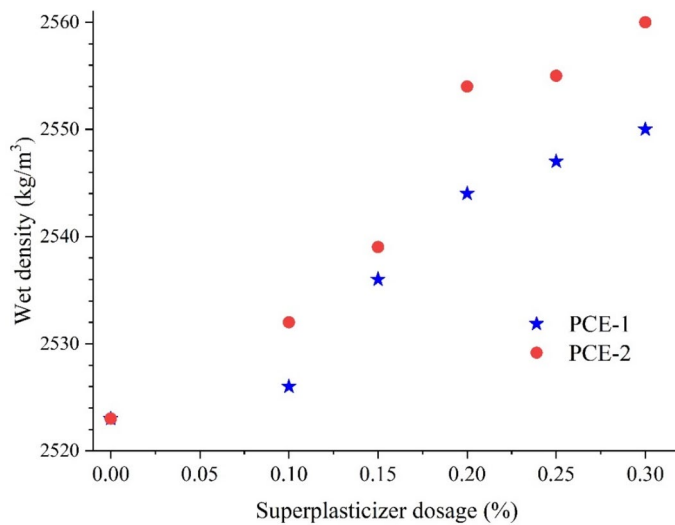


Fig. 8. Wet densities of the prepared concrete mixture with different dosages of PCE-1 and PCE-2 superplasticizers.

superplasticizers in the concretes. This is attributed to the effective role of the superplasticizers in cement particle dispersion, which diminishes the available voids in the concretes consistent with the previous report⁵⁴. Therefore, the prepared concrete became more compact in the presence of PCE-1 and PCE-2 superplasticizers. The wet density of the prepared concrete mixtures with 0–0.3 wt% of PCE-1 or PCE-2 are in the range of 2523–2550 and 2523–2560 kg/m³. The inclusion of PCE-2 in the concrete shows the higher concrete density compared to those with PCE-1, at the same dosages. For instance, the wet density of prepared concrete with 0.3 wt% of PCE-2 shows 1.47% enhancement relative to the control sample, while the finding for concrete made of 0.3 wt% of PCE-1 is 1.07%.

Mechanical properties

Compressive strength of the concrete mixtures made of PCE-1 and PCE-2

The development of compressive and flexural strength of the prepared concrete mixtures incorporating different dosages of PCE-1 and PCE-2 superplasticizers at different aging times were studied by compressive and flexural tests. Figure 9a demonstrates the compressive strengths of the concretes with different amounts of PCE-1 superplasticizer (0, 0.1, 0.15, 0.2, 0.25, and 0.3 wt%) after 3, 7, and 28 days. A comparative study of the mechanical properties of the concretes made of PCE-1 superplasticizer shows that compressive strengths are significantly influenced by PCE-1 concentration. Actually, by increasing the PCE-1 concentration from 0 (control sample) to 0.3 wt% the compressive strength of the concretes follows an increasing trend (Fig. 9a).

The compressive strength of the concretes is improved by prolonging the aging time (curing period) from 3 to 7 and 28 days, because of the well-dispersion of the cement particles by PCE-1 superplasticizer. The water demand is reduced by the incorporation of PCE-1 into the concrete mixture resulting in its compressive strength development⁵⁵. At the interval of 3 days, although by increasing the PCE-1 concentration the compressive strength of concrete was enhanced, the difference between the compressive strength at 0.2, 0.25, and 0.3 is not significant ($p > 0.05$). Whereas at 7- and 28-day curing intervals, the improvement in the compressive strength of the concretes is significant by increasing the PCE-1 dosages ($p < 0.05$). After the curing times of 3, 7, and 28 days, the concrete mixtures made of 0.3 wt% PCE-1 show compressive strength of 28.3, 45.1, and 60.5 MPa, respectively, which are 58.9, 79 and 96.3% higher than the concrete mixtures without PCE-1 (control sample). On

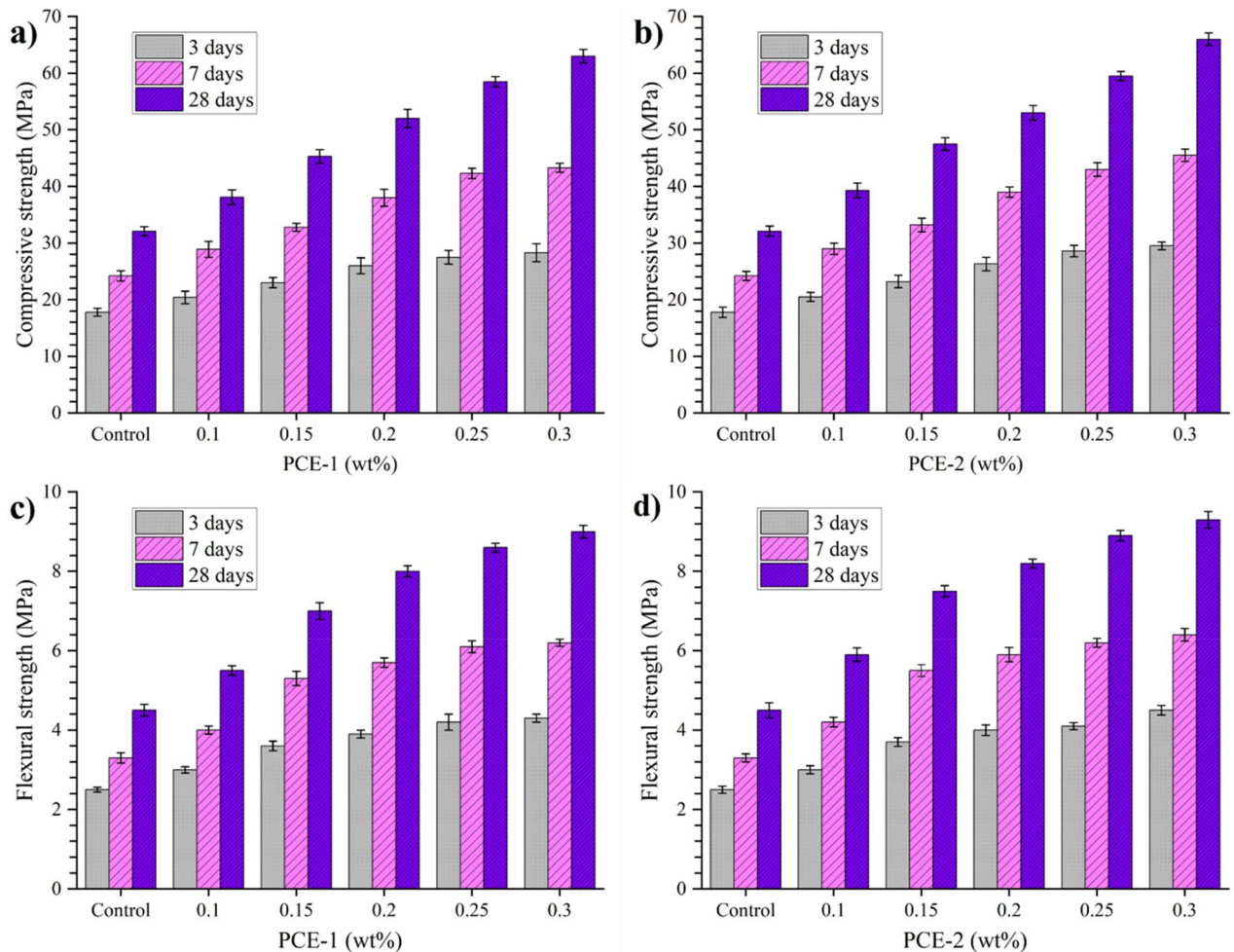


Fig. 9. Compressive and flexural strengths of the prepared concrete mixtures without (control sample) and with different wt% of PCE-1 (a, c) and PCE-2 (b, d) superplasticizer after 3, 7, and 28 days.

the other hand, after 3 to 28 days of curing times, the compressive strength of concretes made of superplasticizer PCE-1 exhibits a faster-improving rate compared to the control concrete.

Additionally, similar trends were observed for the concretes made of PCE-2 superplasticizer, and their compressive strength is remarkably improved by increasing the PCE-2 dosage (0.1, 0.15, 0.2, 0.25, and 0.3 wt%) and curing time (3, 7, and 28 days, Fig. 9b). The progress in compressive strength is more obvious in the concretes made of PCE-2 compared to those with PCE-1 (Fig. 9). For instance, the concrete made of 0.3 wt% PCE-2 after 3, 7, and 28 days of curing period shows a 65.7, 88 and 105.6% improvement in strength relative to concrete mixtures without PCE-2, which show a 6.8, 9, and 9.3% enhancement relative to concretes made of PCE-1 with similar dosage and curing time. The presence of MPEGM with simultaneous carboxylic acid and side-chain polyether groups promotes the adsorption-dispersibility potent of PCE-2 by providing more functional groups to interact with the cement particles. Therefore, the well-dispersion of the cement particles by PCE-2 and the reduced water demands led to improved compressive strength.

Flexural strength of the concrete admixtures made of PCE-1 and PCE-2

The flexural strengths of the concrete mixtures made of different dosages of PCE-1 and PCE-2 at curing periods of 3, 7, and 28 days were investigated by Tensile analysis. According to Fig. 9c and d, the trends of flexural strength of the concretes made of PCE-1 and PCE-2 is consistent with their dosages. In addition, it is obvious that by increasing the PCE-1 and PCE-2 dosages, the flexural strengths of the produced concrete mixtures are significantly affected by the curing period. At the curing period of 3, 7, and 28 days, the flexural strength of concrete mixtures made of 0.1–0.3 wt% of each superplasticizer shows an enhancement in the range of 20–72%, 21–88% and 22–100% for PCE-1 and 20–80%, 27–94% and 31–106% for PCE-2, relative to the control sample. It is evident that by raising the curing period from 3 to 28 days, concrete mixtures with similar composition show a faster flexural strength improving rate compared to the control sample. Besides, it was found that the concrete mixtures containing PCE-1 have a higher flexural strength relative to the concretes made of PCE-1 (with the same content) after 3, 7, and 28 days of water-curing. The results of flexural strength of concretes made of PCE-1 and PCE-2 are consistent with the results of compressive strengths and approve that the incorporation of the above-mentioned superplasticizers to concretes are associated with their reduced water demand which led to promoted mechanical properties. The effect of the curing period and superplasticizer dosage on the flexural strength is similar to the compressive strength.

Ultrasonic pulse velocity

Ultrasonic pulse velocity (UPV) is an in-situ and non-destructive analysis for the evaluation of the strength and quality of cured concrete. This test is performed by measuring the passing velocity (based on the required times) of an ultrasonic pulse through a concrete structure. Achieving higher ultrasonic speed through the concrete is a sign of its continuity and high quality without cracks or voids. The UPV results of the prepared concrete mixtures with different dosages of PCE-1 and PCE-2 at curing intervals of 3, 7, and 28 days are shown in Fig. 10. UPV values of the prepared concrete with 0.1, 0.15, 0.2, 0.25, and 0.3 wt% of PCE-1 and PCE-2 are 2600, 2800, 3100, 3300, and 3400 m/s and 2500, 2800, 3300, 3500, and 3600 m/s, respectively, after 3 days of water-curing. This illustrates that the UPV values of concretes made of 0.1–0.3 wt% of PCE-1 and PCE-2 show a 118.2–154.5% and 113.6–163.6% enhancement compared to concretes without plasticizer (2200 m/s). The amounts of UPV values increase sharply by increasing dosages of the PCE-1 and PCE-2 from 0.1 to 0.25 wt% and then become relatively plateau at higher dosages (0.3 wt%). In addition, the UPV values of the concrete are elevated by prolonging the water-curing period from 3 to 7 and 28 days (Fig. 10). After 7 and 28 days of curing, the incorporated concretes with 0.1–0.3 wt% of PCE-1 and PCE-2 shows 120.7–179.3 and 121.6–189.2% and 124.1–186.2 and 124.3–197.3% enhancement in the UPV value relative to the control concrete. The higher influence of PCE-2 on the UPV value of concrete compared to PCE-1 (at the same dosage and curing period) returns to the well-dispersion of cement particles and removing voids, which result in high-quality and continuity concretes.

Conclusion

In this study, polyethylene glycol maleate (MPEGM) was synthesized through chemical modification of polyethylene glycol (PEG) with maleic anhydride (MA). Molecularly modified polycarboxylate superplasticizer comprising of TPEG and AA (1:6 mol ratio, PCE-1) and the synthesized MPEGM with TPEG and AA (0.5:1:6 mol ratio, PCE-2) were prepared through solution radical polymerization. Afterward, concrete mixtures with different dosages (0, 0.1, 0.15, 0.2, 0.25, 0.3 wt%) of PCE-1 and PCE-2 were prepared. The precise synthesis of MPEGM together with chemical structure and composition of PCE-1 and PCE-2 were identified by FTIR and ¹HNMR analyses. Molecular weight and polydispersity index (PDI) of its copolymer changed from 8.74×10^4 g/mol (PDI of 1.36) to 7.37×10^4 g/mol (PDI of 2.19) by introducing MPEG to PCE-1. The results of water-reducing percentages show that the prepared concretes with 0.1–0.3 wt% of PCE-1 and PCE-2 induce a water reduction percentage of 16–37.3% and 26.5–40%, respectively. The zeta potential measurements reveal that the zeta potential of cement particles changed from +2.8 mV to –7.8 and –9.5 mV in presence of 0.6 g/L of PCE-1 and PCE-2, respectively. This was attributed to the induced electrostatic and steric hindrance forces of superplasticizers. A comparative study between PCE-1 and PCE-2 shows that the prepared concretes with PCE-2 have larger water-reducing percentage and higher fluidity, air content, bleeding water rate, mechanical properties, wet density, and UPV together with longer initial and final setting times. The superiority of PCE-2 to PCE-1 was attributed to its adsorption-dispersibility potent induced by stronger electrostatic and steric repulsion forces. These observations exhibited the promising potentiality of the prepared superplasticizers for fabricating concretes with improved performance.

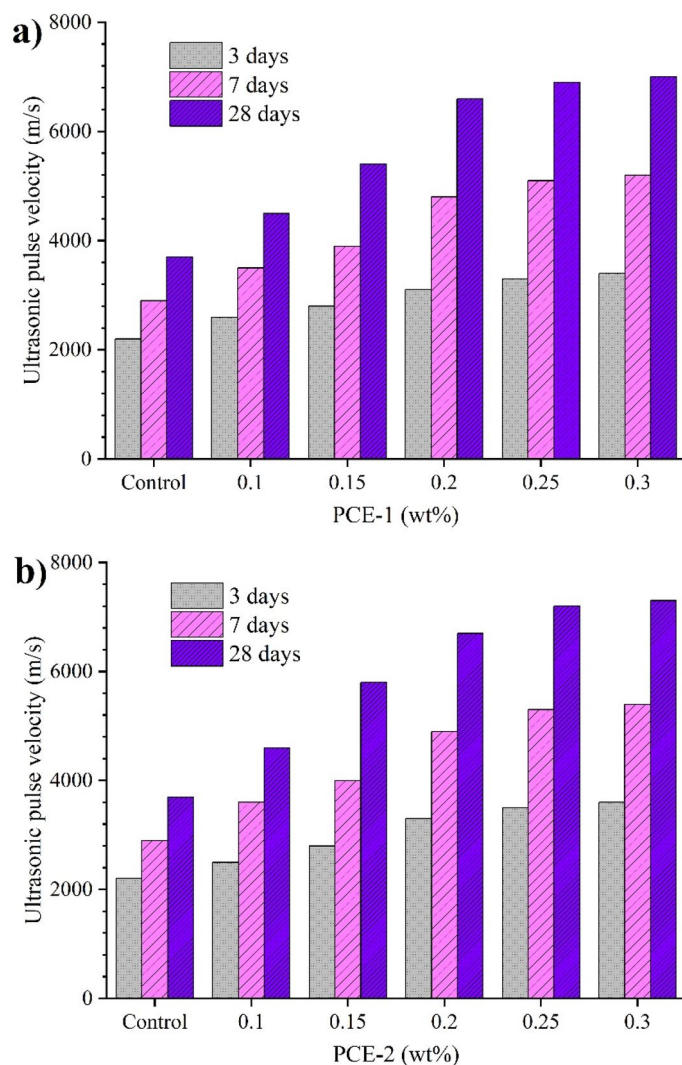


Fig. 10. The UPC results of the concrete made of different dosages of PCE-1 (a) and PCE-2 (b) after 3, 7, and 28 days.

Data availability

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Author contributions

M.M.: Methodology, Formal Analysis, Investigation, Validation, Writing-Original Draft. M.A.: Supervision, Conceptualization, Writing-Review & Editing. F.N.: Validation, Data Curation, Visualization.

Competing interests

The authors declare no competing interests.

Additional information

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