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Synthesis of copolymers of methoxy polyethylene glycol acrylate and 2-acrylamido-2-methyl-1-propanesulfonic acid: Its characterization and application as superplasticizer in concrete

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ABSTRACT

Water-soluble copolymers of methoxy polyethylene glycol acrylate (mPEGA) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) were synthesized by free radicalic polymerization and evaluated as slump-retaining dispersant for cement particles. The slump-retaining effect of the synthesized copolymers was studied in terms of reaction pH, composition, and molecular weight of mPEG side chains. mPEG grafted copolymers (mPEGA-co-AMPS) were characterized by FTIR, ^{1}H NMR. In this study, dilute solution viscometry measurements were performed to compare the molecular weight effect on fluidity of the copolymers and mechanical properties of the mortar samples prepared by the copolymers were investigated to determine the flexural strength and compressive strengths. It was observed that the reaction pH had a noticeable effect on the molecular weight of the PEG-grafted samples thus causing a significant effect on fluidity. mPEGA-co-AMPS synthesized at a pH of 6 has given the highest fluidity result. Copolymers with mPEG side chains with a molecular weight of 1100 gave higher fluidity and viscosity average molecular weight values than the copolymers with mPEG 2000 side chains. Furthermore, for all the samples tested in this research, increase in molecular weight caused an increase in fluidity, however, a decrease in mechanical properties due to the different air contents of these copolymers.

1. Introduction

Superplasticizer (SP) or high-range water reducer is an important chemical admixture that can be added to concrete mixtures to improve workability. Strength of concrete is inversely proportional to the amount of water added or water–cement (w/c) ratio. In order to produce stronger concrete, less water is added, which makes the concrete mixture unworkable and difficult to mix, necessitating the use of plasticizers and superplasticizers.

The superplasticizers can also have some additional functions like accelerating or retarding cement hydration, and air entraining. Superplasticizers belong to a class of water reducers chemically different from the primary water reducers. Primary water reducers decrease the water requirements of concrete by about 10–15%, whereas superplasticizers are capable of reducing the water requirements by about 30–40% [1].

There are three generations of superplasticizers in concrete. The first generation, namely plasticizers, is commonly manufactured from lignosulfonates, a by-product from the paper industry. The second generation superplasticizers have generally been manufactured from sulfonated naphthalene formaldehyde or sulfonated melamine formaldehyde, although the third, new generation products based on polycarboxylic ethers are recently generated and still developing. Traditional lignosulfonate based plasticizers and naphthalene and melamine based superplasticizers disperse the flocculated cement particles through a mechanism of electrostatic repulsion. In normal plasticizers, the active substances are adsorbed on to the cement particles, giving them a negative charge, which leads to repulsion between particles. Naphthalene and melamine superplasticizers are organic polymers. The long molecules wrap themselves around the cement particles, giving them a highly negative charge so that they repel each other. In recent years, comb-type polymers with polyethylene oxide (PEO) grafted side chains for reducing agents have attracted great attention. These comb-type polyethylene glycol (PEG) grafted polycarboxylate ethers were developed as a cement superplasticizer at first in the 1990s in Japan. These polymers had a structural characteristic that provided more fluid concrete, which was more resistant to segregation and bleeding than any prepared concrete with the superplasticizers known previously. For these reasons, nowadays polycarboxylate admixtures have been introduced into the cement systems replacing admixtures based on melamine and naphthalene [2].

In this research, our aim was to design, synthesize and characterize novel water-soluble polycarboxylate ether copolymers (mPEGA-

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co-AMPS) that can be used as a superplasticizer in concrete, and to study the effects of changing the reaction conditions on the flow properties and the mechanical strengths of the copolymers in concrete.

2. Experimental

2.1. Chemicals

2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS) (Aldrich), acrylic acid (AA) (Acros), polyethylene glycol 2000 monomethyl ether (mPEG 2000) (Fluka), polyethylene glycol 1100 monomethyl ether (mPEG 1100) (Fluka), ammonium persulfate (Riedel-de Haen), methane sulfonic acid (MSA) (Merck), hydroquinone (Sigma), sodium hydroxide (NaOH) (Riedel-de Haen), hydrochloric acid (HCl) (Riedel-de Haen), ethanol (EtOH) (Riedel-de Haen), toluene (Merck), hexane (J.T. Baker).

2.2. Cement

The cement used in all mixtures was a normal Portland cement (PC) CEM I 42.5 R, equivalent to ASTM Type I Portland cement [3]. Chemical composition and physical properties of the cement are presented in Table 1.

Table 1
Chemical and physical properties of Portland cement.

Chemical composition (%)	
CaO	62.83
SiO_2	20.54
Al_2O_3	5.44
Fe_2O_3	3.31
MgO	1.55
SO_3	3.10
K_2O	0.92
Na_2O	0.46
Loss on ignition	2.72
Bogue potential compound composition	
C_3S	49.6
C_2S	21.7
C_3A	8.8
C_4AF	10.1
Physical properties	
Specific gravity (g/cm^3)	3.14
Blaine fineness (cm^2/kg)	3648
Initial setting time (min)	150
Final setting time (min)	210

2.3. Synthesis of methoxy poly(ethylene glycol) acrylate (mPEGA)

mPEG (M_w 2000) was condensed with acrylic acid (AA) according to the procedure adapted from literature [4]. mPEG and AA were refluxed in toluene, with methane sulfonic acid (MSA) as the catalyst and hydroquinone as the radicalic polymerization inhibitor, at 90 °C for 7 h. The product was collected by precipitation in n-hexane twice and dried in an oven. The macromonomer methoxy poly(ethylene glycol) acrylate (mPEGA) was obtained. The structure of the macromonomer is represented in Fig. 1. The condensation of mPEG ($M_w = 1100$) was performed in a similar manner.

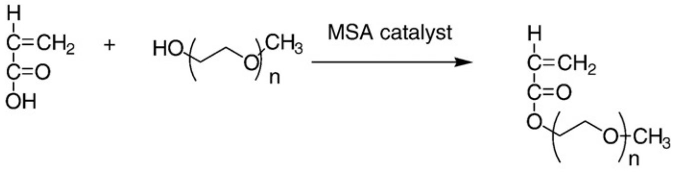


Fig. 1. The synthesis mPEGA macromonomer.

2.4. Synthesis of mPEGA-co-AMPS

mPEGA-co-AMPS was prepared from mPEGA (with M_w 2000 and 1100 separately) and AMPS through free-radical polymerization according to the procedure adapted from literature [5]. Ammonium persulfate (APS) was used as the initiator. mPEGA-co-AMPS with 5 wt.% mPEG ($M_w = 2000$) was prepared as follows. mPEGA (0.6 g) and AMPS (11.4 g) were dissolved in 100 mL of distilled water, and the pH value was adjusted to 8 with 1 N NaOH. APS aqueous solution was added dropwise into the reaction mixture. The mixture was refluxed at 75 °C for 4 h by purging N_2 gas. After the reaction was completed, the mixture was precipitated and washed with ethanol solution. The ethanol was removed by using a rotaevaporator and the remaining precipitate which is mPEGA-co-AMPS was dried in an oven till constant weight. Fig. 2 shows the chemical structure of this copolymer.

In this study, copolymers with different mPEG weight percentages and molecular weight, different reaction pH values were prepared, purified and tested. Scheme 1 shows these copolymers.

3. Methods

3.1. Flow test of cement paste (minislump)

The fresh cement paste with a certain amount of superplasticizer was prepared at a w/c ratio of 0.40. The fluidity of the cement pastes was evaluated by the standard test method ASTM C 143.

3.2. Mortar tests

The mortar mixtures for the mechanical testing were prepared with respect to the TS 2871, the standard for preparing fresh concrete. Both the flexural strength tests and compressive strength tests were performed according to TS EN 196-1.

Density and the air content of the fresh mortars were tested according to EN 1015-6 and EN 1015-7, respectively.

3.3. Dilute solution viscometry

Viscosity of a polymer solution depends on concentration and size (i.e., molecular weight) of the dissolved polymer. By measuring the solution viscosity we should be able to get an idea about molecular weight. Viscosity techniques are very popular because they are experimentally simple.

Let η_0 be the viscosity of the pure solvent and η be the viscosity of a solution using that solvent. Several methods exist for characterizing the solution viscosity, or more specifically, the capacity of the solute to increase the viscosity of the solution. Specific viscosity (η_{sp}) expresses the incremental viscosity due to the presence of the polymer in the solution. Normalizing η_{sp} to concentration gives η_{sp}/c which expresses the capacity of a polymer to cause the solution viscosity to increase; i.e., the incremental viscosity per unit concentration of polymer. As with other polymer solution properties, the solutions used for viscosity measurements will be nonideal and therefore η_{sp}/c will depend on c. The extrapolated value of η_{sp}/c at zero concentration is known as the intrinsic viscosity [η].

Molecular weight of the polymer which is called as viscosity average molecular weight for polymers can be calculated by a simple

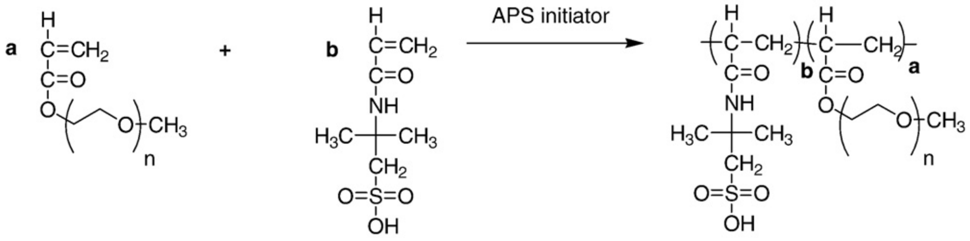


Fig. 2. Free-radical copolymerization between AMPS and mPEGA.

equation called as Mark–Houwink relationship by using intrinsic viscosity [6].

$$[\eta] = kM_v^a$$

M_v is viscosity average molecular weight, k and a are Mark–Houwink constants. There is a specific set of Mark–Houwink constants for every polymer solvent combination. This means that it is not possible to determine molecular weight of a polymer just synthesized because of not having Mark–Houwink constants available. Yet it still can give a qualitative idea for comparisons of $[\eta]$'s which is directly proportional to M_v.

4. Results and discussion

4.1. Structural characterization of mPEGA macromonomer

The structure of mPEGA was characterized by FTIR and ^{1}H NMR spectroscopy. FTIR spectrum showing typical absorption bands at 1732 cm^{-1} (ester C=O stretching), 1281 cm^{-1} and 1242 cm^{-1} (ester C–O stretching, two bands), 2885 cm^{-1} (C–H stretching band of PEG), 1469 cm^{-1} (C–H bending of PEG), 1112 cm^{-1} (C–O ether stretching of PEG), and 1649 cm^{-1} (C=C stretching) was in agreement with the structural characteristic of the macromonomer. The NMR spectrum also showed typical signals attributed to acrylate (5–6 ppm), the methoxy group (O-CH_3) (3.55 ppm), and –CH_2CH_2O– of mPEG (3.63 ppm).

4.2. Structural characterization of the copolymers

The structure of the mPEGA-co-AMPS copolymers was verified from their ^{1}H NMR and FTIR spectra. FTIR spectra of the copolymers (KBr pellets) were recorded with an FTIR Nicolet 5100 spectrometer in the fundamental region of 400–4000 cm^{-1}. Fig. 3 shows the spectra of mPEGA-co-AMPS with 5% mPEG (2000), 15% mPEG (2000) and 25% mPEG (2000). The spectra showed the following absorption bands: 3507 (amide N–H stretching), 1669 cm^{-1} (the stretching band of carbonyl of amide group and ester group are overlapped), 1043 cm^{-1} (ester C–O stretching), 2934 cm^{-1} (C–H stretching of PEG), 3080 cm^{-1} (C–H stretching of the main chain), 1458 cm^{-1} (C–H bending), 1188 cm^{-1} (C–O ether stretching), 1555 cm^{-1} (amide N–H bending), 1390 cm^{-1} (S=O stretching).

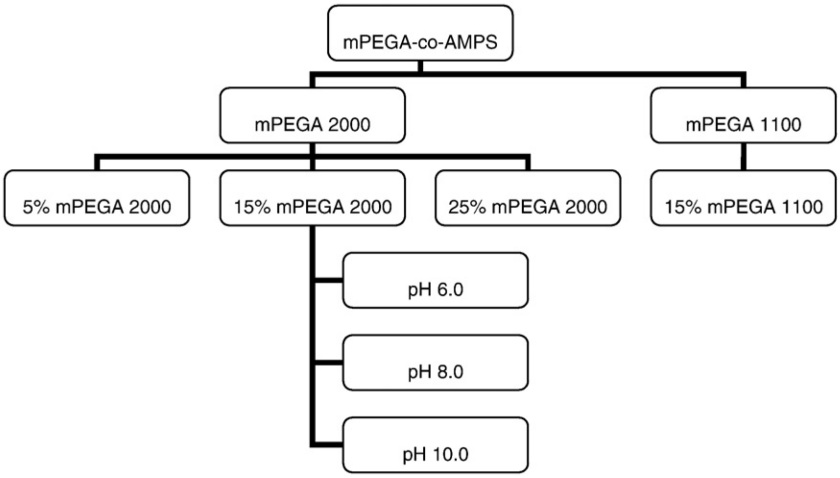
The ^{1}H NMR spectrum of mPEGA(2000)-co-AMPS in Fig. 4 shows the signals at δ 3.58 (2H) (1), 3.26 (2H) (2), 1.96 (1H) (3), and 1.37 (8H) (4, 5).

4.3. Minislump test of the cement pastes with mPEGA-co-AMPS

The major function of superplasticizers is to disperse cement particles and improve the workability of cementitious materials. For this purpose, minislump test was applied to determine the effectiveness of the copolymers as superplasticizer.

4.3.1. Effect of mPEG content

Fig. 5 shows the measured relative minislump values of cement pastes with mPEGA-co-AMPS having various weight percentages of mPEGA 2000. The highest minislump value is observed in the mPEGA-co-AMPS with a feed ratio of 5% mPEGA. It is interesting that both of the copolymers with 5% and 25% mPEGA gave higher fluidity than the copolymer with 15% mPEGA. Superplasticizers depending on many parameters influence the workability properties of the cement pastes. Rheological properties such as slump, viscosity etc. are affected by the chemical composition and the molecular structure of the superplasticizer [7–11]. Furthermore, the chemical composition and the



Scheme 1. The schematic representation of the synthesis of mPEGA-co-AMPS samples under different compositions and pHs.

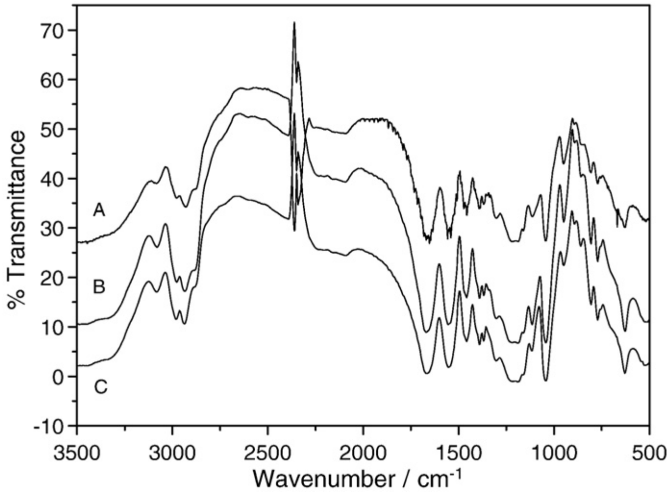


Fig. 3. FTIR spectrum of mPEGA(2000)-co-AMPS with different mPEGA(2000) weight percentages. A: 15% mPEGA(2000). B: 25% mPEGA(2000). C: 5% mPEGA(2000).

specific surface area of the cements have an effect on the behavior of superplasticizers in pastes, mortars and concrete [12–16]. Since the superplasticizer synthesized for this research contains both long, comb-like side chains and ionic groups, they can create not only steric effects but also electrostatic repulsions. So, the amount of AMPS and the PEO units present in the copolymer plays an important role in the fluidity of the cement pastes. In such a medium where a mixture of polar and nonpolar species, unreacted monomers and homopolymers exists, a direct trend of increasing/decreasing fluidity with respect to the mPEGA content may not occur.

4.3.2. Effect of reaction pH

By changing the reaction pH, we tried to examine the effect of acidity of the medium on the structure of the copolymer i.e. the amount of unreacted monomer, homopolymer and copolymer. Moreover, different pHs applied during the polymerization step may have an effect on the molecular weight distribution of the copolymer besides its chemical structure and this can be another research area for examining the fluidity of cement. Fig. 6 shows the fluidity results of the samples with different reaction pHs. mPEGA-co-AMPS synthesized at pH 6 gives slightly more effective results in fluidity tests.

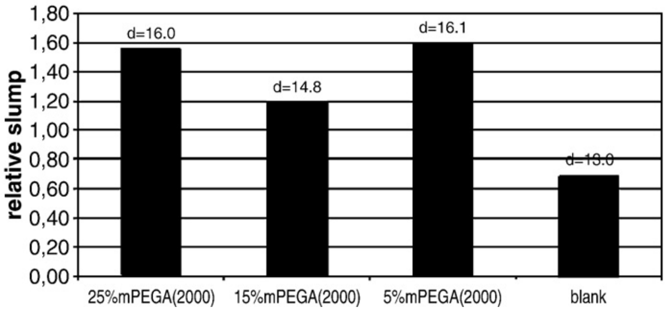


Fig. 5. Relative minislump values of the cement pastes with mPEGA(2000)-co-AMPS at various weighet percentages of mPEGA(2000) (w/c = 0.4).

4.3.3. Effect of molecular weight of mPEG

The length of mPEG side chains has a minor influence on relative slump, since the conformation of the long side chains is generally “mushroom-like”. In the comparison of relative minislump values of mPEGA-co-AMPS with different molecular weights of mPEG, which are shown in Fig. 7, the relative minislump value of mPEGA(1100)-co-AMPS is slightly higher than the one with mPEG 2000.

4.4. Dilute solution viscometry results of mPEGA-co-AMPS

4.4.1. Effect of mPEG content

The mPEGA(2000)-co-AMPS which have different mPEG contents are compared in terms of dilute solution viscometry in Fig. 8. From this comparison, it is observed that higher mPEG content which causes steric effects decreases the polyelectrolytic behavior of the samples; furthermore, in 25% mPEGA(2000)-co-AMPS, there is no polyelectrolytic behavior. When the minislump test results are also

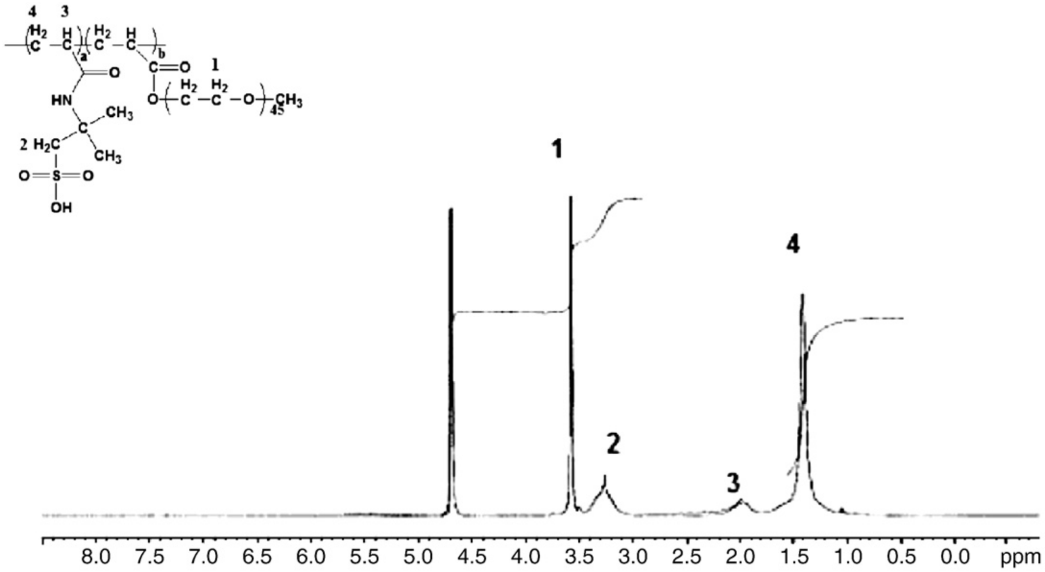


Fig. 4. ^{1}H NMR of 15% mPEGA-co-AMPS (M_w of mPEG = 2000).

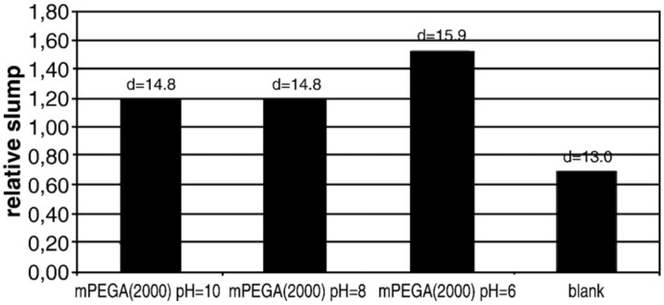


Fig. 6. Relative minislump values of the cement pastes with mPEGA(2000)-co-AMPS at various reaction pH values (w/c = 0.4).

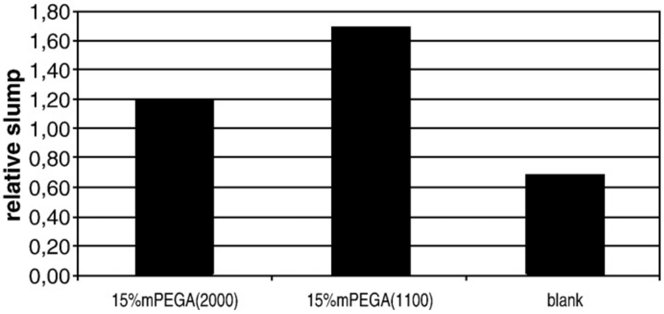


Fig. 7. Relative minislump values of the cement pastes with 15% mPEGA(2000)-co-AMPS and 15% mPEGA(1100)-co-AMPS (w/c = 0.4).

considered, 5% mPEGA(2000)-co-AMPS has the highest fluidity and [η] which is directly proportional to M_v.

4.4.2. Effect of reaction pH

Fig. 9 shows the dilute solution viscosimetry results of mPEGA-co-AMPS synthesized at various pH values. The copolymer synthesized at acidic medium i.e. pH 6, shows the highest polyelectrolytic behavior, with respect to the ones synthesized at pH 8 and 10 and the degree of polymerization is increased at low pH, so the higher molecular weight copolymer is obtained affecting the fluidity in a positive manner.

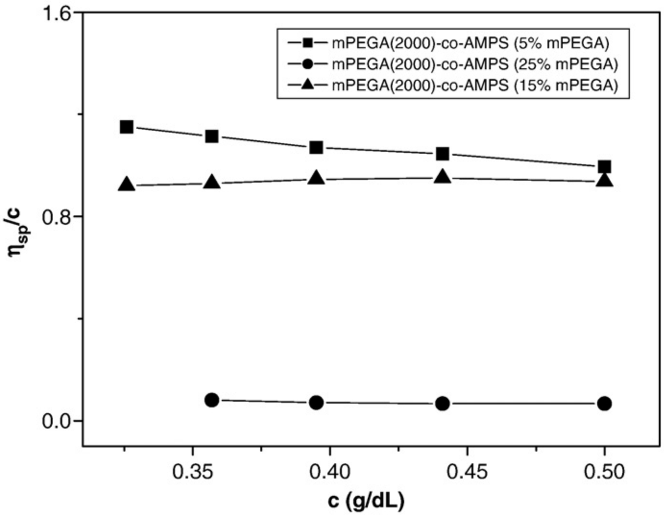


Fig. 8. Dilute solution viscometry results of mPEGA(2000)-co-AMPS with different mPEG contents.

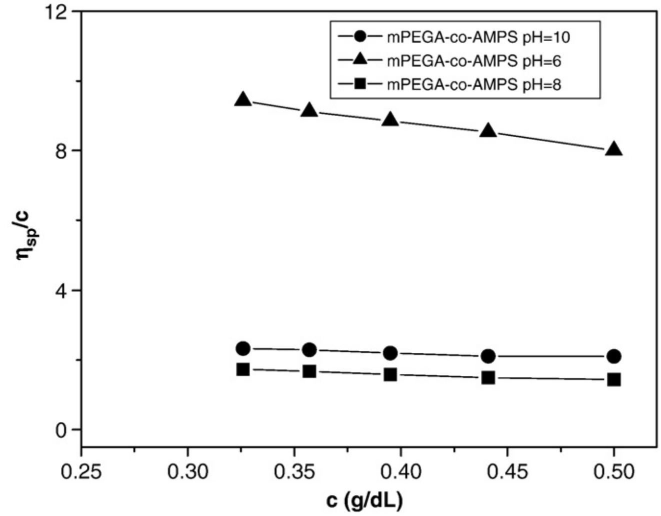


Fig. 9. Dilute solution viscometry results of mPEGA(2000)-co-AMPS with various reaction pH values.

4.5. Mechanical strength tests results

4.5.1. Flexural strength test results

Maximum flexural stresses experienced by the mortar samples at their moment of rupture are given in Table 2.

Samples illustrated with the letters in the Table 2 are defined as:

- A: The blank mortar (with no admixture)
- B: mPEGA-co-AMPS with 15% mPEG (1100) pH = 8
- C: mPEGA-co-AMPS with 15% mPEG (2000) pH = 6
- D: mPEGA-co-AMPS with 25% mPEG (2000) pH = 8.

The stress data obtained from the flexural strength test is inserted into Eq. (1) and the units are converted according to the conversion

Table 2
Maximum flexural stresses experienced by the mortar sample.

		Force (kgf)
A	Sample 1	250
	Sample 2	235
	Sample 3	240
B	Sample 1	190
	Sample 2	205
	Sample 3	175
C	Sample 1	120
	Sample 2	115
	Sample 3	130
D	Sample 1	230
	Sample 2	275
	Sample 3	240

Table 3
Flexural strengths of mortar samples.

	A	B	C	D
kgf/cm^2	68.0	53.4	34.2	69.8
N/mm^2	6.7	5.2	3.4	6.8

Table 4
Maximum compressive stresses experienced by the mortar samples.

		Force (kgf)
A	Sample 1	8870
	Sample 2	7080
	Sample 3	6940
B	Sample 1	5280
	Sample 2	5240
	Sample 3	5020
C	Sample 1	2790
	Sample 2	2360
	Sample 3	2480
D	Sample 1	6370
	Sample 2	6130
	Sample 3	6350

labeled as Eq. (2), the flexural strength results of the mortar samples in kgf/cm^2 and N/mm^2 are represented in Table 3 [17].

$$\sigma_{\text{flex}} = \frac{3}{2} \cdot \frac{P \cdot L}{d^3} \tag{1}$$

$$\sigma_{\text{flex}} = \left[\frac{\text{kgf} \cdot \text{cm}}{\text{cm}^3}\right] = \left[\frac{\text{kgf}}{\text{cm}^2}\right] = \frac{9,8}{100} \cdot \left[\frac{\text{N}}{\text{mm}^2}\right] \tag{2}$$

4.5.2. Compressive strength test results

Maximum compressive stresses experienced by the mortar samples at the moment at which the samples are crashed are given in Table 4.

The compressive strength data calculated in kgf/cm^2 and N/mm^2 from Eq. (3) are given in Table 5.

$$\sigma = \frac{F}{A_0} \tag{3}$$

The water content of all mortar samples is the same, thus, their mechanical properties are also expected to be similar to the blank mortar, however, the samples showed higher fluidity than the blank mortar in minislump tests. Except sample C, all the other four samples give approximately the same mechanical strength with the blank mortar.

Since the copolymers which are water-reducing agents, will reduce the water content of the concrete, their mechanical strengths are expected to improve [18]. Another important factor affecting the mechanical properties is the air entrainment. To confirm this, fresh mortar densities of all the samples are measured and the percentage air contents are calculated. According to the results tabulated in Table 6, both the compressive and flexural strength measurements are influenced by different air contents and the higher air content found in sample C gives the lowest mechanical strength data as previously described. The unexpected increase in the air content of sample C may account for its low flexural strength.

Table 5
Compressive strengths of the mortar samples.

	A	B	C	D
kgf/cm^2	438.1	323.8	159.0	392.7
N/mm^2	42.9	31.7	15.6	38.5

Table 6
Density and air contents of fresh mortars.

	Air content (vol.%)	Density (kg/m^3)
Reference (sample A)	5.65	2133
Sample B	11.45	2000
Sample C	20.48	1798
Sample D	5.05	2146

5. Conclusion

In this study, a series of novel carboxylate type copolymers mPEGA-co-AMPS was designed and synthesized in various compositions and pHs, as a superplasticizer in concrete. The effect of these copolymers on the fluidity of concrete is studied in terms of copolymer compositions, reaction pHs, molecular weight of the copolymers, content and molecular weight of mPEG side chains. The results are summarized as follows:

- 15% mPEGA-co-AMPS sample with a reaction pH 6 gives the highest fluidity result.
- The superplasticizer synthesized for this research contains both long, comb-like side chains and ionic groups; they can create not only steric effects but also electrostatic repulsions. So, the amount of AMPS and the PEO units present in the copolymer plays an important role in the fluidity of the cement pastes.
- Copolymers with mPEG side chains with a molecular weight of 1100 give slightly higher fluidity and viscosity average molecular weight values than copolymers with mPEG 2000 side chains.
- The experimental results have shown that the mechanical properties of mortars are also affected by the molecular weight of mPEG and its amount.
- The mechanical strengths of the mortar samples are directly proportional to their air contents i.e. greater the air content or lower the density, poorer is the mechanical strength. Thus, sample C gave the lowest mechanical strength due to the highest air entrainment to the sample.

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