Synthesis, Characterization and Cement Application of Maleic Anhydride Water-Soluble Grafted Polymer

[1]El-Sayed Moussa Negim, [2]Mahyuddin Ramli, [3]Saber E. Mansour,
[1]Bahruddin Saad and [1]Muhammad Idiris Saleh

[1]School of Chemical Sciences,
[2]School of Housing Building and Planning,
Universiti Sains Malaysia, Pinang, Malaysia
[3]Omar Al-Mukhtar University, Faculty of Science, Chemistry Department, Box 919, Al-Bayda, Libya

Abstract: Methoxypolyoxyethylene-g-Poly maleic anhydride (MPOE-g-PMA) were prepared in presence of titanium isopropoxide as an initiator using a macroradical initiator technique. The grafted copolymers were characterized through Fourier transform infrared (FT-IR) and nuclear magnetic resonance (NMR). The effects of grafted copolymers on the physico-mechanical properties of Ordaniary Portland Cement (OPC) pastes were investigated. The results showed that the addition water mixed to the cement with grafted copolymer improve most of the specific characteristics of (OPC). As the concentration of the grafted copolymer increases, the water-to-cement (W/C) as well as setting time decreases. The combined water content increases with addition of the copolymer to the mixing water. The compressive strength was sharply increased at nearly all hydration ages. The SEM images confirmed that the addition of the organic polymer solutions to the cement powder does not affect the chemical composition of the normal hydration products, but only affects the physical state, shape or morphology and size or crystals of the formed hydrates.

Key words: Cement admixture · Modification of methoxypolyoxyethylene · Physicomechanical properties · Water-soluble surfactant

INTRODUCTION

Chemical admixtures are now widely used in the production of cement with excellent workability, for easy placement without reduction in cement content and strength. These admixtures are extremely effective for dispersing cement particles in water.

Polymeric admixtures are defined as polymers used as a main ingredient effective at modifying or improving cement-based material properties [1-8]. Such a polymeric compound can be polymer latex, redispersible polymer powder, water-soluble polymer or liquid polymer.

Several reports have been concerned with the improvement of the strength and development of Portland cement using admixtures [9-11]. Chemical admixtures or superplasticizers have been used to reduce the water of consistency and to improve the workability of cement pastes and consequently concrete, leading to improvement in mechanical properties and resistance towards environmental deterioration, chemical attack and moistures. Polymeric admixtures which act as water reducer decrease the total porosity, therefore the relationship between porosity and electrical resistivity in cementitious systems were studied [12].

The performance of organic admixtures is closely related to their character including chemical composition, molecular structure and types of functional and hydrophobic groups, molecular weight distribution and mean molecular weight [13].

In the present work poly maleic anhydride-g-methoxypolyoxyethylene (PMA-g-MPOE) were prepared and characterized by FTIR and ^{1}H NMR. So, the main objective is to investigate the influence of the prepared polymers on the physico-chemical and mechanical properties of the cement pastes premixed with these polymers.

Corresponding Author: El-Sayed Moussa Negim, School of Chemical Sciences, Universiti Sains Malaysia, Pinang, Malaysia.
Tel:+6012-4609447, Fax: +6046574854, E-mail: elashmawi5@yahoo.com.

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

OxidesMaterials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	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

MATERIALS AND METHODS

Experimental Procedures

Preparation of PMA-g-MPOE: Preparation of MPOE-MA grafted copolymer by a reaction mixture containing 1 mol MPOE, 1 mol MA and a catalitic amount of titanium isopropoxide was stirred mechanically and gradually heated to 180°C in oil bath under a nitrogen atmosphere. After this, the reaction mixture was maintained at this temperature for 8 h.

The prepared polymers were characterized by FT-IR and ^{1}H NMR 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°.

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 [14] of the cement sample was 3350 cm^2/g.

Preparation and Methods: The prepared copolymer 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 [15, 16]. 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 total porosity and compressive strength [17]. 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 total porosity, ξ of each sample at any interval was calculated from the following equation [18]:

$$\xi = 0.99 \times We \times dp / (1 + Wt)$$

where 0.99 is the specific volume of the free water, We is the evaporable water content, dp is the bulk density, g/cm^3 and Wt is the total water content which is equal to the sum of evaporable water (We) and combined water (Wn) contents. The bulk density (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 [18]. 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 [19]. The microstructure of the hydrated cement pastes was investigated by scanning electron microscopy (SEM) and elemental analysis. The SEM images of the 7-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.
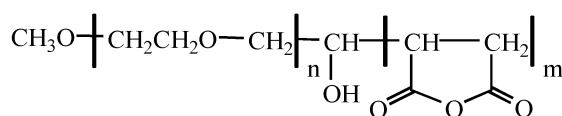
RESULTS AND DISCUSSION

Characterisation of the Modified Surfactant:
The IR spectra of both MPEO and grafted MPEO with maleic anhydride (MA) are shown in Figure 1. The results indicate that both curves appear to have the same characteristic vibration absorbing peaks. There are remarkable differences in the spectrum (b) at 1635, 1410 and 810 cm^{-1} namely, the vibration absorbing peaks of-CH=CH-group of maleic anhydride. Moreover, strong vibration absorption peak of carbonyl group C=O exists at 1740 cm^{-1} in the corresponding curve.

The ^{1}H NMR spectrum gives more support for the structure of the prepared grafted copolymers. The chemical shifts at δ = 3.2 to δ= 3.8 ppm for the proton in MPOE (____OCH$_2$____CH$_2$____) and proton in PMA appear at δ = 2.5 ppm. The signals at δ 6.5-6.7 ppm, characteristic of the (olefinic proton)-CH=CH-in the maleic acid residue. The typical ^{1}H NMR spectrum for MPOE-g-PMA is shown in Figure 2.

The grafted copolymer is expected to have the following structure:

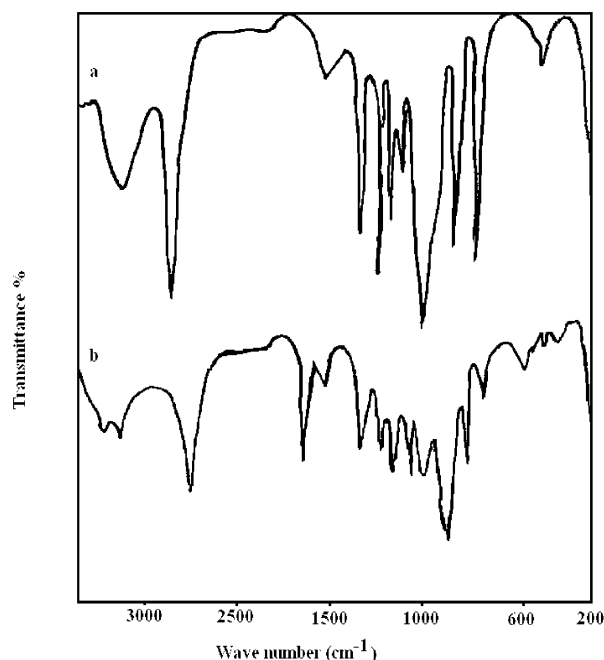$$CH_3O\left[CH_2CH_2O-CH_2\right]\left[\underset{\underset{OH}{|}}{CH}\right]_n\left[CH-CH_2\right]_m$$

MPOE-g-PMA

Application of Graft Copolymer for Cement

Water of Consistency and Setting Time: The water/cement (W/C) ratio is an important factor in ensuring the good quality cement with polymers. The effect of copolymer addition on water/cement ratio required to maintain the desired flow (105-125 mm) is shown in Figure 3. The required quantity of water decreases with the addition of the grafted copolymer. However, the decrease is relatively more in case of increasing the concentration of the copolymer thane that of the cement pastes without copolymer (W/C = 28%). This ratio tends to change irregularly according to the type of polymer concentrations added to Portland cement during the mixing process. This may be due to a relationship between the W/C ratio of Portland cement and the particle size as well as viscosity of the grafted copolymers used, which cause variable water requirements to produce suitable pastes.

On the other hand, the initial and final setting times of cement with grafted copolymer are shown in Figure 4. The initial and final setting times of cement paste without polymer were found to be 150 and 215 min respectively. The initial and final setting times of cement with grafted copolymer for lower addition (0.25%) were observed as 160 and 240 min and for higher additions (1%) were 130 and 190 min, respectively. Grafted copolymer from 0.25% to 1% acts as a retarder. Generally, organic polymers act as retarders and have distinct behavior towards
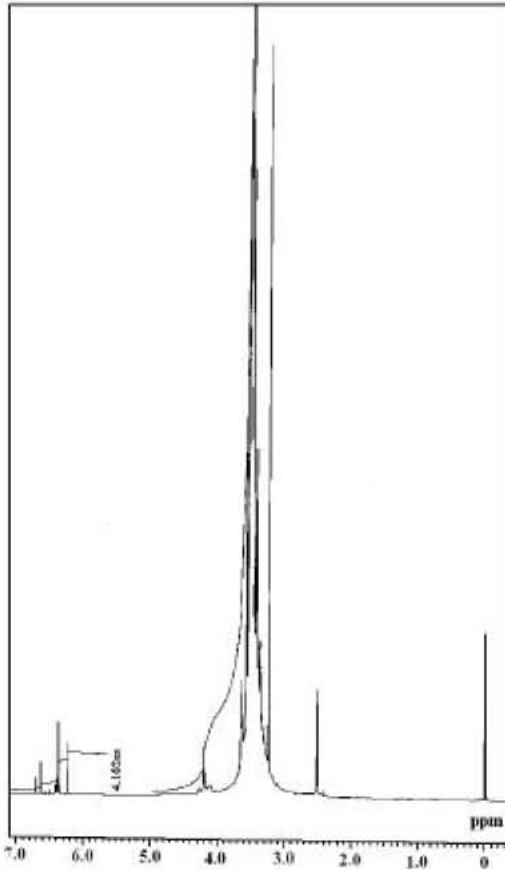

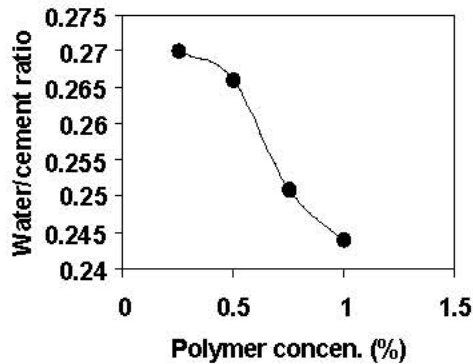Fig. 1: FTIR (a) MOPE and (b) MPOE-g-PMA

Fig. 2: ^{1}H NMR spectrum of MPOE-g-PMA

Fig. 3: W/C ratio necessary to obtain the Vicat standard consistency of OPC with different concentration of MPOE-g-PMA
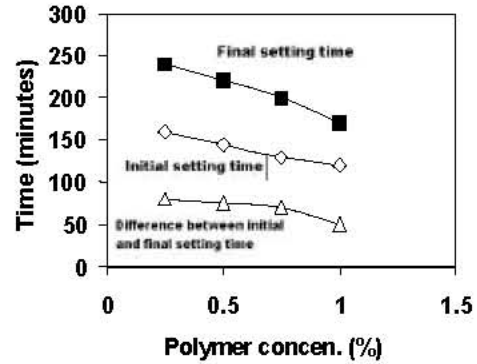

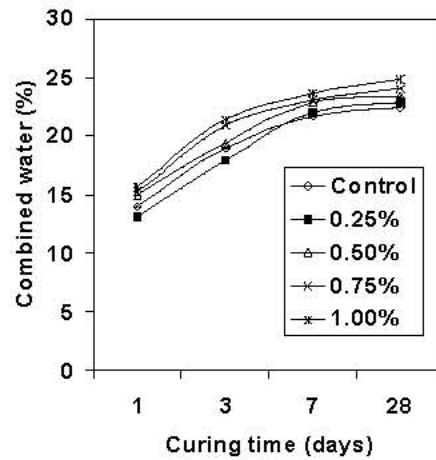Fig. 4: Setting times of O.P.C paste mixed with different concentration of MPOE-g-PMA.

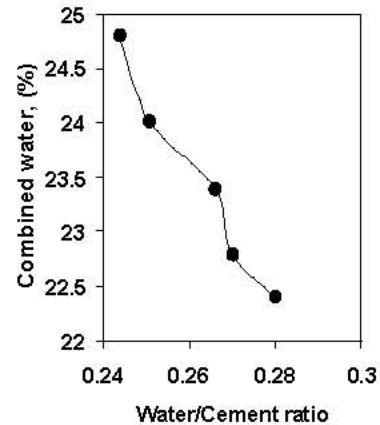Fig. 5: Combined water of OPC mixed with different concentration of MPOE-g-PMA.

Fig. 6: Combined water of OPC mixed with different water/cement ratio of MPOE-g-PMA

the setting of cement [19]. The setting time of cement may be varied according to the physical and chemical properties of organic polymers such as solubility, viscosity, chain length, polarity and functional group(s). It is reported [20] that, generally, organic retarders contain the HC-OH group in their molecules, which retards the rate of adsorption of H_3O^+ ions on cement universal surface and slows the setting reactions. The set retardation [21] may primarily be due to the retardation of the hydration of C_3S through the adsorption of the organic admixture onto calcium hydroxide. It is clear from
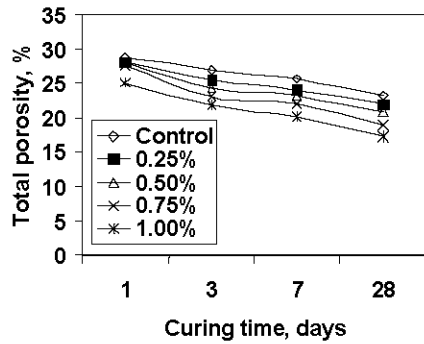
Fig. 7: Total porosity of the OPC pastes and those premixed with different concentrations of MPOE-g-PMA.
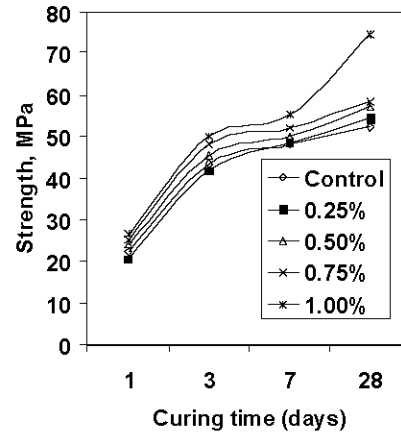

Fig. 8: Compressive strength of OPC mixed with different concentration of MPOE-g-PMA

Fig. 9: Compressive strength of OPC mixed with different water-cement ratio of MPOE-g-PMA

the Figure 4, a decrease on the setting time (between initial and final setting time) occurred with increasing the concentration of the copolymer.

Chemically Combined Water Content: Chemically combined water content of cement pastes was used as a measure of the degree of hydration [22]. The results of chemically combined water contents of the various pastes premixed with grafted copolymer are represented as a function of curing time in Figure 5. It is clear that the chemically combined water content increases gradually with curing time for all hardened cement pastes. This is due to the progress of the hydration with curing time and accumulation of hydration products. From the Figure shows that, the chemically combined water content increases with increase in the polymer concentration.

Figure 6 shows that, the chemically water content increase with decreasing water/cement ratio. It is conceivable that a long lasting close contact of water molecules with cement granules is required for the hydration to occur. In case of presence of grafted copolymer, they could be gathering around cement granules to form a polymer layer, in which the hydrophobic ends of the grafted copolymer are in contact with the cement granule surface and their hydrophilic heads orientate towards surrounding water molecules, similar to the picture of surfactant micelles.

Compressive Strength: The total porosity and compressive strength of the hardened cement pastes of the OPC (control) and those premixed with various concentrations of the prepared polymers (MPOE-g-PMA) are graphically represented as a function of curing time up to 28 days in Figures 7 and 8 respectively. Generally, the
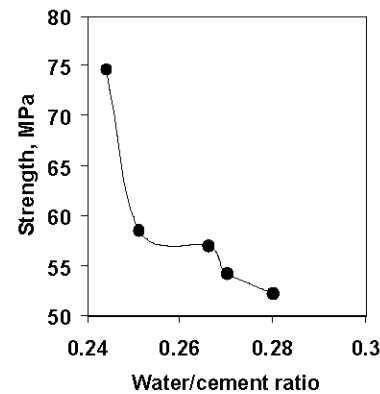
total porosity of the various cement pastes decreased with curing time up to 28 days (Fig.7), while the compressive strength increased (Fig. 8). This is attributed to that the total porosity and the compressive strength of the hardened cement pastes depend mainly upon the rate of hydration. Therefore, as the hydration proceeds, the formation of hydration products started and continuously increased by time. The formed hydration products were deposited into the pore structure that originally filled with free water. Consequently, the total porosity decreased and accordingly the compressive strength increased [23]. The compressive strength of Portland cement paste with a polymer concentration of 0.25% is not quite different from that of the control paste. However, the addition of higher amounts of polymer causes a marked increase in the 28 days compressive strength of pastes. For example, the addition of 1.00% polymer to Portland cement paste leads to strength 30% higher than that of the blank paste. From Figure 9, it appears that differences in strength
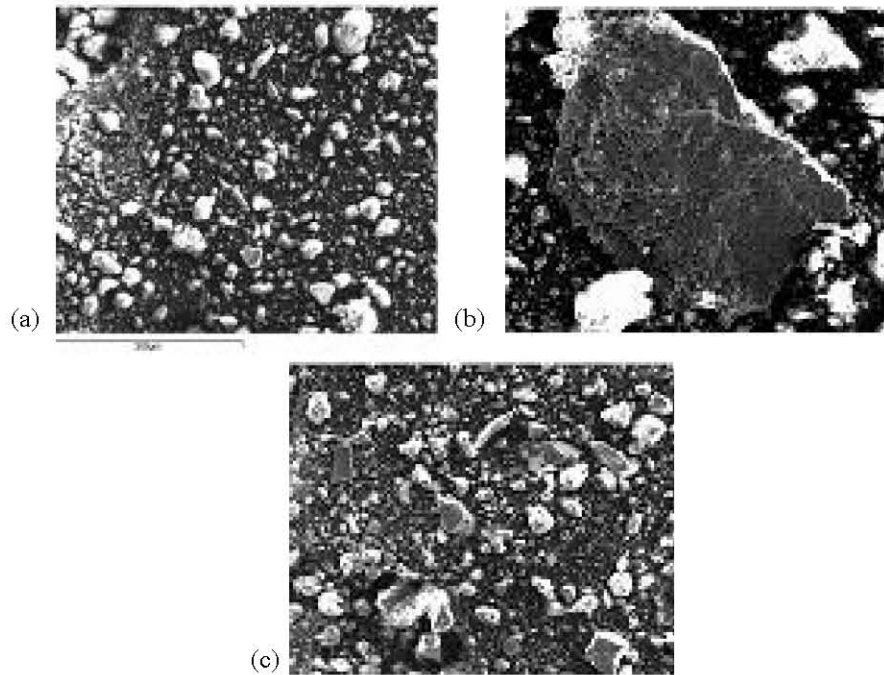
Fig. 10: SEM pictures of (a) OPC hydrated for 7 day & OPC hydrated for 7 day in presence of MPOE-g-PMA (b) 0.25% and (c) 1.00%.

Table 2: Elemental analysis of cement pastes mixed with polymers

Concen. of copolymer (%)	Elements									
	C	O	Na	Mg	Al	Si	S	K	Ca	Fe
0.00		36	0.4	4.1	6.6	17	1.1	0.8	31	1.1
0.25	1.8	49	0.3	1.7	3.5	9.7	1.4	0.4	29	1.3
1.00	5.8	50	0.2	0.2	1.0	3.8	1.5	0.2	35	1.4

produced by grafted polymer can adequately be accounted for on the basis of changes in the w/c ratios of pastes. In general, the compressive strengths of Portland cement pastes with superplasticizer increase in consequence of the lower w/c ratio in the mix.

However, the type of admixture used plays a very significant role in determining the w/c ratio dependence of paste strength. This dependency becomes small in the case of grafted copolymer modified Portland cement pastes. The introduction of grafted copolymer, that is considerably looser in structure due to the lack of symmetry along the chain onto the Portland cement, makes the strength of paste more dependent on polymer concentration. It is apparent that the w/c ratio has a significant effect on the rate of gain of strength of the paste. The pastes with a low w/c ratio gain strength more rapidly than the pastes with higher w/c ratio [24].

SEM Microanalysis: Figure 10 illustrates the SEM micrographs of freshly prepared cement pastes of the pure OPC (control) and those premixed with PMA-g-MPOE. The dispersion of cement particles is different among the kinds of admixture [26, 27]. The cement pastes premixed with 0.25% of the polymer showed a coarse coagulated structure consists of various-sized flocks of cement particles, while the coagulated structure is more uniform and denser with 1.00%.

Elemental Analysis: The changes of concentrations of carbon, sulfur and calcium in the direction of depth from the surface on alite and interstitial materials with regard to a clinker dipped in an aqueous solution of polymer 0.25% and 1.00% which is particularly effective for improving the fluidity of cement pastes. As shown from the data in Table 2, the relative concentration of carbon

on the surface of the adsorbed layer on alite in case of cement paste mixed with polymer is higher than that of interstitial material in cement without polymer. The reason is considered that grafted copolymer is more densely absorbed on the surface of adsorption layer.

CONCLUSIONS

MPOE-g-PMA was prepared and characterized by using FT-IR and ^{1}H NMR. Mixing the cement pastes with each of the prepared polymers decreased the water of consistency, however, the setting times (initial and final) were elongated, i.e. the grafted polymers act as a water reducing (or superplastisizing) and set-retarding agents when mixed with the cement. Mixing the cement pastes with the grafted polymer enhances the combined water contents at all curing ages of hydration. The total porosity of the hardened cement pastes premixed with the grafted polymers decreases, while the compressive strength increases, especially in presence of 1.0 % concentration of the grafted polymer. As the concentration of grafted polymer increases, the properties of the cement pastes are improved. The SEM microanalysis of OPC and those premixed with grafted polymer at 7 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 0.25% of grafted polymer, while the coagulated structure is more uniform and denser with 1.00 % of grafted polymer.

REFERENCES

1. Ohama, Y. And Polymer-based admixtures, 1998. Cem. Concr. Compos, 20: 189-212.
2. Colville, J., A.M. Made and M. Miltenberger, 1999. J. Mater. Civ. Eng., 11(1): 1-5.
3. Ray, I., A.P. Gupta and M. Biswas, 1994. Cem. Concr. Compos, 16: 309-316.
4. Ray, I., A.P. Gupta and M. Biswas, 1995. Cem. Concr. Compos, 17: 9-21.
5. Schulze, J., 1999. Cem. Concr. Res., 29: 909-915.
6. Bureau, L., A. Alliche, P.H. Pilvin and S. Pascal, 2001. Mater. Sci. Eng. A., 308: 233-240.
7. Fu, X. and D.L.L. Chung, 1996. Cem. Concr. Res., 26(1): 69-75.
8. Shaker, F.A., A.S. El-Dieb and M.M. Reda, 1997. Cem. Concr. Res., 27(5): 711-720.
9. Ramachandran, V.S., 1984. Concrete admixtures: Properties, Science and Technology, NOYES Publications, Park Kidge, NJ, USA.
10. Larbi, A. and J.M. Bijen, 1990. Cem. Concr. Res., 20: 139.
11. Chandra, S. and P. Flodin, 1987. Cem. Concr. Res., 17: 875.
12. Tuimdajski, P.J., A.S. Schumacher, S. Perron, P. Gu and J.J. Beaudoin, 1996. Cem. Concr. Res., 26(4): 539.
13. Uchikawa, H., T. Sone and D. Sawaki, 1997. World Cement Research and Development, 28(2): 72.
14. ASTM-Standards, C204-82, 1993. Standard test method for fineness of Portland Cement by Air Permeability apparatus, pp: 887-892.
15. ASTM-Standards and C187-86, 1993. Standard test method for normal consistency of hydraulic cement, pp: 148-150.
16. ASTM-Standards and C191-92, 1993. Standard test method for setting time of hydraulic cement by Vicat apparatus, pp: 866-868.
17. ASTM-Standards and C170-90, 1993. Standard test method for compressive strength of dimentional strones, pp: 828-830.
18. Satarin, V.I. and Y.M Syrkin, 1968. Proc. 5th. Int. Symp. Chem. Tokyo, Japan, 215.
19. Milestone, N.B., 1979. J. Am. Cer. Soc., 62: 321-324.
20. Hansen, W.C., 1960. ASTM Spec. Tech. Publ., 266: 3.
21. Skalny, J. and M.E. Tadros, 1977. J. Am. Ceram. Soc., 60(3-4): 174-175.
22. Brunauer, S. and L.E. Capeland, 1964. The chemistry of concrete, Scient. Am., 210: 83.
23. Hewlett, C.P., 1998. Lea's Chemistry of cement and concret, 4th Edn., John Wiley and Sons Inc., London, Toronto.
24. Neville, A.M., 1997. Properties of Concrete, fourth and final ed., John Wiley and Sons, New York, USA.
25. Uchikawa, H., 1994. Hydration of Cement and Structure Formation and Properties of Cement Paste in the Presence of Organic Admixture. Conference in Tribute to Micheline Moranville Regourd, "Importance of Recent Microstructural Developments in Cement and Concrete" (Sherbrooke, Canada), Concrete Canada, 63.
26. Gad, E.A.M., M.R. Mabrouk and F.H. Mosallamy, 2005. Silicates Industrials, 70(3-4): 59-64.
27. Papo, A. and L. Piani, 2004. Cement and Concrete Research, 34(11): 2097-2101.