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Synthesis and Characterization of Novel Copolymers of Poly (isopentenyl PEG - co-allyl PEG), Their Performance in Cement Mortar and Comparison with Physical Blends

Zeynep DIZDAR[1], Olcay MERT[2], Guralp OZKOC[1, *]

[1]*Kocaeli University Department of Chemical Engineering, Izmit/Kocaeli 41380 TURKEY*

[2]*Kocaeli University Department of Chemistry, Izmit/Kocaeli 41380 TURKEY*

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Abstract

The aim of this study is the synthesis and characterization of the novel copolymers of poly(isopentenyl PEG-co-allyl PEG) (TPEG-co-APEG) and the investigation of their influence on the properties of the cement mortar. The performance of the copolymers was compared with the physical blends of TPEG and APEG having the similar TPEG/APEG ratio. In addition, a commercial MPEG type PC was used as a control in the experiments. The FTIR and 1H-NMR proved that the copolymerization was successfully achieved. GPC enlightened the change of molecular weight of the copolymers. The dispersion, flow retention and the strength of the mortars prepared with copolymers or physical blends were compared. It was found that the strength and the adsorption of the copolymers were better than that of blends, whereas flow retention of the blends was better in comparison to that of the copolymers.

1. INTRODUCTION

In recent years, the interest in preparing high-performance and non-polluting concrete and development of concrete admixtures has grown rapidly [1-4]. Polycarboxylate (PCE) superplasticizers are utilized in constructions to obtain high-flow mortar to be used in self-compacting concrete having a low water-to-cement ratio. In addition, modified PCE superplasticizers yield excellent fluidity retention. PCEs, comb-shaped copolymers, consist of a backbone having negatively charged carboxylate groups and side chains of poly(ethylene oxide) (PEO). Cement particles are adsorbed by the carboxylate groups, while PEO-grafted side chains stretched-out from the cement particle to create steric hindrance and to prevent agglomeration of cement particles. There are many PCE types of chemically different products can be found in the market today, including MPEG-type PCEs that were made from ω-methoxy poly(ethylene glycol) methacrylate ester, APEG-type PCEs that were synthesized from α-allyl-ω-methoxy or ω-hydroxy poly(ethylene glycol) ether, VPEG-type PCEs that were based on vinyl ethers and TPEG-type PCEs that were made from isoprenyloxy poly(ethylene glycol), IPEG-type PCEs that were made from isobutenyl PEG. The APEG, VPEG or TPEG types were produced alternatively to MPEG.

There are many publications on PCE products focused on PCE chemistry, number, length and density of side chains and also the dispersion effects and the adsorption mechanism on to the cement or micro-sized fillers such as fumed-silica. Moreover, some of the publications were about compatibility of concrete with clay or silt. Plank et al. investigated the influence of the lipophilic-hydrophilic balance (HLB) value of PCE on the flow behavior of concrete. It was found that the HLB value of a PCE designates if a PCE will initiate the water-like flow behavior in a concrete. Among the PCEs tested, the APEG-types resulted in the best water-like flow behavior, followed by IPEG and MPEG type PCEs [5, 6]. Liu et al. studied the preparation, characterization and performance of PCE superplasticizer that were synthesized through bulk polymerization. PCEs of TPEG and IPEG exhibited the best fluidities and retaining properties [7].

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*Corresponding author, e-mail: guralp.ozkoc@kocaeli.edu.tr

Another paper was about the dispersion, adsorption and flow retaining behavior of cement mortars containing TPEG-type polyether kind polycarboxylate superplasticizers (PCEs), which were synthesized using isoprenyl-oxy-PEG-ether (TPEG), acrylic acid (AA), maleic anhydride (MA) and sodium methylallyl sulfonate (SMAS). The results indicated that the MA modified TPEG-type PCE having a definite amount of anchor groups and PEO side chains exhibited very good water reducing property and flow retention. This was attributed to the synergy between the steric hindrance and the electrostatic repulsive forces [8]. Plank and Lei studied the synthesis of a vinyl ether-based PCE for the clay tolerant-concrete. Sorption measurements and X-ray diffraction analysis showed that the new PCE interacts with clay only through surface adsorption, whereas conventional PCEs with PEG graft chains were entered chemically into the interlayer space of clay layers [9]. Plank et al. investigated the synthesis and performance of a modified polycarboxylate dispersant with a new building block for concrete having enhanced cement compatibility. The results were compared with conventional APEG- and methacrylate ester (MPEG)-type PCEs. Results suggested that the modified PCE dispersed all cement samples well and hence was more robust against variations in cement composition. The new building block induced higher affinity to the surface of cement [10]. In a different study, researchers were interested in synthesis and performance of methacrylic ester based polycarboxylate superplasticizers possessing hydroxy terminated poly(ethylene glycol) side chains. The results showed that hydroxy terminated poly(ethylene glycol) methacrylate ester had better performance [12]. Plank and Sachsenhauser investigated the effects of α-allyl-ω-methoxypolyethylene glycol-maleic anhydride copolymers having different side chain lengths on the adsorption and dispersing effect of cement. It was found that the amount of polymer adsorbed on cement rapidly decreased with increasing side chain length [13]. In a different study [16], Plank and Hirsch focused on the influence of the zeta potential of early cement hydration products, particularly ettringite, monosulfate, syngenite, portlandite, and gypsum, on superplasticizer adsorption. Very high positive zeta potential resulted in a strong superplasticizer adsorption whereas a negative zeta potential does not allow adsorption. In another research by Keller and Plank, the PCE copolymers based on maleic anhydride and α-allyl-ω-methoxy PEG ethers were synthesized. The researchers focused on the influence on the morphological changes of calcium carbonate crystals. The results showed that PCEs can also modify the growth of cement hydrates [19].

The advantageous and disadvantageous of PCEs extracted from the literature are shown in Table 1. It is seen that one type of PCE is not enough to satisfy all the requirements. Some of the PCE types are good in cement dispersion but not good in retention. The studies reported in the literature have been focused on the dispersion and the adsorption effects, flow behavior of mortar, backbone and number of side chains of PCEs, etc. of alternative PCEs. Differently from the literature, in this study, we synthesized TPEG and APEG based PCEs and also their novel copolymers of poly(isopentenyl PEG-co-allyl PEG) (TPEG-co-APEG) in order to combine advantageous properties in one structure. We have investigated the ratio of APEG to TPEG on the performance in slump retention and compressive strength of mortar, and we have also characterized the copolymers via spectroscopic, choromotographic and thermal techniques. In addition, we have compared the properties of copolymers of TPEG-co-APEG with physical blends of TPEG/APEG having the same TPEG to APEG ratio. A graphical representation of the experimental stages of this paper is given in Figure 1.

Table 1. *The properties of PCEs type on cement or mortar*

PCE type	**Producer**	**Physical Properties**
MPEG	Dispersion of cement [6, 8, 11]	M_n: 2400 g/mol Appearance: White crystal Pure: 99% Dissolve in DMF, water, etc.
TPEG	Slump retention [7, 8] Adsorption on cement [8]	
APEG	Dispersion of silica fume [11, 20], fast floe speed [5, 6]	Mn: 72,06 g/mol Density: 1.18 g/cm^3
IPEG	Dispersing effect, fast flow speed [6]	Purity: 99% M_n: 105.99 g/mol Density: 1.85 g/cm^3

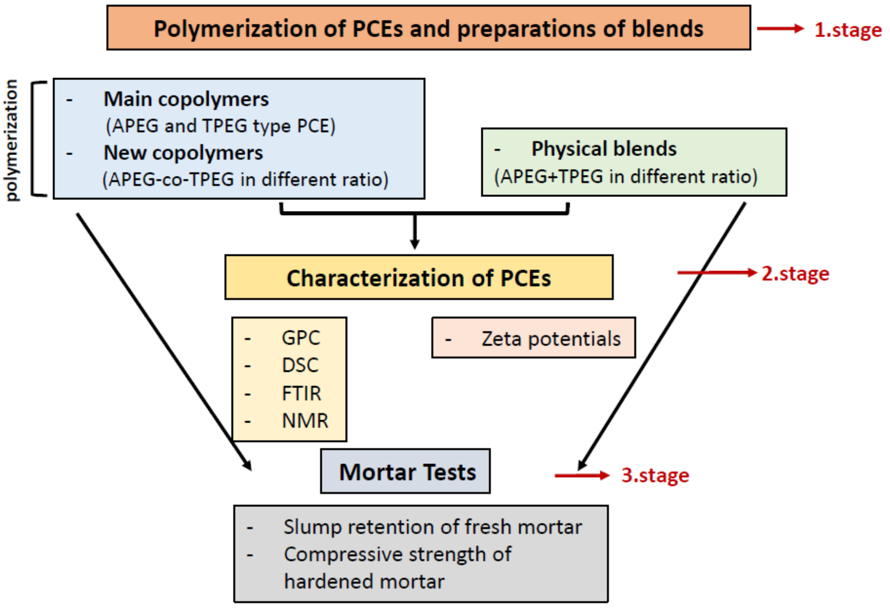


Figure 1*. The schematic representation of the synthesis PCEs, characterization and mortar tests of PCEs*

2. MATERIALS AND METHODS

2.1. Materials

The details of the materials used through-out the experiments were summarized in Table 2. The cement used in this study was a portland cement (CEM I 42.5 R) from Nuh Çimento A.Ş.

2.2. Synthesis of PCEs

Two types PCEs (TPEG and APEG) and their seven copolymers (TPEG-co-APEG) having different compositions were synthesized and characterized. In addition, their physical blends (TPEG+APEG) having the same composition were prepared and compared to copolymers.

APEG type PCE were prepared from macromonomer, AA and MAn through free radical polymerization at a molar ratio of 1:3:4.5, respectively. APS was used as the initiator in all reactions. The macromonomer was dissolved in distilled water in a 100 ml three-neck flask combined with a stirrer, condenser and initiator inlet. Firstly, the macromonomer was completely dissolved, and then AA, MAn, APS and SPM were added. The temperature was increased to 80°C and kept constant. APS aqueous solution that was 0.5% of macromonomer was added drop-wise into the reaction mixture for 1 h under atmospheric pressure. The total reaction time was 4 hours. The concentration of the final product was 30 wt% PCE in water. Synthesis reaction of APEG type PCEs is shown in Figure 2.

TPEG type PCEs were synthesized with the same method as explained in APEG above. Instead of using APEG type macromonomer, TPEG type macromonomer was used in TPEG type PCEs. In synthesis of APEG-co-TPEG PCEs, APEG and TPEG macromonomers were used together at different molar ratios.

Table 2. *Structure and physical properties the materials used in synthesis of PCE*

Materials	**Producer**	**Physical Properties**
TPEG type macromonomer	Turkey	M_n: 2400 g/mol Apperance: White crystal Pure: 99% Dissolve in DMF, water, etc.
APEG type macromonomer		
Acrylic acid	Acar Chemicals	Mn: 72,06 g/mol Density: 1.18 g/cm^3
Sodium hypophosphite monohydrate	Merck	Purity: 99% M_n: 105.99 g/mol Density: 1.85 g/cm^3
Maleic anhydride (MAn)	Sigma	M_n: 98.06 g/mol Density: 1.48 g/cm^3
Ammonium persulfate (APS)	Akkim	M_n: 228.2 g/mol

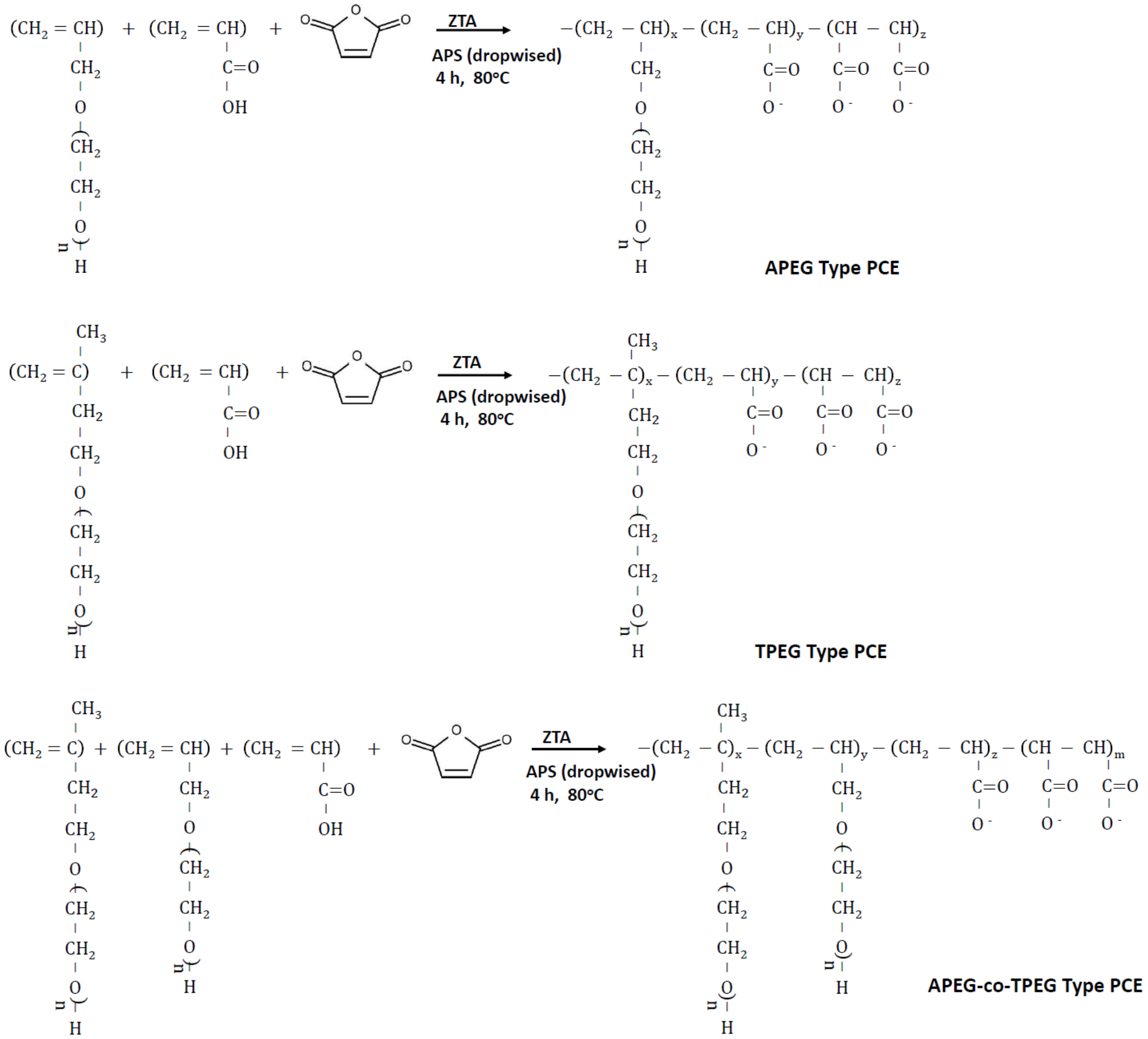


Figure 2. *Synthesis reaction of polycarboxylate copolymers*

2.3. Preparation of Cement Mortars

The mortar was prepared from 450 g of ordinary Portland cement (CEM I 42.5 R) and 1350 g of CEN (European Committee for Standardization) standard norm sand. The cement to sand ratio was 1:3. 211.5 g of water was added to maintain water to cement ratio of 0.47. The mortar was mixed according to the DIN EN 196 standard using a MX-AT 96-107 model mixer from Metaş Machine A.Ş., Ankara/Turkey. Firstly, half of the cement and water were added and then mixed for 30 sec at low speed. Then, the rest of the materials were added gradually during mixing time of 30 seconds and mixed for 15 sec. After that, the content of the mixer mixed at high-speed for 90 sec. For the PCE samples, the dosages (% percent weight of cement) were adjusted to reach a mortar spread flow value of 25 ± 1 cm at room temperature.

2.4. Characterization of PCEs

2.4.1. Gel Permeation Chromatography (GPC)

The PCEs were characterized by Flexar model GPC (Perkin Elmer) containing refractive index and ultraviolet detectors. PL aquagel-OH 30 and 40 columns with an operating range (PEG/PEO) of M_w=100 to 60000 and 10000 to 200000 g/mol were used.

2.4.2. Fourier Transformed Infrared Spectroscopy (FTIR) and ^{1}H-NMR Analysis

Prior to analysis, the PCE solutions were freeze-dried at -110°C under vacuum. In order to determine the chemical structure of the PCEs, FTIR analysis were carried out using a Perkin Elmer Spectrum 100 Universal ATR instrument. The spectral resolution was of 2 cm^{-1}. Each sample was scanned 16 times. For ^{1}H-NMR analysis, samples were first dried then dissolved in d-dimethyl sulfoxide (d-dmso). The ^{1}H-NMR spectra were obtained at room temperature with an Avance-300 spectrometer (Bruker) operating at a frequency of 300 MHz.

2.4.3. Differential Scanning Calorimeter (DSC)

Differential scanning calorimeter analysis (DSC) was performed using a Mettler Toledo DSC1 Star System. The temperature range was -40 to 120°C, and the heating rate was 10°C/min. Nitrogen gas was used as the purge gas.

2.5. Properties of Cement Mortar with PCEs

2.5.1. Fluidity and Flow Retention of Fresh Cement Mortar and Compressive Strength of Hardened Cement Mortar

A fresh mortar spread flow test was analyzed as follows: the mortar was poured into a Vicat cone, which was placed on a glass plate, and filled exactly to the brim. Thereafter, the cone was removed vertically. The resulting spread of the mortar was measured twice. The second measurement is at a 90° angle to the first one. An average value was reported as the spread flow value (Figure 3). For the PCE samples, the dosages were adjusted to reach a mortar spread flow value of 25 ± 1 cm. To investigate the fluidity retention, mortars with PCEs were examined every 30 min within a total period of 120 min. The compressive strength of hardened mortar was measured after 1st, 7th, and 28th days of standard curing according to DIN EN 196.

Figure 3. *The spread flow test of mortar*

2.5.2. Zeta Potential Measurements

The zeta potential was determined with Nano ZS model Zetasizer (Malvern Instruments). CEM I 42,5 R portland cement was used to prepare the cement paste. The zeta potential of the paste was measured as a function of copolymer dosage, such as 0.1%, 0.2% and 0.3%. Diluted cement slurries were prepared using 0.20 g of cement in 100 ml deionized water with different PCEs at different concentrations. All suspensions were mixed for 10 min before the test.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of PCE Samples

The GPC analysis of copolymers and the reference, a commercial MPEG type PCE are shown in Table 3. The GPC was used to obtain the polymer fractions in the superplasticizer samples and to determine the weight-average molecular weight (M_w), number-average molecular weight (M_n) and the polydispersity (PDI). The M_n value for the commercial product (reference) is 6970 g/moles and M_w is 31340 g/moles with a PDI value of 4.4. For the TPEG and APEG, respectively, M_n is 5600 g/moles and 2700 g/moles; and M_w is 40020 g/moles and 9620 g/moles. The polydispersities are found as 7.1 and 3.6 for TPEG and APEG, respectively. For the TPEG/APEG (T/A) copolymers M_n values are between 3200 to 3900 g/moles, and the M_w values are between 15000-21000 g/moles depending on the composition of the copolymer. The corresponding PDI values are in the range of 4.5 to 5.7. Under similar polymerization conditions, it is seen that the TPEG has higher M_n and M_w with a broader molecular weight distribution (PDI: 7.1), whereas APEG exhibited smaller M_n and M_w with much narrower molecular weight distribution (PDI: 3.6). As the copolymers of TPEG/APEG are considered, a significant dependence of either M_n or M_w on composition could not be obtained, but the M_n and M_w values were in between that of TPEG and APEG.

Table 3. *The GPC results for the copolymers and commercial sample*

Copolymer*	**M_w**	**M_n**	**Polydispersity Index (PDI)**
Reference**	31340	6970	4.4
100TPEG	40020	5600	7.1
80T/25A	16050	3530	4.5
75T/20A	20440	3740	5.5
67T/33A	18760	3260	5.7
50T/50A	16380	3780	4.3
33T/67A	15520	3300	4.7
25T/75A	17890	3590	4.9
20T/80A	21670	3980	5.4
100APEG	9620	2700	3.6

The presence of the characteristic chemical groups in superplasticizers was analyzed through FTIR. The FTIR analysis was taken for the specific frequencies of stretching vibrations for aliphatic groups (3200–2500 cm^{-1}), carbonyl groups (1900–1500 cm^{-1}) and ether groups (1250–950 cm^{-1}) (Figure 4). The bands specific for carbonyl groups (1500–1900 cm^{-1}) revealed that samples contained esters (1726–1728 cm^{-1}) and also some amounts of free carboxylic acids (1632 cm^{-1}). In APEG type PCE, free carboxylic acid peak was not strong. In spectra of all samples there was no peak observed for free maleic anhydride (1830 cm^{-1} and 1760 cm^{-1}). The spectra of APEG-co-TPEG copolymer type PCEs showed the bands of hydrophobic aliphatic groups at 2877 cm^{-1} (-CH_2) and bands of hydrophilic oxyethylene groups at 1150–1040 cm^{-1} (CH_2-O-CH_2) from the poly(ethylene glycol) chains.

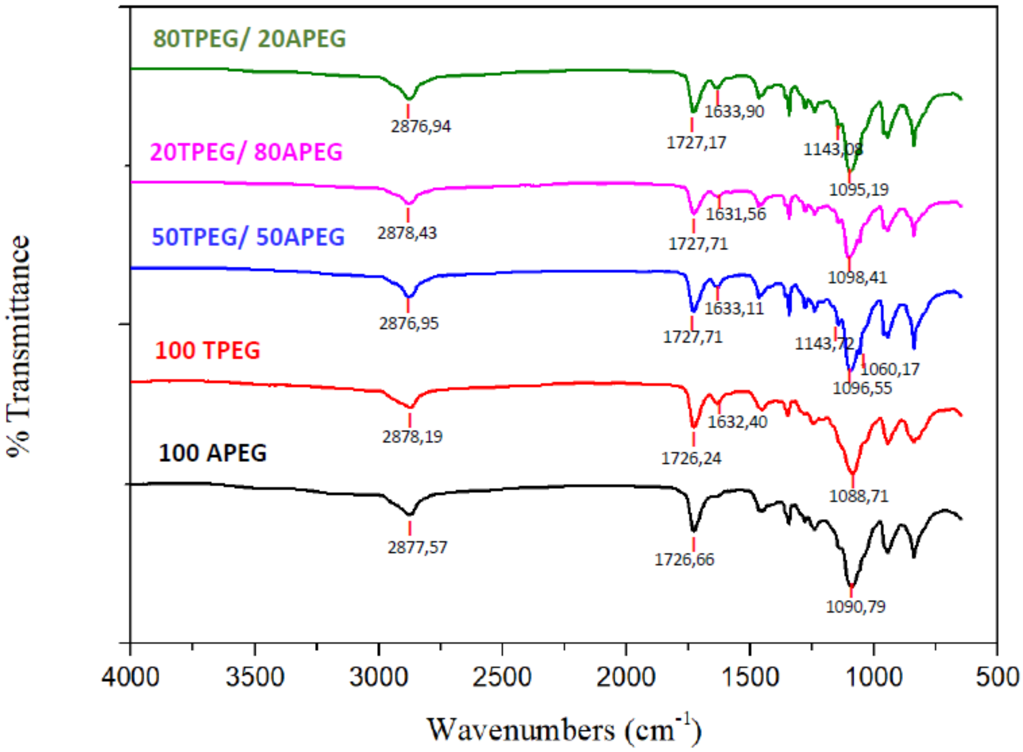


***Figure 4.** FTIR spectra for polycarboxylates*

^{1}H-NMR spectra for (a) TPEG monomer, (b) APEG monomer, (c) TPEG polymer, (d) APEG polymer, and (e) 50 TPEG/ 50 APEG copolymer were given in Figure 5. TPEG and APEG monomers were used to further verify the success of the polymerizations and the determination of repeating number of units in PEG. The solvent peaks of d-dmso and H_2O resonanced at $\delta = 2.50$ and 3.30 ppm in all spectra, respectively. TPEG monomer (Figure 5a) gave signals 1.70 ppm (-CH_3, s), 2.20 ppm (=C-CH_2, t), 3.5 ppm (−OCH_2CH_2–, s, ether groups of PEGs), 3.65 ppm (-CH_2O, t), 4.69, 4.74 (CH_2=, 2s), 4.60 (− OH, s, end group in TPEG). The number average molecular weight of the PEG side chains in TPEG was determined from the ratio of the CH_2=C of alkene and the CH_2 protons of PEG in ^{1}H-NMR. Mn of PEG side chains was found as approximately 2.700 g/mol with 60 units of ethylene oxide. That's why huge intensity of PEG signals was observed when compared to the other peaks in ^{1}H-NMR for all TPEG and APEG monomers and their homo- and copolymers. (Figure 5a-e) The resonances at 0.8–1.0 ppm (CH_3-), 1.0-2.0 ppm (-CH_2), and 2.0-2.8 ppm (-CH-) belonged to the TPEG, AA, and MA units. Also, the peaks between 3.5 and 3.7 ppm were attributed to the CH_2 of polyoxyethylene side group. (Figure 5b) Shifts in resonances in TPEG combined with broadening of peaks represented an indication of successful polymerization. For example, the signal of meta substituent (-CH_3) was shifted from 1.70 ppm to 1.08 ppm (via double bond opening) after the polymerization of TPEG. APEG macromonomer (Figure 5c) displayed signals at 3.5 ppm (−OCH_2CH_2–, s, ether groups of PEGs), 4.0 ppm (-CH_2O, m), 4.60 ppm (−OH, s, end group in APEG), 5.15, 5.25 ppm (CH_2=, m), 5.9 ppm (=CH, m). M_n of PEG side chains in APEG were very similar with those in TPEG according to ^{1}H-NMR peak calculations. The formation of new signals at high field of spectrum (1-3 ppm) together with peak broadening proves the polymerization of APEG. The resonances at 1.2-2.0 ppm (-CH_2), and 2.05-2.75 ppm (-CH-), 3.6 ppm (-OCH_2CH_2) belonged to the APEG, AA, and MA units. (Figure 5d) The formation of saturated methyl, methylene, and methine groups from unsaturated alkenes resulted with new signals in 50 % TPEG/ 50 % APEG copolymer, as well. Both proton signals of repeating units of TPEG and APEG together with AA and MA moieties were overlapped in the regions of 0.8–1.0 ppm (CH_3-), 1.0-2.1 ppm (-CH_2), and 2.1-2.7 ppm (-CH-), 3.6 ppm (-OCH_2CH_2) in ^{1}H-NMR spectrum. (Figure 5e)

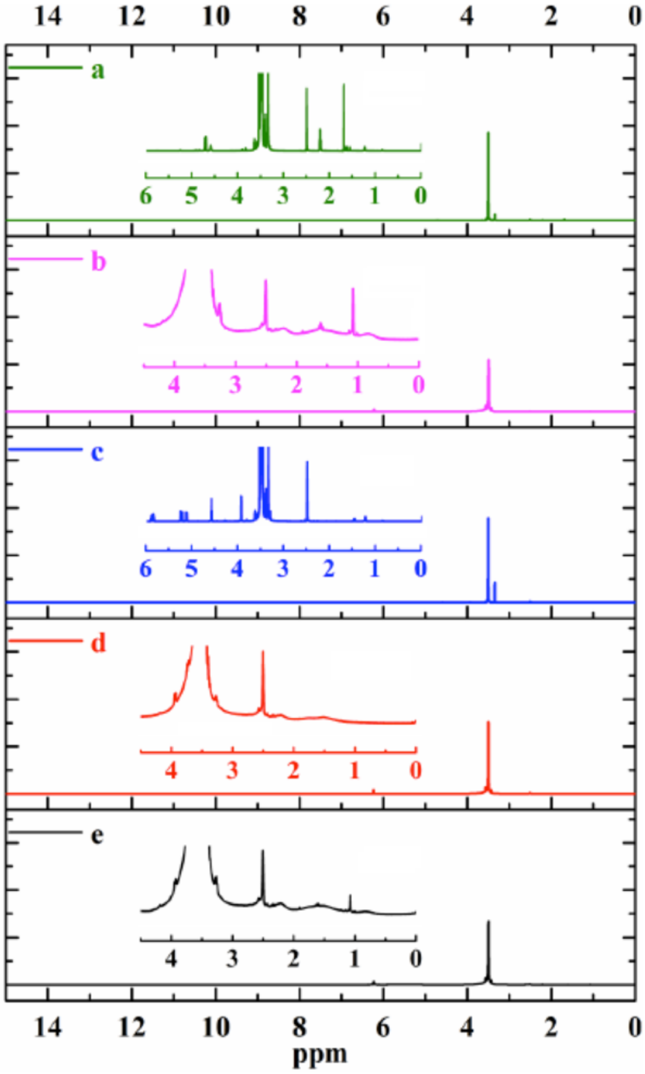
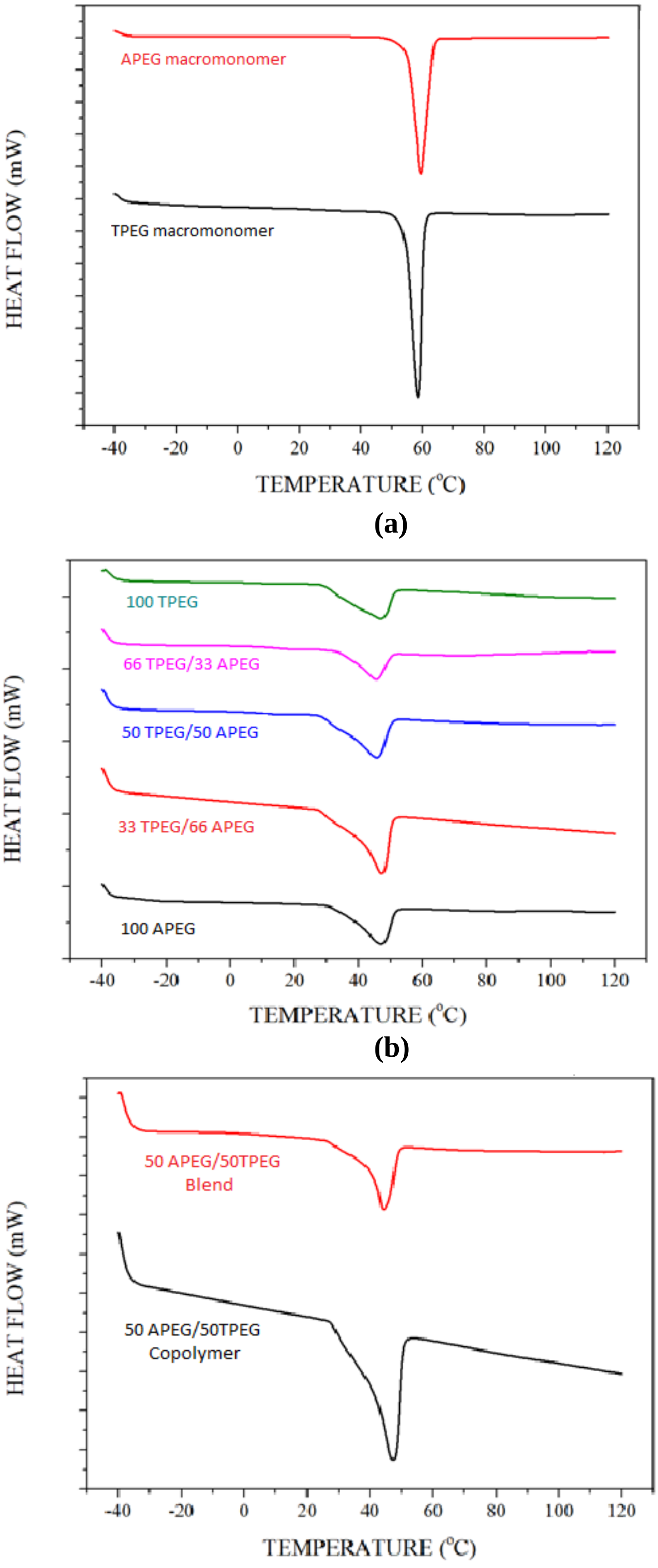


Figure 5. *^{1}H-NMR spectra of a) TPEG macromonomer, b) TPEG polymer, c) APEG macromonomer d) APEG polymer, and e) 50 TPEG/ 50 APEG copolymer*

The DSC thermograms of the APEG and TPEG macromonomers, their polymers and different ratio of APEG-TPEG copolymers were examined between -30 and 110ºC in Figure 6. All polymers displayed amorphous state, as expected, except for PEG side chains according to thermograms. T_m values of APEG and TPEG macromonomers were found to be 56°C and 58 °C, respectively while the melting temperature of copolymers was around 45-46°C (Figure 6). The presence of the AA and MAn moieties diminished the melting temperature of the corresponding APEG or TPEG in the PCE copolymers. This situation proved that the crystallization of APEG-TPEG copolymers was remarkably affected by the presence of the other components. The lowering of melting point is probably due to the thinner crystalline lamella in the copolymer. The DSC thermograms of the different copolymers also revealed that the higher molecular weight caused a lower melting peak (especially at onset) for MePEG/PEG. For example, the onset (starting at melting) temperatures of 100 TPEG/ 0 APEG copolymer (Mw: 40k), 66 TPEG/ 33 APEG copolymer (Mw: 18.8k), and 50 TPEG/ 50 APEG copolymer (Mw: 16.4k) were around 29, 32, and 37ºC, respectively. Similar behaviors were observed in polylactide–PEG and diisopropyl polyglycolide-PEG copolymers in the literature [21, 22]. In Figure 6c, Tm values of 50 TPEG+ 50 APEG blend was found to 43 °C, while the melting temperature of copolymers was around 46°C, there was a difference about 3 °C between Tm values of blend and copolymers.



(a)

(b)

(c)

Figure 6. *DSC thermograms of a.) TPEG, APEG macromonomers, b.) copolymers, and c.) selected blends and copolymers*

3.2. Flowability of Fresh Mortar and Compressive Strength of Hardened Mortar

To investigate the effects of APEG-co-TPEG copolymers and APEG/TPEG blends on flowability properties of fresh mortar, the flow retention was examined during 120 min. The dosage of PCEs was adjusted to control targeted spread value of 25 ± 1 cm. The dosages of copolymers and blends are shown in Table 4.

Table 4. *The dosages of copolymers and blends to control targeted spread value of 25 ± 1 cm*

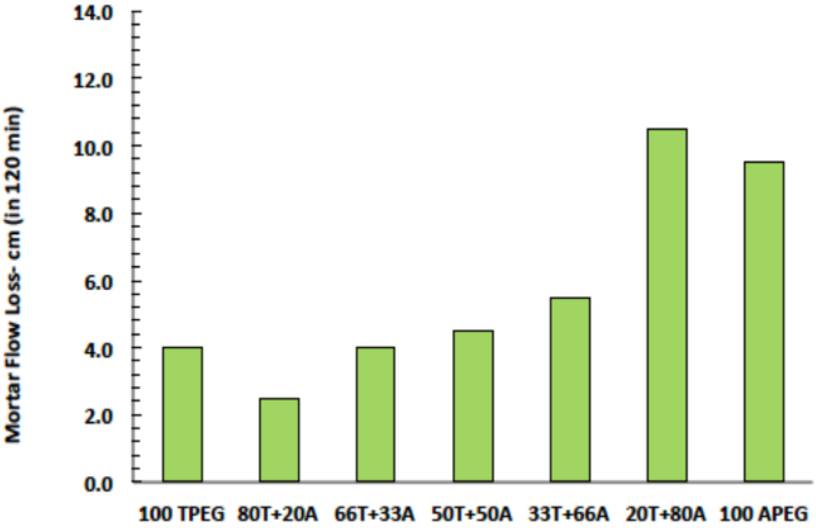
Copolymer	**Dosage %**	**Blends**	**Dosage %**
100TPEG	0.9	100TPEG	0.9
80T/20A	1.0	80T+20A	1.2
67T/33A	1.0	67T+33A	1.2
50T/50A	1.1	50T+50A	1.3
33T/67A	1.3	33T+67A	1.5
20T/80A	1.4	20T+80A	1.5
100APEG	1.4	100APEG	1.4

All the PCE types examined in this study yielded comparable dosage values with the reference materials with acceptable variation. According to Plank et al. the lower the dosage of PCEs to achieve the same flow spread, the stronger the adsorption to the cement particles [6], and generally, the better the dispersion performance of PCEs, the higher the adsorption amount of PCEs on cement [10, 11, 13]. The results indicated that TPEG-type PCEs were the most effective ones as cement dispersants with the lowest dosage (i.e. dosage %=0.9) with respect to MPEG and APEG type PCEs. On the other hand, as the APEG content increased in the either blend or copolymer, the dosage became higher. The different steric locations of carboxylic groups on the chains leads to the different adsorption behaviors of the two PCEs. It is usually thought that one major factors behind the adsorption of PCEs on mineral surfaces is the ability to make complexes with calcium ions or atoms on the surface of minerals [23]. The maximum interaction can occur if the steric location and accessibility of surface calcium atoms or ions match with the position of carboxylate groups exists on the PCE molecule. The COO groups are located at different distances with respect to APEG-PCEs in TPEG type PCEs.

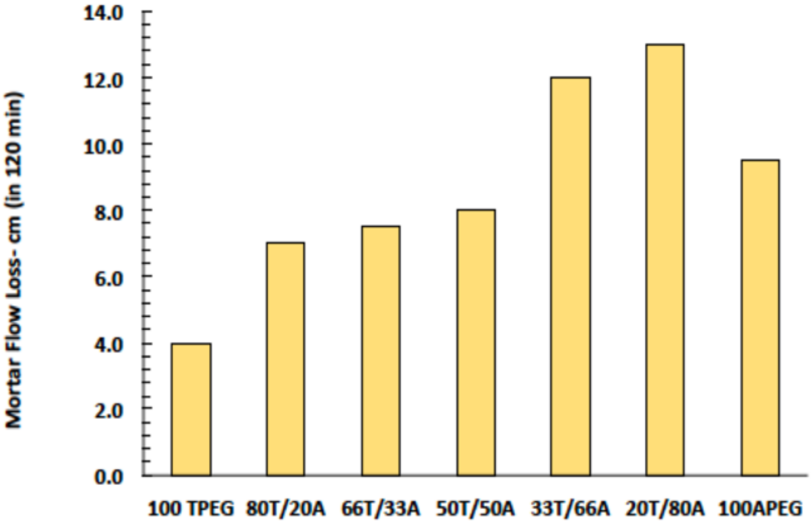
In addition, the copolymer’s dispersing performance was better than that of blends as seen from the results. The reason could be explained in such a way that in the same chemical structure, PCEs interaction can occur easily with cement surface, in contrast, in blends, interaction can be difficult because the excess of ions in the solution [24].

Time dependent flow retention behaviors of the PCEs measured at different dosages are shown in Figure 7. The values represented in plots are the loss of the flow values in 120 min. The loss of flow-spread values of MPEG type PCE and the reference, was measured as 6.5 cm in 120 min. According to the data, the flow retention ability of the cement mortar with blends generally was better than the conventional MPEG-type PCE. However, in contrast, the flow retention ability of the copolymers was not as good as the blends and TPEG-type PCE. Flow retention has been associated to the steric hindrance of the longer side chains [12,15,25]. When the side chains in TPEG structure is longer than that of APEG, TPEG yielded better flow retention. In addition, since the adsorption of copolymers was better in compared to blends, there is not enough ions to enhance the flow retention as the copolymers were used [25].

The compressive strength of hardened mortar was measured after 1st, 7th and 28th days of curing. The compressive strength of mortar with copolymers and blends is shown in Figure 8. The compressive strength of hardened mortar with MPEG type-PCE measured on 1, 7 and 28 days is 18.3, 27.7 and 34.1 MPa, respectively. Meanwhile, the results indicated that the compressive strength of copolymers increased higher than that of blends. The hardened mortar with TPEG-type PCE has the highest strength value and also, 66 TPEG-co-33APEG, 50 TPEG-co-50 APEG, 33 TPEG-co-66 APEG PCEs values were close to its. As a general trend, the copolymers with high adsorption exhibited better compressive strength values.

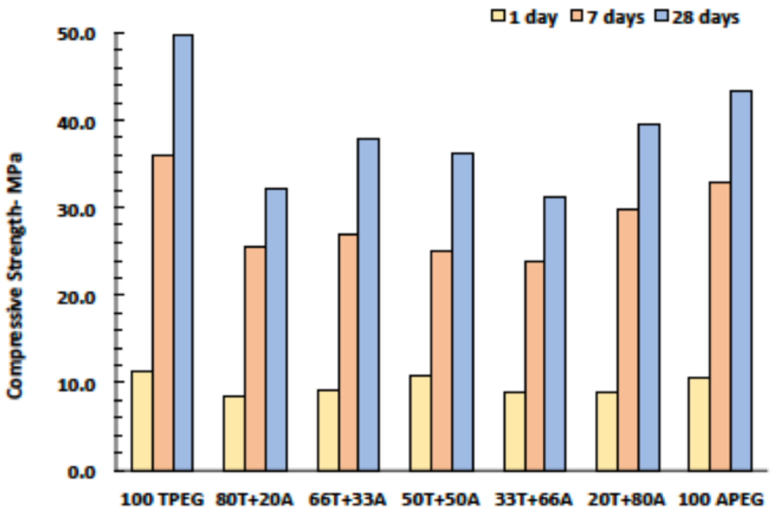


(a) TPEG + APEG BLENDS

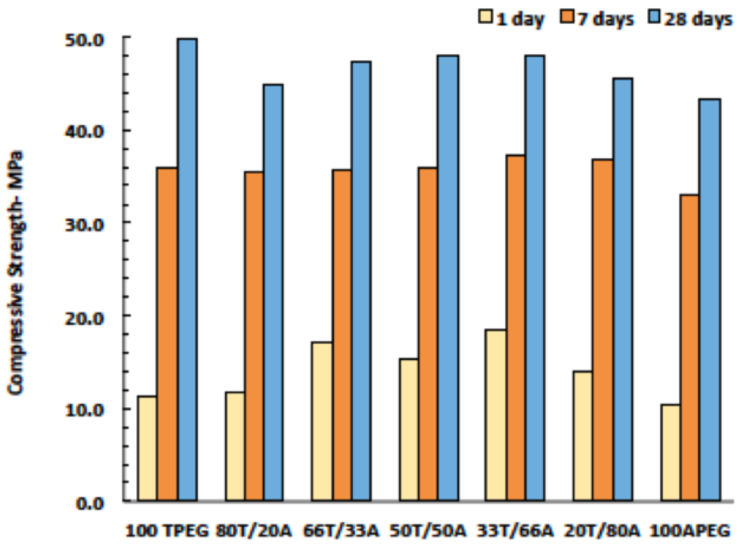


(b) TPEG-APEG Copolymers

Figure 7. *Time dependent fluidity retention of mortar by the time a) Blends, b) Copolymers*



(a) TPEG-APEG Blends



(b) TPEG-APEG Copolymers

Figure 8. *The compressive strength of hardened mortar behavior of the PCEs a) Blends, b) Copolymers*

3.3. Zeta Potential Analysis

In order to investigate the dispersing mechanism of a superplasticizer, measurement of the zeta potential of cement pastes seems to be a useful method. The sharp reduction of the zeta potential through negative zone indicates an electrostatic repulsion between cement particles due to the adsorption of superplasticizer molecules, which makes them more negatively charged. Contrarily, if the value is measured the same as the superplasticizer is introduced, it can be understood that the main mechanism for the dispersion is the steric hindrance between the cement particles that carry the adsorbed polymer molecules [13].

Time-lapse zeta potential measurements showed no change of the initial zeta potential value of -4,4 mV during the first hour after preparation of the cement slurry. This means that the zeta potential was only influenced by the PCE adsorption in the first hour during measurement. In order to investigate the dispersion mechanism for the copolymers and blends, their zeta potentials in cement paste were measured at increasing dosages. The results are shown in Figure 9. The zeta potential values of copolymers and blends were closer to zero point, indicating good dispersing abilities. However, there is no significant difference in zeta potentials between copolymers and blends.

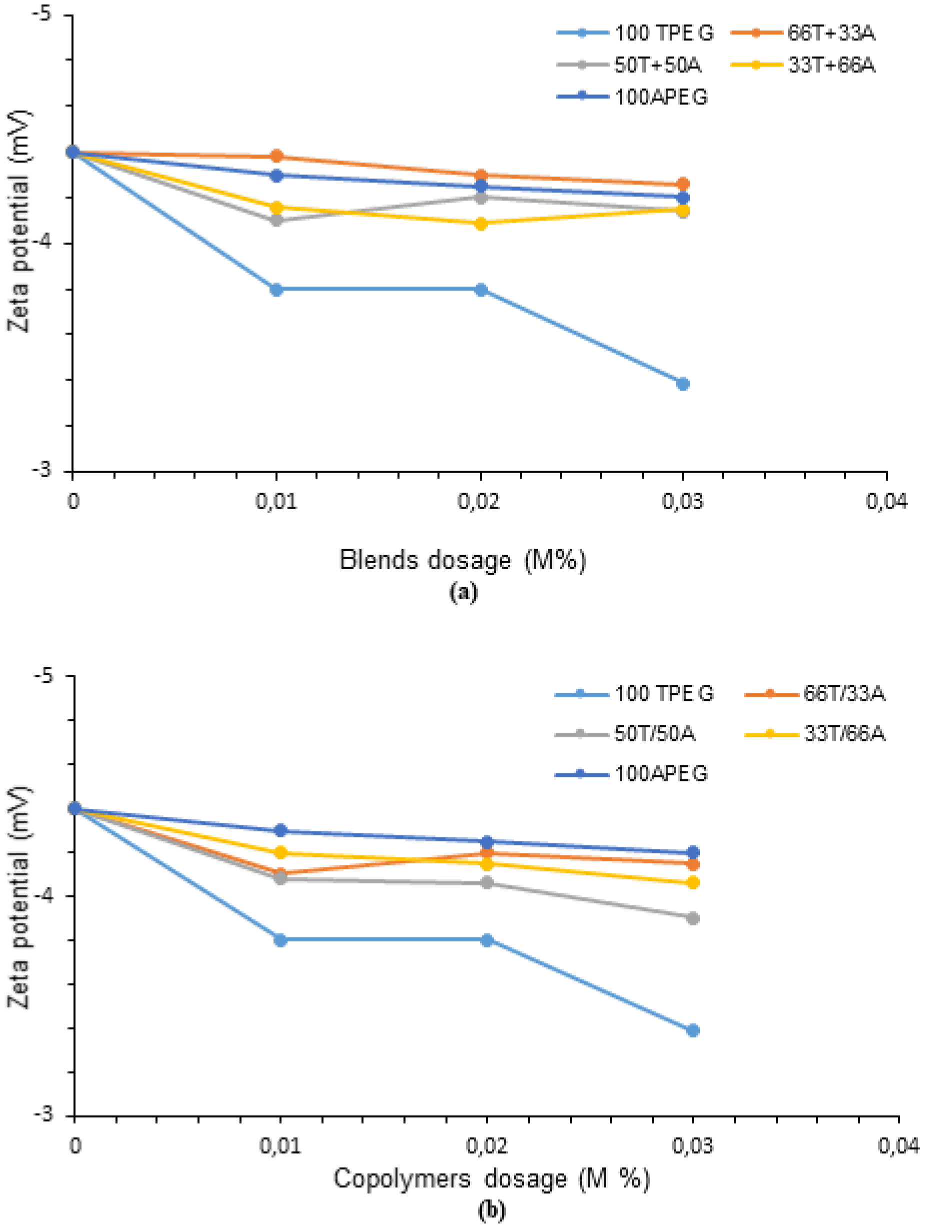


Figure 9. *Zeta potential of cement paste with respect to a.) Blends, b.) Copolymers*

4. CONCLUSIONS

A new type of TPEG-co-APEG based PCE has been successfully synthesized by free radical copolymerization and their properties were compared with blends having the same TPEG to APEG ration in the copolymers. ^{1}H-NMR and FTIR spectra confirmed the characteristic functional groups and proved the formation of copolymers. Gel permeation chromatography results revealed that the highest molecular weight was obtained from TPEG type polymers, whereas the molecular weight of copolymers of TPEG-co-APEG was located between TPEG and APEG. The dispersion, flow retention and the strength of the mortars prepared with copolymers or blends were compared. It was found that the strength and the adsorption of the copolymers were better than blends, whereas flow retention of the blends were better in comparison to the copolymers. Our study demonstrates that the blends and copolymers of TPEG and APEG copolymers can be use in different applications as an alternative to TPEG and MPEG-type PCEs.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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