The Effect of Molar Ratios of the Monomers on the Physico-Mechanical Properties of Ordinary Portland Cement

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Abstract: Hydrophilic copolymer latices based on 2-hydroxy ethyl acrylate (2-HEA) and 2-hydroxy ethyl methacrylate (2-HEMA)] were synthesized with different molar ratios (95/ 05, 90/10 and 85/15) using azo-bis-isobutyro-nitril(ABIN) as initiator and alcoholic solution as solvent.The obtained latices were characterized by FT-IR, ^{1}H NMR, tensile strength, mass spectra, TGA, DSC as well as viscosity. The effect of hydrophilic copolymers with and without sodium hydroxide on the physico-mechanical properties of ordaniary Portland cement (OPC) pastes was investigated. The results showed that the addition of aqueous solutions from the prepared copolymers with and without sodium hydroxide to the cement improve most of the specific characteristics of OPC. As the concentration of the hydrophilic copolymer increases, the setting time increases. The combined water content increases with the addition of copolymer to the mixing water. The compressive strength was sharply increased at all hydration. The results of the solution of the prepared polymers in presence of sodium hydroxide are better than its copolymers without sodium hydroxide.

Key words: Solution copolymer · Ordinary Portland Cement · Setting, Combined water · Compressive strength

INTRODUCTION

Admixtures are ingredients added to the concrete batch immediately before or during mixing. They comprise chemical admixtures, air-entraining agents and miscellaneous other types. They confer beneficial effects to concrete, including reduced water requirement, increased workability, controlled setting and hardening, improved strength, better durability, desired coloration and volume changes.

Concrete technology uses admixtures to improve the rheological properties of concrete. However, the reaction between admixtures and cement has not been well understood due to complexity [1]. The consequences of the admixture/cement interaction depend on the physicochemical parameters of the cement and the admixtures [2-13].

The performance of organic admixtures is closely related to their character including chemical composition, molecular structure, types of functional and hydrophobic groups, molecular weight distribution and mean molecular weight[14].The most important factors influencing rheological properties of cement binder mixtures considered are: aggregate type, graining, volume part of cement paste in mixture, w/c ratio, presence, type and properties of admixtures and laps of time from the end of mixing [15-17]. Depending on the enhanced property, admixture can be classified as water reducers, superplasticizers, accelerators, retarders, air-entraining agents, corrosion inhibitors, alkali-aggregate expansion inhibitors and shrinkage reducing admixtures. When a admixture is used as a water reducer at a given workability, it improves the properties of hardened concrete and, in particular, increases strength and

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Table 1: Chemical composition of raw materials, wt%

| Raw Materials | Oxides | | | | | | | | |
	L.O.I	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3
P. C. clinker	0.32	21.48	6.03	4.22	65.29	0.68	0.11	0.21	0.39
Raw gypsum	22.16	0.58	0.14	0.11	30.08	0.13	0.09	0.07	45.36

durability due to the reduction in capillary porosity and permeability, both related to a lower water/cement ratio (W/C) [17, 18].

The aim of the present work is to prepare hydrophilic copolymer of high solid content by using different molar ratios of 2-hydroxy ethyl acrylate (2-HEA) and 2-hydroxy ethyl methacrylate (2-HEMA). The obtained hydrophilic lattices were characterized by different techniques as FT-IR, ^{1}H NMR, tensile strength, mass spectra, TGA, DSC and viscosity. The work was further extended to investigate the application of the obtained copolymer to modify the workability of cement pastes.

MATERIALS AND METHODS

Synthesis and Characterization of P(2-HEA-Co-2-HEMA): Hydrophilic copolymers (2-HEA-co-2-HEMA) with various ratios of hydrophilic chains [M1(95: 05), M2 (90: 10), M3 (85: 15)] respectively were synthesized by solution polymerization using ABIN as initiator and ethanol as solvent at 60°C. The polymers synthesized were re-precipitated several times from ethanol to diethyl ether and dried in a vacuum desiccator at 30°C until a constant weight achieved. The viscosity of polymer solution was measured at 25±0.1°C using an Ubbelohde viscometer. The FT-IR analysis of the prepared polymers was carried out using Perkin Elmer FT-IR. The ^{1}H NMR spectra of the prepared polymers were carried out using A JEOL EX-270 NMR spectrometer, 270 MHz for ^{1}H NMR was used with super conducting magnet Oxford and 5 mm Dual probe head for ^{1}H and [13]C - analysis. Typical conditions are spectral width 4000 Hz for ^{1}H and 15000 Hz for ^{13}C; 32 K data points and flip angle of 45°.

Thermograimetric analyzer (TGA) was recorded on TGA/SDTA851[e], METTLER TOLEDO. Glass transition temperature of samples were measured using differential scanning calorimetry (DSC), on a NETZSCH DSC200 PC, using aluminum crimped pans under N_2 flow at 20 mL min^{-1}. The measurements were carried out between -50 °C and 200°C at a heating rate of 10°C Min^{-1}. The tensile properties of the blend films were measured by using MTS 10/M tensile testing machine at a crosshead speed of 50 mm/min. An average of at least four measurements was taken and the 1-kN load cell was used.

Ordinary Portland Cement (OPC): The raw materials used in the present study are Portland cement clinker and raw gypsum, which were provided by Vostok Cement Company. Each of these raw materials was separately ground in a steel ball mill until the surface area of 3650 and 2900 cm^2/g, respectively was reached. The chemical composition of the raw materials is shown in Table 1. The ordinary Portland cement (M0) was prepared by mixing 96wt% Portland cement clinker and 4wt% raw gypsum in a Porcelain ball mill for one hour to ensure complete homogeneity of the cement. The Blaine fineness[19] of the cement sample was 3350 cm^2/g.

Preparation of Samples: At time of sample preparation, water mixed with the water soluble copolymer was added gradually to about 200 g of the dry cement powder in order to determine the water of consistency and setting time using Vicat apparatus [20, 21]. Workability test using the flow table was conducted as per BS 1881, Part 105: 1984. A cone made of metal sheet (height 300mm, bottom diameter 200mm, top diameter 100mm) is filled with concrete to the top in three layers and rodded in specified way. The cone is then lifted and the concrete allowed slumping. The amount of slump is measured and recorded to the nearest 5mm. To about 500 gm of the dry cement powder, water mixed with the hydrophilic copolymer was added using the predetermined water of consistency. The cement pastes were directly moulded into one-inch cube stainless steel moulds. After moulding, the mould was manually vibrated for 3-4 minutes and then on a vibrator for other 3 minutes to assure the complete removal of air bubbles and voids to produce suitable pastes. The moulds were kept in a humidity chamber at 100% R. H and constant room temperature for 24 hours, demoulded and then cured in tap water till the time of testing (1, 3, 7 and 28 days) for compressive strength [22]. Three samples were taken for each hydration age and the mean value was considered. The curing water was renewed every week. The broken specimens from the determination of compressive strength were immersed in 1: 1 methanol-acetone mixture to stop the hydration. The mechanism of hydration was also studied by measuring the chemically combined water cement, which was carried out based on ignition loss [23].

RESULTS AND DISCUSSION

Characterization of the Prepared Hydrophilic Copolymers

FT-IR Spectra of P (2-HEA-co-2-HEMA): The FT-IR spectrum was used to monitor the formation of copolymers. The FT-IR of the copolymer shows in Figure 1. The observed peaks are at 1717 cm^{-1}, corresponding to carbonyl group, 3437 cm^{-1} corresponding to (OH stretch), 2927 cm^{-1} corresponding to CH_2-aliphatic and 1362 cm^{-1} corresponding to CH_3 - C in 2-HEMA unit.

1H NMR Spectra of P (2-HEA-Co-2-HEMA): The ^1H NMR spectrum gives more support for the structure of the prepared copolymer. The ^1H NMR spectrum of the prepared copolymer is shown in Table 2 and Figure 2. It is clear from the table that the chemical shits at δ = 1.53 - 1.67 ppm for proton in CH_2(a), δ =3.99 - 4.00 ppm for proton in CH_2(c), δ = 3.42 - 3.55 ppm for proton in CH_2(d), δ = 2.24 - 2.28 for proton in CH(b) and δ = 0.973 ppm for proton in CH_3(e).

Mass Spectra of P (2-HEA-co-2-HEMA): The characteristic peaks of the mass spectra of the prepared copolymer of (2-HEA -co -2-HEMA) are shown in Table 3 and Figure 3.

It is clear from the Table 3, that there are characteristics peaks such as;peaks No. 53 and 139 confirm the structures of the prepared copolymers.

Low Critical Solution Temperature (LCST) of P(2-HEA-co-2-HEMA): Compositions of copolymers were obtained using FT-IR and dependence of composition ratios upon initial monomer ratios is presented in Figure 4.

It was studied that P(2-HEA-co-2-HEMA) obtained by free radical copolymerization has high molecular weight (about one million) and very narrow molecular weight dispersion, which is due to azeotropic copolymerization. Apparently, azeotropic copolymerization is related to the same activity of 2-HEA and 2-HEMA in copolymerization reaction. Influence of the temperature on viscosity of aqueous solutions of copolymers was investigated. It was shown that reduced viscosity decreases at increasing of temperature, as presented in Figure 5. Apparently, it is related to enhancing of hydrophobic interaction and composition of macromolecular chains. Thermo-sensitivity of linear HEA-HEMA copolymers results in occurring of LCST, as presented in Figure 6. It was shown that LCST decreases at increasing of content of hydrophobic component (2-HEMA) in copolymer.

Tensile Strength of P(2-HEA-co-2-HEMA): The tensile strength of the copolymer film with respect to the variable compositions of 2-HEA and 2-HEMA in the copolymer with and without NaOH are shown in Figure 7. It can be seen that the highest tensile strength value was observed in the M3 copolymer with 15% 2-HEMA and the lowest tensile value leads to M1 copolymer with 5% 2-HEMA. This is due to the increased cross-linking content in the copolymer with increasing the ratio of 2-HEMA. On the other hand, the tensile strength of the copolymer in presence of NaOH is higher that without NaOH. This is presumably due to the increased ionic strength and hydrogen bonding density of the copolymer in presence of NaOH.

Thermal analysis of P(2-HEA-co-2-HEMA): Thermogravimetric analysis (TGA) was employed to investigate the thermal stabilities and the influence of the amount of ionic content on initial degradation temperature (IDT) in the P(2-HEA-co-2-HEMA) with and without NaOH. Figure 8 shows the IDT of the copolymer increases with increasing the ratio of 2-HEMA in the copolymer. This behaviour is in good agreement with the results obtained by other authors [24,25] for thermal degradation of methylcellulose, according to whom the mechanism of methylcellulose degradation includes the parallel processes of dehydration and demethoxylation (-OCH_3, -CH_2OCH_3). The IDT increases as pH of the copolymer increases in presence of NaOH. It can be seen that the apparent thermal stability of the polymers with regards to level of ionic content increases with the increase of the level of pH due to the presence of ionic interactions which originate either from a proton transfer or coulombic interactions between the carbonyl and hydroxyl group. The thermal transitions of the copolymer were determined by differential scanning calorimetry (DSC) analysis. The T_g varies continuously with ratios of monomers in the copolymer. To describe such type of composition dependence of the T_g of copolymers, the so-called Fox equation was used [26]:

$$\frac{1}{Tg} = \frac{W1}{Tg1} + \frac{W2}{Tg2}$$

Table 2: Chemical shifts of P(2-HEA-co-2-HEMA).

Polymers	Resonance Signal (PPM)	Proton	Assignment
[2-HEA-co-2-HEMA]	1.53 - 1.67	-CH$_2$- (a)	
	2.24 - 2.28	-CH- (b)	
	3.99 - 4.00	-CH$_2$- ©	
	3.42 - 3.55	-CH$_2$- (d)	
	0.973	-CH$_3$- (e)	

Table 3: Mass spectra of P(2-HEA-co-2-HEMA).

No. of peak	Mass	Fragment
16	68	
33	89	
53	116	
65	130	
139	246	

Table 4: Tg of the P(2-HEA-co-2-HEMA).

Polymers	T_g^a	T_g^b
M1	-12.22	-14.22
M2	-9.37	-10.3
M3	-6.47	-8.1

[a] Predicted using Fox equation

[b] measured using DSC
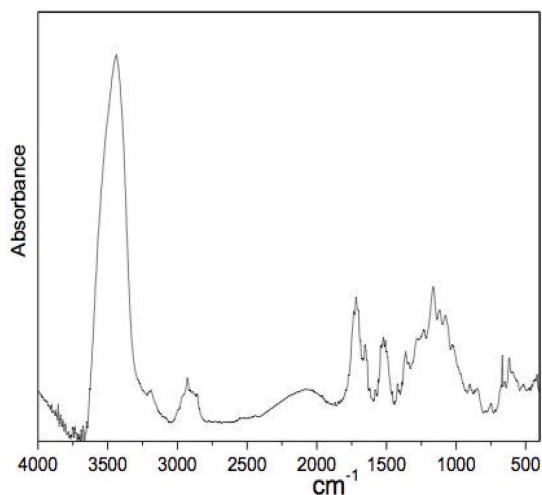
Fig. 1: The FTIR spectrum of P(2-HEA-co-2-HEMA).
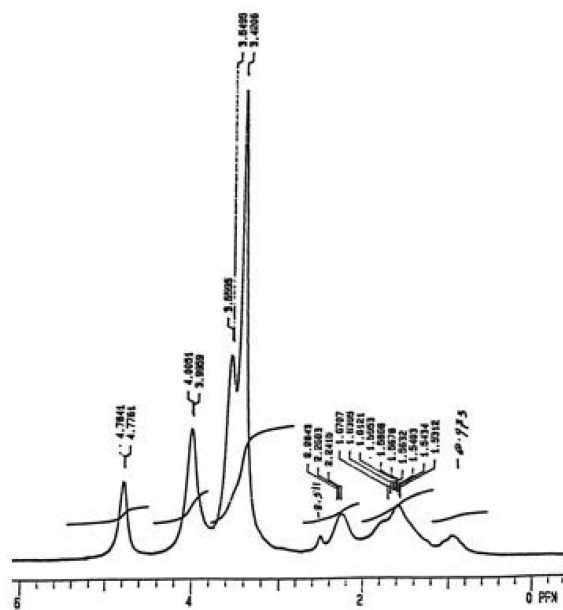
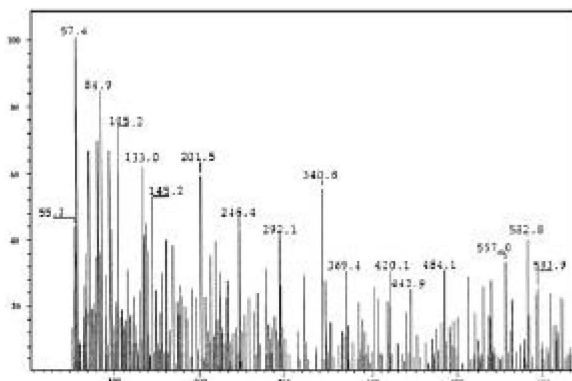Fig. 2: ^{1}H NMR spectrum of P(2-HEA-co-2-HEMA).

Fig. 3: Mass spectrum of P(2-HEA-co-2-HEMA).

Where T$_g$ is the glass transition temperature of the copolymer, T$_{g1}$ and T$_{g2}$ are the glass transition temperatures of the two homopolymers and w$_1$ and w$_2$ are the weight fractions of the two repeat units in the copolymer.

Differential scanning calorimetry is a conventional technique to judge the miscibility of a copolymer. The results of DSC analysis of copolymer are summarized in Table 4, the experimentally measured T$_g$ values closely
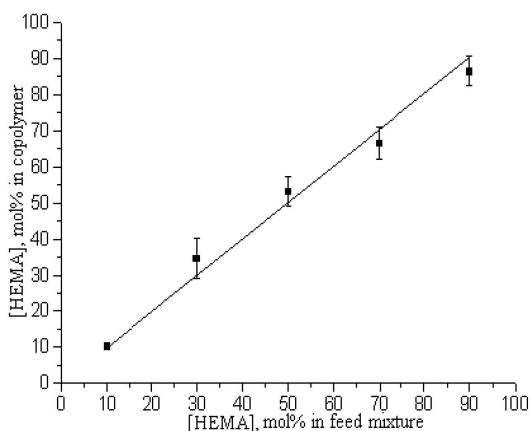
Fig. 4: Dependence of composition ratios of P(2-HEA-co-2-HEMA) copolymers upon initial monomer ratios in feed mixture.
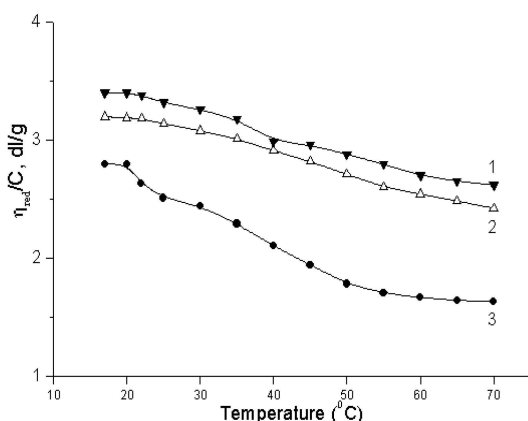

Fig. 5: Dependence of reduced viscosity of P(2-HEA-co-2-HEMA) copolymers on the temperature in aqueous solutions. [2-HEA]:[2-HEMA], mol%:. 1 - 90:10; 2 - 80:20; 3-70:30.
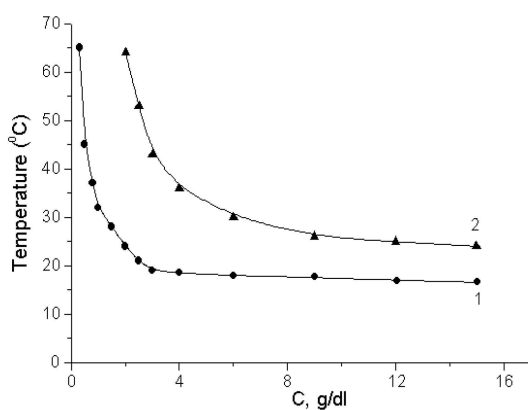

Fig. 6: Dependence of LCST of 2-HEA-co-2-HEMA copolymers upon the temperature in aqueous solutions. [2-HEA]:[2-HEMA], mol%: 1 - 80:20; 2 - 90:10.
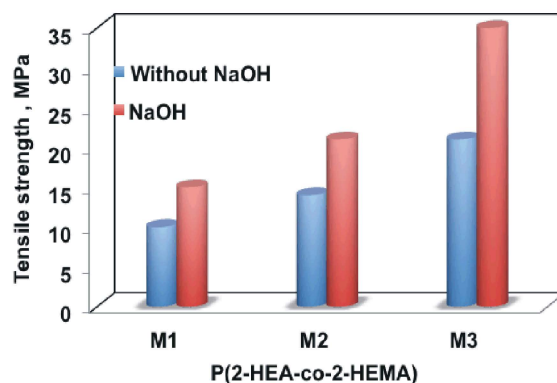

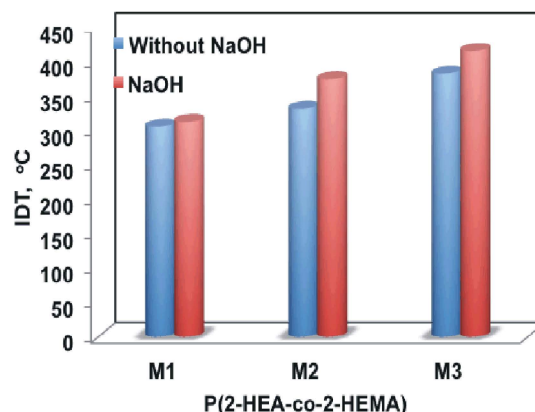Fig. 7: Tensile strength of P(2-HEA-co-2-HEMA) with and without NaOH

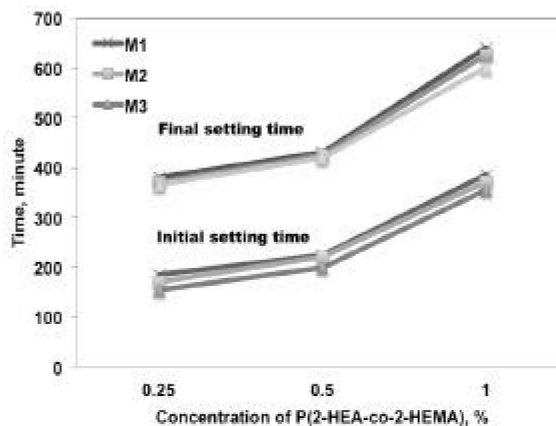Fig. 8: The effect of the P(2-HEA-co-2-HEMA) on the IDT of the film.

Fig. 9: Setting times of the OPC pastes premixed with different ratios and concentrations of P(2-HEA-co-2-HEMA) without NaOH.

follow the predictions of the Fox equation. Generally, it is known that T_g is directly proportional to crosslinking density and indirectly proportional to chain flexibility. Results are consistent with this statement. From Table 4,

it can be seen that the T_g of copolymer moves toward the higher temperatures as the 2-HEMA increases. Tgis shifted from -12.22°C to -6.47°C as the 2-HEMA increases from 5 to 15% respectively. The increase of T_g with increasing of 2-HEMA is mainly due to increased cross-linking segments in the copolymer structure.

Application of P(2-HEA-co-2-HEMA) for Cement Water/Cement Ratio and Setting Time: Generally, the water/cement (W/C) ratio for the various cement pastes, mortars or concretes has a major effect on their specific properties because most failure accompanied with cement structures are essentially due to either too much or too low water that being added during mixing process[24].

W/C ratio of Portland cement pastes decreases from 28% to 25% with the addition of copolymer to OPC pastes. This ratio tends to change irregularly according to the type of copolymers and its concentrations added to Portland cement during mixing process. This may be due to a relationship between W/C ratio of Portland cement and the particle size as well as viscosity of the hydrophilic polymers used which cause variable water requirements to produce suitable pastes.

On the other hand, the setting time (initial and final) of the pure Portland cement pastes increases sharply with the addition of hydrophilic copolymers with and without sodium hydroxide. The setting times also increase sharply with the increase of polymer concentrations and decrease gradually with the increase the ratio of [2-HEMA] in the hydrophilic copolymers as shown in Figures 9 and 10. The increase in setting time associated with concentration of the copolymer can be decreased by increasing the side chain length, increasing the backbone length, or increasing the degree of polymerization in the backbone [27] led to shorter setting time than its copolymer solutions without sodium hydroxide. Setting time may be accelerated or retarded based on the admixture's chemistry, dosage rate and interaction with other admixtures and cementing materials in the concrete mixture.
[28, 29].

Workability: Workability is the term used for freshly mixed concrete that is easy to transport, able to flow, has the desired strength and resist segregation. Among the factors that affect the workability include quantity and characteristics of cement, gradation and shape of aggregates, amount of water, admixtures and other additives [30]. The results of the cement pastes

workability tests for P(2-HEA-co-2-HEMA) with various compositions are represented in Figure 11. The results showed that the workability of OPC pastes increased with the addition of hydrophilic copolymer than that of pure OPC. Whatever, the workability of OPC pastes premixed with hydrophilic copolymer decreased with increasing the ratio of 2-HEMA in the copolymer. Enhancement of the cement paste workability is mainly interpreted in terms of improved consistency due to both the 'ball bearing' action and the dispersing effect of polymer [31]. On the other hand, as it is shown in the Figure 11, the highest workability was observed in the copolymer premixed with OPC in presence of sodium hydroxide. This result my be due to the increase in ionic strength of the medium, thus the ionic interaction between cement particle and the copolymer increases, more electrostatic interactions are expected to cause an increase in fluidity [32].

Chemically Combined Water Content: It is generally well known that the chemically combined water content is an indirect evidence of the quantitative increase of the newly hydration products formed in the hardened cement pastes during the hydration process [27]. On this basis, the results of chemically combined water contents of the various cement pastes premixed with different hydrophilic copolymers solutions with and without sodium hydroxide are graphically plotted as a function of curing time in Figures 12, 13. As it is clear, the values of combined water content increase gradually as the curing time proceeds up to 28 days of hydration [34]. This is mainly due to the continuous formation of the hydration products that are formed during the hydration process [27]. Also, it leads to an increase in the formation of additional amounts of calcium silicate hydrates as a result of pozzolanic reaction [35]. The combined water contents of the cement pastes premixed with hydrophilic polymers tend to be higher than the pure Portland cement that mixed with water only at all curing periods. Furthermore, as the ratio of [2-HEMA] in the hydrophilic copolymers increases the combined water contents increase sharply. As shown from Figure 13 the combined water contents of the cement pastes premixed with hydrophilic copolymer solutions in presence of sodium hydroxide tend to be higher than its polymer solution without sodium hydroxide. This is essentially attributed to the fact that the addition of copolymers did not form any polymer films or membranes around the cement grains, but only polymerizes or crystallizes inside the pore structure of the hardened cement pastes [30].
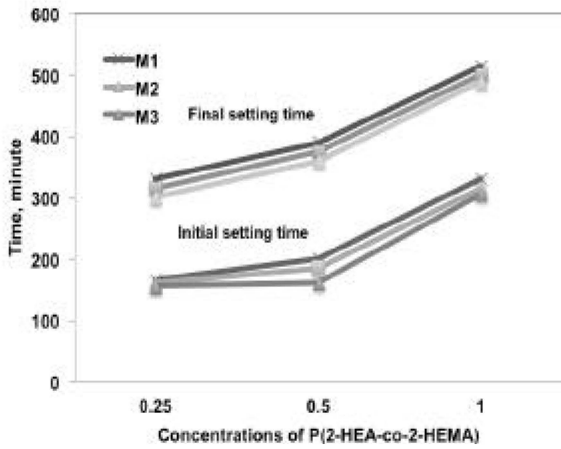
Fig. 10: Setting times of the OPC pastes premixed with different ratios and concentrations of P(2-HEA-co-2-HEMA) without NaOH.
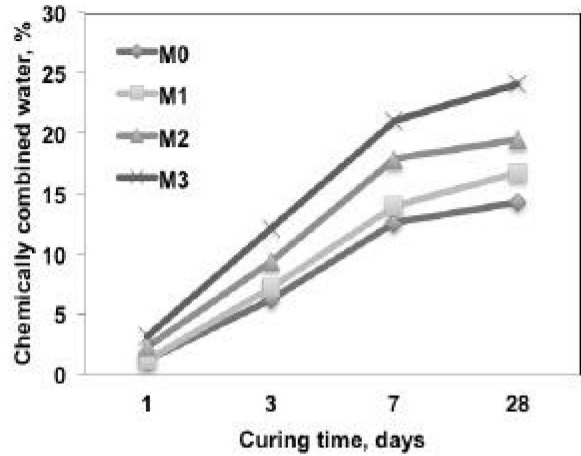

Fig. 13: The effect of P(2-HEA-co-2-HEMA) on the chemically combined water of OPC pastes in presence of NaOH
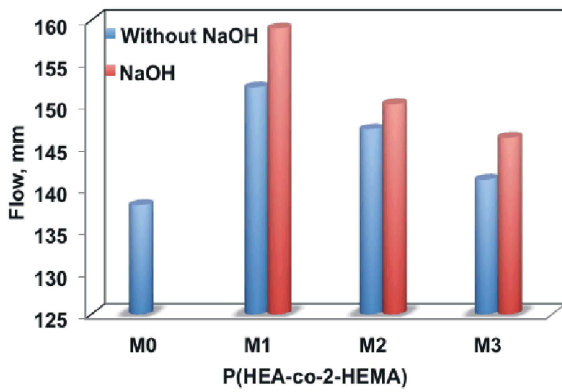

Fig. 11: The effect of P(2-HEA-co-2-HEMA) on the flow of OPC pastes with and without NaOH
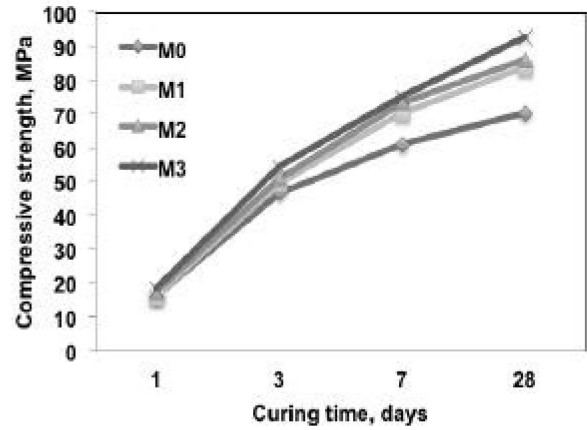

Fig. 14: The effect of P(2-HEA-co-2-HEMA) on the compressive strength of OPC pastes without NaOH
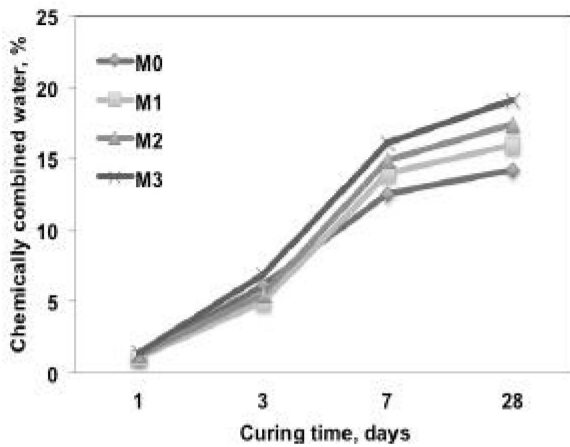

Fig. 12: The effect of P(2-HEA-co-2-HEMA) on the chemically combined water of OPC pastes without NaOH.
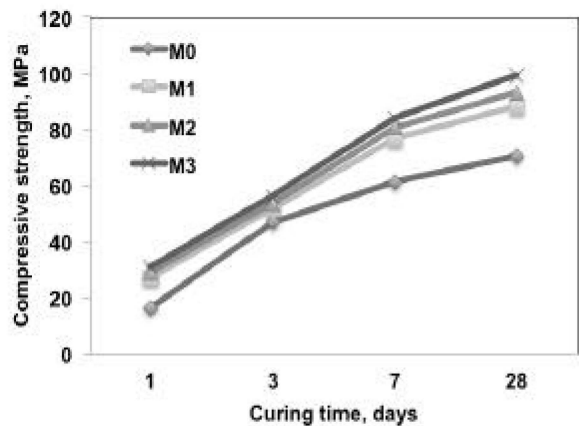

Fig. 15: The effect of P(2-HEA-co-2-HEMA) on the compressive strength of OPC pastes in presence of NaOH.

Compressive Strength: Figure 14 shows the compressive strength of the cement pastes premixed with P(2-HEA-co-2-HEMA) of various ratios of 2-HEA and 2-HEMA at W/C-ratio of 0.25. The compressive strength of cement pastes containing hydrophilic copolymers with three various ratios are nearly the same at 1 day and thereafter, through at an early age of 3 days, M_3 with a weaker retarding effect led to slightly higher strength than the remained ratios of copolymers and OPC. At 28 days the compressive strength is highest with cement paste containing M3 followed by M2 and M1. Immediately after the first contact of cement with water, an exchange of ionic species between the solids and liquid phase is initiated and the process of cement hydration begins.

When the hydrophilic copolymer based water-reducing admixture is added to the system, it adsorbs onto the hydrating cement compounds, which results in improved dispersion of cement particle [36]. In addition, both the character and rate of hydration reactions are usually influenced. All aspects of cement chemistry and cement hydration are thoroughly described elsewhere [37, 38].

Figure 15 shows the compressive strength of the cement pastes premixed with solutions of hydrophilic copolymers in presence of (sodium hydroxide) tends to be higher than those of the pure OPC at all curing periods. As it is, clear that the compressive strength of all samples increases with curing time as the ratio of [2-HEMA] in the copolymer increases.

From Figures 14 and 15, it is shown that the compressive strength of the cement pasts premixed with hydrophilic copolymer solutions in presence of sodium hydroxide tends to be higher than its copolymer solutions without sodium hydroxide and the pure Portland cement at all curing periods. Development of high strength of the initial stages is the main application for admixtures of this type [39]. Although the hydrophilic copolymers can be used as a straight addition to obtain higher workability with some increase in initial strength, it is more usual to combine some slight water reduction (hydrophilic copolymers) with the acceleration (sodium hydroxide) effect of the admixture to achieve very significant increases in strength. There is some evidence [39] that the effective pore diameter distribution is changed by the addition of sodium hydroxide and that there is some change in the hydration species of tricalcium silicates. The general picture is that, as far as permeability is concerned, it is reduced by sodium hydroxide and the net effect therefore of water reduction by the admixture and permeability reduction by the sodium hydroxide would be to produce a more impermeable concrete.

CONCLUSIONS

- Hydrophilic copolymers of (2-HEA) with (2-HEMA) in three different ratio ca. [(95: 05), (90: 10) and (85: 15)] were prepared and characterized in relation to FT-IR, ^{1}H NMR, Mass spectra, TGA, DSC and viscosity.
- Mixing of Portland cement powder with water that is premixed with the hydrophilic polymer solutions with and without sodium hydroxide evidently improves most of the specific characteristics of the cement pasts.
- The W/C-ratio decreases, i.e. the hydrophilic polymer solutions with and without sodium hydroxide act as a water reducing agent when mixed with the cement powder.
- The chemically combined water content of the solutions of hydrophilic polymer in presence of sodium hydroxide also enhances and seems to be higher than that of its copolymers without sodium hydroxide and the pure Portland cement pastes nearly at all curing ages.
- The compressive strength of the solutions of hydrophilic polymer in presence of sodium hydroxide increases sharply compared with those of its polymers without sodium hydroxide and the pure hardened cement pastes. As the concentration of (2-HEMA) in the copolymer increases, the properties of the cement pastes are also improved.

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