

Effect of Phthalic Anhydride-Based Hyperbranched Polyesteramide on Cement Characteristics

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ABSTRACT: Hyperbranched polyesteramides (HB₁ and HB₂) were prepared by the bulk reaction between phthalic anhydride (PhAn) with either diisopropanolamine (DiPA) or diethanolamine (DEA), respectively. The hyperbranched polyesteramides were characterized by IR, GPC, ¹H-NMR, and thermal analysis (TGA and DSC). The effects of solutions of 1, 3, and 5 wt % HB₁ and HB₂ on the properties of Ordinary Portland Cement (OPC) and Portland Limestone Cement (PLC) were studied. Measurements of water of consistency, setting times, bulk density, apparent porosity, and compressive strength for the cement pastes were performed. Some selected cement pastes were characterized by IR and SEM photos. The results showed that HB₁

and HB₂ slightly increased the compressive strength, the combined water and density while decreased the apparent porosity. IR of the formed phases showed increase in the intensities of the spectra for the cement pastes mixed with HB₁ and HB₂ when compared with those of the blank cement pastes. SEM images showed that the incorporation of HB₁ and HB₂ affected only shape or morphology and crystallinity of the formed hydrates. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3054–3064, 2011

Key words: hyperbranched polyesteramides; polymeric admixtures; ordinary Portland cement; Portland limestone cement

INTRODUCTION

Recently, hyperbranched polymers have appeared as fast growing emerging area of research because of their excellent characteristics which resulted from their high functionality as a good example of structure–property relationship.^{1,2} Hyperbranched polymers are easily prepared via several preparative methods such as step growth polycondensation and self-condensing vinyl polymerization.^{3,4} Nowadays, hyperbranched polymers are used in several everyday life needs such as surface and enzyme modifiers, drug carrier, polymer electrolytes, coatings, etc.^{5–11} Accordingly, as a new application, it was thought in this publication to use some members of the hyperbranched polyesteramides as polymeric admixtures for cement pastes. In general, polymer-modified cement, concrete and mortar are produced by adding polymer dispersions, redispersible powders, water-soluble polymers or liquid polymers to the fresh mixture of the building materials. The polymer molecules adsorb on the cement particles and a polymer film forms. The polymers dispersed in water by surfactants badly influence the cement hydration and consequently the polymer film forma-

tion where using of surfactants hinders the polymer film formation and the cement hydration.¹² In the absence of surfactants, water-soluble polymers are supplied on a molecular scale, allowing lower amounts of polymer to be used where an easier and more uniform film formation on the hydrated crystals is expected.¹² The main effect of the polymer is to disperse the agglomerated cement particles.^{13–15} That dispersion, depending on the molecular architecture of the polymer, can be predominantly attributed to the steric hindrance or the combination of steric hindrance and electrostatic repulsion.¹³ The effect of some water-soluble polymer admixtures on the hydration characteristics of Portland cement pastes was studied¹⁶ where it was found that the addition of styrene/butyl acrylate (SBA) to Portland cement with mixing water accelerated the early rate of hydration mechanism, but it has no or a marginal effect at later stages. Knapen and Van Gemert¹⁷ investigated the effect of the presence of water-soluble polymers on the cement hydration reactions by means of isothermal calorimetry, thermal analysis, FTIR spectroscopy, and SEM investigation. Despite an initial retardation of the hydration reactions, a higher degree of hydration was found after 90 days for 1% polyvinyl alcohol-acetate, methylcellulose and hydroxyethylcellulose-modified mortars because of a better dispersion of the cement particles in the mixing water. Methylcellulose also affected the

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TABLE I
Chemical Composition of the Used Cements, wt %

Oxides Materials	L.O.I	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃
OPC	2.64	20.12	5.25	3.38	63.13	1.53	0.55	0.3	2.54
PLC	6.44	16.099	4.028	3.801	60.095	1.240	0.649	0.257	1.436

morphology of the Ca (OH)₂ crystals. Polymer bridges were detected between the layered crystals, gluing the layers together and strengthening the microstructure. In addition, the internal cohesion of the polymer-modified cement pastes was improved. In the presence of the polymers, more cohesive microstructure with a smaller amount of micro-cracks was created. The main objective of this publication is to study the effect of phthalic anhydride-based hyperbranched polyesteramides on the physicochemical and morphological properties of two types of cement, Ordinary Portland cement (OPC) and Portland limestone cement (PLC).

EXPERIMENTAL

Chemicals and materials

Diisopropanolamine (98%) and diethanolamine (99%) were delivered from Fluka Chemicals. Phthalic anhydride (99.98%) was received from Arablab, Dubai, UAE. All chemicals were used as received. The OPC and PLC with Blaine surface areas of 3300 cm²/g and 3100 cm²/g, respectively, were provided from Helwan and Torah Cement Companies, Egypt. The chemical compositions of OPC and PLC are shown in Table I.

Instrumentation

IR spectra were recorded by Pye-Unicum SP-1100 in the range of 400–4000 cm⁻¹. Gel permeation chromatography (GPC) was carried using GPC-1100 Agilent technologies with refractive index detector with 100–10⁴–10⁵ Å ultrastraygel columns connected in series using polystyrene (PS) as standard and *N, N'*-dimethylformamide (DMF) as eluent. ¹H-NMR spectrum was obtained by Jeol JNM-EX 270 MHz, using tetramethylsilane (TMS) as internal standard and DMSO-*d*₆ as the main solvent. Thermal gravimetric analyses (TGA) of the polymers was carried out by using TGA Q 5000 TA instrument, in the range from 40 to 750°C with heating rate 10 K/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements of the polymers were carried out using differential scanning calorimeter Q 1000 TA in the range from –80°C to 150°C with scanning rate of 20 K/min under nitrogen atmosphere. The standard water of consistency (or w/c ratio) of each sample as well as the setting times (initial and final) of the

cement pastes were directly determined by Vicat apparatus.^{18,19} Bulk density (B.D) and apparent porosity (A.P.) of the hardened cement pastes were calculated from eqs. (1) and (2), respectively:²⁰

$$\text{B.D. (g/cm}^3\text{)} = W_1 / (W_1 - W_2) \times 1 \quad (1)$$

$$\text{A.P. \%} = (W_1 - W_3) / (W_1 - W_2) \times 100 \quad (2)$$

where W_1 is the saturated weight, W_2 is the suspended weight, and W_3 is the dry weight. Compressive strength measurements of the cement pastes were carried out using a hydraulic testing machine of the Type LPM 600M₁ SEIDNER (Germany) having a full capacity of 600 KN.¹¹ The loading was applied perpendicular to the direction of the upper surface of the cubes. The chemically-combined water content at each time interval was also determined on the basis of ignition loss.^{21,22} The SEM images of the fractured surfaces, coated with a thin layer of gold, were obtained by JEOL-JXA-840 electron analyzer at accelerating voltage of 30 KV.

Preparation of HB₁ and HB₂

HB₁ and HB₂ were prepared as previously described in the literature^{23–27} and as the following: A mixture of (DiPA or DEA) and PhAn with a molar ratio for (DiPA or DEA) /PhAn of 1.15/1 was introduced into three-necked flask placed into thermostated oil bath and equipped with a mechanical stirrer and a vacuum pump. The reaction mixture was gradually heated to 70°C, with continuous stirring, and then more slowly to 170°C. A vacuum was created during the heating to remove the condensates. The formed hyperbranched polymers were washed with acetone, filtered and then dried at 50°C for 24 h. The yield of HB₁ and HB₂ was 92.55% and 90.78%, respectively. The reaction was followed up by determining the acid values along the reaction period to confirm the completion of reaction.²⁵ The acid values of HB₁ and HB₂ were measured by taking a sample of the reaction mixture every hour. The sample was dissolved in distilled water and then titrated against 0.1N KOH, using phenolphthalein as indicator. At the end point, the color was changed from colorless to pink. The acid values were calculated from eq. (3) and illustrated in Table II:

$$\text{Acid value (mg KOH/g)} = V \times N \times 56.1 / W \quad (3)$$

TABLE II
The Changes of Acid Value of HB₁ and HB₂ with Reaction Time

Reaction time (h)	1	2	3	4	5	6	7
KOH (mg)/HB ₁ (g)	299.15	250.56	233.58	190.12	150.81	111.45	90.14
KOH (mg)/HB ₂ (g)	312.45	262.15	245.86	199.45	170.45	132.18	110.25
Reaction time (h)	8	9	10	11	12	13	14
KOH (mg)/HB ₁ (g)	80.45	66.48	50.46	35.46	25.86	25.41	-
KOH (mg)/HB ₂ (g)	101.49	94.12	77.15	55.45	40.15	34.61	33.15

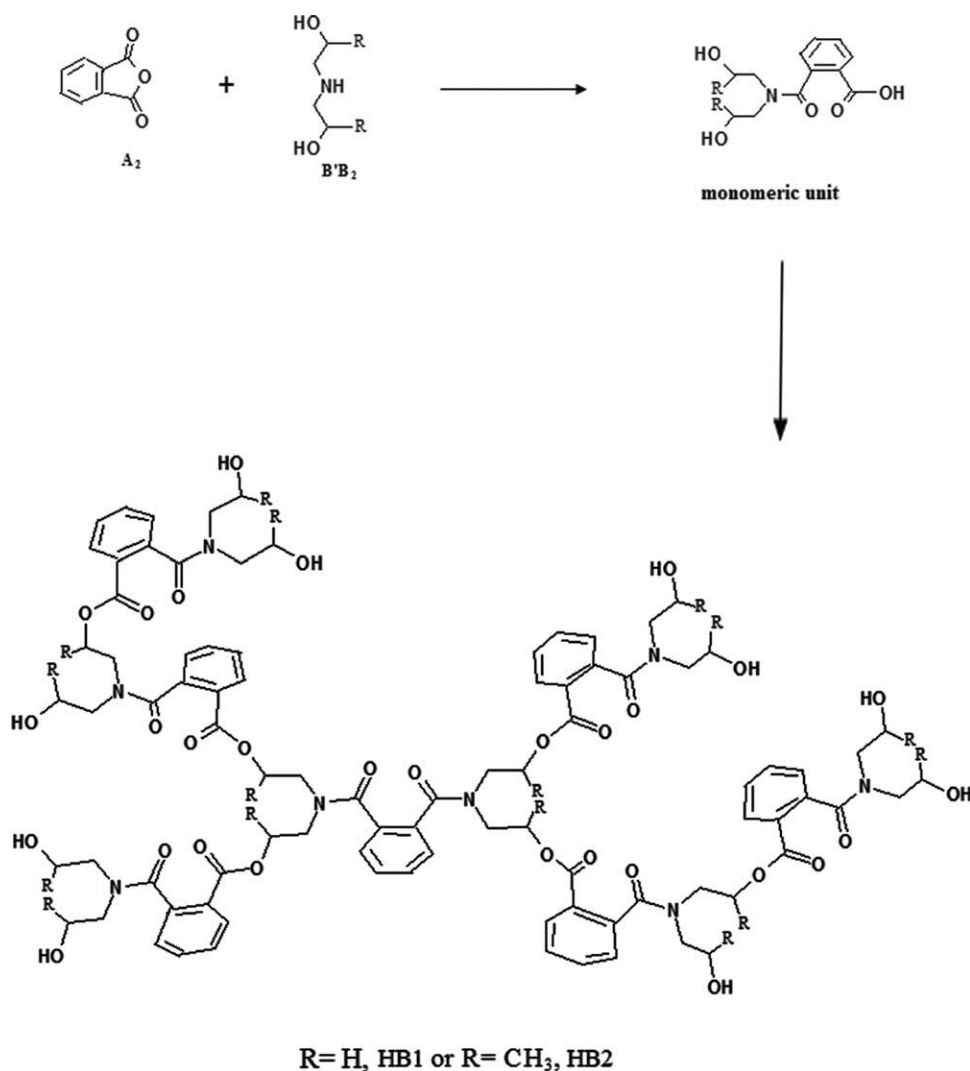
The amount of KOH (mg) was 675.53 mg at zero time.

where V is the ml of 0.1N KOH consumed for sample, N is the normality of KOH, W is the weight of the sample in gm, and 56.1 is the molecular weight of KOH.

Preparation of cement mixes

HB₁ and HB₂ solutions (0, 1, 3, and 5 wt %) were prepared and then added to both cement

types (OPC and PLC). The cement pastes were molded into one inch cubic stainless steel molds, vibrated manually for 2 min and then on a mechanical vibrator for other 2 min. The molds were stored inside a humidity cabinet for 24 h at 23°C ± 1°C and 100% R.H. demoulded and then cured under water till the time of testing for compressive strength after 1, 3, 7, 28, and 90 days.



Scheme 1 The formation reaction of HB₁ and HB₂ hyperbranched polymers.

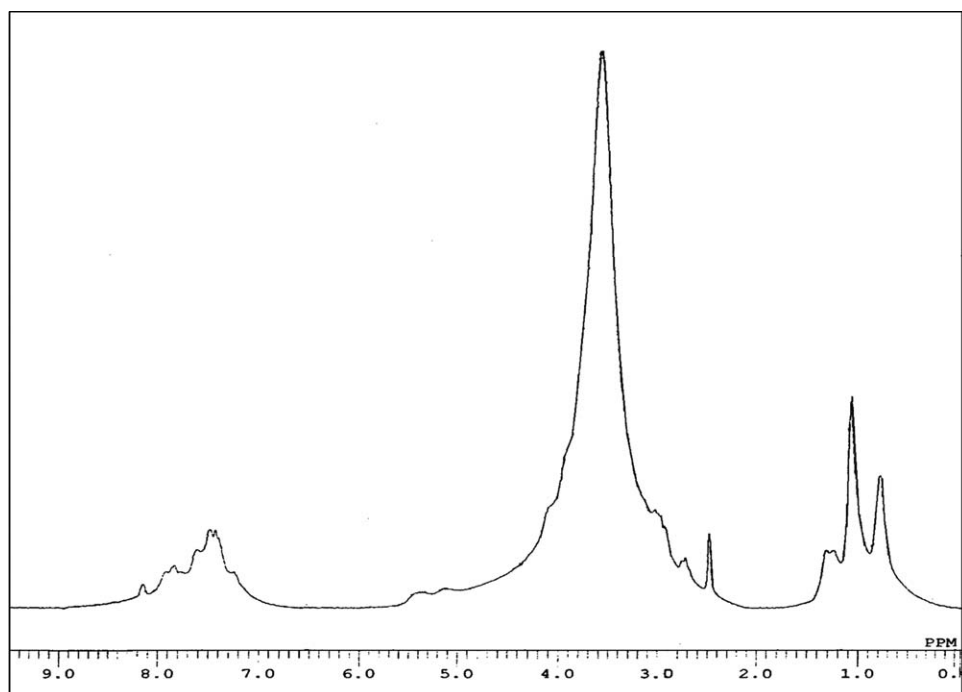


Figure 1 ¹H-NMR spectra of HB₁.

RESULTS AND DISCUSSION

Characterization of the prepared polymers

The hyperbranched polyesteramides HB₁ and HB₂ were synthesized as mentioned in the literature and as illustrated in Scheme 1 via esterification reaction between phthalic anhydride (PhAn) as A₂

monomer with either diisopropanolamine (DiPA) or diethanolamine (DEA) as B'B₂ monomers.²⁷ The esterification reaction was followed by measuring the acidity of the reaction mixture where the changes of acid values with reaction time were recorded as shown in Table II. In general, the acidity decreased with increasing time, which indicated

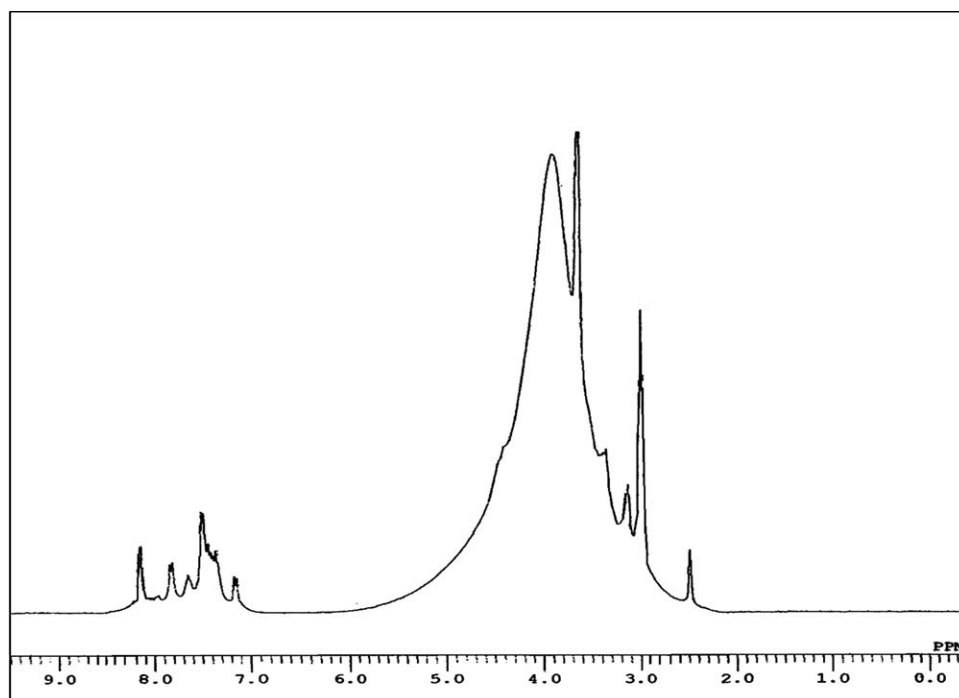


Figure 2 ¹H-NMR spectra of HB₂.

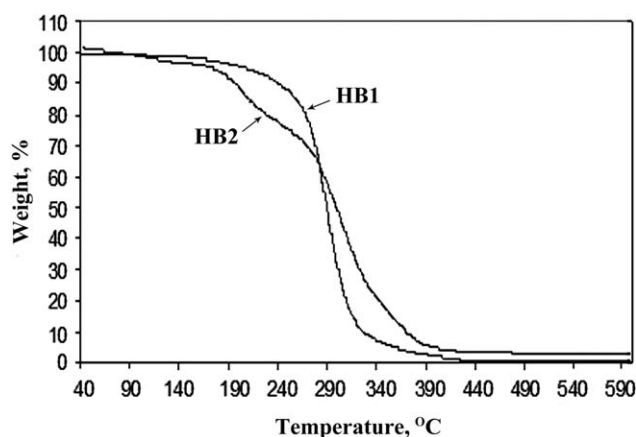


Figure 3 TGA curves of HB₁ and HB₂.

that the esterification proceeded by the condensation reaction between the carboxylic and the alcohol groups present in the monomeric units. Also, the acid value of HB₂ was higher than that of HB₁, which indicated higher reactivity of HB₂ than HB₁.¹⁶ The number average molecular weight (M_n) and polydispersity index (PDI) of HB₁ were found to be 2400 g/mol and 1.64, respectively, whereas those of HB₂ were found to be 2100 g/mol and 1.27, respectively, by GPC relative to polystyrene standards. IR spectra for HB₁ and HB₂ revealed a broad absorption band at 3401–3392 cm^{-1} (ν O–H) which implied the presence of large number of hydroxyl groups in both of HB₁ and HB₂. Hereby, two absorption peaks appeared at 1623–1612 cm^{-1} (ν C=O in amide groups) and 1721–1720 cm^{-1} (ν C=O in ester groups). That indicated the reaction of the secondary amine in DiPA and DEA with the anhydride group in PhAn producing amide and carboxyl groups. Then, as the temperature gradually increased, a condensation reaction occurred converting the carboxyl groups to ester in an esterification reaction. The bands from 1276 to 1269 to 1065–1064 cm^{-1} were attributed to C–O and C–N stretching. ¹H-NMR spectra of HB₁ and HB₂ are shown in Figures 1 and 2.²⁷ Thereby, in case of HB₁, signals of chemical shifts from 7.24 to 8.16 ppm appeared and were referred to the protons of the benzene ring. Also, the signals at chemical shifts from 0.78 to 1.31 ppm were associated with the methyl protons and that from 2.73 to 3.02 ppm were assigned to methylene protons. The signal at chemical shift of 3.56 ppm was ascribed to the methine protons. The signals at chemical shifts from 5.12 to 5.43 ppm were assigned to the proton of hydroxyl group. ¹H-NMR spectrum for HB₂ indicated signals of chemical shifts from 7.15 to 8.17 ppm related to the protons of the benzene ring. The signal at 4.48 ppm was assigned to the proton of hydroxyl group. The signals at chemical shifts of 2.97–3.38 ppm and 3.62–

3.90 were referred to methylene protons of O=CN–CH₂ and O=CO–CH₂, respectively. The TGA curves of HB₁ and HB₂ are shown in Figure 3. The TGA thermograms of HB₁ and HB₂ indicated slight weight loss of 3 and 6% up to 180°C, respectively. That was attributed to the loss of moisture. The weight loss of HB₂ was much higher than that in case of HB₁ by heating in the range of 100–265°C, where HB₁ lost 18% of its original weight while HB₂ lost 28.5% of its original weight. The reason might be that there were more carboxyl groups in HB₂ than in case of HB₁. These carboxyl groups easily reacted with alcohol groups to produce water, which evaporated at high temperatures. Therefore, HB₂ lost more weight during heating. When the temperature reached 280–340°C, TG curves of HB₁ and HB₂ descended sharply. The reason might be that the amide carbonyl groups and the ester bonds in the hyperbranched polyesteramides decomposed at 300–360°C.²⁷ DSC measurements recorded the glass transition temperatures (T_g) of HB₁ and HB₂ as 42°C and –19°C, respectively.

Utilization of the prepared polymers as cement admixtures

The prepared hyperbranched polymers were tested as admixtures for cement where several parameters were measured such as water of consistency, setting times, bulk density, apparent porosity, and compressive strength. The measurements of the water of consistency and setting times (initial and final) are

TABLE III
Water of Consistency and Setting Times (Initial and Final) Measurements of OPC and PLC Pastes and those Premixed with 1, 3, and 5% of HB₁ and HB₂

Polymer	Type of cement	Polymer (wt %) ^a	Water of consistency (%)	Setting time (min)	
				Initial set	Final set
HB ₁	OPC	0	30.00	130	250
		1	29.66	135	250
		3	29.33	135	255
		5	29.00	140	260
		PLC	0	25.00	60
		1	25.00	65	110
		3	24.66	65	115
		5	24.33	70	120
HB ₂	OPC	0	30.00	130	250
		1	29.33	130	255
		3	28.66	140	260
		5	28.33	140	260
		PLC	0	25.00	60
		1	24.00	60	115
		3	23.66	65	115
		5	23.00	70	125

^a Polymer concentration in mixing water.

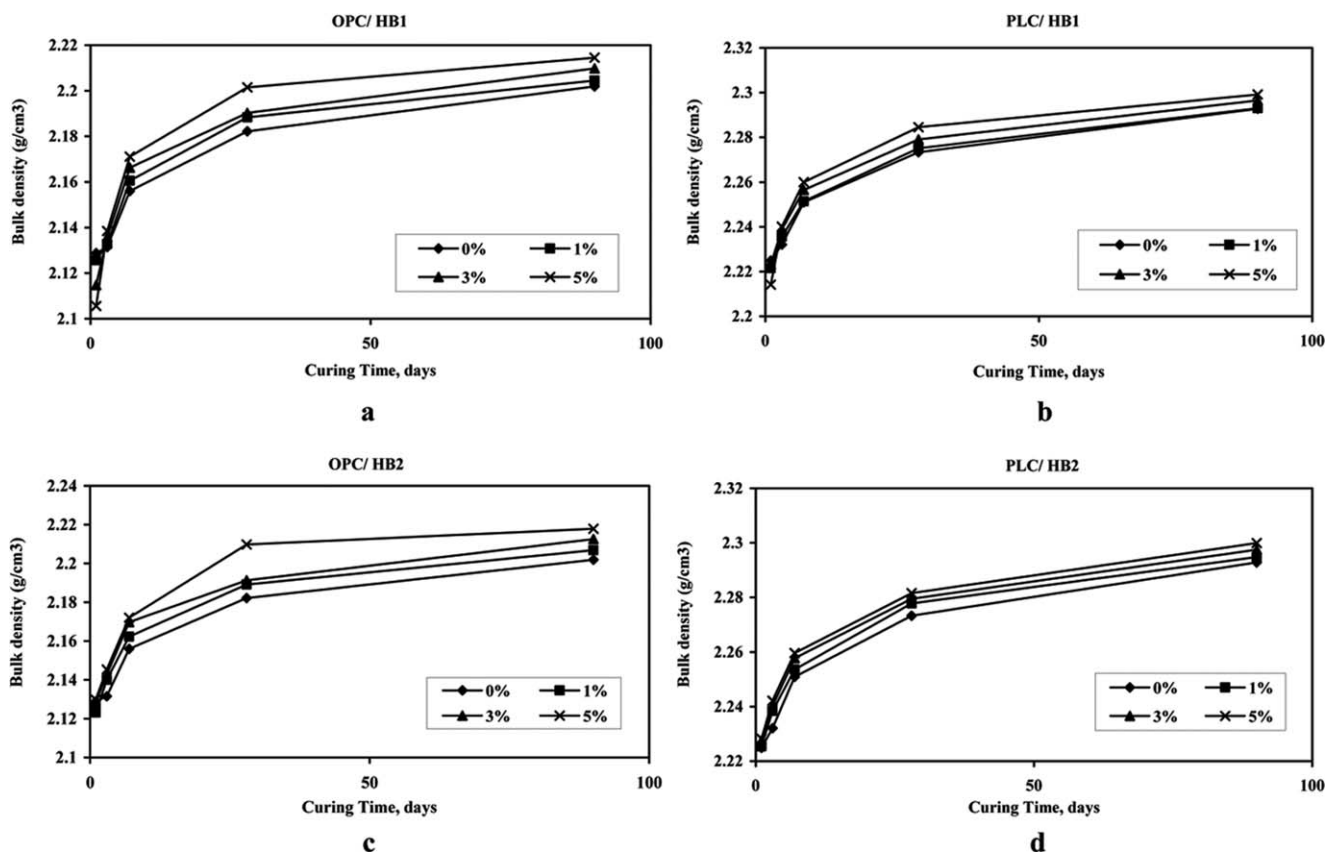


Figure 4 Bulk density of OPC and PLC cement pastes premixed with variable concentrations of HB₁ and HB₂.

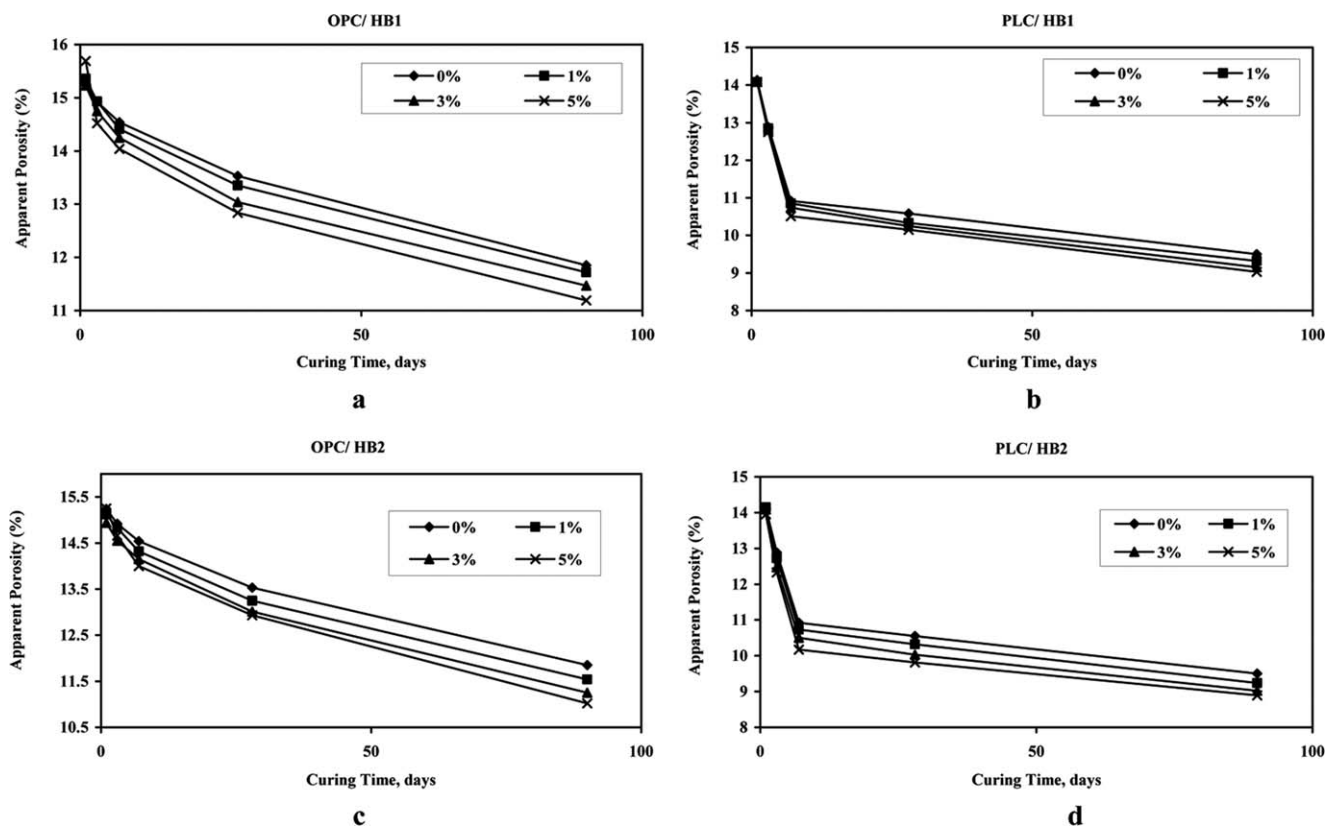


Figure 5 Apparent porosity of OPC and PLC cement pastes premixed with variable concentrations of HB₁ and HB₂.

TABLE IV
Combined Water Content Measurements of OPC and PLC Pastes and those Premixed with 1, 3, and 5% of HB₁ and HB₂, Hydrated up to 90 days

Property	Polymer	Cement	Polymer concn. (wt %) ^a	Curing time, days					
				1	3	7	28	90	
Chemically combined water (%)	HB ₁	OPC	0	11.51	11.94	12.53	13.67	14.39	
			1	11.67	11.98	12.68	13.83	14.63	
			3	11.61	12.13	12.71	14.06	14.99	
		PLC	5	10.91	12.22	12.94	14.26	15.13	
			0	10.96	12.36	13.49	14.74	15.44	
			1	11.19	12.45	13.56	14.82	15.69	
	HB ₂	OPC	3	10.91	12.49	13.75	15.18	15.95	
			5	10.95	12.58	13.94	15.27	16.05	
			0	11.51	11.94	12.53	13.67	14.39	
		PLC	1	10.56	12.15	12.86	13.94	14.88	
			3	10.68	12.35	13.16	14.16	15.36	
			5	11.34	12.55	13.37	14.37	15.82	
	Compressive strength (MPa)	HB ₁	OPC	0	10.95	12.36	13.49	14.74	15.44
				1	10.83	12.56	13.78	14.97	15.85
				3	10.28	12.47	14.19	15.45	16.19
			PLC	5	10.86	12.64	14.27	15.65	16.29
				0	30.4	51.2	57.6	64	67.2
				1	28.8	49.6	57.6	62.4	67.2
HB ₂		OPC	3	28.8	52.8	59.2	65.6	68.8	
			5	27.2	51.2	60.8	67.2	70.4	
			0	33.6	54.4	65.6	88	91.2	
		PLC	1	33.6	52.8	65.6	88	92.8	
			3	32	56	67.2	89.6	96	
			5	32	57.6	68.8	91.2	97.6	
HB ₁		OPC	0	30.4	51.2	57.6	64	67.2	
			1	27.2	52.8	59.2	65.6	68.8	
			3	24	54.4	62.4	67.2	70.4	
		PLC	5	25.6	54.4	62.4	68.8	72	
			0	33.6	54.4	65.6	88	91.2	
			1	32	54.4	67.2	89.6	94.4	
HB ₂	OPC	3	33.6	56	70.4	91.2	97.6		
		5	30.4	59.2	70.4	92.8	99.2		
		0	33.6	54.4	65.6	88	91.2		
	PLC	1	32	54.4	67.2	89.6	94.4		
		3	33.6	56	70.4	91.2	97.6		
		5	30.4	59.2	70.4	92.8	99.2		

^a Polymer concentration in mixing water.

indicated in Table III. Generally, the water of consistency gradually decreased with increasing the polymers concentration up to 5% in both types of cements. The water of consistency was reduced by using 5% HB₁ from 30 to 29% with respect to OPC and from 25% to 24.33% with respect to PLC. On the other hand, the water of consistency decreased by using 5% HB₂ from 30% to 28.33% in case of OPC and from 25 to 23% in case of PLC. So, the water of consistency was highly reduced by 3.33–5.57% with OPC and by 2.68–8.00% with PLC in comparison with that of the blank. Thus, HB₁ and HB₂ acted as water-reducers. On the other hand, HB₁ and HB₂ increased the setting times (initial and final) of either OPC or PLC. The initial setting time increased by using 5% of HB₁ and HB₂ from 130 to 140 min with OPC and from 60 to 70 min with PLC. The final setting time increased by using HB₁ and HB₂ from 250 to 260 min. with OPC and from 110 to 120 and 125 min. with PLC by using 5% HB₁ and HB₂, respectively. So, HB₁ and HB₂ performed as setting-

retarders. The reduction in water of consistency and the elongation of setting times was attributed to the adsorption of the highly polar polymer molecules on the cement particles and the formation of a polymer film. An electrostatic repulsion between the negatively charged cement particles was formed, which reduced the interparticle attraction between the cement particles leading to prevent flocculation or agglomeration. Finally, well-dispersed system was obtained which allowed the water to penetrate between the particles without excess of water. In addition, this partial or full encapsulation of the cement hydrates by the polymer molecules retarded the hydration process.^{28,29}

The bulk density and apparent porosity measurements were illustrated in Figures 4 and 5. Generally, the bulk density of all cement pastes gradually increased with curing time while the apparent porosity decreased. That was attributed to the continual deposition of the formed hydration products in the pore structure of the hardened cement

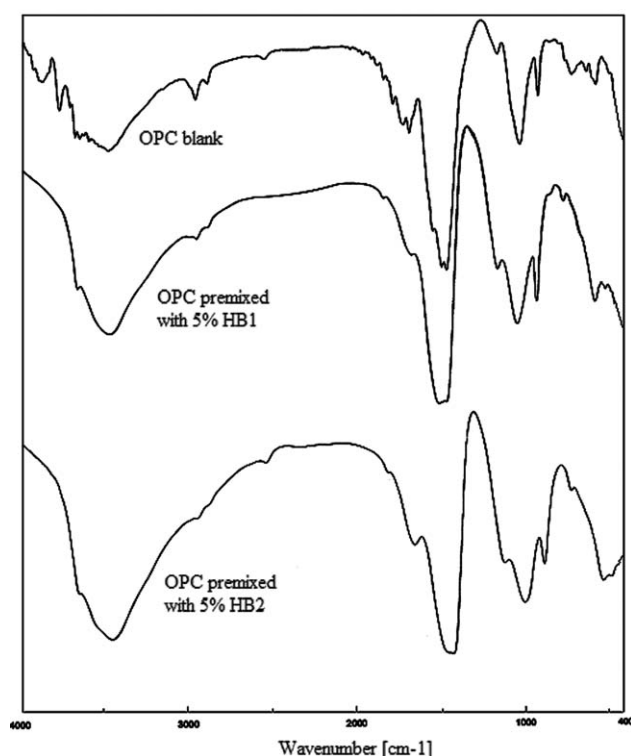


Figure 6 IR spectra of cement pastes after 90 days for samples OPC blank, OPC premixed with 5% of HB₁ and HB₂.

pastes.²⁰ Furthermore, the bulk density increased and the apparent porosity decreased with increasing polymers concentration. The bulk density increased from 2.2019 to 2.2145 g/cm³ by using 5% HB₁ with OPC and from 2.2928 to 2.2991 g/cm³ with PLC after 90 days, while decreased the apparent porosity from 11.85 to 11.19% with OPC and from 9.50 to 9.03% with PLC after 90 days. However, the bulk density increased by using 5% HB₂ from 2.2019 to 2.2179 g/cm³ with OPC and from 2.2928 to 2.2999 g/cm³ with PLC after 90 days, while the apparent porosity decreased from 11.85% to 11.02% with OPC and from 9.50% to 8.89% with PLC after 90 days. That was attributed to the improvement in the hydration process by the polymer addition. Subsequently, the amount of hydrates increased which filled more pore spaces in comparison with blank samples in addition to the polymer film formation which contributed in filling the pore spaces.

The chemically combined water content and compressive strength measurements are indicated in Table IV. Generally, both of the combined water and the compressive strength values of all cement pastes increased with curing time. That was mainly attributed to the gradual and continuous formation of the hydration products resulting from the hydration of the main phases of cement, particularly C₃S and β-C₂S.²⁰ Furthermore, the combined water content and compressive strength of all cement pastes

increased with increasing polymer concentration at all curing times, except for the first 24 h. The chemically combined water increased from 14.39% to 15.13% with OPC by using 5% HB₁ and from 15.44% to 16.05% with PLC after 90 days, while the compressive strength increased from 67.2 MPa to 70.4 MPa with OPC and from 91.2 MPa to 97.6 MPa with PLC after 90 days. However, the combined water content increased by using 5% HB₂ from 14.39% to 15.82% with OPC and from 15.44% to 16.29% with PLC after 90 days while the compressive strength increased from 67.2 MPa to 72 MPa with OPC and from 91.2 MPa to 99.2 MPa with PLC after 90 days. The higher values of the combined water content by incorporation of HB₁ and HB₂ with either OPC or PLC were due to the dispersion effect of the adsorbed polymer on the cement grains, which in turn prevented their aggregation and improved the hydration process. However, the increase in compressive strength was mainly due to the reduction in water of consistency and the better hydration obtained by the polymer addition. At the first 24 h, the retardation in the hydration process by the polymer film formation resulted in lower compressive strength compared with the blank samples.

IR spectra of the hydrated OPC and PLC pastes and those premixed with 5% of HB₁ and HB₂ after 90 days of hydration are shown in Figures 6 and 7. The sharp absorption band at 3645–3627 cm⁻¹ was related to the free OH group coordinated to Ca⁺²,

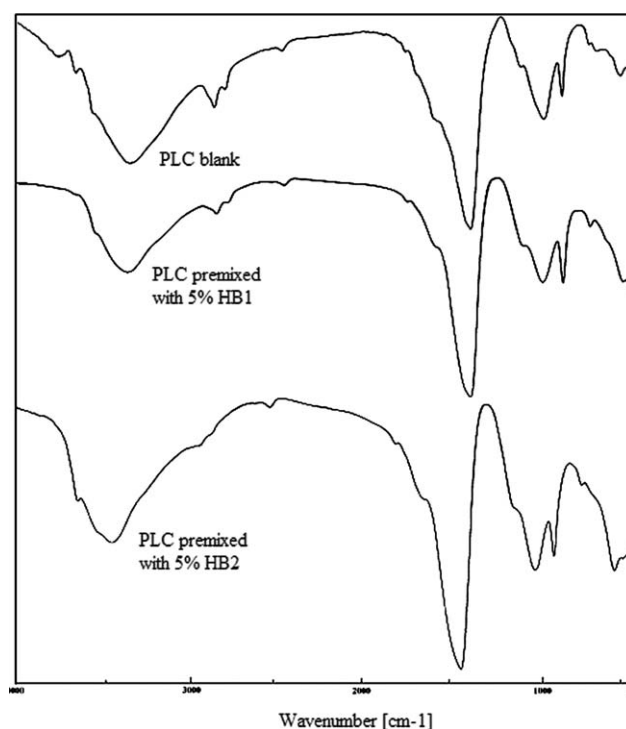


Figure 7 IR spectra of cement pastes after 90 days for samples PLC blank, PLC premixed with 5% of HB₁ and HB₂.

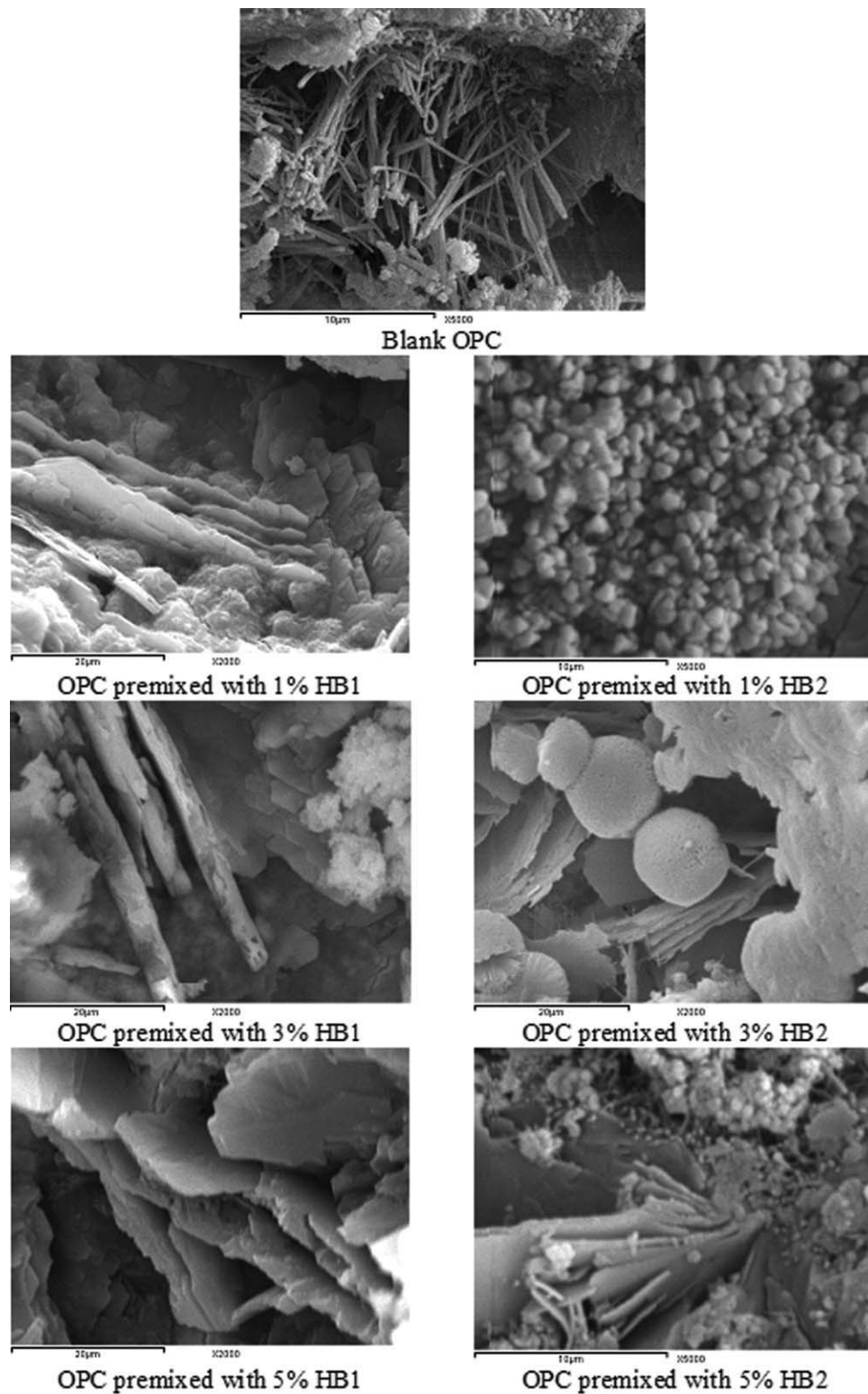


Figure 8 SEM images of cement pastes for samples OPC blank, OPC premixed with 5% of HB₁ and HB₂.

i.e., free lime. The intensity of the broad absorption band at $3447\text{--}3420\text{ cm}^{-1}$, which was due to the OH group associated to H^+ bond related to the symmetrical stretching frequency of water, increased in presence of polymer. The two bands at $2964\text{--}2925$

and $2859\text{--}2856\text{ cm}^{-1}$ were due to $-\text{CH}_2$ and $-\text{CH}_3$ from the residual organic mixture. The two absorption bands at $1648\text{--}1643$ and $1428\text{--}1426\text{ cm}^{-1}$ were ascribed to the main silicate band involving Si—O stretching vibration bands of CSH, while the band at

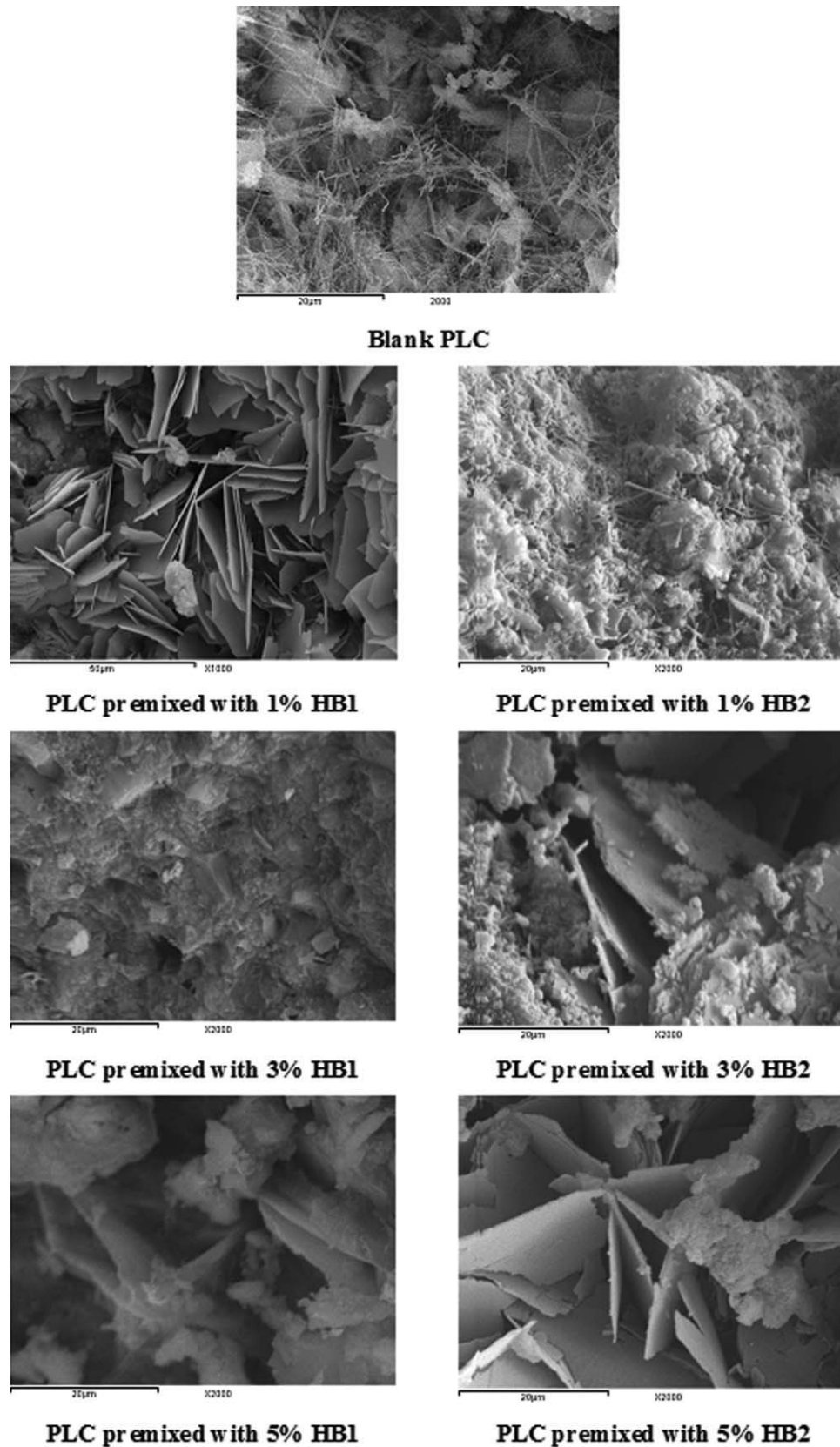


Figure 9 SEM images of cement pastes for samples PLC blank, PLC premixed with 5% of HB₁ and HB₂.

1109–1120 cm^{-1} was due to CAH. No new phases were detected by IR, only increased intensities of the formed phases were observed by the addition of HB₁ and HB₂ than those of the blank cement pastes. These observations indicated the improvement in the cement hydration process. Also, the intensities of the absorption bands associated with sample premixed with HB₂ were slightly higher than those associated with the sample premixed with HB₁. The scanning electron microscopy (SEM) images of OPC and PLC pastes and those premixed with 1, 3 and 5% of HB₁ and HB₂ after 90 days of hydration are illustrated in Figures 8 and 9. The needle-like crystals of ettringite were clearly detected with OPC and PLC blank pastes. These needles were decreased or mostly disappeared in presence of HB₁ and HB₂. That was mainly due to the conversion of ettringite ($\text{C}_3\text{A}\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$) to monosulphate ($\text{C}_3\text{A}\cdot \text{CaSO}_4\cdot 12\text{H}_2\text{O}$) or to the fact that the hydrates were surrounded with the polymer coat or thin films which prevented its growth. Those facts proved that better hydration was obtained by the addition of the polymers. HB₁ and HB₂ also affected the morphology of the Ca (OH)₂ crystals.

Generally, in absence of polymers, crystals of Ca (OH)₂ are generally weak and unable to withstand the stresses that are generated during the early hydration when the rearrangement of hydrates takes place in a limited space.¹⁷ However, in the presence of HB₁ and HB₂, the structure of Ca (OH)₂ was modified to the extent that the crystals became capable of withstanding those stresses where layered deposition of Ca(OH)₂ plates were detected.¹⁷

CONCLUSIONS

The presence of HB₁ and HB₂ had great effect on the cement hydration. A small increase in the rate of hydration of pastes modified with HB₁ and HB₂ was observed. A reduction in the water of consistency was recorded by the polymers addition. Better hydration process was obtained in presence of the polymer. Also, HB₁ and HB₂ influenced the morphological structure of the hydrates where the ettringite needles decreased or mostly disappeared in presence of HBPA. In addition, plates of Ca(OH)₂ crystals were detected. HB₂ gave better effect on the cement pastes than HB₁ because of its higher reactivity.

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