Modification of Cement with Succinic Anhydride-Based Hyperbranched Polyesteramide

Amal Amin,[1] Hassan M. Darweesh,[2] Ahmed M. Ramadan,[3] Samir M. M. Morsi,[1]
Magdy M. H. Ayoub[1]

[1]Polymers and Pigments Department, National Research Center, Dokki, Giza, Egypt
[2]Department of Refractories, Ceramics and Building Materials, National Research Centre, Dokki, Giza, Egypt
[3]Chemistry Department, Faculty of Science, Helwan University, Egypt

ABSTRACT: Two hyperbranched polyesteramides (HYP_1 and HYP_2) were prepared by reacting succinic anhydride (ScAn) with both of diisopropanolamine (DiPA) and diethanolamine, respectively, via one-pot polycondensation reaction. The prepared polymers were analyzed using gel permeation chromatography, infrared spectra, and 1HNMR. The resulting hydroxyl-ended resins have been successfully applied as polymeric admixtures in two types of cements such as Ordinary Portland cement and Portland limestone cement. The water of consistency decreased by addition of the hyperbranched polymers in both types of cements. Better hydration was observed by incorporation of small amounts of polymers. The infrared spectra and scanning electron microscopy photos of Ordinary Portland cement and Portland limestone cement pastes premixed with HYP_1 and HYP_2 showed no effect on the chemical composition of the cement hydrates where only the morphology and the crystallinity of the formed hydrates were changed. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 1483–1489, 2012

Key words: hyperbranched polymers; polyesteramides; polymeric admixtures; portland-limestone cement

INTRODUCTION

Hyperbranched polymers are highly branched, polydisperse, three-dimensional macromolecules which, due to their unique structures and properties, have attracted increasing attention.[1,2] Unlike dendrimers, the hyperbranched polymers can be synthesized via one step reactions. Therefore, they represent economically promising products for large-scale industrial applications.[3] Their applications are essentially based on the nature and the large number of the functional groups within their skeleton.[4] Herein, the water soluble hyperbranched polyesteramides HYP_1 and HYP_2 as shown in Figure 1 have been prepared via polycondensation reaction between ScAn (with A_2 functional groups) and DiPA or diethanolamine (DEA) (with $B\backslash B_2$ functional groups) monomers.[5–7] The resulting hyperbranched polyesteramides have been utilized as polymeric admixtures in cement as new application of the hyperbranched polymers as was described in our previous publications.[6,7] Generally, water-soluble polymers are frequently added to cement mortars and concrete to improve some of their specific properties. The modified cement pastes with water-soluble polymers usually show higher water retention than the blank ones. The hydrophilic property of the polymers fixes the water molecules in the fresh mixture, preventing the dry-out by evaporation or absorption into the surrounding porous material.[8] The water-retaining capacity often results in thickening and viscosity enhancing behavior. Less free water is available for bleeding and the segregation tendency decreases due to the increased viscosity of the cement paste. The homogeneity of the paste is also improved where better dispersion is obtained.[9,10] Water-soluble polymers are dissolved in the mixing water on a molecular scale in contrast to the polymer dispersions where no surfactants are needed. However, the addition of small amounts of water-soluble polymers usually influences the properties of the hardened material. Two processes can take place during hardening such as cement hydration and polymer film formation.[11] On these bases, the main objective of this paper was to investigate the influence of succinic anhydride based hyperbranched polyesteramides on the physicomechanical properties of Ordinary Portland cement (OPC) and Portland limestone cement (PLC).

EXPERIMENTAL

Chemicals and materials

Diisopropanolamine (98%), diethanolamine (99%), and succinic anhydride (98%) were delivered from Fluka Chemicals and were used as received. The

Correspondence to: A. Amin (aamin_07@yahoo.com).
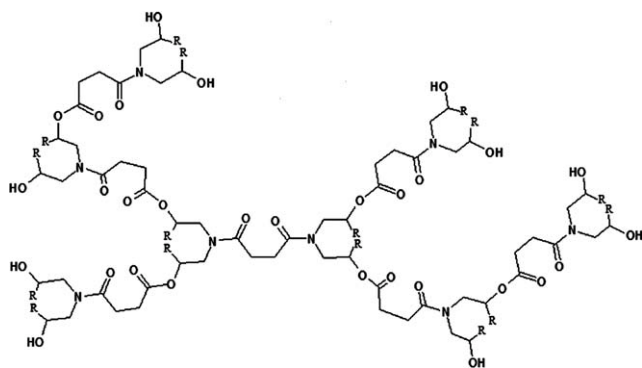
Figure 1 Structure of hyperbranched polymer HYP$_1$ and HYP$_2$. R: H, HYP$_1$ or R: CH3, HYP$_2$.

OPC and PLC with blaine surface areas of 3300 cm^2/g and 3100 cm^2/g, respectively, had been provided from Helwan Cement Company, Egypt. The chemical composition of OPC and LPC is shown in Table I.

Instrumentation

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 (^{1}HNMR), and scanning electron microscopy (SEM).[6,7] The standard water of consistency as well as the setting times (initial and final) of the cement pastes were directly determined by Vicat apparatus.[12,13] Bulk density (BD) and apparent porosity (A.P) of the hardened cement pastes were calculated from equations 1 and 2, respectively:[14,6,7]

$$BD(g/cm^3) = W1/(W1 - W2) \times 1 \quad (1)$$

$$AP\% = (W1 - W3)/(W1 - W2) \times 100 \quad (2)$$

Where $W1$ = saturated weight, $W2$ = suspended weight, and $W3$ = dry weight.

Compressive strength of the hardened cement pastes was measured by using a hydraulic testing machine LPM 600 M1 SEIDNER (Germany) having a full capacity of 600 KN.[15,6,7]

The chemically combined water content of the hardened cement pastes at each time interval was also determined on the basis of ignition loss.[14] The SEM images of the fractured surfaces of the hardened cement pastes, coated with a thin layer of gold,
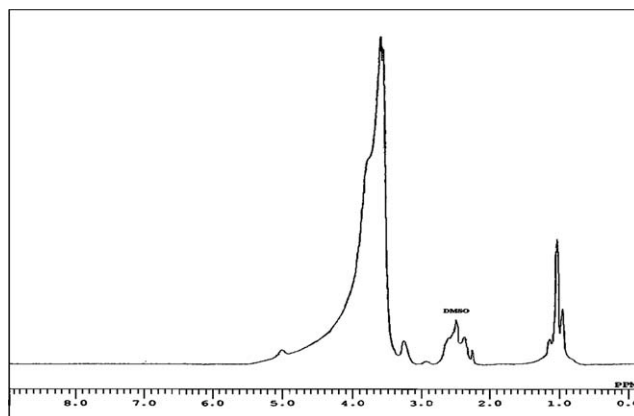
Figure 2 ^{1}H-NMR of HYP$_1$.

were obtained by JEOL-JXA-840 electron analyzer at accelerating voltage of 30 KV.

Preparation of hyperbranched polyesteramides

HYP$_1$ and HYP$_2$ were prepared as previously described in the literature,[15,16] and as mentioned in our publications,[6,7] as in the following: A mixture of (DiPA or DEA) and ScAn with a molar ratio for (DiPA or DEA)/ ScAn 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 170°C, with continuous stirring. A vacuum was created during the heating to remove the condensates. The formed hyperbranched polymers were washed with acetone then dried at 50°C for 24 h. The yield of HYP$_1$ and HYP$_2$ was 96.81% and 94.72%, respectively.

Preparation of cement mixes

The two hyperbranched polyesteramides, HYP$_1$ and HYP$_2$ were added to OPC and PLC by dissolving them in the mixing water with the dosages of 0, 1, 3, and 5 wt % and the cement pastes were processed as published in our previous communications.[6,7]

RESULTS AND DISCUSSION

Water soluble polyesteramides hyperbranched polymers HYP$_1$ and HYP$_2$ (Fig. 1) were prepared via one pot polycondensation reaction.[5–7,16–18] It was proved that HYP$_2$ has higher reactivity as cement admixture

TABLE I
Chemical Composition of OPC and PLC Raw Materials, wt %

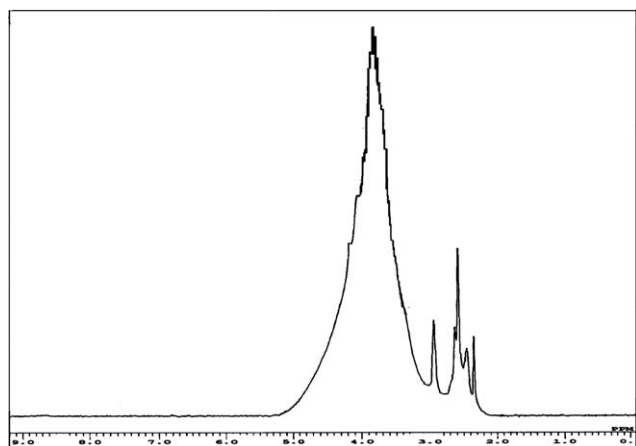| Oxides Materials	L.O.I	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	Na$_2$O	K$_2$O	SO$_3$
OPC	2.64	20.12	5.25	3.38	63.13	1.53	0.55	0.3	2.54
PLC	6.44	16.099	4.028	3.801	60.095	1.240	0.649	0.257	1.436

Figure 3 ^{1}H-NMR spectrum of HYP$_2$.

than that of HYP$_1$ because of the presence of more carboxyl groups in HYP$_2$ by measuring the acid values during their formation reactions as previously described in the literature.[5–7]

GPC measurements recorded the number average molecular weights (Mn) for HYP$_1$ and HYP$_2$ as 1800

TABLE II
Water of Consistency and Setting Times (Initial and Final) Measurements of OPC and PLC Pastes and Those Premixed with 1, 3, and 5% of HYP$_1$ and HYP$_2$

Polymer	Type of cement	Polymer (wt %)^a	Water of consistency (%)	Setting time (min) Initial set	Setting time (min) Final set
HYP$_1$	OPC	0	30	130	250
		1	29.33	135	260
		3	29	145	265
		5	28.33	145	270
	PLC	0	25	60	110
		1	24.33	60	115
		3	23.7	65	120
		5	23.33	75	130
HYP$_2$	OPC	0	30	130	250
		1	29	150	255
		3	28.7	165	270
		5	28	165	275
	PLC	0	25	60	110
		1	23	65	120
		3	22.7	75	125
		5	22.33	75	140

^{a} Polymer concentration in mixing water.

TABLE III
Bulk Density and Apparent Porosity Measurements of OPC and PLC Pastes and Those Premixed with 1, 3, and 5% of HYP$_1$ and HYP$_2$, Hydrated up to 90 Days

Property	Polymer	Cement	Polymer concn. (wt %)^a	Curing time, days 1	3	7	28	90
Bulk density (g/cm^3)	HYP$_1$	OPC	0	2.13	2.13	2.16	2.18	2.20
			1	2.14	2.14	2.18	2.18	2.20
			3	2.12	2.19	2.20	2.20	2.21
			5	2.08	2.17	2.19	2.23	2.25
		PLC	0	2.23	2.23	2.25	2.27	2.29
			1	2.20	2.24	2.27	2.28	2.30
			3	2.22	2.25	2.27	2.29	2.30
			5	2.19	2.26	2.29	2.30	2.32
	HYP$_2$	OPC	0	2.13	2.13	2.16	2.18	2.20
			1	2.09	2.15	2.18	2.19	2.21
			3	2.15	2.18	2.20	2.22	2.24
			5	2.09	2.24	2.24	2.25	2.27
		PLC	0	2.23	2.23	2.25	2.27	2.29
			1	2.18	2.24	2.26	2.28	2.30
			3	2.21	2.25	2.28	2.29	2.32
			5	2.20	2.25	2.28	2.30	2.32
Apparent porosity (%)	HYP$_1$	OPC	0	15.24	14.92	14.54	13.53	11.85
			1	14.77	14.71	13.53	12.48	10.89
			3	15.13	14.65	13.17	11.43	10.15
			5	15.77	14.22	12.58	11.22	9.48
		PLC	0	14.13	12.88	10.92	10.57	9.50
			1	13.89	12.59	10.55	10.02	8.96
			3	13.32	12.45	10.13	9.37	8.79
			5	14.18	12.15	9.93	9.19	8.56
	HYP$_2$	OPC	0	15.24	14.92	14.54	13.53	11.85
			1	14.83	13.55	11.48	10.34	10.19
			3	16.07	13.75	11.44	10.20	9.84
			5	16.28	13.00	10.36	9.64	9.26
		PLC	0	14.13	12.88	10.92	10.57	9.50
			1	13.36	11.82	10.39	9.93	8.95
			3	13.19	11.60	10.15	9.65	8.53
			5	14.69	11.33	9.91	9.15	8.15

^{a} Polymer concentration in mixing water.

TABLE IV
Combined Water Content Measurements of OPC and PLC Pastes and Those Premixed with 1, 3 and 5% of HYP$_1$ and HYP$_2$, Hydrated up to 90 Days

Property	Polymer	Cement	Polymer concn. (wt %)[a]	Curing time, days				
				1	3	7	28	90
Bulk density (g/cm^3)	HYP$_1$	OPC	0	11.51	11.94	12.53	13.67	14.40
			1	10.42	12.34	12.94	13.98	14.90
			3	10.73	12.71	13.86	14.33	15.92
			5	11.27	13.37	14.42	15.16	16.93
		PLC	0	10.95	12.36	13.50	14.74	15.44
			1	10.69	13.39	14.40	15.15	16.67
			3	11.09	13.50	14.57	15.59	17.26
			5	10.19	13.62	14.97	15.79	17.97
	HYP$_2$	OPC	0	11.51	11.94	12.53	13.67	14.40
			1	12.05	12.12	13.14	14.16	15.90
			3	12.08	12.32	14.12	14.52	16.95
			5	10.92	13.56	14.36	15.25	17.52
		PLC	0	10.95	12.36	13.50	14.74	15.44
			1	11.82	13.92	14.32	15.48	16.72
			3	12.05	13.94	15.31	15.95	17.49
			5	10.78	14.38	15.47	16.45	18.19
Compressive strength (MPa)	HYP$_1$	OPC	0	30.4	51.2	57.6	64	67.2
			1	17.6	52.8	57.6	67.2	70.4
			3	28.8	52.8	62.4	70.4	73.6
			5	27.2	59.2	64	70.4	76.8
		PLC	0	33.6	54.4	65.6	88	91.2
			1	41.6	56	68.8	89.6	97.6
			3	36.8	60.8	73.6	89.6	100.8
			5	32	62.4	76.8	91.2	105.6
	HYP$_2$	OPC	0	30.4	51.2	57.6	64	67.2
			1	27.2	54.4	59.2	70.4	78.4
			3	24	57.6	64	75.2	81.6
			5	24	59.2	67.2	76.8	83.2
		PLC	0	33.6	54.4	65.6	88	91.2
			1	36.8	56	70.4	91.2	99.2
			3	36.8	59.2	72	92.8	107.2
			5	33.6	65.6	75.2	96	110.4

[a] Polymer concentration in mixing water.

g/mol and 1400 g/mol, respectively, whereas the polydispersity values (D) were recorded as 1.56 and 1.43, respectively. IR spectra of HYP$_1$ and HYP$_2$ showed a broad absorption band at 3441–3396 cm^{-1} (ν O—H) which implied the presence of a large number of hydroxyl groups in the polymers. The characteristic absorption bands of the anhydride groups at 1865 cm^{-1} and 1785 cm^{-1} disappeared in the IR spectra of HYP$_1$ and HYP$_2$, while two new absorption bands at 1624–1622 cm^{-1} (ν C=O in amide groups) and 1727–1724 cm^{-1} (ν C=O in ester groups) appeared. The band at 2979–2953 cm^{-1} was referred to C—H stretching and those bands from 1260 to 1234 to 1074–1064 cm^{-1} were attributed to C—O and C—N stretches in the IR spectra of HYP$_1$ and HYP$_2$.

^{1}H-NMR spectrum of HYP$_1$ as shown in Figure 2 recorded signals of chemical shifts at 0.95–1.14 ppm, 2.26–2.37 ppm, and 2.6–2.9 ppm which were referred to the signals of methyl protons, methylene protons of —CH$_2$CON— and the methylene protons of —CH$_2$COO—, respectively. The signals at chemical shifts of 3.26–3.57 ppm and 3.6 ppm were attributed to the methylene protons of —CH$_2$NC=O and the methine protons. The signal at 5.01 ppm was assigned to the proton of hydroxyl group. ^{1}H-NMR spectrum for HYP$_2$ as illustrated in Figure 3 indicated signals of relatively similar chemical shifts to those for HYP$_1$ with some deviations where the chemical shifts at 3.59–4.08 ppm were attributed to the methylene protons of —CH$_2$N—C = O, —CH$_2$O—C=O, and —CH$_2$OH. The signal at 4.2 ppm was assigned to the proton of the hydroxyl group.

The prepared polymers were inserted in cement pastes. Then, several parameters were studied. The measurements of water of consistency and setting times (initial and final) are indicated in Table II. Generally, the water of consistency decreased with increasing the concentration of HYP$_1$ and HYP$_2$ in OPC and PLC pastes where 5% of HYP$_1$ and HYP$_2$ reduced the water of consistency by 5.56 and 6.67% with OPC and by 6.68 and 10.68% with PLC. That was mainly due to the adsorption of the polymers
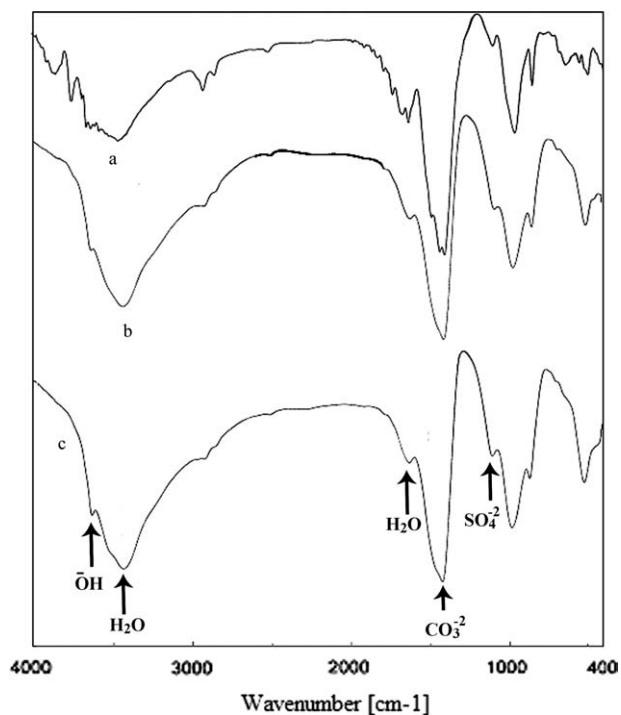
Figure 4 IR spectra of OPC pastes after 90 days for sample (a) without polymer, sample (b) premixed with 5% HYP_1, and sample (c) premixed with 5% HYP_2.
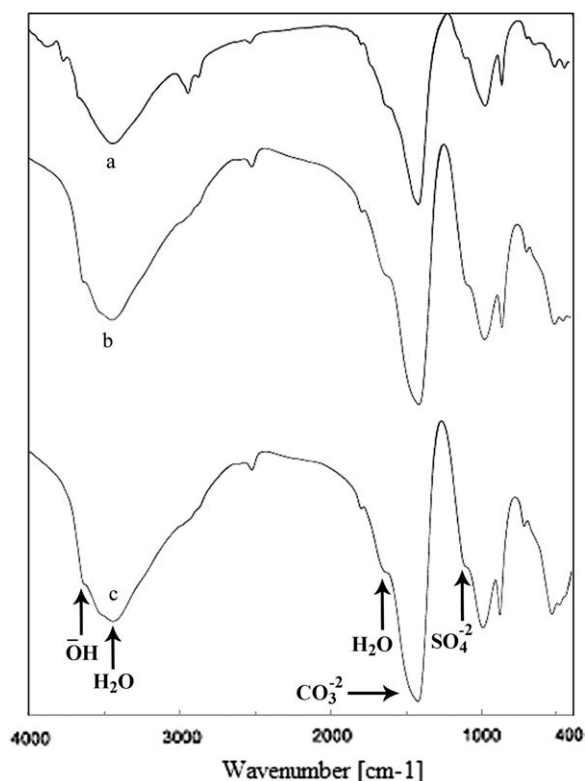

Figure 5 IR spectra of PLC pastes after 90 days for sample (a) without polymer, sample (b) premixed with 5% HYP_1, and sample (c) premixed with 5% HYP_2.
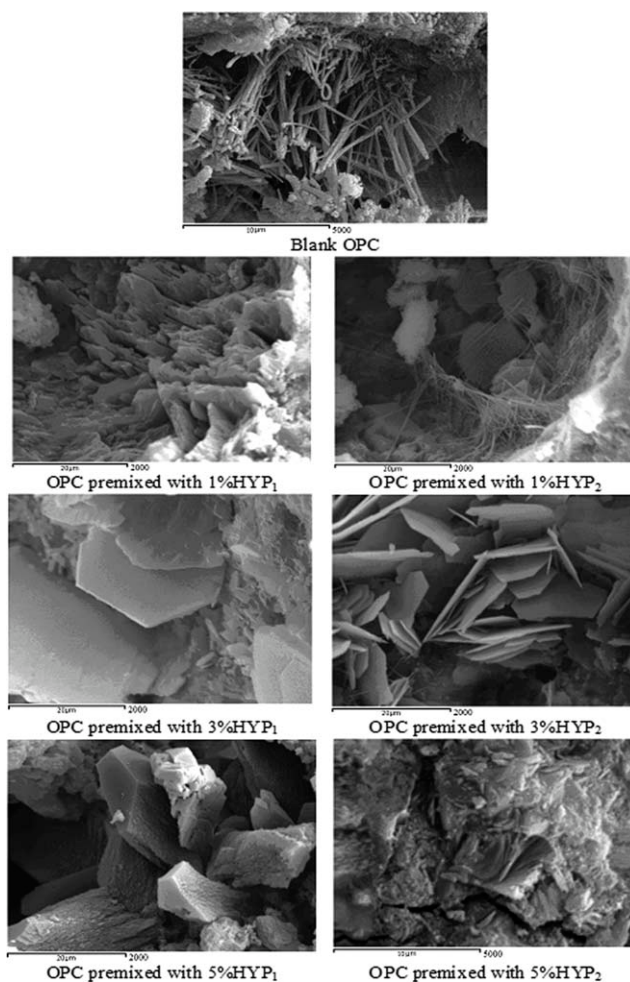

Figure 6 SEM images of blank PLC and pastes premixed with 1, 3, and 5% of HYP_1 and HYP_2 hydrated up to 90 days at magnification power ×5000 and ×2000.\

molecules on the cement particles which led to the formation of polymer film. Then, an electrostatic repulsion was formed which reduced the interparticle attraction between the cement particles preventing flocculation or agglomeration. Finally, a well-dispersed system was obtained where no excess water was needed to penetrate between the particles.[19] Thus, HYP_1 and HYP_2 can act as water reducing admixtures. On the other hand, the setting times (initial and final) of OPC and PLC pastes increased with increasing HYP_1 and HYP_2 concentrations in the OPC and PLC pastes. That was attributed to the partial or full encapsulation of the cement hydrates with polymer films, which retarded the hydration process.[11] So, HYP_1 and HYP_2 can act as setting retarding admixtures.

The BD and apparent porosity measurements of OPC and PLC pastes and those premixed with 1, 3, and 5% of HYP_1 and HYP_2 were recorded as illustrated in Table III. Generally, the BD of all hardened cement pastes increased with curing time while the apparent porosity decreased. That was attributed to

the continual deposition of the formed hydrates in the pore structure of the hardened cement pastes.[11] Moreover, the BD increased while the apparent porosity decreased with increasing the concentration of polymers in OPC and PLC pastes. That was attributed to the increase in the amount of cement hydrates in the presence of HYP_1 and HYP_2 which filled the pore spaces of the hardened cement paste.

The combined water content and the compressive strength measurements of OPC and PLC pastes and those premixed with 1, 3, and 5% of HYP_1 and HYP_2 are shown in Table IV. Generally, the combined water of all cement pastes increased with curing time which was due to the progress in the hydration process.[11] Higher values of combined water contents were obtained by the incorporation of HYP_1 and HYP_2 in OPC and PLC pastes. That was referred to the improvement in the hydration process which resulted from the dispersion effect of HYP_1 and HYP_2 on the cement hydrates. The compressive strength increased with curing time as a consequence of the progress in the hydration process. Additionally, higher compressive strength values were obtained by increasing the concentrations of HYP_1 and HYP_2 in OPC and PLC pastes at all curing ages, except at the first 24 h of hydration where the polymers retarded the hydration process. That fact was ascribed to the decrease in the obtained water of consistency which resulted from the addition of HYP_1 and HYP_2 to OPC and PLC pastes leading to higher values of compressive strength. The incorporation of HYP_2 into OPC and PLC pastes increased the compressive strength slightly higher than that in case of HYP_1 which was referred to the higher reactivity of HYP_2.

The IR spectra of the hydrated OPC and PLC pastes and those premixed with 5% of HYP_1 and HYP_2, respectively, are shown in Figures 4 and 5. Some characteristic bands were observed such as the calcium hydroxide bands at 3644-3630 cm^{-1}, combined and adsorbed water of C—S—H phases at 3445–3420 cm^{-1} which increased in presence of HYP_1 and HYP_2. Also, several other bands were observed such as molecular water at 3445–3420 cm^{-1} and 1648–1638 cm^{-1}, carbonate phases at 1428–1425 cm^{-1} and 877–875 cm^{-1}, sulfate phases at 1120–1112 cm^{-1} and hydrated calcium silicates at 995–984 cm^{-1}. No new phases were formed by the addition of HYP_1 and HYP_2, only increased intensities of the already present bands were observed.

The SEM images of OPC and PLC pastes, respectively, and those premixed with 1, 3, and 5% of HYP_1 and HYP_2 are shown in Figures 6 and 7. Generally, the needles of ettringite phase ($C_3A.3CaSO_4.32H_2O$), which formed during the reaction of C_3A with gypsum in presence of water, were clearly demonstrated in images of blank OPC and PLC pastes. These needles
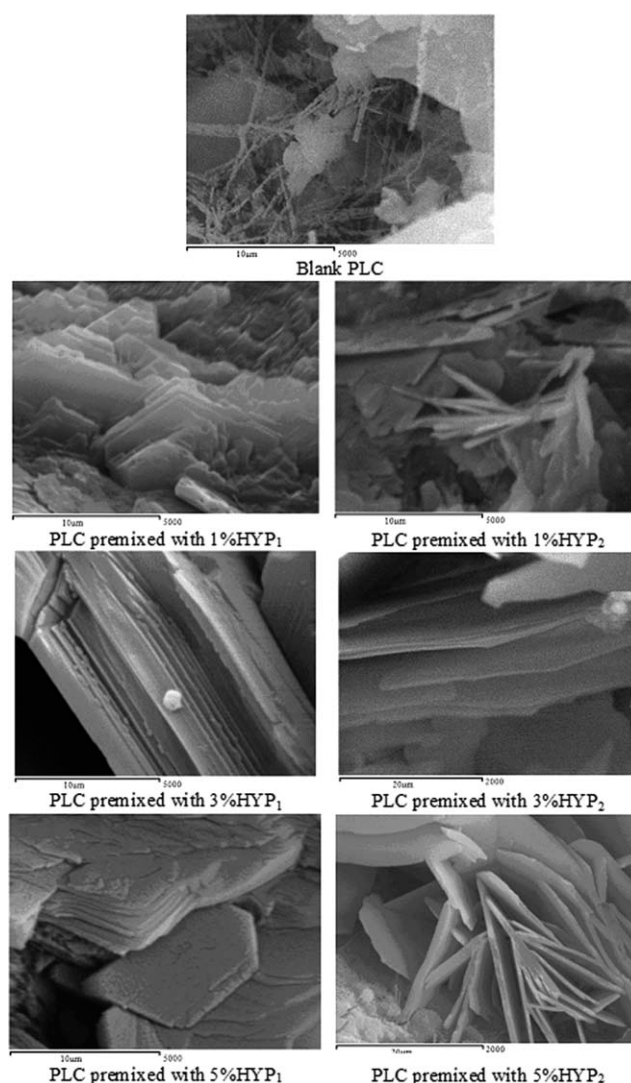
Figure 7 SEM images of blank PLC and pastes premixed with 1, 3, and 5% of HYP_1 and HYP_2 hydrated up to 90 days at magnification power ×5000 and ×2000.

decreased or mostly disappeared in presence of HYP_1 and HYP_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 film which prevented its growth. Those observations indicated better hydration of the pastes in the presence of HYP_1 and HYP_2. Hyperbranched polyesteramides also affected the morphology of the $Ca(OH)_2$ crystals which were resulted from the hydration of C_3S and β-C_2S phases of the cement. In presence of the polymers, layered deposition of undistorted $Ca(OH)_2$ crystals was demonstrated and arranged in stacks. The polymers acted as a bonding agent that glued the crystal layers together. Thus, the microstructure was strengthened in presence of polymers. As $Ca(OH)_2$ crystals represented the weak phase in the binder matrix and the surfaces of those crystals formed preferred cleavage sites, so, the strengthening of the microstructure improved the

overall strength of the binder matrix. That in turn was reflected positively on the specific characteristics of the cement, particularly the mechanical strength.[8]

CONCLUSIONS

HYP_1 and HYP_2 improved the overall cement hydration process in two types of cements such as OPC and PLC. No new phases were formed by the polymer addition, which indicated that HYP_1 and HYP_2 did not affect the chemical structure of the cements but only affected the physicomechanical properties. HYP_1 and HYP_2 influenced the morphological structure of the hydrates. The ettringite needles decreased or mostly disappeared in presence of the polymers. Additionally, plates of Ca $(OH)_2$ crystals were detected. Generally, HYP_1 and HYP_2 can act as water-reducing and setting-retarding admixtures.

References

1. Grigoras, M. High Perform Polym 2009, 21, 304.
2. Mahapatra, S.S.; Karak, N. J; Macromol Sci, Pure Appl Chem 2009, 46, 296.
3. Ohta, Y.; Fujii, S.; Yokoyama, A.; Furuyama, T.; Uchiyama, M.; Yokozawa, T.; Angew Chem Int Ed 2009, 121, 6056.
4. Seiler, M. Chem Eng Technol 2002, 25, 237.
5. Van Benthem, R.; Rietberg, J.; Stanssens, D. Eur. Pat. 1 036 106 2000.
6. Amin, A.; Morsi, S.; Darweesh, H. H. M.; Ayoub, M. M. H.; J Appl Polym Sci 2011, 121, 309–320.
7. Amin, A.; Morsi, S.; Darweesh, H. H. M.; Ayoub, M. M. H.; J Appl Polym Sci 2011, 120, 3054–3064.
8. Knapen, E.; Van Gemert, D. Cem Concr Res 2009, 39, 6.
9. Paiva, H.; Silva, L.; Labrincha, J.; Ferreira, V Cem Concr Res 2006, 36, 1257.
10. Fu, X.; Fu, X.; Lu, W.; Chung, D. Cem Concr Res 1996, 26, 1007.
11. Beeldens, A.; Van Gemert, D.; Schorn, H.; Ohama, Y.; Czarnecki, L.; Mater Struct 2004, 280, 601.
12. STM C 187–98 (1998). Standard Test Method for Normal Consistency of Hydraulic Cement.
13. STM C 191 (2008). Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle.
14. Hewlett, P. C.; Lea's Chemistry of Cement and Concrete, 4th ed.; John Wiley & Sons Inc; New York, 1998.
15. ASTM C 170–90 (1993). Standard Test Method for Compressive Strength of Dimension Stone.
16. van Benthem, R. A. T. M.; Meijerink, N.; Gelade', E.; de Koster, C. G.; Muscat, D.; Froehling, P. E.; Hendriks, P. H. M.; Vermeulen, C. J A. A.; Zwartkruis, T. J. G. Macromolecules 2001, 34, 3559.
17. Muscat, D.; van Benthem, R. A. T. M. Top Curr Chem 2001, 212, 41.
18. Fang, K.; Xu, Z.; Jiang, X.; Zhang, X.; Fu, S. Polym Bull 2008, 60, 533.
19. Rixom, R.; Mailvaganam, N.; Chem Admixtures for Concrete, 3rd ed.; E & FN Spon; London, 1999.