



## Preparation and characterization of effective Polycarboxylate ether-based superplasticizers and assessment of their performance in grout mixes

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### Abstract

This study investigates the synthesis and characterization of polycarboxylate ether-based superplasticizers (PCE-based SPs) used in concrete. The PCE-based SPs were synthesized using methacrylic acid, methoxy polyethylene glycol methacrylate, thioglycolic acid, and ammonium persulfate through free radical copolymerization mechanism. Various analytical methods, including specific gravity, solid content, FT-IR, <sup>1</sup>HNMR, GPC, TG, and XRD, were employed to characterize the prepared PCE-based SPs. The microstructure of hydrated cement pastes was examined using XRD and SEM. The impact of the chemical composition of the polycarboxylates on the rheological properties of grout mixes and the performance of the superplasticizers was evaluated through slump, flow table, and compression tests on different grout mixtures. The formulated superplasticizers demonstrated effective dispersal properties and excellent slump performance. Notably, the PC-4 mix achieved a maximum flow of 230 mm in the flow table test at a water-cement ratio of 0.25, and it exhibited high compressive strength values after 28 days of curing. XRD and SEM analysis indicated that the PC-4 hydrated paste had a denser and more compact structure, attributed to the formation of excessive hydration products compared to the neat OPC paste.

**Keywords:** Methoxy polyethylene glycol methacrylate; Polycarboxylate ether; Superplasticizers; Grout; Free radical polymerization.

### 1. Introduction

As urbanization continues to progress, the construction industry has seen rapid growth, leading to an increased demand for concrete admixtures. In particular, high-performance polycarboxylic acid water-reducing agents have become crucial in providing high-quality concrete for diverse construction projects. This has made the advancement and application of polycarboxylic acid water-reducing agents and additional concrete additives a focal point for research [1-3].

The development of multifunctional polycarboxylate has shown significant progress over the years, displaying various capabilities such as maintaining slump, controlling coagulation, and reducing shrinkage. Their incorporation influences the bond between Portland cement particles and alters the physicochemical characteristics of their solid-liquid interface, ultimately impacting the flow properties of cement paste [4]. Recently, the global community has encountered various challenges, including environmental limitations and escalating energy and raw materials costs. In response to these issues, this study explores the potential of the polycarboxylate industry as a viable solution to address the gaps created by these challenges. Polycarboxylate ethers (PCEs), introduced nearly twenty years ago, are considered the most advanced form of high-range water reducers and superplasticizers compared to other products like polycondensates [3, 5]. It consists of a carbon chain with anionic COOH groups and polyethylene oxide side chains. These anionic carboxylate groups strongly interact with the cationic mineral surface of the cement particles leading to the adsorption of PCEs chains. The polyethylene oxide side chains on the cement particles are stretched and induces a steric hindrance beside the typical electrostatic repulsion process. Also, the elongated side chains function to physically distance the cement particles, facilitating water encasement around them and preventing their agglomeration [3, 6]. This dispersion effect of PCEs was reported for other suspensions like suspensions of lime stone, silica, and barium titanate [7-9]. The advantage of polycarboxylate, as a synthetic superplasticizer, is that it can reduce water content by up to 40%, unlike other superplasticizers such as sulfonated naphthalene formaldehyde (SNF), acetone formaldehyde (AF), and sulfonated melamine formaldehyde (SMF) condensates can't cause this decrease in the W/C ratio. One of the other advantages of synthetic plasticizers is their ability to provide a wide range of material properties and characteristics. Polycarboxylate ethers (PCE), also called PCs or comb polymers, and they are a kind of environmentally friendly superplasticizer that has gradually become the most important alternative concrete water-reducer in the industry because of their high water-reduction rate, long slump retention, and adjustable molecular structure to suit various construction requirements [10-13].

Li investigated in his study [14] that polycarboxylate can reduce the surface tension of the solution and increase the wetting,

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permeation, and adsorption of the cement surface, while also exhibiting good dispersion retention performance. Additionally, the study reported by Mohammed [15] showed that the use of polycarboxylate can significantly improve the strength of the cementitious grout, with increases of up 290% and 360% reported, based on the specific polymer type, polymer content, water-to-cement ratio, and curing duration. Furthermore, different types of polycarboxylate polymers have been found to reduce water content and increase the performance and strength of concrete [16]. This work focuses on the synthesis of polycarboxylate by polymerizing two monomers, methacrylic acid and MPEG-MA (methoxy polyethylene glycol methacrylate), with the use of ammonium persulfate (APS) as a free radical initiator [17] and thioglycolic acid (TGA) as a chain transfer agent [18], under various polymerization conditions. The performance of the synthesized polycarboxylates as superplasticizers in cement grout is also evaluated, as polycarboxylate ethers (PCE) or comb polymers are the most recently developed superplasticizers in the building and construction fields.

**Table 1:** The composition of chemicals and physical characteristics of cement

Chemical composition									
Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	LSF	Mn <sub>2</sub> O <sub>3</sub>	Cl	C3A
3.81	4.09	63.35	1.6	2.45	0.41	0.97	0.22	0.04	3.2
Physical properties									
Fineness (0.08/%)		Density(g/cm <sup>3</sup> )		Specific area (m <sup>2</sup> /kg)			Standard consistency (%)		
0.6		3.15		349			25.8		

## 2. Experimental

### 2.1. Materials

Methacrylic acid (MAA, Sigma, >99%), ammonium persulfate (APS, sigma, 98 wt.%), thioglycolic acid (TGA, sigma, AR), and sodium hydroxide (NaOH) were purchased from El-Gomhouria Co., Ltd. (Cairo, Egypt). Methoxy polyethylene glycol methacrylate (MPEG-MA) (Mn = 950) was purchased from Sigma Aldrich Co. The study utilized normal ordinary Portland cement (Cement I 42.5 N), provided by Sinai Company Cement Group Co., Ltd.). The physical characteristics and chemical composition of the Portland cement underwent analysis, as detailed in Table 1. The high-quality sand originated from Elsaf Company with a fineness of 4.13, whereas the ISO standard sand adhered to ISO679: 1989 and EN196-1 manufacturing guidelines (Cairo, Egypt).

### 2.2. Synthesis of PCE-based SPs

The polycarboxylate ether-based superplasticizers (PCE-based SPs) were created via aqueous free radical copolymerization of MAA and MPEG-MA macromonomer in a four-necked round bottom flask equipped with a thermometer, N<sub>2</sub> gas inlet, refluxing condenser, and stirrer. The polymerization medium (distilled water) was purged with N<sub>2</sub> for 1 hr. and proceeded to slowly raise the temperature to 70 °C. Then, the weighted amount of MPEG-MA macromonomer was added to the medium. After 1 hour, the weighted mixture of chain transfer agent TGA and initiator APS dissolved in 6 g of water was fed continuously over 7 hours. Then, a weight of MAA was fed continuously over 4 hours using a peristaltic pump's droplets. Once the addition was finished completing the stirring for one more hour at 70 °C and then cooled to ambient temperature. Conclusively, the pH was modified to 7 through the application of a 30 wt% NaOH solution to produce a slightly viscous polymer solution. The chemical structure of PCE-based SP can be observed in Scheme 1, while the ingredient ratios for the created PCE-based SPs are detailed in Table 2.

**Table 2** Feed composition data of PCE-based SPs

Components	Percentages (Moles)								
	PC-1	PC-2	PC-3	PC-4	PC-5	PC-6	PC-7	PC-8	PC-9
MPEG-MA	0.0063	0.0042	0.0063	0.0063	0.0063	0.0063	0.0063	0.0063	0.0063
APS	0.00022	0.00022	0.00022	0.00044	0.00066	0.00044	0.00044	0.00044	0.00044
MAA	0.023	0.046	0.023	0.023	0.023	0.023	0.023	0.023	0.023
TGA	0.0012	0.0012	0.0022	0.0012	0.0012	0.0012	0.0012	0.0012	0.0012
Conditions									
Temperature (°C)	70	70	70	70	70	80	90	70	70
Time (h)	12	12	12	12	12	12	12	24	48

### 2.3. Characterization of PCE-based SPs

#### 2.3.1. Spectral analysis

FT-IR spectra were carried out at the Faculty of Pharmacy, Ain Shams University, Cairo, Egypt. The results were registered on a Mac FT-IR spectrometer (KBr technique) within a wavenumber interval of 4000 – 400  $\text{cm}^{-1}$ . Band intensities were expressed either as transmittance (T%).  $^1\text{H-NMR}$  spectra ( $\text{D}_2\text{O}$ ) were registered on a Varian Mercury-300BB NMR300 spectrometer at the Micro-analytical Centre, Cairo University, Egypt.

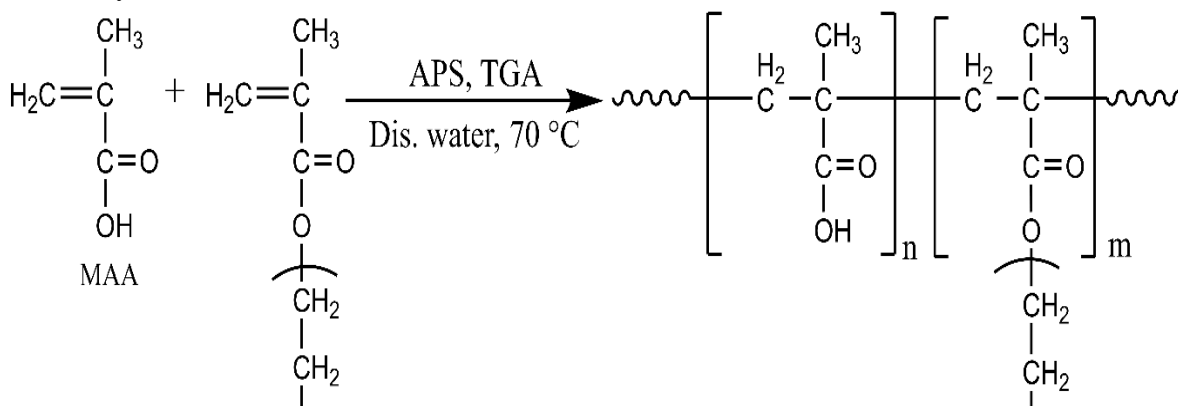
#### 2.3.2. Chromatography analysis

Analysis conducted via gel permeation chromatography (GPC) was performed at the National Research Center, El Buhouth St., Dokki, Cairo, Egypt. The molar masses ( $M_w$  and  $M_n$ ) and the polydispersity index (PDI) of the superplasticizer samples were analyzed using an Agilent 1260 Chromatography System equipped with UV and RID Dual Detectors. This system employed a chromatographic column (PL aqua gel-OH MIXED-H 8  $\mu\text{m}$ , 4.6 $\times$ 250 mm) to separate the polymer fractions. The carrying phase used was a boric acid-sodium borate buffer solution with a pH of 8.5, flowing at a rate of 0.350 mL/min. For calibration, standard samples of sodium polyacrylate polymers with predetermined molar masses were utilized.

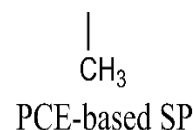
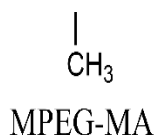
#### 2.3.3. Thermo-gravimetric analysis (TG)

Thermogravimetric analysis (TG) and its derivative (DTG) were quantified using a Setaram TGA 500 apparatus at a heating rate of 10  $^\circ\text{C}/\text{min}$  for a mass sample of about 20 mg in the  $\text{N}_2$  atmosphere and a temperature range from 25  $^\circ\text{C}$  to 700  $^\circ\text{C}$ .

#### 2.3.4. X-ray diffraction (XRD)



Scheme 1. The chemical scheme for the synthesis of Polycarboxylate ether-based superplasticizer.



X-ray diffraction was measured at the National Research Center, El Buhouth St., Dokki, Cairo, Egypt. A Philips PW-1730 unit was utilized. Records were taken at  $2\theta$  intervals from 5 to 60 $^\circ$ .

#### 2.3.5. Scanning Electron Microscope (SEM)

The scanning electron microscope was measured by QUANTA FEG250 at the National Research Center, El Buhouth St., Dokki, Cairo, Egypt.

### 2.4. Test methods

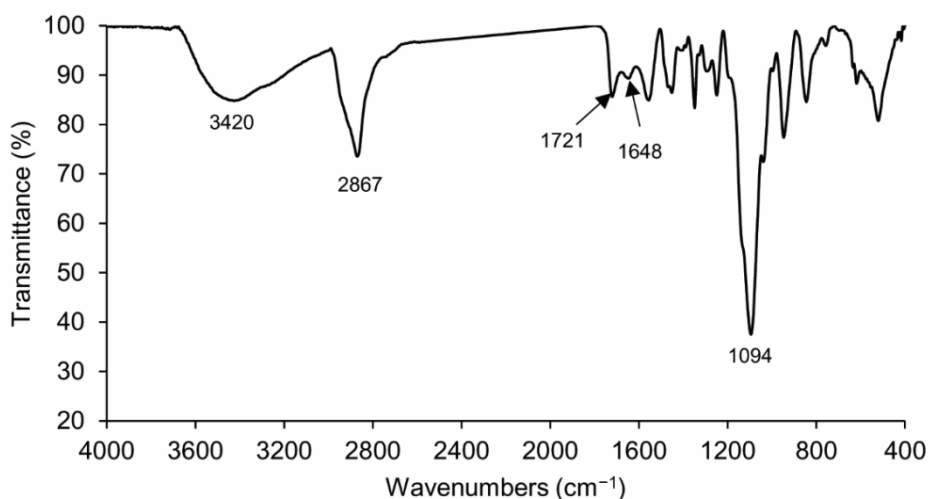
#### 2.4.1. Solid content and Specific gravity

The solid content and the specific gravity of PCE-based SPs were measured by a moisture analyzer instrument (Mettler Toledo), and the portable density meter Anton parr DMA 35. The specific gravity results were measured at 20  $^\circ\text{C}$ . The yield percentage was determined using the solid content results by the following equation:

$$\text{Yield (\%)} = \frac{\text{Solid content}}{\text{Total weight of monomers}} \times 100$$

#### 2.4.2. Evaluation of the PCE-based SPs Performance

The fluidity and workability of the prepared mortar with/without PCEs were tested according to the ASTM C-method with mini-slump cone dimensions (9 cm for height, 1.5 cm for upper radius, and 3 cm for bottom radius), and the test was done without dropping the table to show the flow difference between grout mixed with PCE samples. Generally, each PCE was mixed with water and then added to the mortar with a water-cement (W/C) ratio of 0.25 and a polycarboxylate content of 0.4% based on the weight of the cement with a cement-to-sand ratio of 1:1. The water reduction ratio (W) of superplasticized grout was calculated using the following formula:



**Fig. 1** FTIR spectrum of polycarboxylate ether (PC-4)

$$W = \frac{W_o - W_1}{W_o} \times 100$$

Where:  $W_o$  is the quantity of water required for the cement mortar to reach a spread of  $180 \pm 5$  mm;  $W_1$  is the quantity of water required for the cement mortar after adding the polycarboxylate (0.4%) to achieve a spread within the range of  $180 \pm 5$  millimeters. Several measurements were conducted to determine an average value.

#### 2.4.3. Setting time

Following the grout sampling and wet sieving through a 4.75-mm sieve to extract mortar, eliminate and discard the retained aggregate. Test the setting times of the sample (initial and final) sieve using the STHG-80B Digital Penetration Testing Apparatus according to ASTM C403.

#### 2.4.4. Compressive strength

The compression strength of various grouts was assessed following the guidelines stipulated in ASTM C109. The impact of cross-linked PCEs on the development of compressive strength in cement mortars, both with and without the presence of the polymers PCE-based SPs, was evaluated across different curing stages. A combination of OPC, sand, water, and PCE-based SPs sample (1.6% of 25% PC solid content) was carefully combined in a mass proportion of OPC: standard sand: water = 1:1:0.9. Subsequently, the mixture was cast into a mold sized at 70 mm  $\times$  70 mm  $\times$  70 mm. The compressive strength at intervals of 1, 3, 7, and 28 days was gauged utilizing a universal pressure tester (TYE-2000B). Each specimen underwent three separate tests, from which the average compressive strength was ascertained and documented

### 3. Results and discussion

#### 3.1. Synthesis and characterization of the Polycarboxylate ether

Synthesis of the polycarboxylate ether can be explained as follows: On heating the mixture of MAA and MPEG-MA in the presence of ammonium persulfate (APS) initiator, the APS molecules begin to decompose giving active radical species of  $(NH_4OSO_2O^\bullet)$ . These radicals attack the comonomers and initiate the copolymerization reaction. The thioglycolic acid (TGA) as a chain transfer agent is used to control the molecular weight and to avoid the formation of very high molecular weight which is not recommended for SP [18].

##### 3.1.1. FTIR analysis

Figure 1 displays a representative FTIR spectrum of the synthesized polycarboxylate ether (PC-4). The absorption bands that appeared in the spectrum confirmed the polymerization of MAA and MPEG-MA monomers in the synthesis of polycarboxylate samples. OH groups were indicated by the appearance of a band at  $3420\text{ cm}^{-1}$  [19, 20], and the band at  $2867\text{ cm}^{-1}$  derives from the C-H stretching vibration. The bands at  $1721$  and  $1648\text{ cm}^{-1}$  are attributed to the stretching vibration of C=O in MPEG-MA and MAA, respectively [20, 21]. Besides, the two bands at  $1094\text{ cm}^{-1}$  and  $947\text{ cm}^{-1}$  are owed to the existence of the ether bonds (C-O-C) of poly(ethylene oxide) side chains. The bands of the double bond at about 1600 were not observed in the spectrum, denoting that MAA and MPEG-MA have come in the synthesis polymerization.

##### 3.1.2. NMR analysis

Figure 2 displays the  $^1\text{H-NMR}$  of the synthesized polycarboxylate ether (PC-4)  $\text{D}_2\text{O}$ . The H atoms of ethylene oxide repeating units appear at  $\delta = 3.711 - 3.779$  ppm [20, 22]. The peak at 4.79 ppm stood for  $\text{D}_2\text{O}$  used for dissolving the sample. The peak at 1.8 – 2 ppm corresponds to the methylene groups in the backbone chain. The methoxy group at the side chain end shows

proton resonances at  $\delta = 3.457$  ppm. The peak for the methyl group linked to the main chain was observed at  $\delta = 1 - 1.4$  ppm [21]. The H atoms related to the double bonds did not appear at 5.7 ppm [20], supporting the results of FTIR.

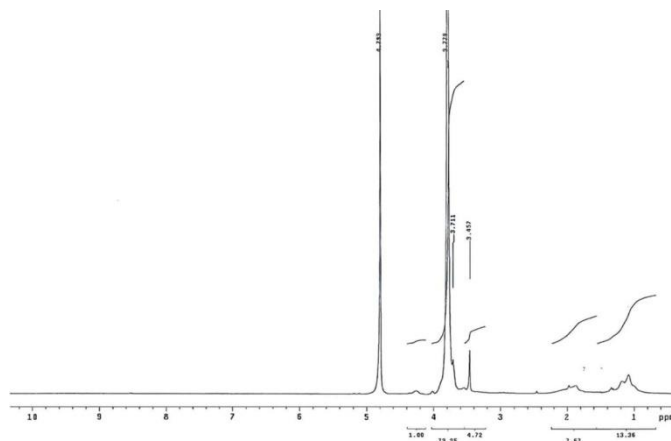


Fig. 2  $^1\text{H}$  NMR spectrum of polycarboxylate ether (PC-4).

### 3.1.3. GPC analysis

Gel permeation chromatography (GPC) analysis is a commonly used method in polymer science for accurately determining these parameters and gaining valuable insights into the structural features of the polymer [14]. The observations of the GPC analysis for all PCE samples are illustrated in Table 3 in terms of the number average molecular weight ( $M_n$ ), the weight average molecular weight ( $M_w$ ) and the polydispersity index (PDI). Figure 3 illustrates a representative GPC analysis specifically conducted on the PC-4 sample.

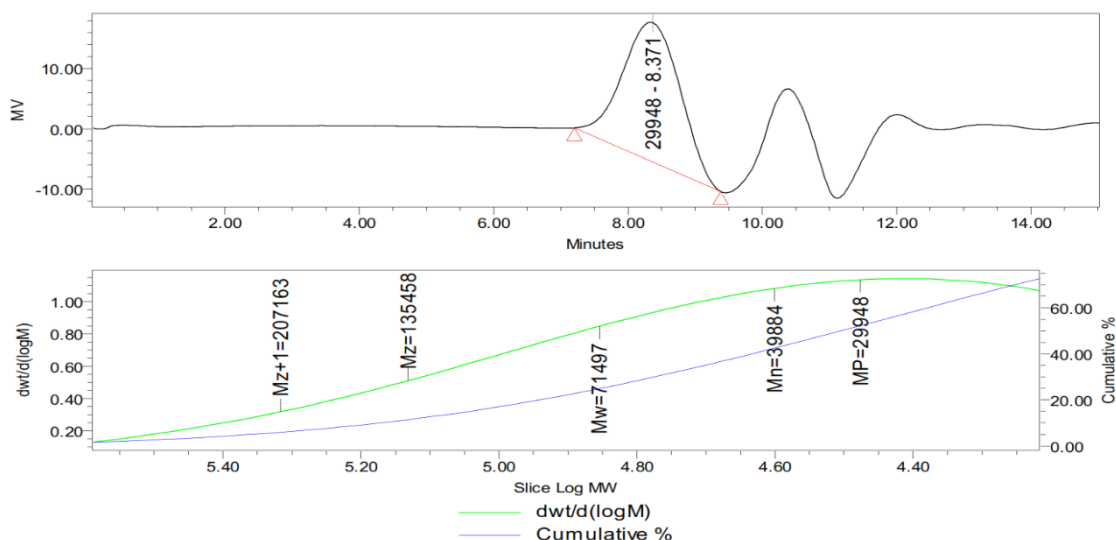


Fig. 3 Typical GPC analysis of the synthesized PCE

The graph showcases the elution profile, with the retention time on the x-axis and the intensity or concentration on the y-axis. The GPC analysis provides understanding of the molecular weight characteristics of the PCEs. The data obtained from the GPC analysis reveal that the molecular weights of the PCEs decrease with an increase in the amount of MPEG-MA macromonomer used in the synthesis. This indicates that a rise in the concentration of MPEG-MA macromonomer leads to the generation of polymer chains of reduced length [15]. The values in Table 3 also indicate that as the temperature during the polymerization process increases, the  $M_w$  of the polycarboxylate polymer also increases. Conversely, a rise in the concentration of the APS initiator has been found to lead to a reduction in the molecular weights of the PCEs. This phenomenon can be attributed to the fact that as the concentration of radical species increases, a larger number of active growing chains are created. Consequently, the presence of numerous active growing chains results in the creation of shorter polymer chains. Moreover, the polymerization time has a direct impact on the  $M_w$  of the PCEs. Extending the duration of polymerization, it allows for the attachment of a greater number of monomers to the developing polymer chains. This leads to the formation of longer chains, resulting in polymers with elevated molecular weights. This increase in molecular weight can have a range of impacts on the characteristics of the polymer [16]. PDI, derived from the proportion of  $M_w$  to  $M_n$ , serves as a quantitative indicator for assessing the dispersion of molecular weights within polymer samples. Within this research, the PDI values were slightly higher than unity ( $\text{PDI} \leq 2$ ), indicating that the molecular weight dispersion for all synthesized PCEs is relatively narrow, with the polymer chains exhibiting a high degree of uniformity. Overall, the GPC analysis and the corresponding data presented in Table 3 suggest that the  $M_w$  of the PCEs is influenced by factors such as the amount of MPEG-MA macromonomer, reaction temperature, initiator concentration, and polymerization time. The observed trends

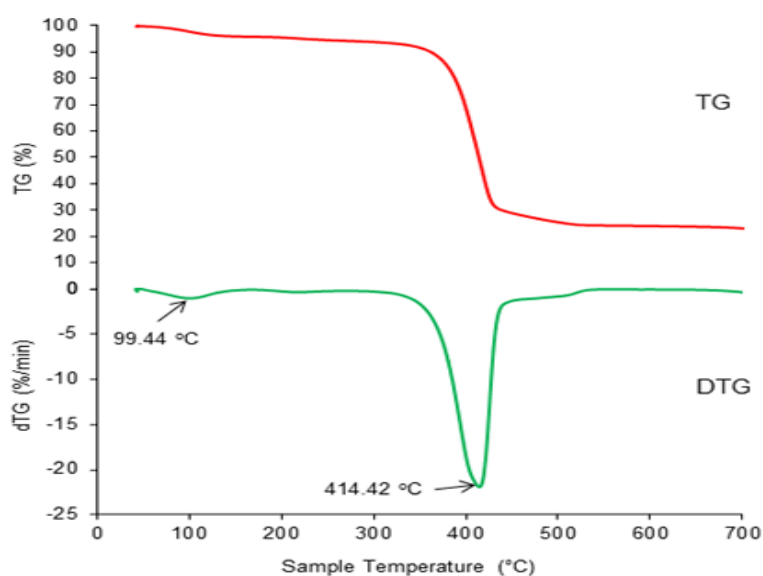
provide valuable insights into the synthesis process and can aid in tailoring the characteristics of the synthesized sample of PCE for specific applications.

**Table 3** Molecular weights (Mn and Mw) and polydispersity indexes of the synthesized PCEs

Sample	Mn (g/mol)	Mw (g/mol)	Polydispersity (PDI)
PC-1	43,553	79,045	1.815
PC-2	51,577	105,005	2.036
PC-3	54,846	113,158	2.063
PC-4	39,884	71,497	1.794
PC-5	37,112	60,620	1.633
PC-6	44,001	79,257	1.801
PC-7	63,180	132,364	2.095
PC-8	48,154	97,373	2.022
PC-9	49,842	97,496	1.956

### 3.1.4. TG analysis

The relationship between the weight-loss percentage and temperature for the polycarboxylate ether was measured. In Figure 4, the TG and DTG curves were drawn for PC-4. The thermal curve exhibits two distinct regions of weight loss. The initial region of weight loss in the temperature range of 53.5 °C to 139 °C (DTG peak at 99.44 °C) was due to the evaporation of water adsorbed in the PCE sample. The second weight loss was in the interval of temperature at 358 °C to 433.28 °C (higher DTG peak at 414.42 °C), which is attributed to the decomposition of PCE chains and resulted in the maximum recorded weight loss of 57.20%.



**Fig. 4** TG-DTG analysis of the synthesized PCE

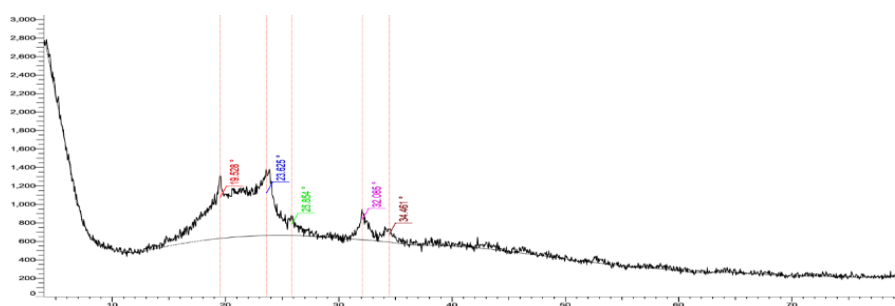
### 3.1.5. XRD analysis

A typical XRD analysis for PC-4 is shown in Figure 5. As observed, four peaks at  $2\theta$  19.52 °, 23.62 °, 32.09 °, and 34.46° appeared in the XRD pattern, indicating the semicrystalline nature of the tested sample (PC-4).

### 3.2. Evaluation of yield percentage and specific gravity

Table 4 presents comprehensive data on the yield percentages of each PCE sample, offering valuable insights into the influence of varying synthesis conditions on the overall yield percent. It becomes evident through the results that the yield percent is intricately tied to several key factors, including polymerization temperature, monomer composition, polymerization time, and initiator concentration. The recorded yield (%) values depicted a range spanning from 84.48% to 96.96%, with a discernible hierarchy observed among the different PCE samples, ranked in descending order as PC-7, PC-1, PC-2, PC-6, PC-9, PC-4, PC-3, PC-5, and PC-8. The highest yield percentage, reaching an impressive 96.96%, was successfully achieved for

the PC-7 sample under specific synthesis conditions: an MAA: MPEG-MA molar ratio of 3.65:1, a polymerization temperature of 90 °C, a polymerization time of 12 hours, and an APS initiator molar ratio.



**Fig. 5** XRD analysis of the synthesized PCE (PC-4)

One significant observation unveiled in the data showcases that elevating the polymerization temperature from 70 °C in the PC-5 sample to 90 °C in the PC-7 sample resulted in a substantial 10.85% increase in the yield percentage. This notable increase can potentially be attributed to the heightened activity of MPEG-MA in actively participating in the polymerization reaction under elevated temperature conditions. Moreover, a closer examination of the impact of polymerization duration on the yield percentage reveals interesting findings. Increasing the polymerization duration from 12 hours in the PC-4 sample to 48 hours in the PC-9 sample led to a modest 4.77% increase in the yield percentage. This marginal increase could be linked to the rising concentrations of MAA and MPEG-MA comonomers in the medium as the reaction time extended, consequently boosting the polymer formation rate and thereby affecting the yield percentage. Interestingly, alterations in the comonomer composition did not significantly influence the polymer yield, highlighting the robustness of the synthesis process under varying composition ratios. Additionally, the data illuminates the function of APS initiator quantity in modulating the polymer yield. Here, an incremental increase in the APS quantity corresponded to an increase in polymer yield, as evidenced by the rise from 86.38% in PC-3 to 86.62% in PC-4 with an APS quantity shift from  $22 \times 10^{-5}$  mol to  $44 \times 10^{-5}$  mol. However, beyond this point, the yield percentage decreased to 86.11% in PC-5, indicating a threshold in the APS quantity that maximizes the polymer yield. The rationale behind this phenomenon lies in the generation of a higher number of radical species with increased APS quantity, consequently fostering an increase in polymer yields. Nonetheless, a further escalation in the APS quantity could lead to the formation of a higher amount of nonprecipitable oily oligomeric fractions, resulting in decreased polymer yields post the  $44 \times 10^{-5}$  mol APS threshold. Furthermore, the specific gravity results featured in Table 4 offer crucial insights into the physical properties of the prepared samples. values ranging from 1.055 to 1.076 od Specific gravity were identified in all samples, displaying clear differences due to varying solid content values for the PCE samples. The significance of evaluating specific gravity in concrete mix design is underscored by these findings, as it serves as a fundamental parameter for ensuring the desired characteristics and performance of concrete formulations.

### 3.3. Rheological Test

Rheology behavior can be studied by measuring the flow table and slump test for the fresh grout mixes. All PCE-based SP samples were measured at a fixed water-to-cement ratio (0.25) to evaluate the different performances of PCE-based SPs. The grout composition for the blank sample (without PCE-based SPs) and PCE-based SP mixes, the values of a slump, and the flow table test at initial (0 time) and 30 minutes were summarized in Table 5. The results of the slump test of PCE-based SPs are better than blank grout samples without SPs although the water-to-cement ratio of the standard is higher than all PCE-based SPs mixes. The change of polymerization conditions such as MAA&MPEG-MA composition and initiator concentration, in addition to the polymerization temperature and reaction time, gave a deviation in PCE-based SPs performance due to the change in molecular weight and polydispersity index of the obtained PCE-based SPs. With increased initiator (APS) concentration in PC3 to PC5 samples the Mwt and PDI of PCE-based SPs decrease and give the best result for PC-4 grout mix for both slump test and flow table[17]. Decrease the monomer concentration in the PC-2 mix given the lower flow table diameter (65 mm) compared with other PC mixes at the same polymerization conditions due to the decreased active matter of the final prepared polymer. Furthermore, the increase in the polymerization temperature in PC-6 and PC-7 mixes at 80 and 90°C, respectively decreases the rheological behavior of the grout. Also, for PC-8 and PC-9 mixes, increasing the polymerization time by 24 and 48 hrs has a negative effect on the flow table values which are 140 and 120 mm, respectively. PC-4 mix exhibited good retention fluidity at 30 minutes for the flowability test compared with other PC mixes. The photographic pictures of the flowability of the grout test for all PCE-based SP grout mixes were presented in Figure 6 at the initial time. The PC-4 picture showed the best rheological behavior.

### 3.4. Setting time

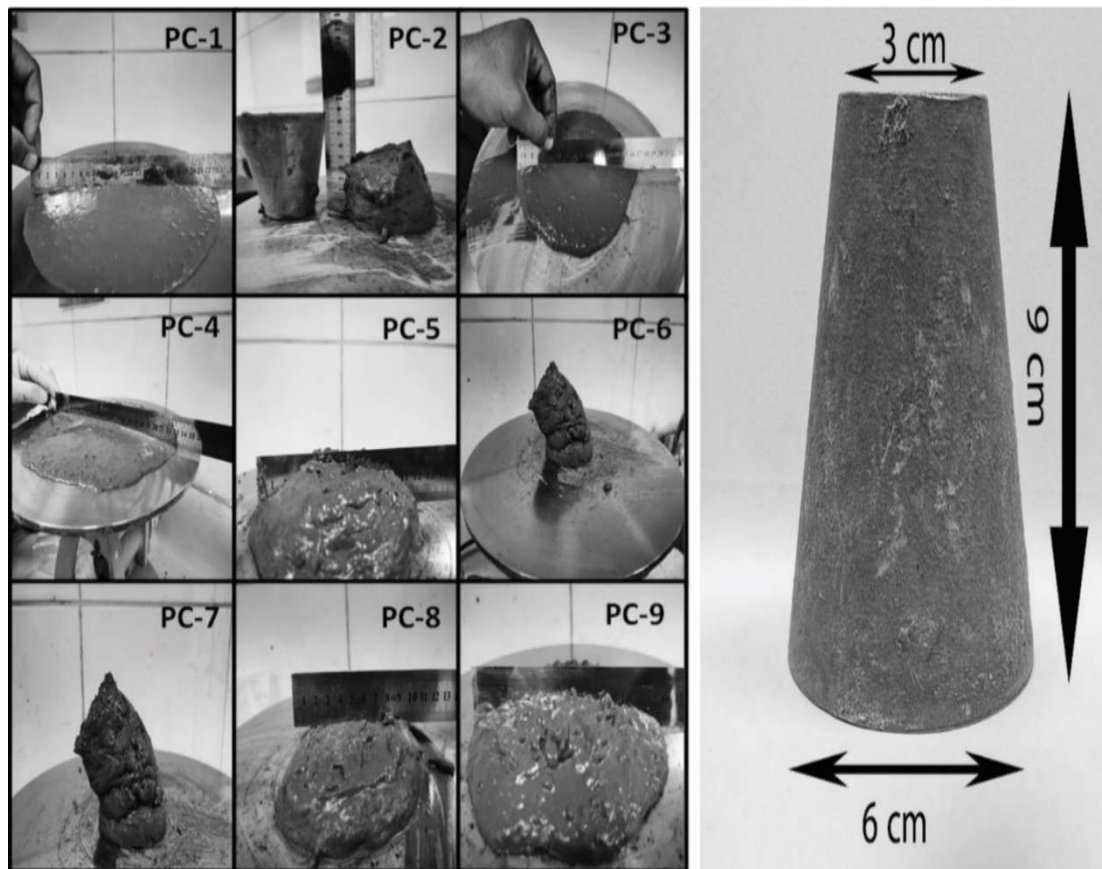
The process of cement hydration exerts a direct impact on the setting time of the cement paste [18]. Subsequent to the introduction of water, a sequence of chemical reactions unfolds, ultimately resulting in the solidification of the cement substrate. The setting times of the cement paste samples (initial and final) containing or lacking SPs are demonstrated in Table 6. seen in Table 6 that the setting times of the cement samples (initial and final) samples containing PCE were longer than



those of the blank sample. This is because the carboxyl groups in the PCE interacted with the calcium ions in the cement system to form various chelates [19]. The growth of solid-phase nucleation and hydration products was prevented, which delayed the cement hydration [20]. The setting times for the PC-4 sample (initial and final) are the longest compared with other samples due to its high performance and efficiency on the cement grain surface, which acts as a barrier between cement particles and water molecules.

**Table 4** Density and yield results of polycarboxylate samples

Characteristics	PC-1	PC-2	PC-3	PC-4	PC-5	PC-6	PC-7	PC-8	PC-9
Specific gravity	1.076±0.002	1.060±0.002	1.070±0.002	1.070±0.002	1.055±0.002	1.077±0.002	1.063±0.002	1.069±0.002	1.064±0.002
Yield (%)	93.71	93.60	86.38	86.62	86.11	93.54	96.96	84.48	91.39
Colour	Pale yellow	Pale yellow	Pale yellow	Pale yellow	Pale yellow	Pale yellow	Pale yellow	Pale yellow	Pale yellow



**Fig. 6** Photographic pictures for initial flow test of PCE-based SPs grout samples

**Table 5** Flow table and slump test results of grout mixes with/without different polycarboxylate sample.

Mix	Blank	PC-1	PC-2	PC-3	PC-4	PC-5	PC-6	PC-7	PC-8	PC-9
Cement (g)	500	500	500	500	500	500	500	500	500	500
Sand (g)	496	496	496	496	496	496	496	496	496	496
Water (g)	225	125	125	125	125	125	125	125	125	125
Dosage of PCE (g)		2	2	2	2	2	2	2	2	2
<b>Flow and slump test results (mm)</b>										
Flow Table, Initial	No	230	No	170	230	120	No	No	120	140
Slump Test, Initial	No	Collapse	65	Collapse	Collapse	No	No	No	No	No
Flow Table, 30 min	No	No	No	No	120	No	No	No	No	No
Slump Test, 30 min	No	No	No	No	No	No	No	No	No	No

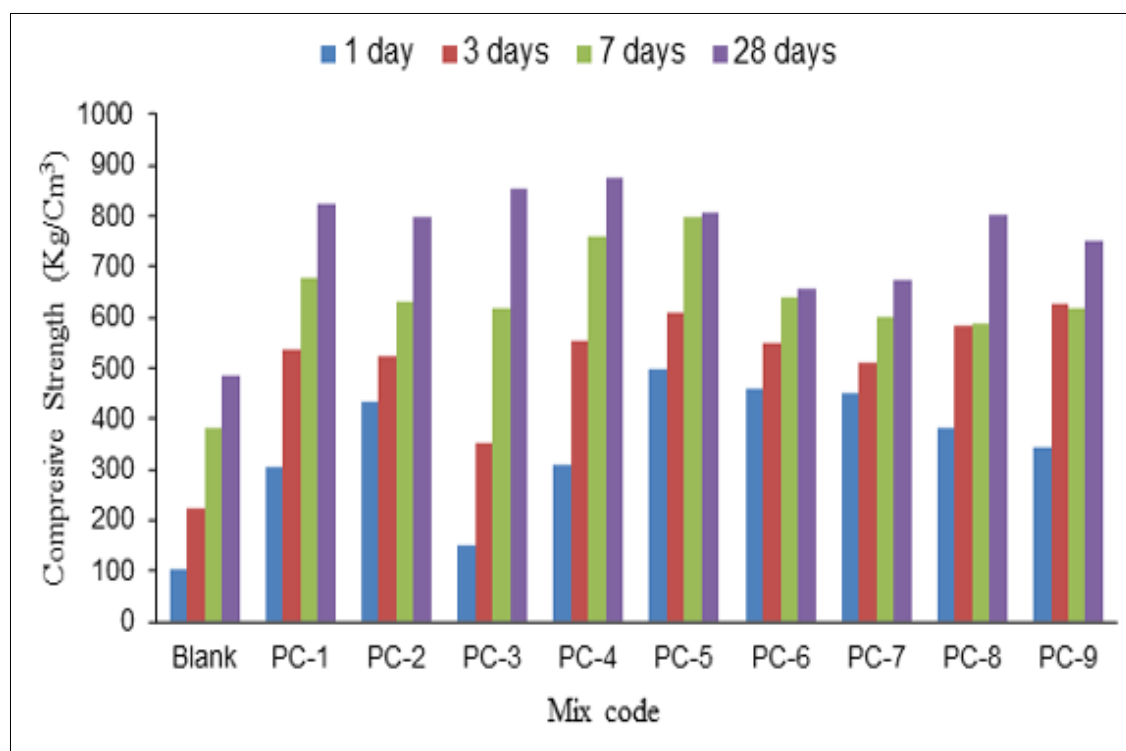


**Table 6** Initial and final setting time and compressive strength test results of grout mixes with/without different polycarboxylate samples

	Blank	PC-1	PC-2	PC-3	PC-4	PC-5	PC-6	PC-7	PC-8	PC-9
Setting time										
Initial setting min	51	263	210	267	274	192	200	205	215	213
Final setting min	238	409	377	480	420	354	372	360	390	402
Compressive strength										
1 day (kg/cm <sup>3</sup> )	104	304.4	432.4	151.6	308	496	458	450	384	345
3 days (kg/cm <sup>3</sup> )	225.2	537.6	524.4	352.2	554	608	551	511	584	626
7 days (kg/cm <sup>3</sup> )	383.2	678.8	632	619.6	760	798	638	600	586	616
28 days (kg/cm <sup>3</sup> )	487	823	797	853	875	805	658	675	800	751

### 3.5. Compressive strength

The assessment of mortar and concrete performance heavily relies on compressive strength, the most crucial mechanical property. Figure 7 displays the compressive strength of ten distinct mixtures with and without PCE-based superplasticizers at various curing ages (1, 3, 7, and 28 days). The data outlined in Table 6 reveals a consistent uptrend in compressive strength values across all samples as the curing age extends. This enhancement is attributed to the increased formation of hydration products like calcium silicate hydrates (CSH) and calcium aluminosilicate hydrates (CASH) [21]. This improvement is credited to the enhanced dispersion effects enabled by the carboxylic and hydroxyl groups on the polycarboxylate backbone, along with the steric repulsion and complexing interactions between PCE-based superplasticizers and the outer layer of cement particles [22]. For PCE-based SPs mixes, the best compressive strength results were obtained for PC-4 and PC-5 mixes, which are polymerized with high doses of APS as a free radical source at 70 °C. After the above temperature, the performance of PCE-based SPs decreased with increasing temperature. Conversely, increasing the polymerization time up to 24 and 48 hours for PC-8 and PC-9, respectively, adversely influences on the compressive strength, especially at the early curing age of hydration 1, 3, and 7 days. There is a relationship between Mw of the polycarboxylate polymer and its efficiency.

**Fig. 7** Compressive strength test for mortar mixes with/without PCE-based SPs at different curing ages (1, 3, 7, and 28 days of hydration)

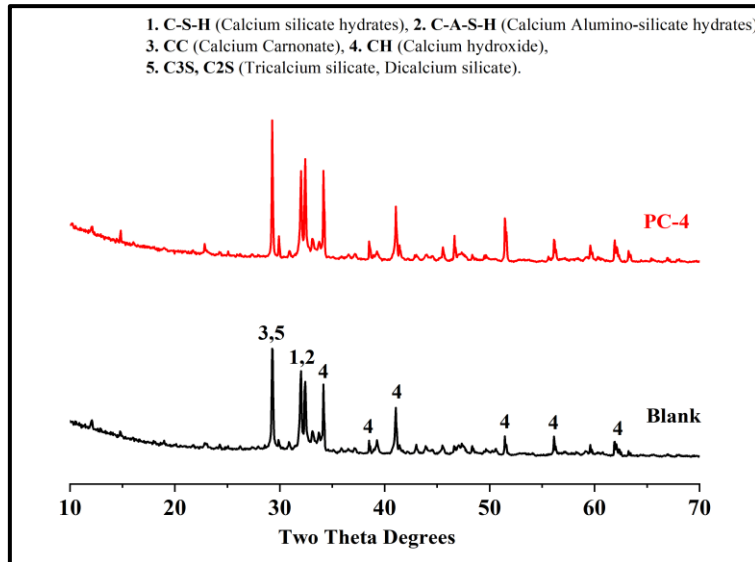


Fig. 8 XRD patterns for Blank and PC-4 hydrated cement paste samples at 28 days of hydration.

### 3.6. X-Ray diffraction of PC-4 hydrated cement paste

XRD of two selected samples: Blank sample (hydrated cement paste without Polycarboxylate) and PC-4 (OPC paste with PC-4) cured at 28 days of hydration at room temperature as demonstrated in Figure 8. All XRD patterns demonstrate the presence of different hydration products such as calcium silicate hydrates (C-S-H) and calcium aluminum silicate hydrates (C-A-S-H) Calcium hydroxide (CH, Portlandite) and some unreacted Clinker phases (Dicalcium silicate and Tricalcium silicate). The presence of unreacted cement phases especially Dicalcium silicate can be ascribed to less reactivity of  $C_2S$  up to 28 days of hydration. The presence of  $CaCO_3$  can be related to the carbonation of  $Ca(OH)_2$  (portlandite) due to the rise of its alkalinity which increases the  $OH^-$  ions in the water curing system. As shown in XRD patterns, the PC-4 sample exhibited sharp peaks of hydration products (1, 2, and 4) in comparison to the blank sample which can be illustrated by the presence of polycarboxylate chains that have dual actions. The first increases the electrostatic force among the cementitious particles and increases the electrical double layers followed by an increase in the gel formation during the early ages of hydration. The second, polycarboxylate chains act as deflocculating agents by the action of ion exchange and steric repulsion forces. The presence of polycarboxylate enhances the cement hydration process of clinker phases and increases hydration products such as C-S-H and C-A-S-H [23]

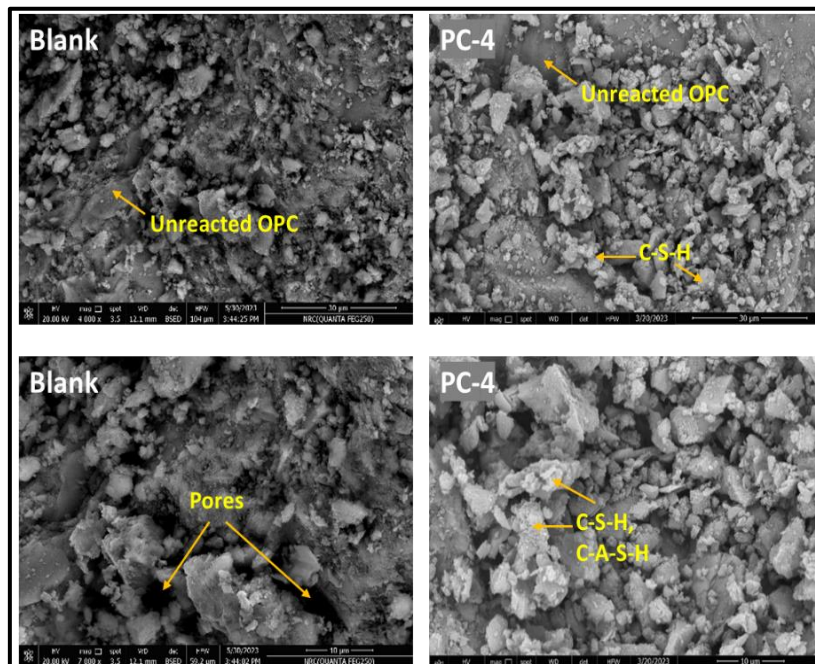


Fig. 9 SEM images for Blank and PC-4 hydrated cement paste samples for two magnifications Values X-4000 and X-7000 at 28 days of hydration

### 3.7. Morphological observations of PC-4 hydrated cement paste

Figure 10 shows the SEM for the hydrated blank paste at 28 days of hydration without polycarboxylate addition and compares its surface texture with the PC-4 hydrated paste. The SEM results show the presence of unreacted cement particles, and hydrated cement products as white accumulated and dispersed points (in the form of calcium silicate hydrates [C–S–H] and sodium aluminum silicate hydrates [N–A–S–H]), and pores with different sizes [24]. SEM image for the PC-4 sample shows a denser and more compact structure between sand grains and hydrated cement products due to the dispersion efficiency of the polycarboxylate chains. conversely, SEM images for the blank sample exhibit larger pore sizes compared with the PC-4 sample. The presence of high porosity in the blank sample decreases the compressive strength value. In addition, these results are confirmed by XRD patterns for the same samples by the formation of excessive hydration products in the case of PC-4 hydrated paste.

### 4. Conclusions

A series of polycarboxylate ethers (PCE) was synthesized via radical polymerization technique in an aqueous solution. The investigation of polycarboxylate performance for PCs grout mixes and comparison of their effect with the neat OPC sample were evaluated by setting times, slump tests, and compressive strength. The polycarboxylate efficiency highly depends on the synthesis conditions of the polycarboxylate polymer, such as reaction temperature, reaction time, monomer composition, and initiator concentration. All synthesized polycarboxylate samples have excellent rheological and mechanical properties on grout cement samples. The compressive strength of PCs-grout mixes was given higher values compared with a blank sample without polycarboxylates at different curing ages. PC-4 exhibits better efficiency than all other PCs in terms of flowability, setting times, and compressive strength of grout mixes. XRD and SEM results show better morphology and microstructure for the hydrated cement paste compared with the neat OPC. This research can provide new strategies for the development of higher-performance polycarboxylate, which could improve the actual workability of concrete.

### Conflict of interest

The authors declare no conflict of interest.

### Availability of data and materials

All authors confirmed that the raw data presented in this study are available on request from the corresponding author.

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