Utilization of Hydrophilic Copolymers as Superplasticizers for Cement Pastes Part I: Poly [acrylic Acid-co-styrene]

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Abstract: Three composition ratios of poly[acrylic acid (AA)-co-styrene (St)] were prepared in alcohol solution using azo-bis-isobutyro-nitrile as initiator (ABIN). The hydrophilic copolymers were characterized by FT-IR, ¹H NMR, Mass spectra, viscosity and scanning electron microscopy (SEM). The effect of hydrophilic copolymers with and without sodium hydroxide on the physico-mechanical properties of ordinary Portland cement (OPC) pastes was studied. The results showed that the addition of aqueous solutions from the prepared copolymers with and without sodium hydroxide to the cement improves most of the specific characteristics of (OPC). As the ratio of AA in the hydrophilic copolymer increased, the water of consistency decreased, whereas the setting times (initial & final) were elongated. The combined water content and compressive strength of the hardened cement pastes were increased at all ages of hydration. The prepared copolymers in presence of NaOH achieved better improving effects than those prepared in absence of NaOH. The SEM images showed that the addition of these polymers to the cement material improves the dispersibility and workability of cement pastes.

Key words: Copolymer · Ordinary portland cement · Water consistency · Setting time · Combined water · Porosity · Compressive strength · SEM

INTRODUCTION

Superplasticizers are nowadays widely employed in cement technology, since they give a better workability at a fixed water/cement ratio, or, on the other hand, they allow to obtain the same workability as that of the plain cement paste but with a great reduction in water content; hence, cement pastes can be prepared with low porosity and, consequently, with higher mechanical strengths and durability [1-6]. The consistency of the polymer-modified systems is markedly improved at lower water-cement ratios over that of ordinary cement mortar and concrete, because of the plasticizing and air-entraining effects of the polymer [7, 8].

The traditional polymeric cement modifiers are cellulose derivatives including methyl cellulose, carboxymethyl cellulose and hydroxyethyl cellulose, polyvinyl alcohol, polyethylene oxide, polyacrylamide, etc. [9]. Hydrophilic polymers are dissolved in the mixing water on a molecular scale in contrast to polymer dispersions where no surfactants are needed. However, the addition of small amounts of hydrophilic polymers usually influences the properties of the hardened material. Two processes can take place during hardening such as cement hydration and polymer film formation [10]. Previous papers have been published that dealt with superplasticizers and their effect on the mechanical and physicochemical properties of cement paste, mortar and concrete [11-14]. Several papers were presented regarding cement hydration and mechanism of interaction with superplasticizers [15-17].

The present study deals with the preparation and characterization of poly [acrylic acid (AA)-co-styrene (St)] via FT-IR, ¹H NMR, mass spectra and viscosity. The work further investigates the application of the prepared copolymer to modify the workability and mechanical strength of the cement pastes. The plasticizing effect of both types of polymers was evaluated by SEM images.

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MATERIALS AND METHODS

Experimental Procedures;
Synthesis and Characterization of Copolymers: A hydrophilic homopoly Acrylic acid (AA) or M_1 and a copolymer styrene (St) or AA-co-St with various ratios of hydrophilic chains (M_2 = 99: 01, M_3 = 97: 03, M_4 = 95: 05) were synthesized by solution polymerization using ABIN as an initiator and ethanol as a solvent at 60°C. The copolymers synthesized were reprecipitated several times from ethanol to diethyl ether and dried in vacuum desiccators at 30°C until a constant weight was achieved. The polymer was prepared in the presence or absence of sodium hydroxide solution.

The prepared polymers were characterized by FT-IR, ^{1}H NMR spectra, viscosity and mass spectra. 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°C. The viscosity of polymer solution was measured at 25 ± 0.1°C using an Ubbelohde viscometer.

Raw Materials: The raw materials used in the present study are Portland cement clinker (PCC) and raw gypsum (G). Each of those raw materials was separately ground in a steel ball mill until the surface area of 3650 and 2800 cm^2/g, respectively were achieved. The chemical composition of the raw materials is shown in Table 1. The mineralogical composition of the PCC sample is C_3S, 58.79 %; β- C_2S, 17.68 %; C_3A, 8.08 %; C_4AF, 9.72 %. The Ordinary Portland Cement (M_0) was prepared by mixing 96 wt. % PCC and 4 wt. % G in a porcelain ball mill for one hour using 3 balls to assure complete homogeneity of the cement. The Blaine surface area[18] of the cement sample was 3350 cm^2/g.

Preparation and Methods: The prepared copolymer (either in the absence or presence of NaOH) was added to mixing water and then added gradually to 300 g of the dry cement in order to determine the water of consistency and setting time using Vicat apparatus [19, 20]. The determined water of consistency premixed with the copolymer was added to 500 g of the dry cement.

The resulting cement pastes were directly moulded into one-inch cube stainless steel moulds. The moulds were manually agitated for 2 minutes and then on a vibrator for another 2 minutes to assure the complete removal of air bubbles and voids and to produce suitable pastes. The moulds were kept in a humidity chamber at 100 % R. H and a constant room temperature over night, then demoulded and cured under water till the time of testing (1, 3, 7 and 28 days) for compressive strength[21]. The compressive strength was carried out using a hydraulic testing machine of Type LPM 600 M1 SEIDNER (Germany) having full capacity of 600 KN. The loading was applied perpendicular to the direction of the upper surface of the cubes.

The combined water content (dp) was determined from the following equation: $dp = W_1 / W_1 - W_2$ g/cm^3, where W_1 is the saturated surface dry weight in air (g) and W_2 is the submerged weight in water (g).To stop the hydration at any age of hydration, a representative sample of about 10 g after the determination of compressive strength was taken, ground in an alumina mortar containing 50 ml of 1:1 (methanol: acetone) solution mixture and then filtered through a sintered glass funnel (G4). The sample was washed with 50 ml fresh diethyl ether, dried at 70°C for one hour and then kept inside an airtight bottle as described elsewhere [22].

The curing water was renewed every week. The combined water content (Wn) of samples predried at 105°C for 24 hours was determined as the ignition loss at 1000°C for 30 minutes [13]. The microstructure of the hydrated cement pastes was investigated by scanning electron microscopy (SEM) and elemental analysis. The SEM images of the 28-days hydrated cement pastes was employed by the Microanalysis INCA (Oxford instrument-UK), combined with scanning electronic microscope Super prob. 733-Joel (Japan). For this purpose, the samples were coated by a thin layer of gold palladium to be electrically conductive and to increase its contrast of display.

Table 1: The chemical composition of the raw materials, mass %

Oxides Materials	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	SO$_3$	Na$_2$O	K$_2$O	L.O.I
PCC	21.48	6.03	4.22	64.29	0.68	0.39	0.21	0.11	1.32
G	0.58	0.14	0.11	30.08	0.13	45.36	0.07	0.09	22.16

RESULTS AND DISCUSSION

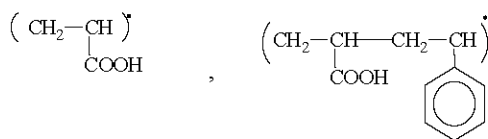### Characterization of Hydrophilic Polymers

FT-IR Spectra: The FT-IR spectra of the prepared homo (AA) and its copolymer with (St) are shown in Table 2 and Figure 1. It is clear that there are some differences in the characteristic peaks of the prepared polymers due to co-polymerization.

The FT-IR spectra of OPC mixed with the prepared homo- (AA) and its copolymers with St are shown in Table 3 and Figure 2. Tables 2 and 3 illustrate that the values of stretching frequencies of carbonyl group of the prepared polymers are in the range of $1715 - 1726$ cm^{-1} and for the polymers mixed with the cement are in range of $1641 - 1643$ cm^{-1}. As it is shown, the C=O was shifted to lower frequencies on complexation [24]. This attributed to complexation between the hydrated cement components and the functional groups present in the hydrophilic polymers [25-28].

^{1}HNMR Spectra: The ^{1}H NMR spectra of the prepared homo- (AA) and its copolymer with St are shown in Table 4 and Figure 3. There are noticeable chemical shifts in the characteristic peaks of the copolymers rather than that of its homopolymer due to the occurrence of copolymerization process.

Mass Spectra: The characteristic peaks of the mass spectra of the prepared copolymer of AA-co-St are shown in Table 5 and Figure 4.

Table 5 shows that there are characteristic peaks such as

$$\left(CH_2-\underset{\underset{COOH}{|}}{CH} \right) \quad , \quad \left(CH_2-\underset{\underset{COOH}{|}}{CH}-CH_2-\underset{\underset{\bigcirc}{|}}{CH} \right)$$

which confirm the structure of the prepared polymers.

Viscosity of the Prepared Polymers: Viscosity of the prepared homo acrylic acid and its copolymer with styrene are shown in Table 6.

Application of Hydrophilic Copolymer and Their Salts for Cement

Water of Consistency and Setting Time: The water of consistency as well as setting times (initial & final) of the OPC pastes (M_0) and those premixed with different ratios and concentrations of hydrophilic polymer AA-co-St in absence (M_1-M_4) and presence (Ma-Md) of NaOH are

represented in Tables 7 and 8, respectively. It is clear that the water of consistency of the OPC (M0) decreases from 28% to 26.5% with increasing the ratio of (AA) in the copolymers and then becomes constant even with increasing the hydrophilic copolymer concentrations. On the other hand, the setting times (initial & final) were retarded and increased by the addition of the admixture, i.e. as the ratio of AA in the copolymer decreased. That was attributed to the negative electrical charge which prevents adhesion and flocculation of particles and prolongs setting time [29].

As shown from Tables 7 and 8, hydrophilic copolymer solutions in absence of sodium hydroxide (M1-M4) led to retard setting time more than that in its presence (Ma-Md). It was proposed that the retardation is caused by adsorption of organic molecules onto the surface of anhydrous cement compounds, which creates a barrier to the hydration of cement [30].

Chemically Combined Water Content: The chemically combined water contents of the OPC (M_0) and cement pastes premixed with varying proportions of freshly prepared hydrophilic polymers AA-co-St in absence (M_1-M_4) and presence (Ma-Md) of NaOH are plotted as a function of curing time up to 28 days in Figures 5 and 6, respectively.

The combined water generally increases as the curing time proceeds up to 28 days of hydration. This is mainly attributed to the continuous formation of hydration products resulting from the hydration of the main phases of the cement [31]. The combined water contents of the cement pastes premixed with the various ratios of polymer either with that prepared in absence or presence of NaOH solution are higher than those of the corresponding pure OPC pastes at all curing ages of hydration. Figures 5 and 6 showed that the combined water content of all samples increased as the ratio of AA in the copolymer increased. The results show that the interaction occurs between the polymers and Ca^{2+}, SO_4^{2-} and OH released by the cement during hydration. This reaction makes it possible for the carbonyl radicals of the acrylic polymers to "catch" the Ca^{2+} from the liquid phase of the pastes whilst SO_4^{2-} becomes "trapped" in the latter [31].

On the other hand, cement pastes premixed with solutions of copolymers in presence of sodium hydroxide (Ma-Md) tend to be higher than the solution in absence of sodium hydroxide (M1-M4), this is essentially due to the possibility for the carboxyl group to make contact with the cement particles and cement hydrates is decreased [28].

Table 2: FT-IR Data of the prepared homo- and copolymers

M1 (Cm^{-1})	M2 (Cm^{-1})	Vibration assignment
1715	1726	C=O stretch
-	3432	OH stretch
3110	-	OH broad
2677	2931	CH$_2$-aliphatic
-	1637	C = C

Table 3: FT-IR Data of OPC mixed with the prepared homo (AA) and poly[AA-co-St]

M0 (Cm^{-1})	M1 (Cm^{-1})	M2 (Cm^{-1})	Vibration assignment
-	1641	1643	C=O stretch
3432	3419	3434	OH broad
-	-	1597	C=C
-	2899	2927	CH$_2$-aliphatic

Table 4: Chemical shifts of the prepared homo- and copolymers

Resonance Signal (PPM)	Proton	Assignment
1.15 B 1.80	–CH$_2$- (a)	
2.10 B 2.32	–CH– (b)	
0.875 B 1.258	–CH$_2$- (a)	
2.11 B 2.53	–CH– (b)	
7.13		

Table 5: Mass spectra of the prepared copolymer of (AA-co-St)

No. of peak	Mass	Fragments
5	54	
18	72	
22	77	
39	99	
42	104	
86	176	

Table 6: Viscosity of homo-(AA) and [AA-co-St]

Polymers	η
M$_1$	0.8389
M$_2$	0.7022
M$_3$	0.6297
M$_4$	0.6008

Table 7: Water of consistency as well as setting time of Portland Cement paste mixed with [AA-co-St] in absence of NaOH

Polymer	Concentration %	W/C ratio %	Setting time, min.	
			Initial	Final
M0	----------	28.0	150	360
M1	0.25	26.5	160	320
	0.50	26.5	180	380
	1.00	26.5	195	430
M2	0.25	26.5	220	420
	0.50	26.5	250	480
	1.00	26.5	285	590
M3	0.25	27.0	240	500
	0.50	27.0	265	520
	1.00	27.0	290	610
M4	0.25	27.5	270	510
	0.50	27.5	285	530
	1.00	27.5	320	650

Table 8: Water of consistency as well as setting time of Portland Cement paste mixed with [AA-co-St] in presence of NaOH

Polymer	Concentration %	W/C ratio %	Setting time, min.	
			Initial	Final
M0	----------	28.0	150	360
Ma	0.25	26.5	130	300
	0.50	26.5	145	340
	1.00	26.5	160	405
Mb	0.25	26.5	190	320
	0.50	26.5	210	355
	1.00	26.5	225	405
Mc	0.25	27.0	205	350
	0.50	27.0	230	385
	1.00	27.0	240	450
Md	0.25	27.5	210	370
	0.50	27.5	235	400
	1.00	27.5	260	495

SEM Micrographs: The SEM micrographs of freshly prepared cement pastes of the pure OPC (M_0) and those premixed with AA (M_1) and AA-co-St (M_2) hydrated up to 28 days are shown in Figure 7. It is clear that the molecules of the organic polymer admixtures are precipitated and block the pore system of the hardened cement pastes to act as reinforcement and seem to be bound with hydrated mineral skeleton of CSH and/or CAH. The addition of the organic polymer admixtures to the cement powder during the mixing, the same hydration products are often formed, but with different shapes, microstructures and degrees of crystal size.

Elemental Analysis: The adsorptive behavior of organic admixtures to clinker minerals at the stage of cement hydration was further investigated by analyzing
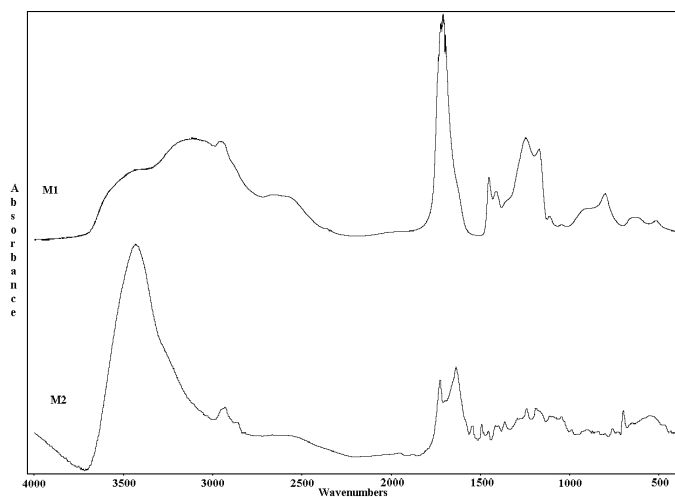

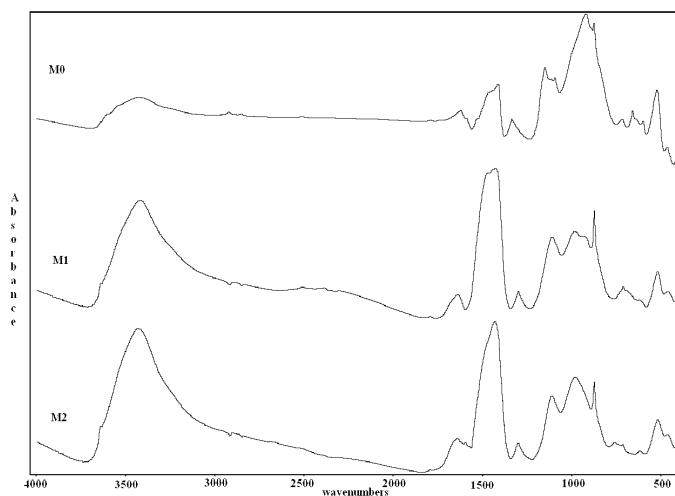Fig. 1: FT-IR spectra of prepared polymers

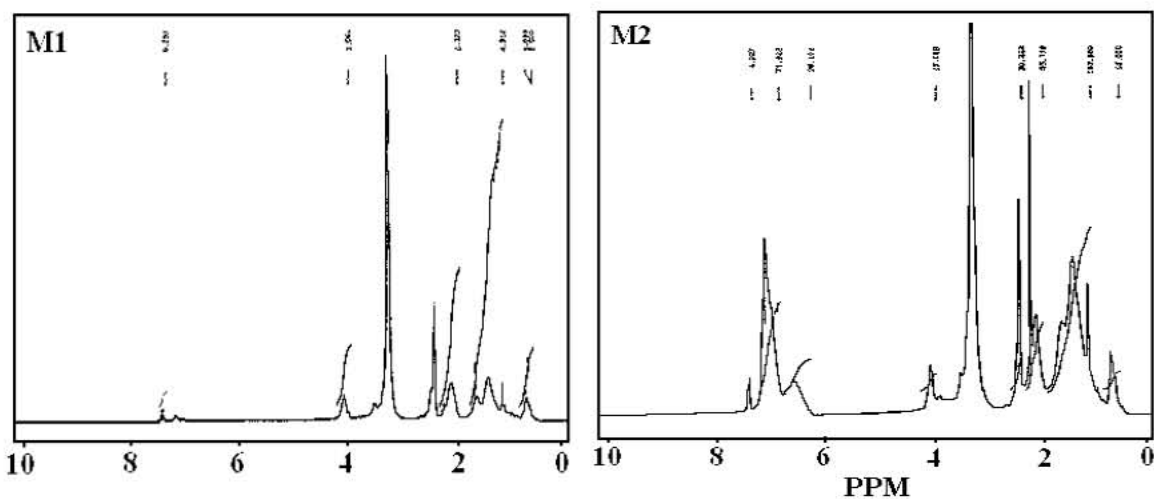Fig. 2: FT-IR spectra of the prepared polymers mixed with cement pastes

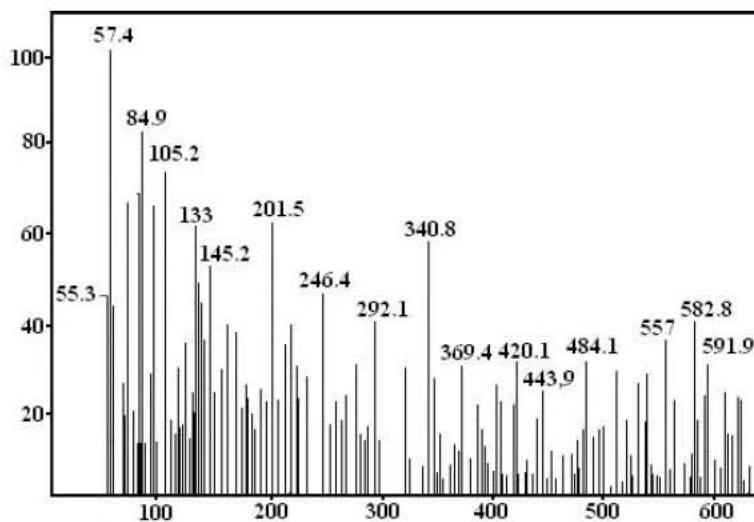Fig. 3: Proton NMR spectra of the prepared polymers

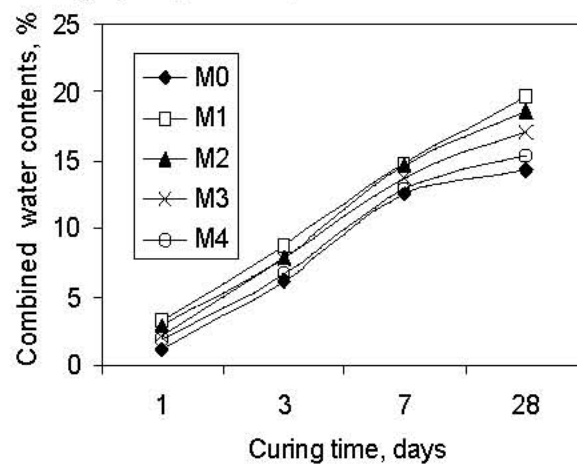Fig. 4: Mass spectra of the prepared copolymer [AA-co-St]

Fig. 5: Combined water contents of the OPC pastes (M0) and those premixed with hydrophilic polymer in absence of NaOH (M1-M4).
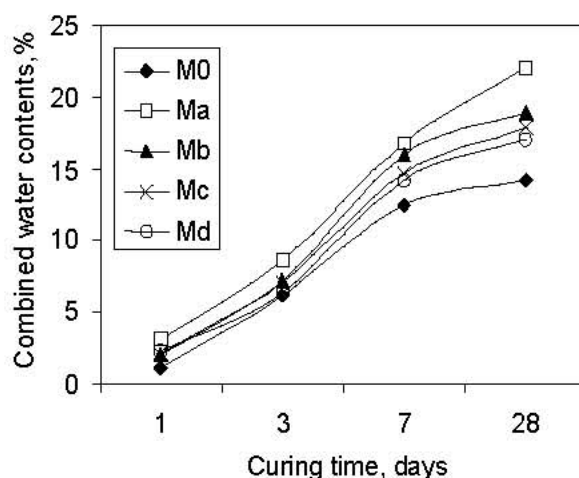
Fig. 6: Combined water contents of the OPC pastes (M0) and those premixed with hydrophilic polymer in presence of NaOH (Ma-Md)

Fig. 7: SEM images of the OPC pastes (M_0) and (M_1) and (M_2) hydrated up to 28 days

Table 9: Elemental analysis of cement pastes mixed with polymers

Elements	C	O	Na	Mg	Al	Si	S	K	Ca	Fe
Cement		36	0.4	4.1	6.6	17	1.1	0.8	31	1.1
M1	5.8	50	0.2	0.2	1.0	3.8	1.5	0.2	35	1.4
M2	1.8	49	0.3	1.7	3.5	9.7	1.4	0.4	29	1.3

the main components of admixtures, C and S and the main component of clinker minerals, Ca, in the direction of depth from the surface. The concentration changes of C, S and Ca on the alite phase of the clinker (C_3S) and interstitial phase are shown in Table 9.

As shown from the data in Table 9, the relative concentration of carbon on the surface of the adsorbed layer on alite in case of cement paste mixed with M1 is higher than that of interstitial material in cement without admixture and than those of alite and interstitial materials in the case of cement paste mixed with M2. The reason is considered that poly (AA) is more densely absorbed on the surface of adsorption layer. Considering that approximately a half of the total surface area of cement

clinker particle is composed of alite, the increase of the electric charge density by the formation of the dense adsorption layer on the alite surface would be one of the reasons for the improvement of fluidity of cement paste by poly acrylic acid admixture [32].

Compressive Strength: The compressive strength of the hardened cement pastes of the OPC (M_0) and those premixed with various ratios of the prepared polymers (AA-co-St) in absence (M_1-M4) and presence (Ma-Md) of NaOH are graphically represented as a function of curing time up to 28 days in Figures 8 and 9 respectively. It is generally obvious that the compressive strength of cement pastes increases sharply with the curing time up
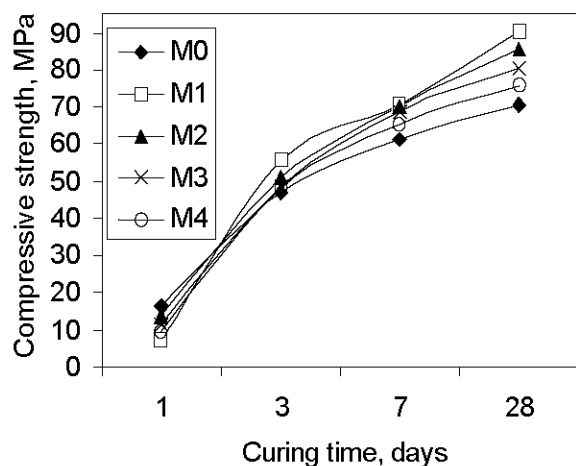
Fig. 8: Compressive strength of the OPC pastes (M0) and those premixed with hydrophilic polymer in absence of NaOH (M1-M4).
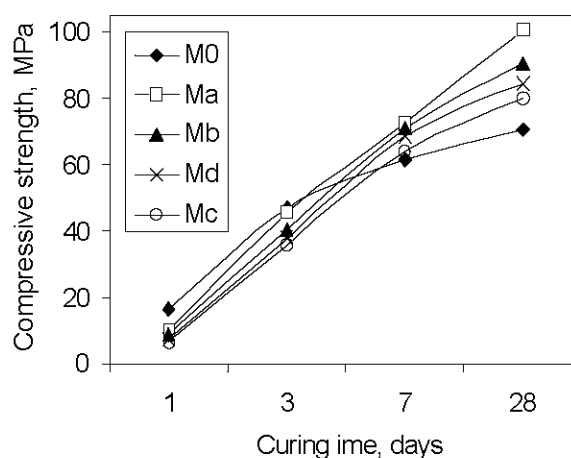

Fig. 9: Compressive strength of the OPC pastes (M0) and those premixed with hydrophilic polymer in presence of NaOH (Ma-Md).

to 28 days. This is mainly due to the continual formation of hydration products, which tend to deposit into the pore structure of hardened cement pastes. This leads to a noticeable decrease in the total porosity. Therefore, the bulk density improves and the compressive strength is significantly enhanced.

As shown from Figures 8 and 9, the compressive strength of the cement pastes premixed with the copolymers increases with the increasing in the ratio of AA in the copolymers because the admixture includes a copolymer of an acrylic acid ($CH_2 = CH – COOH$) with a lot of ester bonds ($– C – O – C –$) in the side chain. This structure increases the steric repulsive force and contributes to the dispersion of solid particles. The repulsive force is considered to be one of the most important forces contributing the fluidity of the cement pastes [33]. Figure 9 showed the compressive strength of the cement pastes premixed with copolymer in presence of sodium hydroxide (Mb-Md) tends to be lower during the early ages of hydration up to 3 days and then becomes higher during the latter ages up to 28 days.

Moreover, the compressive strength of all samples is higher than that of the OPC (M0) at 7 and 28 days. This is mainly because the adhesive action, due to polymerization or crystallization of the polymeric materials, could the grains of the cement with each other associating them. Moreover, the excess of the polymer deposits and polymerizes within the pore system of the hardened cement pastes. The growth of crystalline structure acts as nuclei for other ingredients. This may be continued to enlarge crystals and strong arms-bearing high strength [34]. In addition, the compressive strength of the cement

pastes premixed with the hydrophilic copolymer in presence of NaOH tends to be higher than those of both premixed with copolymers without NaOH and the pure OPC (M_0) at all curing ages of hydration due to that solutions of copolymers in presence of NaOH (Ma-d) with a weaker retarding effect lead to higher strength than solutions of (M1-M4) and OPC (M0).

CONCLUSIONS

Hydrophilic polymer of AA (M_1) and AA-co-St in three different ratios ca. (M_2 =99: 01, M_3 = 97: 03 and M_4 = 95: 05) were prepared and characterized by using FT-IR, ^{1}H NMR, mass spectra, viscosity and SEM images. Mixing the cement pastes with each of the prepared polymers decreased the water of consistency, however, the setting times (initial & final) were increased, i.e. the hydrophilic copolymers with and without sodium hydroxide act as a water reducing (or superplastisizing) and set-retarding agents when mixed with the cement. Mixing the cement pastes with the hydrophilic copolymer enhances the combined water contents at all curing ages of hydration, particularly in presence of sodium hydroxide.

The compressive strength increases, especially in presence of NaOH compared with those of the pure cement pastes. As the concentration of AA in the copolymer increases, the properties of the cement pastes are improved. The SEM micrographs of M_0 and M_1 and M_2 hydrated up to 28 days showed that the dispersability of cement particles is different from each other and a coarse coagulated structure consisting of

various-sized flocks of cement particles is formed with cement pastes premixed with AA-co-St (M₂), while the coagulated structure is more uniform and denser with homo AA (M₁).

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