Employing of Some Hyperbranched Polyesteramides as New Polymeric Admixtures for Cement

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ABSTRACT: Hyperbranched polyesteramides ($HBPA_1$ and $HBPA_2$) were synthesized by the bulk polycondensation of maleic anhydride (MA_n) as an A_2 monomer with both of diisopropanolamine (DIPA) and diethanolamine (DEA), respectively, as $B'B_2$ monomer. The prepared polymers were analyzed with IR, GPC, ^{1}H NMR, TGA, and DSC. The hyperbranched polyesteramides were applied as polymeric admixtures in two different types of cement, namely ordinary Portland cement (OPC) and Portland limestone cement (PLC). Several parameters were studied to evaluate the action of $HBPA_1$ and $HBPA_2$ polymers as cement admixtures. Adding $HBPA_1$ and $HBPA_2$ decreased the water of consistency and increased the compressive strength with no effect on the chemical composition of the cement phases. The combined water content and bulk density displayed the same trend as compressive strength. The IR spectra of the formed phases for the mixed cement pastes with $HBPA_1$ and $HBPA_2$ illustrated increased intensities of the absorption bands than those of the pristine cement pastes. The SEM photos showed that the incorporation of $HBPA_1$ and $HBPA_2$ in cement phases affected the morphology and microstructure of the formed hydrates. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 309–320, 2011

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

INTRODUCTION

Hyperbranched polymers have attracted a considerable interest in the recent years due to their unique features.[1–5] The interest in such three-dimensional macromolecules stems from their interesting properties both in solution and in bulk owing to their novel, highly branched, globular, void-containing shapes, and un-entangled structures.[6,7] Hyperbranched polymers have high solubility, low viscosity, and large number of terminal functional groups.[6,8]

The polydisperse hyperbranched polymers have been generally recognized as the economically more feasible counterparts of the monodisperse dendrimers.[9] However, dendrimer molecules are necessarily constructed in multistep synthesis[10,11] while hyperbranched molecules can be manufactured in one-step polymerization procedure.[12,13] The ease of preparation makes the hyperbranched polymers more readily available for potential applications[14] such as multifunctional initiators[15] and for rheology control compounds for surface modification,[16] medical applications,[17] membranes,[18] nanofillers for polymer nanocomposites,[19] nonlinear optics,[20] and nonporous generators for low dielectric constant insulators.[21,22] Hyperbranched polyesteramides constitute new and promising class of resins.[23,24] They can be synthesized following a very straightforward melt polycondensation procedure which allows the use of a broad range of raw materials for optimal versatility where the synthesis does not require any catalyst. The successful application development for hyperbranched polyesteramides is primarily based on the high number of end groups and the multifunctionality on the same molecule. Thus, a variety of specific applications have been considered for hyperbranched polyesteramides, such as crosslinkers for powder coatings, air drying coatings, dyeable polypropylene fibers, oil field chemicals, rheological modifier in paper coatings, and breaking of azeotropes.[25]

The polymers are used as cement admixtures by their addition to cement at minor amounts and in the form of latices, re-dispersible polymer powders, water-soluble polymers, liquid resins and monomers.[26–28] These additions are performed to confer several beneficial effects on the resulting material, which is known as polymer-modified cement, including reduction in water requirements, increased workability, controlled setting, accelerated hardening,

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improved strength, better durability, desired coloration, and volume changes.[27,28] Water-soluble polymer-modified systems are widely used at very low polymer/cement ratios. The traditional water-soluble polymeric cement modifiers are cellulose derivatives including methyl cellulose, carboxymethyl cellulose and hydroxyethyl cellulose, polyvinyl alcohol, polyethylene oxide, polyacrylamide, etc.[27] The effect of the presence of water-soluble polymers on the cement hydration reactions was investigated where a higher degree of hydration was found after 90 days for 1% polyvinyl alcohol acetate, methyl cellulose and hydroxylethyl cellulose modified mortars.[28] That behavior was referred to a better dispersion of the cement particles in the mixing water. Also, it was found that the addition of styrene/butyl acrylate polymer to Portland cement with mixing water accelerated the early rate of hydration mechanism, but have no or a marginal effect at later ages. The compressive strength values were higher at early ages and slightly lower at later ages.[29] Generally, in normal cement pastes, the particles come into close contact with each other and there is a tendency for cement particles to form large flocks due to Van der Waals attraction forces holding particles together. However, in polymer/cement pastes, the polymer molecules adsorb on the cement particles and a polymer film forms. Consequently, negatively charged cement particles are formed by the adsorption of the polymer molecules onto the cement surface. Hence, electrostatic repulsion is generated between the cement particles reducing the interparticle attraction and preventing flocculation or agglomeration where well-dispersed system is obtained.[30,31] That fact leads to better properties of the formed cement pastes such as better hydration by using less water to penetrate between the particles where the combined water content is the main indication for better hydration. Hence, the amount of hydration products is increased by the deposited polymers in the pore spaces of the hardened cement pastes, in addition to the formed polymer film which fills up the pores of the cement pastes. Consequently, the density increases and the porosity decreases. All these factors positively contribute to the compressive strength of the resulting cement.

Accordingly, due to the high functionality and polarity of the hyperbranched polyesteramides, our research group thought to involve them as polymeric additives or admixtures in the cement pastes where extra enhancement in the properties of the polymer/cement pastes was expected. Therefore, the main objective of the current work was to prepare maleic anhydride-based hyperbranched polyesteramides as illustrated in Figure 1 through melt polycondensation of maleic anhydride (MA_n) with both of diisopropanolamine (DIPA) and diethanolamine (DEA). Then, the resulting polymers were inserted in cement pastes where two kinds of cements were used such as Ordinary Portland cement (OPC) and Portland Limestone cement (PLC). Successive studies were carried out on the resulting polymers/cement pastes to investigate the effect of those polymers on the properties of resulting cement pastes in case of OPC and PLC for their future use as new polymeric admixtures. On that way, several traditional parameters related to polymer/cement pastes were measured such as water of consistency, setting time, bulk density, apparent porosity, combined water content, and compressive strength.

EXPERIMENTAL

Chemicals and materials

Diisopropanolamine (98%), diethanolamine (99%), and maleic anhydride (98%) were purchased from Fluka Chemicals and were used as received. The OPC and PLC with blaine surface areas of 3300 and 3100 $cm^2\ g^{-1}$, respectively, were delivered from Helwan and Torah Cement Companies, Egypt. The chemical compositions of OPC and PLC are shown in Table I. All other chemicals were of commercial grades and were used as received.

Instrumentation and measurements

The prepared polymers and the formed polymer/cement pastes were characterized by using different techniques such as Infrared spectra (IR), gel permeation chromatography (GPC), nuclear magnetic resonance (^1H NMR), and thermal analyses such as thermal gravimetric analyses (TGA) and differential scanning calorimetry (DSC). IR spectra were recorded by Pye-Unicum SP-1100 in the range of 4000–400 cm^{-1}. Molecular weights ($\bar{M}_n$) and polydispersities ($D = \bar{M}_w/\bar{M}_n$) were determined via GPC. GPC measurements were carried out by using GPC-1100 Agilent technologies with refractive index detector with $100\text{-}10^4\text{-}10^5$ A° ultrastyragel columns connected in series using polystyrene (PS) as standard and *N*,*N*-dimethylformamide (DMF) as eluent. ^1H NMR spectra were obtained by Jeol JNM-EX 270 MHZ by using tetramethylsilane (TMS) as internal standard and DMSO-d_6 as the main solvent. TGA was carried out by using TGA Q 5000 TA instrument, in the range from 40 to 750°C with heating rate 10 $K\ min^{-1}$ under nitrogen atmosphere. DSC measurements were carried out by using differential scanning calorimeter Q 1000 TA in the range from −80–150°C with scanning rate of 20 $K\ min^{-1}$ under nitrogen atmosphere. The phase compositions of some selected samples were investigated using IR and scanning electron microscopy (SEM) techniques. 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.

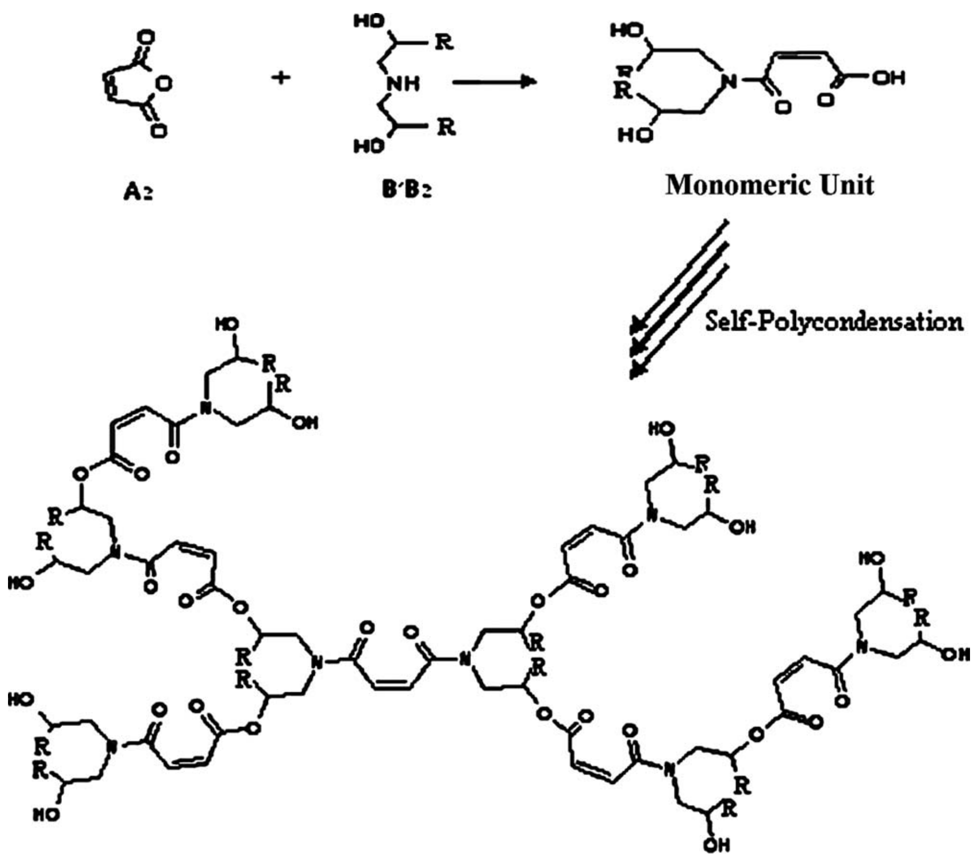


Figure 1 Formation reaction of $HBPA_1$ and $HBPA_2$ hyperbranched polyesteramides where R = CH_3 for $HBPA_1$, R = H for $HBPA_2$.

Several abbreviations are commonly used with respect to the cement phases and were mentioned in the present publication such as:

CSH = Calcium Silicate Hydrate phase or (3 $CaO \cdot 2SiO_2 \cdot 4H_2O$) where this is the main reaction product of cement hydration and is the main source of concrete strength.

CAH = Calcium Aluminate Hydrate phase or $CaOAl_2O_3 \cdot 10H_2O$ which is a result of the reaction between the Aluminate phases of Portland cement and water.

C_3a = Tri-calcium Aluminate phase or $3CaO.Al_2O_3$

Test methods of cement samples

Several parameters were measured for the resulting hyperbranched/cement pastes such as:

Water of consistency and setting times measurements. Water of consistency (w/c) is the quantity of water required to produce a cement paste of standard consistency where the setting times are the periods of time required for the cement performance to begin and to end. Both of water of consistency and setting times were measured directly by Vicat apparatus.[32,33]

Bulk density and apparent porosity measurements. The bulk density and apparent porosity measurements of the cement pastes were carried out before they were subjected to compressive strength determination. The following equations were used to calculate the bulk density and apparent porosity.

$$\text{Bulk density } (\text{g cm}^{-3})^{34} = W_1/(W_1 - W_2) \times I \quad (1)$$

$$\text{Apparent porosity, }\%^{34} = (W_1 - W_3)/(W_1 - W_2) \times 100 \quad (2)$$

TABLE I
Chemical Composition of the Cement Raw Materials (wt %)

Oxides materials	L.O.I[a]	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	B.Area (cm^2 g^{-1})
OPC	2.64	20.12	5.25	3.38	63.13	1.53	0.55	0.3	2.54	3300
PLC	6.44	16.099	4.028	3.801	60.095	1.240	0.649	0.257	1.436	3100

[a] L.O.I. is the loss on ignition.

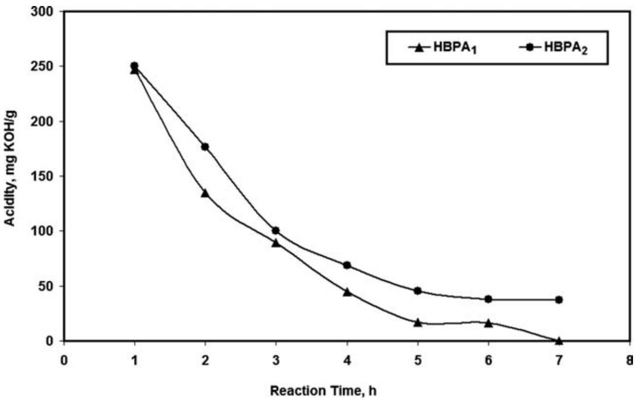


Figure 2 The changes of acid value of $HBPA_1$ and $HBPA_2$ with reaction time.

where W_1, W_2, and W_3 are the saturated, suspended and dry weights of the polymer/cement pastes, respectively.

I: Density of solvent (e.g., $I = 1$ for water).

Compressive strength measurements. Compressive strength of the hardened cement paste for each sample was measured by using a hydraulic testing machine of the Type LPM 600 M1 SEIDNER (Germany) having a full capacity of 600 KN. The loading was applied perpendicular to the direction of the upper surface of the polymer/cement samples.[35]

Chemically combined water measurements. The kinetics of hydration in terms of chemically-combined water content at each time interval were determined on the basis of ignition loss.[32] Chemically bound water is defined as that portion present in interlayer spaces, or more firmly nonevaporable water (W_n) where the following equation was used

$$W_n = W_1 - W_2/W_2 \times 100 \tag{3}$$

W_1 = Weight before ignition, W_2 = ignited weight where the combined water (W_n) is considered as the ignition loss.

Preparative methods

Preparation of hyperbranched polyesteramide

The polyesteramides hyperbranched polymers ($HBPA_1$ and $HBPA_2$) were prepared as previously described in the literature[23,24] as shown in Figure 1 and as the following:

A mixture of DIPA or DEA and MA_n with molar ratio 1.15/1 for DIPA or DEA/MA_n was introduced into three-necked flask which was placed into thermostated oil bath and equipped with mechanical stirrer and a vacuum pump to remove any formed condensates during the esterification reaction. The reaction mixture was heated at 60°C for 3–4 h. Then, the heat was gradually raised to 140°C with continuous stirring. The esterification reaction was monitored by measuring the acid values during the reaction with the reaction time as mentioned in the literature.[36] Aliquots of the reaction mixture were taken where each reaction sample was dissolved in 50 mL distilled water then it was titrated against 0.1N KOH by using phenolphthalein as indicator. The color changed from colorless to pink where the acid value was calculated from equation 4

$$\text{Acid value} = A \times N \times 56.1/W \tag{4}$$

A = amount of consumed KOH, N = normality of KOH (i.e., 0.1N)

W = Weight in grams of the sample, 56.1 = molecular weight of KOH.

The variations in acid value are shown in Figure 2. The acidity decreased with increasing time, which indicated that the formed carboxyl groups from the reaction between MA_n and DIPA or DEA, reacted with the alcohol groups where the esterification reaction progressively proceeded. The results indicated that $HBPA_2$ had more remained carboxylic groups without esterification than that in case of $HBPA_1$. The formed hyperbranched polymers were washed with acetone, filtered and dried at 50°C for 24 h. The yields of both of $HBPA_1$ and $HBPA_2$ were 97.42 and 95.65%, respectively.

Preparation of cement mixes

The two hyperbranched polyesteramides, $HBPA_1$ and $HBPA_2$ were dissolved in the mixing water with the dosages of 0, 1, 3, and 5 wt % and then were added to both cement types (OPC and PLC). The pastes were then molded into one inch cubic stainless steel molds, vibrated manually for two minutes and on a mechanical vibrator for other two minutes. The molds were stored inside a humidity cabinet for 24 h at 23°C ± 1°C and 100% R.H. then were

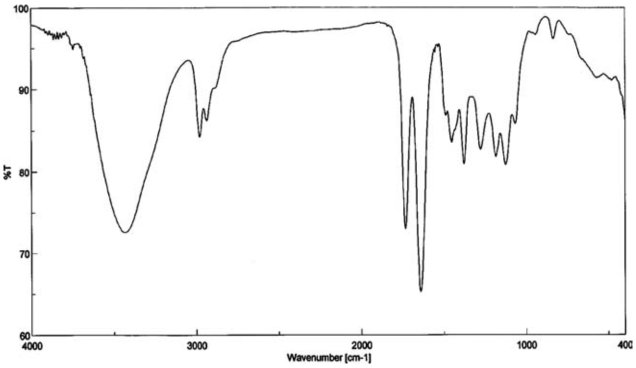


Figure 3 IR spectrum of $HBPA_1$.

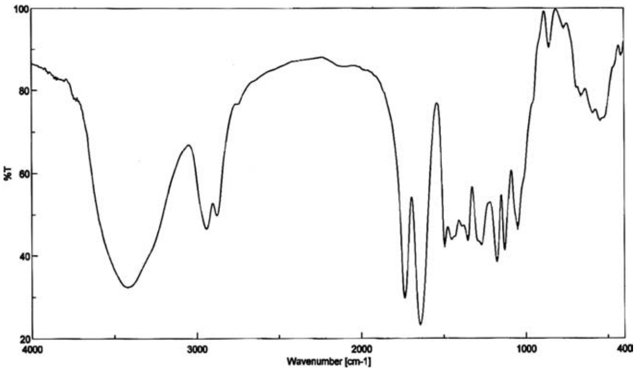


Figure 4 IR spectrum of $HBPA_2$.

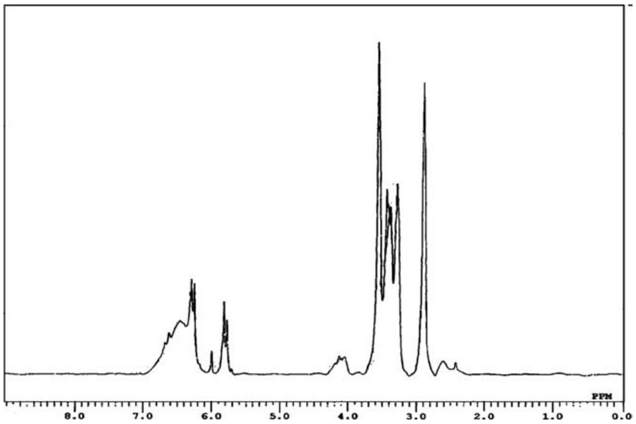


Figure 6 ^1H NMR spectrum of $HBPA_2$.

demoulded and cured under water till the time of testing for compressive strength after 1, 3, 7, 28, and 90 days.

RESULTS AND DISCUSSION

Two hyperbranched polyesteramides $HBPA_1$ and $HBPA_2$ (Fig. 1) were prepared via bulk condensation of maleic anhydride with both of diisopropanolamine and diethanolamine, respectively. $\bar{M}_n$ values for $HBPA_1$ and $HBPA_2$ were found to be 3500 and 2000 g mol^{-1}, respectively, whereas the D values were recorded as 2.54 and 3.53 for the same polymers. The IR spectra of the prepared polymers (Figs. 3 and 4) revealed similar several bands such as υ (C—H), stretching, as two bands at 2978–2940 cm^{-1} and 2934–2876 cm^{-1} and other bands at 1494–1487 cm^{-1}, 1451–1450 cm^{-1}, and 1377–1353 cm^{-1} which were referred to CH_2 and CH_3 bending. The band at 1734–1731 cm^{-1} was ascribed to the α-unsaturated carbonyl of the ester group and the band at 1643–1641 cm^{-1} was attributed to the absorption from amide carbonyl groups. The broad absorption band at 3432–3421 cm^{-1} was assigned to hydroxyl groups (H-bonded). The bands at 943–856 cm^{-1} and 1066–1050 cm^{-1} were attributed to =C—H bending and that bands at 1129–1125 cm^{-1}, 1184–1175 cm^{-1}, and 1276–1269 cm^{-1} were attributed to C—O and C—N stretching. ^1H NMR spectrum for $HBPA_1$ (Fig. 5) indicated signals of chemical shifts at 6.02–6.8 ppm which were referred to the protons of alkenes. Also, the signals at chemical shifts of 1.03 and 1.11 ppm were associated with the methyl protons and that from 2.6 to 3.32 ppm were assigned to the methylene protons. The signals at chemical shifts of 3.88–4.47 ppm were referred to the methine protons. The signal at 5.1 ppm was assigned to the proton of the hydroxyl group. ^1H NMR spectrum for $HBPA_2$ (Fig. 6) indicated signals of chemical shifts at 5.78–6.31 ppm which were ascribed to the protons of alkenes. The signal at 6.4 ppm was assigned to the proton of hydroxyl group. The signals at chemical shifts of 2.9–3.29 ppm and 3.39–4.19 were referred to methylene protons of $O{=}CN{-}CH_2$ and $O{=}CO{-}CH_2$, respectively. The TGA thermograms of the hyperbranched polyesteramides ($HBPA_1$/$HBPA_2$), as shown in Figure 7, indicated slight weight loss of 5 and 10% for both of $HBPA_1$ and $HBPA_2$ up to 190°C, respectively. That weight loss was attributed to the loss of moisture. The weight loss in case of $HBPA_2$ was much higher than in case of $HBPA_1$ when they were heated to the same temperature in

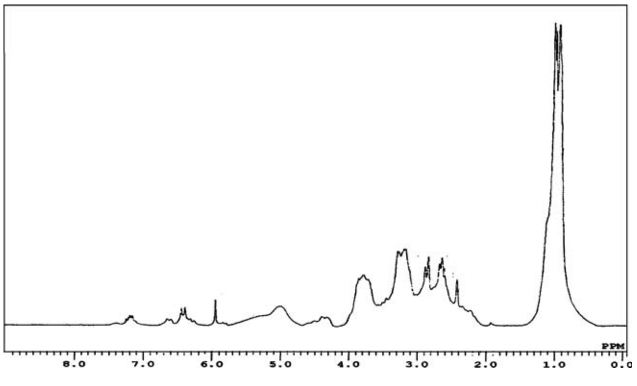


Figure 5 ^1H NMR spectrum of $HBPA_1$.

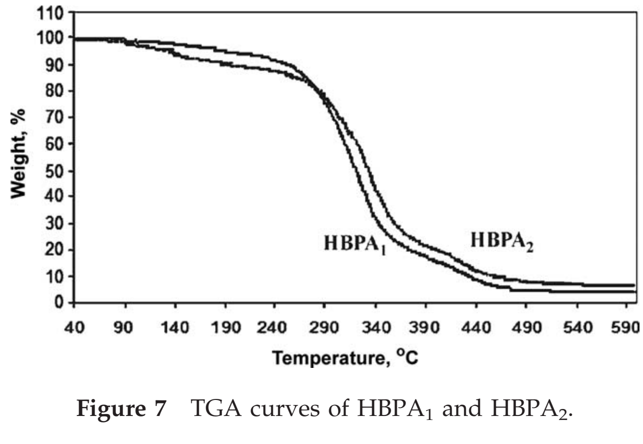


Figure 7 TGA curves of $HBPA_1$ and $HBPA_2$.

TABLE II
Water of Consistency and Setting Times (Initial and Final) of Blank OPC and PLC Pastes and Those Premixed with 1, 3, and 5 % of $HBPA_1$ and $HBPA_2$

Polymer	Cement	Polymer concenteratio (wt %)[a]	Water of consistency (%)	Setting time (min)	
				Initial setting	Final setting
$HBPA_1$	OPC	0	30	130	250
		1	27.7	140	260
		3	27	140	265
		5	26.7	150	280
	PLC	0	25	60	110
		1	23.7	65	125
		3	22	70	135
		5	21	80	135
$HBPA_2$	OPC	0	30	130	250
		1	27.7	145	270
		3	27	160	280
		5	26	170	285
	PLC	0	25	60	110
		1	22.7	70	130
		3	21	80	140
		5	20	85	145

[a] Polymer concentration in mixing water.

the range of 100–290°C. The reason might be attributed to the presence of more unreacted carboxyl groups in $HBPA_2$ than in case of $HBPA_1$.[23,24] These carboxyl groups easily reacted with alcohol groups to produce water, which was evaporated by heating. Therefore, $HBPA_2$ lost more weight during heating. When the temperature reached 290°C, TG curves of $HBPA_1$ and $HBPA_2$ descended sharply. The reason might be that the amide carbonyl groups and the ester bonds in the hyperbranched polyesteramides decomposed at 300–360°C.[6] DSC measurements recorded the glass transition temperatures (T_g) of $HBPA_1$ and $HBPA_2$ as 30°C and -24°C, respectively.

The prepared polymers were inserted in cement pastes. Then, several parameters were studied such as water of consistency, setting time, bulk density, apparent porosity, combined water content and compressive strength to see the effect of the hyperbranched polymers $HBPA_1$ and $HBPA_2$ on the cement pastes.

Water of consistency and setting times (initial and final) measurements are shown in Table II. Generally, water of consistency gradually decreased with increasing of polymers contents up to 5% in both types of cement. Furthermore, the reduction of water of consistency by using the same concentrations of polymers with PLC was more than that in case of OPC. The water of consistency was reduced, in case of 5% $HBPA_1$, from 30 to 26.67% with OPC and from 25 to 21% with PLC, while 5% $HBPA_2$ decreased the water of consistency from 30 to 26% with OPC and from 25 to 20% with PLC (Table II). So, the water of consistency was highly reduced by 11.1–13.3% with OPC and by 16–20% with PLC in comparison with that of the blank. Thus, as mentioned in the literature, it was concluded that this polymer acted as plasticizer and/or superplasticizer where the plasticizers were generally defined as the special category of water-reducing agents which allows much greater water reduction or alternatively extreme workability of the concrete without undesirable side effects such as excessive air entrainment or set retardation.[30,31]

On the other hand, $HBPA_1$ and $HBPA_2$ increased setting times (initial and final) of either OPC or PLC (Table II). Initial setting time increased in case of 5% $HBPA_1$ from 130 to 150 min with OPC and from 60 to 80 min with PLC. Hereby, the final setting time increased from 250 to 280 min. with OPC and from 110 to 135 min with PLC (Table II). The initial setting time increased with respect to 5% $HBPA_2$ from 130 to 170 min with OPC and from 60 to 85min with PLC. Also, the final setting time increased from 250 to 285 min. with OPC and from 110 to 145 min with PLC (Table II). Moreover, the setting times were faster with PLC than with OPC. So, $HBPA_1$ and $HBPA_2$ can act as water reducing admixtures and also as retardants.

The bulk density and the apparent porosity measurements are indicated in Table III with respect to the blank OPC and PLC cement pastes and those premixed with 1, 3, and 5% of $HBPA_1$ and $HBPA_2$. The bulk density gradually increased with curing time while the apparent porosity decreased. That behavior was attributed to the continual deposition of the formed hydration products in the pore structure of the hardened cement pastes. Thus, the apparent porosity was expected to decrease and hence the bulk density enhanced.[34] Moreover, the bulk density increased with increasing the polymer concentration. That was attributed to the improvement in the hydration process and subsequently the amount of hydration products increased with respect to the blank samples which filled the pore spaces of the hardened cement paste. The results with $HBPA_2$ were slightly higher than that obtained in case of $HBPA_1$.

The combined water content and compressive strength measurements are illustrated in Table IV with respect to the blank OPC and PLC cement pastes and those premixed with 1, 3, and 5% of $HBPA_1$ and $HBPA_2$. Generally, the combined water content of all cement pastes increased with curing time. That was mainly attributed to the gradual and continuous formation of hydration products resulting from the hydration of the main phases of cement, particularly C_3S and β-C_2S.[34] The higher obtained values by incorporation of small amounts of polymers with either OPC or

TABLE III
Bulk Density and Apparent Porosity of Blank OPC and PLC Pastes and Those Premixed with 1, 3, and 5 % of $HBPA_1$ and $HBPA_2$ Hydrated Up to 90 Days

Property	Polymer	Cement	Polymer concentration (wt %)[a]	Curing time (days)				
				1	3	7	28	90
Bulk density ($g\ cm^{-3}$)	$HBPA_1$	OPC	0	2.13	2.13	2.16	2.18	2.20
			1	2.21	2.22	2.22	2.23	2.24
			3	2.19	2.23	2.24	2.26	2.29
			5	2.14	2.21	2.27	2.28	2.29
		PLC	0	2.23	2.23	2.25	2.27	2.29
			1	2.23	2.26	2.26	2.29	2.31
			3	2.22	2.25	2.29	2.30	2.31
			5	2.23	2.27	2.29	2.30	2.32
	$HBPA_2$	OPC	0	2.13	2.13	2.16	2.18	2.20
			1	2.18	2.20	2.21	2.22	2.25
			3	2.20	2.23	2.26	2.27	2.27
			5	2.25	2.26	2.27	2.28	2.30
		PLC	0	2.23	2.23	2.25	2.27	2.29
			1	2.19	2.23	2.27	2.29	2.30
			3	2.25	2.26	2.28	2.29	2.32
			5	2.26	2.26	2.29	2.31	2.33
Apparent porosity (%)	$HBPA_1$	OPC	0	15.24	14.92	14.54	13.53	11.85
			1	12.46	11.15	10.57	10.15	9.69
			3	12.64	10.53	9.62	8.05	7.99
			5	14.56	10.43	8.87	8.03	7.57
		PLC	0	14.13	12.88	10.92	10.58	9.50
			1	11.69	10.22	8.79	8.10	8.08
			3	11.96	9.89	8.08	7.28	7.10
			5	13.26	9.65	7.68	6.76	6.27
	$HBPA_2$	OPC	0	15.24	14.92	14.54	13.53	11.85
			1	10.66	10.26	9.11	8.89	8.56
			3	11.35	9.80	8.86	7.97	7.10
			5	9.66	8.55	7.90	6.56	6.20
		PLC	0	14.13	12.88	10.92	10.58	9.50
			1	11.60	10.93	9.44	8.92	7.97
			3	12.31	11.01	8.68	7.80	6.36
			5	9.71	8.68	8.04	5.95	5.57

[a] Polymer concentration in mixing water.

PLC were ascribed to the dispersion effect of the polymers to the cement particles which in turn improved the hydration process.[29,34] Consequently, the addition of $HBPA_1$ and $HBPA_2$ to the cement pastes caused better hydration. The combined water content in case of $HBPA_2$ had higher values than in case of $HBPA_1$. Although, the active groups such as —OH, —OCOR, and —$CONR_2$ in $HBPA_1$ and $HBPA_2$ were the same but $HBPA_2$ was more effective than $HBPA_1$ which was ascribed to the fact that $HBPA_2$ had more remained carboxyl groups without esterification than that in case of $HBPA_1$ as shown in Figure 2. Accordingly, $HBPA_2$ is much more polar than $HBPA_1$. Therefore, adsorption of $HBPA_2$ on the cement particles was higher than in case of $HBPA_1$.[23,24] Thus, the dispersion of cement particles was more with cement pastes premixed with $HBPA_2$ than those premixed with $HBPA_1$.

Compressive strength of the hardened cement pastes was generally increased with curing time (Table IV). That was mainly attributed to the continual formation of hydration products which deposited into the pore structure of the cement pastes. So, the apparent porosity gradually decreased while the compactness increased. Accordingly, the compressive strength was improved and enhanced.[34,36] Higher compressive strength values were obtained for both types of cement by increasing the polymer concentration in comparison with those of the blank samples at all curing ages, except at the first 24 h of hydration. That was mainly due to the high activation effect of the hyperbranched polyesteramides at later stages and to the decrease of the apparent porosity which resulted from further increase of the hydration products.[36]

Furthermore, the dispersing effect[30,31] as revealed by SEM of the hyperbranched polymers/cement pastes indicated improvement in the workability of such pastes and hence an enhancement of the compressive strength was obtained.[34] The compressive strength of $HBPA_2$ was slightly higher with OPC

TABLE IV
Combined Water and Compressive Strength of Blank OPC and PLC Pastes and Those Premixed with 1, 3, and 5% of $HBPA_1$ and $HBPA_2$ Hydrated Up to 90 Days

				Curing time (days)				
Property	Polymer	Cement	Polymer concentration (wt %)[a]	1	3	7	28	90
Combined water (%)	$HBPA_1$	OPC	0	11.51	11.94	12.53	13.67	14.40
			1	11.91	12.91	13.81	14.29	15.68
			3	12.30	12.97	13.92	14.64	16.33
			5	13.63	13.64	14.90	15.44	17.62
		PLC	0	10.95	12.36	13.50	14.74	15.44
			1	11.98	13.71	14.41	15.44	17.02
			3	10.53	13.80	14.76	15.56	17.58
			5	10.36	14.74	15.06	15.57	18.04
	$HBPA_2$	OPC	0	11.51	11.94	12.53	13.67	14.40
			1	11.53	12.83	13.39	15.36	16.19
			3	11.48	12.94	13.77	15.90	17.93
			5	11.30	13.18	14.26	16.47	18.82
		PLC	0	10.95	12.36	13.50	14.74	15.44
			1	11.29	12.92	14.17	15.61	16.85
			3	11.15	13.17	14.90	15.88	17.62
			5	10.90	13.80	15.46	16.55	18.31
Compressive strength (MPa)	$HBPA_1$	OPC	0	30.4	51.2	57.6	64	67.2
			1	30.4	52.8	62.4	70.4	75.2
			3	28.8	54.4	65.6	72	81.6
			5	27.2	56	65.6	73.6	86.4
		PLC	0	32.6	54.4	65.6	88	91.2
			1	35.2	56	70.4	91.2	100.8
			3	32	57.6	72	92.8	107.2
			5	32	59.2	75.2	94.4	113.6
	$HBPA_2$	OPC	0	30.4	51.2	57.6	64	67.2
			1	27.2	54.4	62.4	76.8	83.2
			3	27.2	56	68.8	81.6	84.8
			5	25.6	57.6	70.4	83.2	89.6
		PLC	0	32.6	54.4	65.6	88	91.2
			1	36.8	57.6	73.6	94.4	104
			3	33.6	59.2	73.6	96	113.6
			5	32	62.4	75.2	97.6	115.2

[a] Polymer concentration in mixing water.

and PLC than that with respect to $HBPA_1$ particularly with 5% concentration. Also, the obtained compressive strength values with PLC pastes were much higher than those with OPC pastes. The higher strength was attributed to the lower w/c ratio in case of the PLC than in case of the OPC. So, the activation effect of the polymer increased the rate of hydration which enhanced the cement characteristics of such hardened cement pastes. Generally, the increase of hydration had a positive effect on the compressive strength.

The IR spectra of blank OPC and those premixed with 5% of $HBPA_1$ and $HBPA_2$ are shown in Figure 8, while those of PLC are shown in Figure 9. The sharp absorption band at 3644–3641 cm^{-1} was related to the free OH group coordinated to Ca^{+2} (i.e., free lime). The intensity of the broad absorption band at 3445–3420 cm^{-1}, which was ascribed to the OH group associated to H-bond related to the symmetrical stretching frequency of water, increased in presence of $HBPA_1$ and $HBPA_2$. The two bands at 2959 and 2856 cm^{-1} were related to $—CH_2$ and $—CH_3$ from the residual organic mixture. The two absorption bands at 1647–1642 cm^{-1} and 1428–1425 cm^{-1} are related to the main silicate band involving Si—O stretching vibration bands of CSH, while the band at 1120–1114 cm^{-1} was ascribed to CAH. The intensities of the two absorption bands at 989–983 cm^{-1} and 875 cm^{-1} characterizing CO_3^{-2} and SO_4^{-2} were irregular due to the rate of carbonation or sulfonation of CSH and/or CAH, respectively, where the vibrations of CO_3^{-2} were smaller than those of SO_4^{-2}. It was clear that the intensities of the absorption bands of Si—O, CAH, CO_3^{-2} and SO_4^{-2} were slightly higher with hyperbranched polymers/cement pastes. The intensities of the characteristic peaks were slightly improved with $HBPA_2$ where marginal effect of the two hyperbranched polymers was detected.

The scanning electron microscopy (SEM) images of the OPC pastes and those premixed with 1, 3, and 5% of $HBPA_1$ and $HBPA_2$ are shown in Figure 10, while those of PLC are shown in Figure 11.

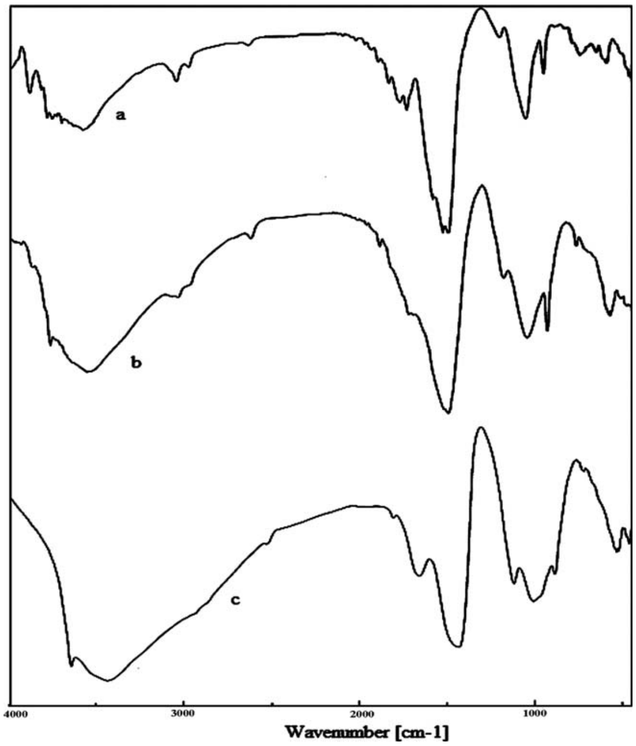


Figure 8 IR spectra of OPC pastes after 90 days for sample (a) without polymer, sample (b) premixed with 5% $HBPA_1$, and sample (c) premixed with 5% $HBPA_1$

Thereby, the needles of ettringite phase ($C_3A.3CaSO_4.32H_2O$), which were formed due to the reaction of C_3A with gypsum in presence of water, were clearly demonstrated for OPC and PLC blank pastes. These needles decreased or mostly disappeared in presence of the hyperbranched polymers as shown in Figures 10 and 11 with respect to 1, 3, and 5% of $HBPA_1$ and $HBPA_2$. That was ascribed whether to the conversion of ettringite to monosulphate ($C_3A.CaSO_4.12H_2O$) or to the fact that the hydration products were surrounded with the polymer films which prevented their growth. These observations indicated better hydration of the pastes in the presence of $HBPA_1$ and $HBPA_2$. The hyperbranched polyesteramides also affected the morphology of the Ca $(OH)_2$ crystals, resulted from the hydration of C_3S and β-C_2S phases of the cement. Layered deposition of Ca $(OH)_2$ crystals were demonstrated and arranged in stack in presence of the polymers as shown in Figures 10 and 11. That was attributed to the binding effect between the hyperbranched polyesteramides and Ca $(OH)_2$. The microstructure was strengthened by gluing the crystal layers together. The strengthening by polymer bridges improved the overall strength of the binder matrix because Ca $(OH)_2$ crystals represented the weak phase in the binder matrix and the surfaces of those crystals formed preferred cleavage sites.[28]

That in turn was reflected positively on the specific characteristics of the cement, particularly the mechanical strength. On the other hand, the phases that formed with PLC pastes were the same as with OPC pastes but with well-developed crystals, particularly with the hyperbranched polymers. It could be concluded that the formed phases in case of OPC premixed by $HBPA_1$ and $HBPA_2$ were the same with PLC but with different morphologies and crystallinities. Moreover, the dispersibility properties due to the presence of $HBPA_2$ clearly appeared with the two types of cement. Also, the crystal morphology was clearly detected where the crystals were larger and more compacted. Accordingly, $HBPA_2$ had more effect on the two types of cement than $HBPA_1$.

CONCLUSIONS

The prepared hyperbranched polyesteramides ($HBPA_1$ and $HBPA_2$) reduced the water of consistency for either OPC or PLC cement pastes. Both of $HBPA_1$ and $HBPA_2$ activated the cement phases and improved the rate of hydration. Also, the combined water contents at all curing ages of hydration and mechanical strength were improved, particularly at later

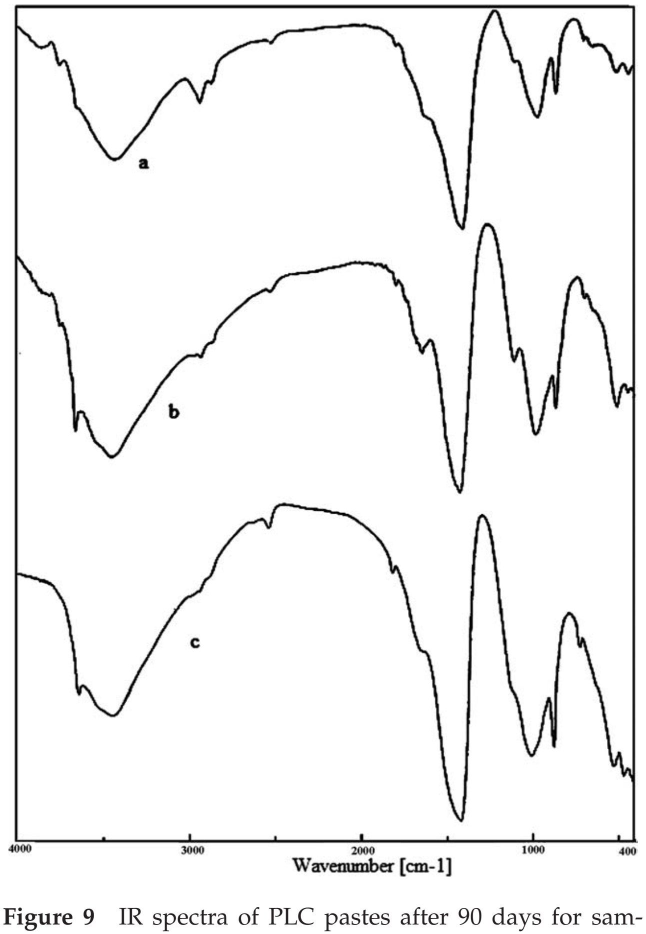


Figure 9 IR spectra of PLC pastes after 90 days for sample (a) without polymer, sample (b) premixed with 5% $HBPA_1$, and sample (c) premixed with 5% $HBPA_1$

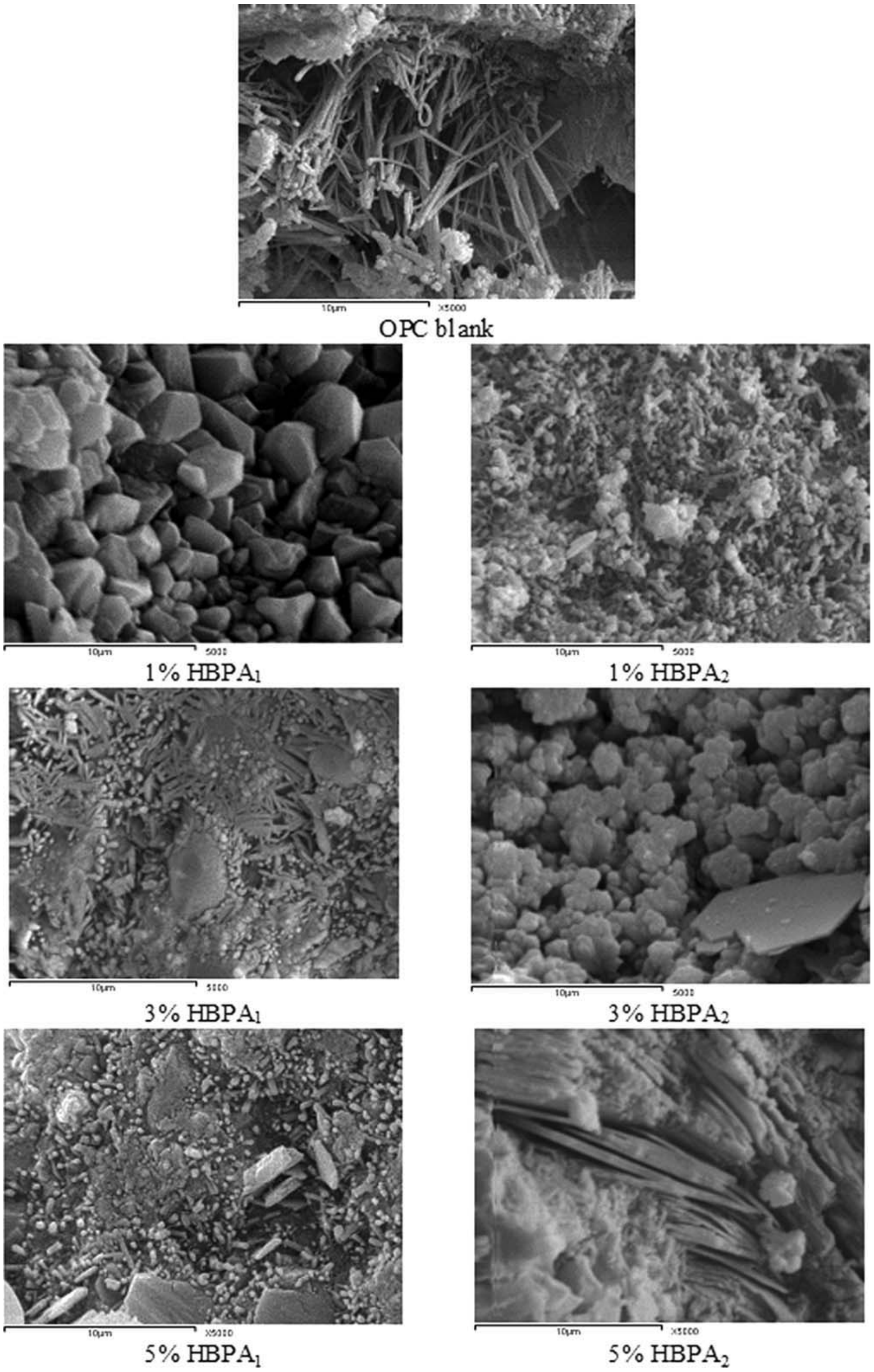
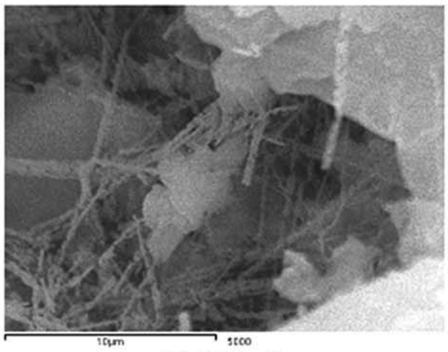
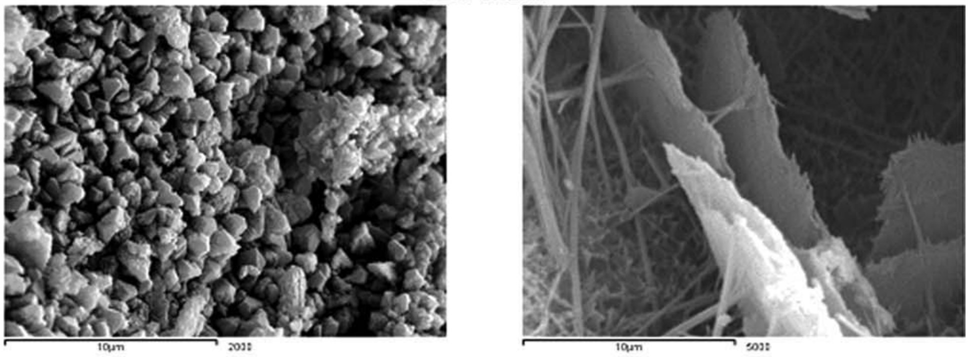


Figure 10 SEM images of blank OPC and pastes premixed with 1, 3, and 5% of $HBPA_1$ and $HBPA_2$ hydrated up to 90 days at magnification power ×5000.

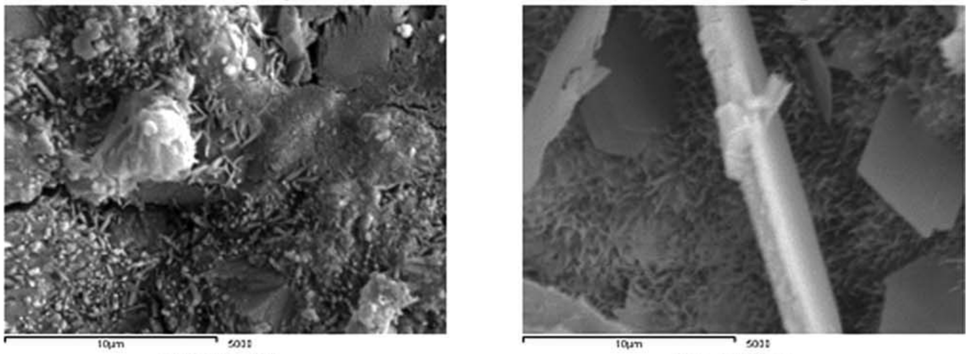
stages of hydration. No new phases were detected by IR, only increased intensities for the formed phases were observed by the addition of polymers. The SEM images showed that the incorporation of the polymer in cement phases did not affect the OPC or PLC hydrates, but it only affected the physical state, shape, or morphology and crystallinity of the formed hydrates. The presence of $HBPA_1$ and $HBPA_2$ influenced the morphology of the Ca $(OH)_2$ crystals. Therefore, they can be used as water-reducing agents and plasticizers or superplasticizers. Eventually, the two hyperbranched polyesteramides displayed the



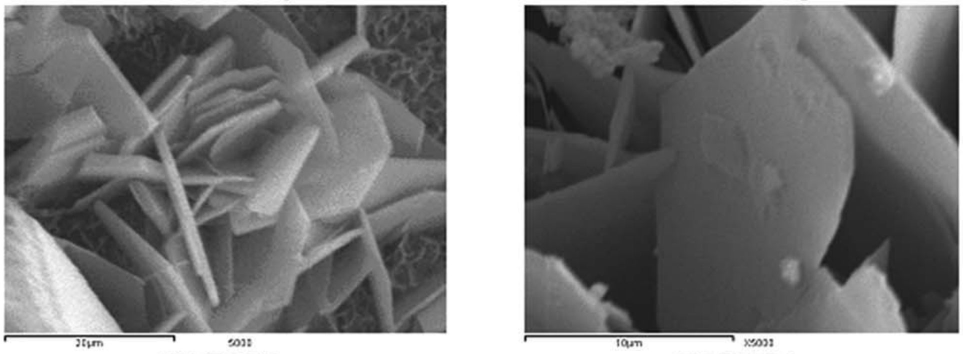
PLC blank



1% HBPA$_1$ 1% HBPA$_2$



3% HBPA$_1$ 3% HBPA$_2$



5% HBPA$_1$ 5% HBPA$_2$

Figure 11 SEM images of blank PLC and pastes premixed with 1, 3, and 5% of HBPA$_1$ and HBPA$_2$ hydrated up to 90 days at magnification power ×5000 (1% HBPA$_1$ was at magnification power ×2000).

same trend on OPC and PLC cements but with preferential efficiency in case of HBPA$_2$.

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