Research Article

New Polymeric Admixture for Cement Based on Hyperbranched Poly Amide-Ester with Pentaerythritol Core

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Hyperbranched poly amide-ester (HBPAE) was synthesized by a solution condensation polymerization through one-step process using pentaerythritol as a central core and AB₂ prepolymerized monomer which was rapidly prepared at room temperature (25°C) using commercially available maleic anhydride (MA) and diethanolamine (DEA) monomers in the presence of p-toluene sulfonic acid as a catalyst. The prepared polymer was characterized by GPC, IR, ¹H-NMR, and thermal analysis (TGA and DSC). The influence of the polymer addition to the cement paste was investigated by measuring the effect of 1, 3 and 5 wt% HBPAE solutions on the properties of ordinary portland cement (OPC). Accordingly, several parameters were investigated such as water of consistency, setting times, bulk density, apparent porosity, compressive strength, and combined water content of the polymer/cement pastes. The SEM images proved that the incorporation of HBPAE with the OPC cement did not affect the chemical composition of hydrates, but it only affected the physical state, shape, size, morphology, and crystallinity of the formed hydrates. The results showed that the polymer addition to OPC pastes improved the physicomechanical properties of cement.

1. Introduction

In the recent years, significant efforts have been focused on synthesis and application of the hyperbranched polymers as they exhibit many special merits such as highly branched three-dimensional globular architecture, low viscosity, high solubility, abundance of functional end groups, and internal cavities in the molecule, which can be easily designed to meet specific needs in various applications [1–3].

Hyperbranched polymers can be easily prepared in one-step reactions and typically have randomly distributed branches that make them attractive alternatives for numerous applications in comparison with their regular counterparts (dendrimers) which need more expensive and drastic conditions to be properly prepared [4–6].

Hyperbranched polymers are potentially applied in various fields from drug delivery to coatings where increasing scientific interest for them over the past several decades is evident and confirmed by the increasing number of publications [7–12].

The concept of the polymer modification for the cement mortars and concretes is not new, since a considerable research and development of a polymer modification have been performed for the past decades [13, 14]. Consequently, various polymer-based admixtures have been developed to produce the currently popular construction materials because of their good cost-performance balance [15]. The addition of concrete admixtures is a frequently used application in the concrete production, recent studies of which proved their favorable effects on the characteristics of

TABLE 1: Chemical composition of the used OPC cement, wt%.

Materials oxides	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

concrete [16–20]. The use of admixtures becomes inevitable in terms of saving time and improving the characteristics of both fresh and hardened concretes [21] such as workability, resistance against physical and chemical external effects, and being economical.

Nowadays, hyperbranched polymers are successfully employed in the building industry as cement admixtures due to their extraordinary desirable properties [22].

Accordingly, this paper investigated the influence of using hyperbranched poly amide-ester (HBPAE) derived from maleic anhydride, diethanolamine, and pentaerthritol as a new polymeric cement admixture on the physicochemical characteristics of the modified cement pastes.

2. Materials and Methods

2.1. Chemicals and Materials. Diethanolamine (DEA), maleic anhydride (MA), p-toluene sulfonic acid (p-TSA), and pentaerthritol (PER) were delivered from Fluka Chemicals, and N, N'-dimethylformamide (DMF) was supplied from Sigma Aldrich Chemicals. The OPC with a surface area of 3300 cm²/g was delivered from El-Masria Cement Company, Egypt. The chemical composition of OPC is listed in Table 1.

2.2. Instrumentation and Measurements. The prepared polymer was characterized via different investigation techniques such as infrared spectra (IR), gel permeation chromatography (GPC), nuclear magnetic resonance (¹HNMR), and thermal analyses such as thermal gravimetric analyses (TGA) and differential scanning calorimetry (DSC). IR spectra were recorded by FTIR-JASCO in the range of 4000–400 cm⁻¹. The samples were pressed into potassium bromide (KBr) pellets. The gel permeation chromatography (GPC) measurements were carried out using GPC-I100 Agilent technologies with reactive index detector with 100–10⁴–10⁵ Å Ultrastaygel columns connected in series using polystyrene (PS) as standard and N, N'-dimethylformamide (DMF) as eluent where the number average molecular weight ($\overline{M}_n$) and polydispersity ($\overline{M}_w/\overline{M}_n$) values were determined.

¹HNMR spectrum was obtained by Varian Mercury 300 MHz, using tetramethylsilane (TMS) as internal standard and DMSO as the main solvent. TGA was carried out by using TGA-50 shimadzu instrument, in the range 40–400°C; the heating rate was 10 K/min and under nitrogen atmosphere. The DSC measurement was carried out by using differential scanning calorimeter DSC-60 shimadzu in the range from 20°C to 140°C, with a scanning rate of 20 K/min, and under nitrogen atmosphere.

2.3. Test Methods of the Cement Samples

2.3.1. Water of Consistency and Setting Time. Standard Vicat apparatus was used to determine the water of consistency

(w/c) as a standard measure of plasticity of a cement paste. Setting times were performed at 28 ± 2°C according to ASTM specification [23, 24].

2.3.2. Bulk Density and Apparent Porosity. Bulk density (B. D.) and apparent porosity (A. P.) of the hardened cement pastes [25] were calculated from the following equations:

$$\begin{aligned} \text{B. D. (g/cm}^3\text{)} &= \frac{W_1}{W_1 - W_2} \times 1, \\ \text{A. P. (\%)} &= \frac{W_1 - W_3}{W_1 - W_2} \times 100, \end{aligned} \quad (1)$$

where W_1 is saturated weight, W_2 is suspended weight and W_3 is dry weight, of the cement paste samples.

2.3.3. Compressive Strength. Compressive strength [26] was carried out 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 on one inch cubic samples perpendicular to the direction of the upper surface of the polymer/cement samples.

2.3.4. Chemically Combined Water Content. The chemically combined water content at each time interval was also determined on the basis of ignition loss [27] using the following equation:

$$W_n = W_1 - \frac{W_2}{W_2} \times 100, \quad (2)$$

where W_1 is Weight before ignition, W_2 is ignited weight and W_n is combined water of the cement paste samples.

2.4. Synthesis of Hyperbranched Poly Amide-Ester (HBPAE)

2.4.1. Synthesis of AB₂ Monomer. AB₂ monomer was prepared by amidation reaction of DEA and MA at a molar ratio of 1/1 where 0.1 mol of MA was dissolved in (100 mL) of chloroform in three-necked round-bottom flask at 25°C. 0.1 mol of crystal DEA was rapidly poured into MA solution. The reaction mixture was stirred with a magnetic stirrer at 60°C under reflux for 4 h and under nitrogen to obtain the AB₂ monomer.

2.4.2. Synthesis of HBPAE. The prepared hyperbranched poly amide-ester as shown in Scheme 1 was synthesized through pseudo-one-step process where 0.4 mol of the previously prepared AB₂ monomer solution, 0.1 mol of pentaerthritol and 0.5 wt% of p-TSA catalyst were introduced, respectively, to 250 mL three-necked flask. Vacuum pump and a reflux distillation equipment with water condenser were installed. The flask was put into an oil bath adjusted at constant temperature of 120°C. The mixture was stirred with a magnetic stirrer

SCHEME 1: Synthesis of hyperbranched poly amide-ester.

for 6 h under vacuum conditions. The crude products were dissolved in (100 mL) DMF, then precipitated, and washed by a mixture of solvents of ethyl ether/acetone (1/1). The precipitate was dried in vacuum.

2.4.3. Preparation of Cement Mixes. For the preparation of cement samples, three different polymer solutions with variable concentrations were prepared such as 1%, 3%, and 5%. Each solution was mixed separately with ordinary Portland cement to study its performance on the properties of the cement pastes.

Water of consistency and setting time measurements were carried out on the blank-cement samples of each type by adding water gradually to cement and testing it with Vicat apparatus. The same procedure was repeated by adding the polymer solutions instead of water to study the effect of adding the polymer.

Cubic samples of blank and polymer/cement admixtures were made and immersed in water basin for different time

periods (1, 3, 7, and 28 days); then they were subjected to be tested for compressive strength, bulk density, apparent porosity, and chemically combined water content for these samples.

3. Results and Discussion

The hyperbranched polymer (HBPAE) was synthesized via pseudo-one-step reaction between pentaerythritol as a central core and AB₂ prepolymerized monomer (Scheme 1) [28]. The HBPAE was characterized by GPC, IR, ¹H-NMR, TGA, and DSC. IR spectrum of the prepared polymer as in Figure 1 revealed the appearance of strong absorption band of hydroxyl group at 3413 cm⁻¹, ester group stretching at 1728 cm⁻¹ and the absorption band of amide carbonyl groups at 1644 cm⁻¹. The band at 1050 cm⁻¹ was attributed to =C-H bending and those at 1127, 1174, and 1293 cm⁻¹ were attributed to C-O and C-N stretches. ¹H-NMR spectrum of HBPAE showed, as in Figure 2, distinguished signals of

FIGURE 1: IR spectrum of the hyperbranched poly amide-ester.

FIGURE 2: ¹H NMR spectrum of the prepared hyperbranched poly amide-ester.

chemical shifts (δ , ppm) at 2.5–3.2, 3.5–4.1, 4.2–4.5, 4.6 and 6.5 which were referred to (O–CH₂ CR₃; R=CH₂–OCO–N(CH₂CH₂)₂OCO–), (O=CN–CH₂), (O=CO–CH₂), (–CH₂CH₂OH), and the protons of alkenes. TGA of HBPAE, as shown in Figure 3, exhibited excellent thermal stability. The weight loss was just 10% up to 176.4°C. The weight losses reached 20% when the temperature was raised to 200°C. TG curve of the hyperbranched poly amide-ester descended when the temperature reached the range of 220–250°C. This behavior might be due to the decomposition of amine and ester bonds in the hyperbranched poly amide-ester. DSC measurements recorded T_g value as 72.22°C. The GPC results indicated the number average molecular weight of HBPAE as 3578 g/mol and the polydispersity value as 2.83.

The prepared hyperbranched HBPAE polymer was tested in cement as a new application where several parameters were measured such as water of consistency, setting times, bulk density, apparent porosity, and compressive strength.

The water of consistency as well as setting times (initial and final) of the OPC cement pastes premixed with variable

FIGURE 3: TGA of the prepared hyperbranched poly amide-ester.

FIGURE 4: Water of consistency and setting times (initial and final) measurements of OPC premixed with 1%, 3%, and 5% of HBPAE.

concentrations of HBPAE are represented in Figure 4. Generally, the water of consistency gradually decreased with increasing the polymer content up to 5%. Using polymer concentration of 5%, the water of consistency decreased from 30% to 23.33% for OPC. The water of consistency was highly reduced by 5.34–6.76% for OPC, when compared with that of the blank. So, it was concluded that this polymer acted as water reducer [29]. Although the polymer lowered the water of consistency, it increased the setting times (initial and final). The initial and final setting times increased from 120 to 165 minutes and 230 to 280 minutes with increasing HBPAE concentration. This behavior meant that the HBPAE behaved as a retarder. The reduction in water of consistency and the elongation of setting times at the same time were attributed to the adsorption of the highly polar polymer molecules on the cement particles and hence the subsequent formation of a polymer film. An electrostatic repulsion between the negatively charged cement particles formed, which reduced the interparticle attraction between the cement particles

FIGURE 5: Bulk density of OPC cement pastes premixed with 1%, 3%, and 5% HBPAE.

FIGURE 6: Apparent porosity of OPC cement pastes premixed with 1%, 3%, and 5% HBPAE.

and then prevented flocculation or agglomeration for them. That partial or full encapsulation of cement hydrates by the polymer molecules retarded the hydration process. So, the used polymer acted as a water reducing admixture and also as a setting retarder.

The bulk density and the apparent porosity are plotted as a function of curing time in Figures 5 and 6, respectively. Generally, the bulk density of all cement mixes increased gradually with curing time while the apparent porosity decreased. This is mainly due to the continual deposition of the formed hydration products in the pore structure of the hardened cement pastes. Thus, the apparent porosity decreases, and hence the bulk density enhances. Moreover, the bulk density was further improved with increasing the polymer concentration. The higher density values with HBPAE may be attributed to the improvement in the hydration process and subsequently the increase in the hydration products compared with those of blank samples.

The chemically combined water contents of OPC cement pastes premixed with 1%, 3% and 5% HBPAE are represented as a function of polymer concentration as in Figure 7. The combined water contents of all cement pastes are generally

FIGURE 7: Chemically combined water contents of OPC cement pastes premixed with 1%, 3%, and 5% HBPAE.

FIGURE 8: Compressive strength measurements of OPC pastes and those premixed with 1%, 3%, and 5% of HBPAE up to 28 days.

increased with curing time up to 28 days. This is 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 $\beta-C_2S$. The combined water contents increased with polymer concentration. The higher values of combined water contents by incorporation of small amounts of polymer with OPC are due to the dispersion effect of the polymer on the cement grains, which in turn prevents their aggregation and thus improves the hydration process [30].

The compressive strength of OPC cement pastes premixed with 1%, 3% and 5% HBPAE was plotted as a function of curing time as shown in Figure 8. The compressive strength of the hardened cement pastes generally increased with curing time. This is mainly due to the continual formation of the hydration products which deposited into the pores of the cement pastes. Thereby, the apparent porosity decreased gradually and the compactness increased. Hence, the bulk density increased by time of hydration. As a result, the compressive strength improved and enhanced. Higher compressive strength values were obtained for OPC cement by increasing the polymer concentration when compared with

FIGURE 9: The SEM micrographs of The OPC pastes (a) premixed with 1%, 3% and 5% of HBPAE ((b), (c), and (d)) hydrated upto 28 days.

those of the blank samples at all curing periods, except at the first 24 hours of hydration. That behavior was to some extent due to both of the high activation effect of the hyperbranched poly amide-ester at later stages and the decrease of the apparent porosity which was resulted from further increase of the hydration products. Furthermore, the dispersing effect of the hyperbranched polymers/cement pastes improved the workability of such pastes. Therefore, an enhancement of the compressive strength was obtained. The SEM images of the OPC cement pastes (a) premixed with 1%, 3% and 5% of HBPAE ((b), (c), and (d)) are shown in Figure 9.

Generally, the needle-like crystals of ettringite phase ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$) that formed due to the hydration reaction of C_3A with gypsum ($CaSO_4 \cdot 2H_2O$) in presence of water were clearly detected for OPC pastes (a). This phase decreased in presence of 1% HBPAE (b) while it completely disappeared with 3% and 5% HBPAE ((c), (d)), respectively. This was due to the conversion of ettringite to monosulphate phase ($C_3A \cdot CaSO_4 \cdot 12H_2O$). This indicated a better hydration of cement phases in its presence. The HBPAE also affected the morphology of Portlandite or $Ca(OH)_2$ and CSH phases, resulting from the hydration of C_3S and/or β - C_2S phases of the cement, where the $Ca(OH)_2$ crystals represent the weak phase in the binder matrix and the strengthening by both polymers improved the overall strength development of the binder matrix [30, 31]. This in turn was reflected positively on the specific characteristics of the cement, particularly

the mechanical strength. On the other side, the phases that formed with both types of polymers were the same as with the pure OPC pastes but with different morphologies and crystallinities, and well-developed crystals were noted with 5% due the dispersion effect where the crystals were larger, condensed, and more compacted.

4. Conclusion

The fundamental extraordinary desirable properties of the dendritic polymers have been demonstrated by using hyperbranched poly amide-ester as cement admixtures. Hyperbranched poly amide-ester which ended with $-OH$ groups can be synthesized by pseudo-one-step process between pentaerythritol and AB_n prepolymerized monomer obtained by the reaction of maleic anhydride and diethanolamine in the presence of p-toluene sulfonic acid as catalyst. The prepared HBPAE reduced the w/c ratio for OPC cement pastes compared to the blank. Therefore, it can be used as a water-reducing agent or a cement admixture. The HBPAE activates the cement phases and improves the rate of hydration. Also, the combined water content and the compressive strength were improved and enhanced by using HBPAE at all curing ages of hydration particularly at later stages. The SEM images showed that the addition of the HBPAE to cement did not affect the OPC hydrates, but it only affected the physical state, shape, morphology, and crystallinity of the formed hydrates.

Acknowledgments

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