

Employing of novel poly (amine-ester) with Pentaerithritol core as a new polymeric admixture for cement

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ABSTRACT

A novel hyperbranched poly (amine-ester) (HBPAE) with a high number of hydroxyl end groups has been prepared and successfully applied as new polymeric admixture for ordinary Portland cement (OPC) after its complete characterization via GPC, IR, ¹H-NMR, TGA and DSC. The effect of polymer addition on the cement paste was investigated by measuring the effect of 1, 3 and 5 wt. % HBPAE solutions on the properties of OPC. The results clarified that the addition of HBPAE to OPC pastes decreased the water of consistency while increased the compressive strength with no effect on the chemical composition of the cement phase. The SEM images indicated that the incorporation of HBPAE in cement phase affected the physical state, shape, size, morphology and microstructure of the formed hydrates. Generally, the addition of hyperbranched poly amine-ester (HBPAE) improved the physico-mechanical properties of cement.

Keywords-hyperbranched polymers, poly (amine-ester), cement admixtures, physico-mechanical properties, ordinary Portland cement.

I. Introduction:

In the last decades, highly branched polymers such as hyperbranched polymers which are randomly branched, three-dimensional and polydisperse macromolecules with a large number of functional end groups, have attracted considerable attention due to their remarkable physical and chemical properties such as reduction of melt and solution viscosity, high solubility, large number of reactive functional end groups, approximately spherical molecular shape and the absence of chain entanglement in comparison to their linear analogues [1-3]. The concept of hyperbranched polymer was first presented by Flory in 1952 [4]. However, they did not match great interest until 1988 when Kim and Webster [1] reported hyperbranched polyphenylenes as melt viscosity modifiers for polystyrene, which renewed the interest in hyperbranched materials. Since then, a wide variety of hyperbranched polymers in different chemical architectures were prepared [5-9]. One of the advantages of hyperbranched polymers is their simple one-pot synthesis which reduces the preparative costs. [4,10,11] Nowadays, hyperbranched polymers are involved in versatile applications from coatings and additives to modifiers. Accordingly, as a new trend, some hyperbranched polymers were successfully employed as cement admixtures due to their properties [12] on the way of the enthusiastic industrial demands to develop new polymeric cement admixtures can be used in

producing the currently popular construction materials based on their cost-performance balance [13-15]. Now, there are different known polymeric chemical admixtures such as modified lignosulfonated polymers (LS), naphthalene formaldehyde sulfonated polymers (N), melamine formaldehyde sulfonated polymers (S), and polycarboxylate derivatives (CE) [16-18]. The addition of the admixtures during the concrete production has favorable effects on the characteristics of concrete [19,20] in terms of saving time and enhancing the characteristics of both fresh and hardened concrete [21] such as workability, resistance against physical and chemical external effects, and being economical etc. Accordingly, in the present study, pentaerithritol based hyperbranched poly (amine-ester) was prepared as a new polymeric cement admixture. The effect of its addition was investigated on the physico-mechanical characteristics of the modified cement pastes.

II. EXPERIMENTAL

2.1. Materials

Diethanolamine (DEOA), methyl acrylate (MA), P-toluene sulphonic acid (p-TSA), pentaerithritol (PER) were delivered from Fluka Chemicals. N, N'-dimethylformamide (DMF) was supplied from Sigma- Aldrich Chemicals. The OPC with surface area of 3300 cm²/g was delivered from El-Masria

Cement Company, Egypt. The chemical composition of OPC is indicated in (Table 1).

2.2. Synthesis of hyperbranched poly amine-ester (HBPAE)

In 250 ml round bottom flask, N, N-diethylol-3-amine methyl propionate (AB₂ monomer, I) was synthesized via Michael addition of methyl acrylate (8.6 g, 0.1 mol) and diethanolamine (10.5 g, 0.1 mol) in methanol solvent (100 ml) at 40 °C with stirring for 4h. Through vacuum distillation, faint yellow oily liquid (I) was obtained. In another successive pseudo one step reaction, 0.1 mol of pentaerithritol (PER), 0.4 mol of (I) and 0.5 wt % of p-toluene sulphonic acid as the catalyst were stirred at 120 °C where HBPAE was obtained. The residual unreacted monomers were removed by vacuum distillation.

2.3. Preparation of cement mixes

Three different polymer solutions with variable concentrations of cement samples 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 times (initial and final) measurements were carried out on the blank-cement samples of each type by adding water gradually to cement and tested with Vicat apparatus. The water to cement ratio was 1:3. 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 with dimensions 2×2×2 (cm) were prepared and immersed in water basin for different time periods (1, 3, 7, 28 days) then they were subjected to be tested for compressive strength, bulk density, apparent porosity and chemically combined water content for these samples.

2.4. Characterization

IR spectra were recorded via IR- JASCO in the range of 4000-400 cm⁻¹. The samples were pressed into potassium bromide (KBr) pellets. Gel permeation chromatography (GPC) measurements were carried out using GPC-1100 Agilent technologies with reactive index detector with 100-104-105 A° ultrastragel columns connected in series using polystyrene (PS) as standard and N, N'-dimethylformamide (DMF) as eluent where the number average molecular weight (\bar{M}_n) and polydispersity (\bar{M}_w/\bar{M}_n) values were determined. ¹H NMR spectrum was obtained by Varian Mercury 300 MHz, using tetramethylsilane (TMS) as internal standard and DMSO as the main solvent. Thermal gravimetric analyses (TGA) were carried out using TGA-50 Shimadzu instrument, in the range of 40 – 400 °C with heating rate as 10 K/min under nitrogen

atmosphere. Differential scanning calorimetry (DSC) was carried out by using differential scanning calorimeter DSC-60 Shimadzu in the range from 20 - 140 °C with a scanning rate of 20 K/min under nitrogen atmosphere. The phase compositions of some selected samples were investigated via 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.

2.5. Test methods of the cement samples

Water of consistency (w/c) is the measure of plasticity and it 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. Standard Vicat apparatus was used to determine the water of consistency (w/c) as well as setting times (initial and final) of the cement pastes which were performed at 28±2 °C according to ASTM specification [22-24].

Bulk density (B. D) and apparent porosity (A. P.) measurements of the hardened cement pastes [24] were calculated from the following equations:

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

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

Where W_1 = saturated weight, W_2 = suspended weight and W_3 = dry weight of the cement paste samples where the samples were dried at oven adjusted at 100 °C for 1h.

Compressive strength is the capacity of a material to withstand axially directed pushing forces. When the limit of compressive strength is reached, materials are crushed. Compressive strength [25] 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.

Chemically-combined water is defined as that portion present in interlayer spaces, or more firmly non-evaporable water (W_n). The chemically-combined water content at each time interval was also determined on the basis of ignition loss [26] using the following equation:

$$W_n = W_1 - W_2 / W_2 \times 100 \quad \text{equation (3)}$$

W_1 = Weight before ignition, where the sample was kept in a desiccator containing calcium carbonate for 1 h before weighing it, W_2 = ignited weight where W_n = combined water of the cement paste samples.

III. RESULTS & DISCUSSION

3.1. Characterization of the prepared polymers

The hyperbranched polymer (HBPAE) was synthesized via pseudo-one-step reaction between pentaerythritol as a central core and AB₂ prepolymerized monomer (Scheme 1). IR spectrum of the synthesized hyperbranched polymer revealed several absorption bands as shown in (Fig. 1), the bands at 2942 cm⁻¹ and 1728 cm⁻¹ were ascribed to C-H stretching and the α -unsaturated carbonyl of the ester group. The broad absorption band at 3401 cm⁻¹ was assigned to the hydroxyl groups which were H-bonded and those bands at 1064 cm⁻¹, 1112 cm⁻¹ and 1265 cm⁻¹ were attributed to C-O and C-N stretches. GPC results indicated that the number average molecular weight and the polydispersity values were 3695 g/mol and 2.656, respectively. ¹H-NMR spectrum of HBPAE showed as in (Fig. 2), distinguished signals of chemical shifts at 2.05 ppm which were assigned to (R'OCH₂CR'³-; R' = -CO-CH₂CH₂-N and R'' = -C(CH₂OCO-)₃). The signals (ppm) at 2.44-2.58 and 2.82-2.98 were ascribed to -N(CH₂CH₂OH) and (-N(CH₂CH₂OH)₂). However, those bands at 3.48-3.54 ppm were ascribed to (-OCOCH₂CH₂NR₂). Signals at 4.4 ppm were assigned to (-CH₂CH₂OH). TGA of HBPAE as shown in (Fig. 3) exhibited relative thermal stability up to 176°C where the weight loss was just 10%. The weight loss reached 20% at 205°C, however, TGA curve of the HBPAE descended in the range of 190°C - 250°C which might be due to the decomposition of amine and ester bonds in the hyperbranched poly amine-ester. DSC measurements recorded T_g value as 11°C. The previous data showed that the expected structure of the resulting polymer with hydroxyl, ester, and amine groups.

3.2. Employing the prepared polymers as cement admixtures

Water of consistency as well as setting times (initial and final) of the OPC cement pastes premixed with variable concentrations of HBPAE are indicated in (Table 2) and are represented in (Fig. 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 5.34-6.34 % for OPC, compared with that of the blank. So, it was concluded that this polymer acted as water reducers [27]. Although the polymer lowered the water of consistency but it increased the setting times (initial and final). As shown in (Table 2), 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 formed between the negatively charged cement particles which reduced the interparticle attraction between the cement particles, which 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.

Bulk density and apparent porosity of the prepared HBPAE are plotted as a function of curing time in (Figs. 5, 6), respectively. Generally, the bulk density of all cement mixes increased gradually with curing time while the apparent porosity decreased. This was mainly due to the continual deposition of the formed hydration products in the pore structure of the hardened cement pastes. Thus, the apparent porosity decreased and hence the bulk density enhanced. Moreover, the bulk density was further improved with increasing the polymer concentration. The higher density values in case of HBPAE were 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 (Fig. 7). The combined water contents of all cement pastes generally increased with curing time up to 28 days. This was mainly attributed to the gradual and continuous formation of hydration products resulting from the hydration of the main phases of cement, particularly C₃S and β -C₂S. The combined water contents increased with polymer concentration. The higher values of combined water contents by incorporation of small amounts of polymer with OPC were due to the dispersion effect of the polymer on the cement grains, which in turn prevented their aggregation and thus improved the hydration process [28].

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 (Fig. 8). The compressive strength of the hardened cement pastes generally increased with curing time. This was 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 those

of the blank samples at all curing periods, except at the first 24 hours of hydration. That behavior was due to some extent to both of the high activation effect of the hyperbranched poly (amine-ester) at later stages and also to 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 (Fig. 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 C3A with gypsum ($CaSO_4 \cdot 2H_2O$) in presence of water were clearly detected for OPC pastes (A). This phase completely disappeared with 1%, 3% and 5 % HBPAE (B, C and D), respectively. This was due to the conversion of ettringite to monosulphate phase ($C_3A \cdot CaSO_4 \cdot 12 H_2O$). For 1% HBPAE the ettringite needle-like disappeared while the formation of calcium CSH is not detected indicating lower effect as compared to 3% and 5% HBPAE. A better hydration of cement phases take place the presence of 3% and 5% of the polymer and the higher effect is attributed to 5% HBPAE. The prepared hyperbranched polymer affected also the morphology of Portlandite or $Ca(OH)_2$ and CSH phases, resulted from the hydration of C_3S and/or $\beta-C_2S$ phases of the cement, where the $Ca(OH)_2$ crystals represented the weak phase in the binder matrix and the strengthening by both polymers improved the overall strength development of the binder matrix [29]. 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.

IV. CONCLUSION

New hyperbranched poly amine-ester (HBPAE) was prepared and used as cement admixture. HBPAE activated the cement phases and improved the rate of hydration. Therefore; it can be used as a water-reducing cement admixture. Also, the combined water content and the compressive strength were improved 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 or morphology and crystallinity of the formed hydrates.

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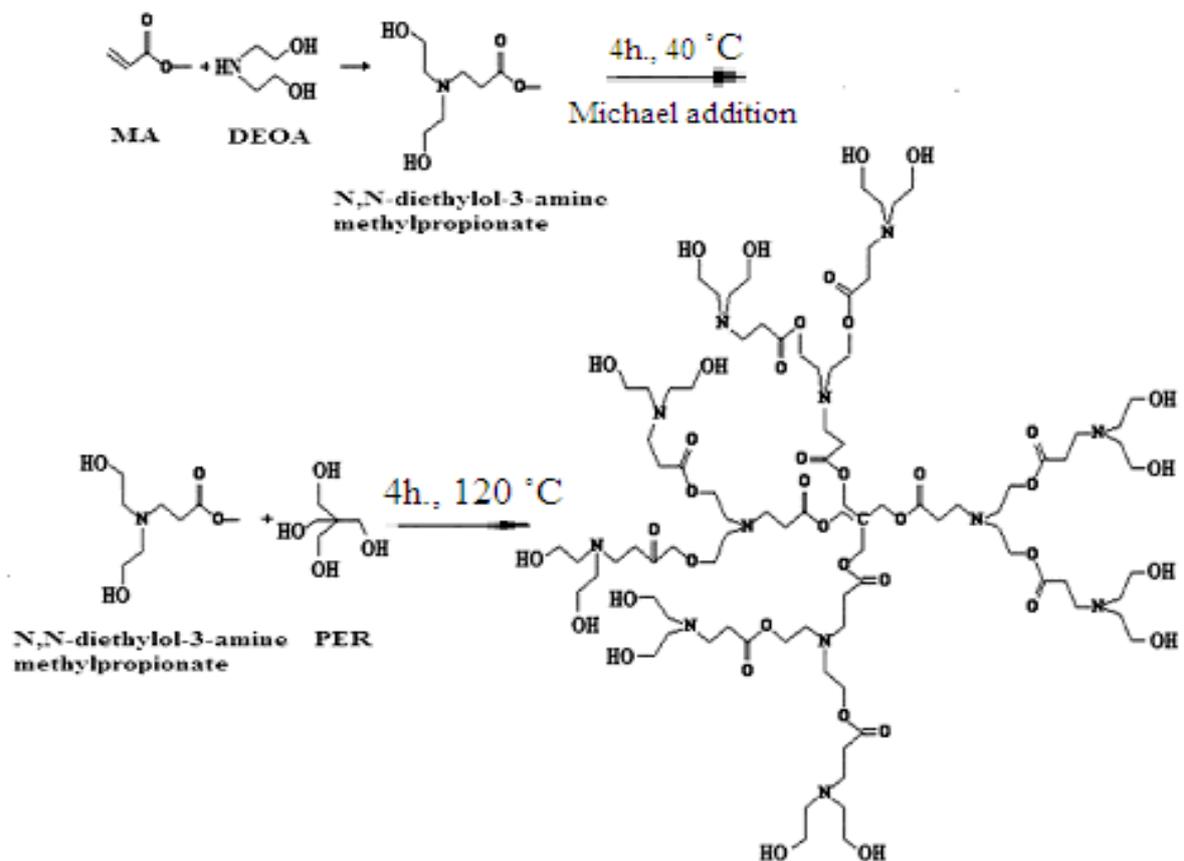
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Table 1 Chemical composition of the used OPC cement, wt. %.

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

Table 2: Water of consistency and setting times (initial and final) measurements of OPC premixed with 1, 3 and 5% of HBPAAE.

Polymer (wt. %)	Water of consistency (%)	Setting time, (min)	
		Initial Set	Final Set
0	30.00	120	230
1	27.66	140	250
3	24.66	155	265
5	23.66	165	280



Scheme 1: Synthesis of hyperbranched poly amine-ester (HBPAE)

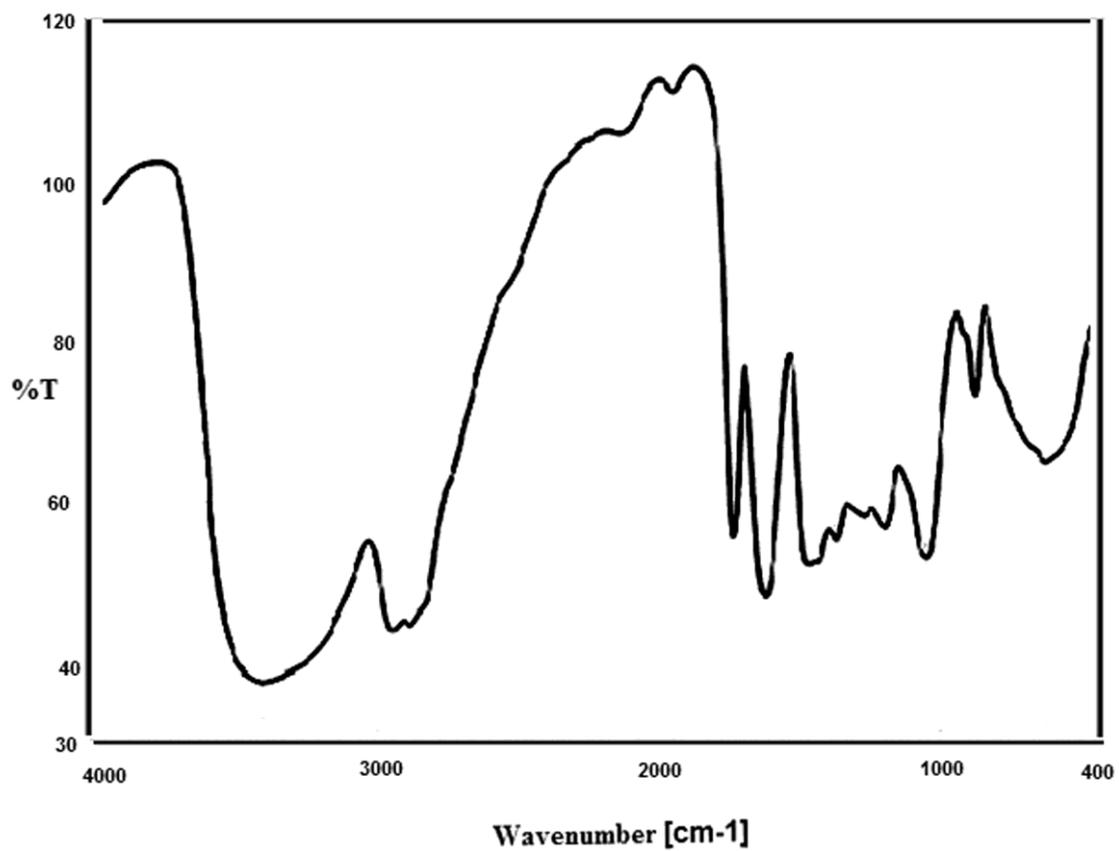


Figure 1: IR spectrum of the HBPAE

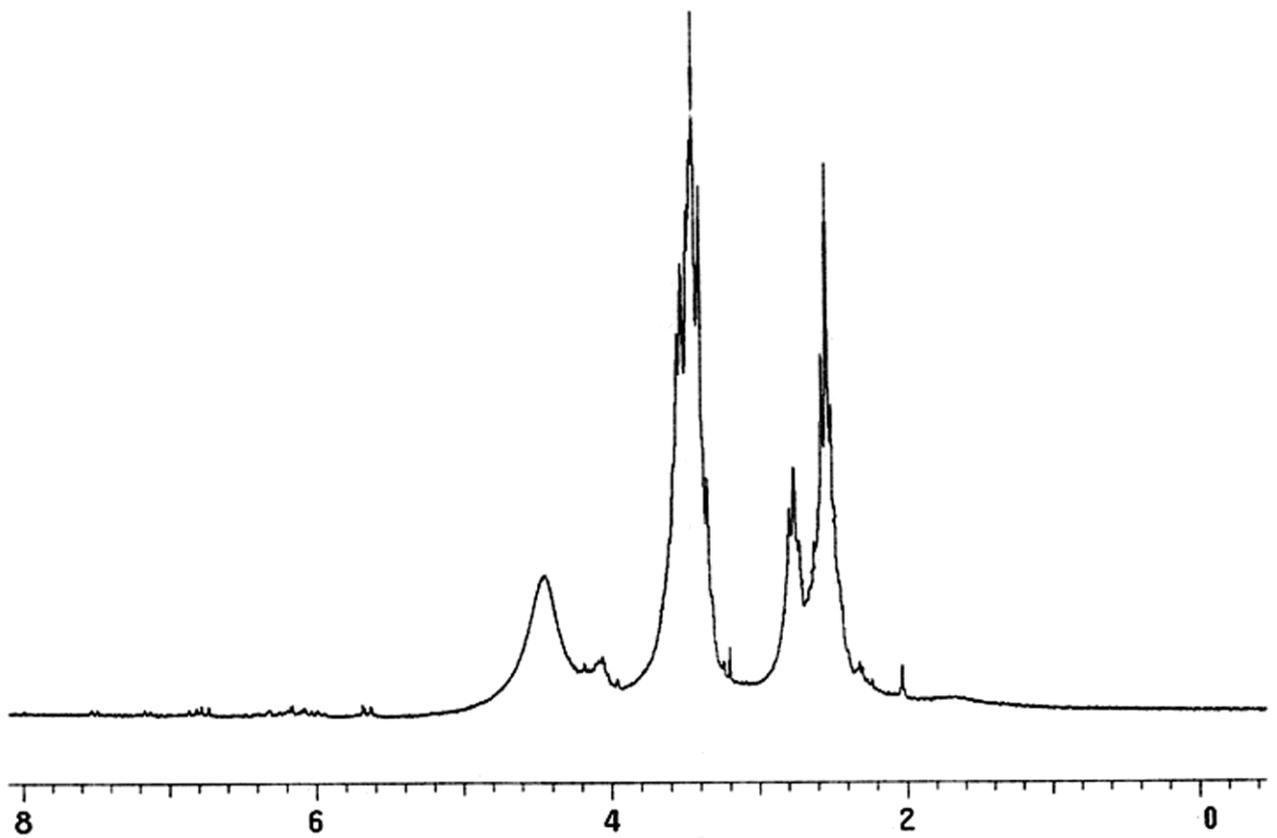


Figure 2: ¹H NMR spectrum of HBPAE

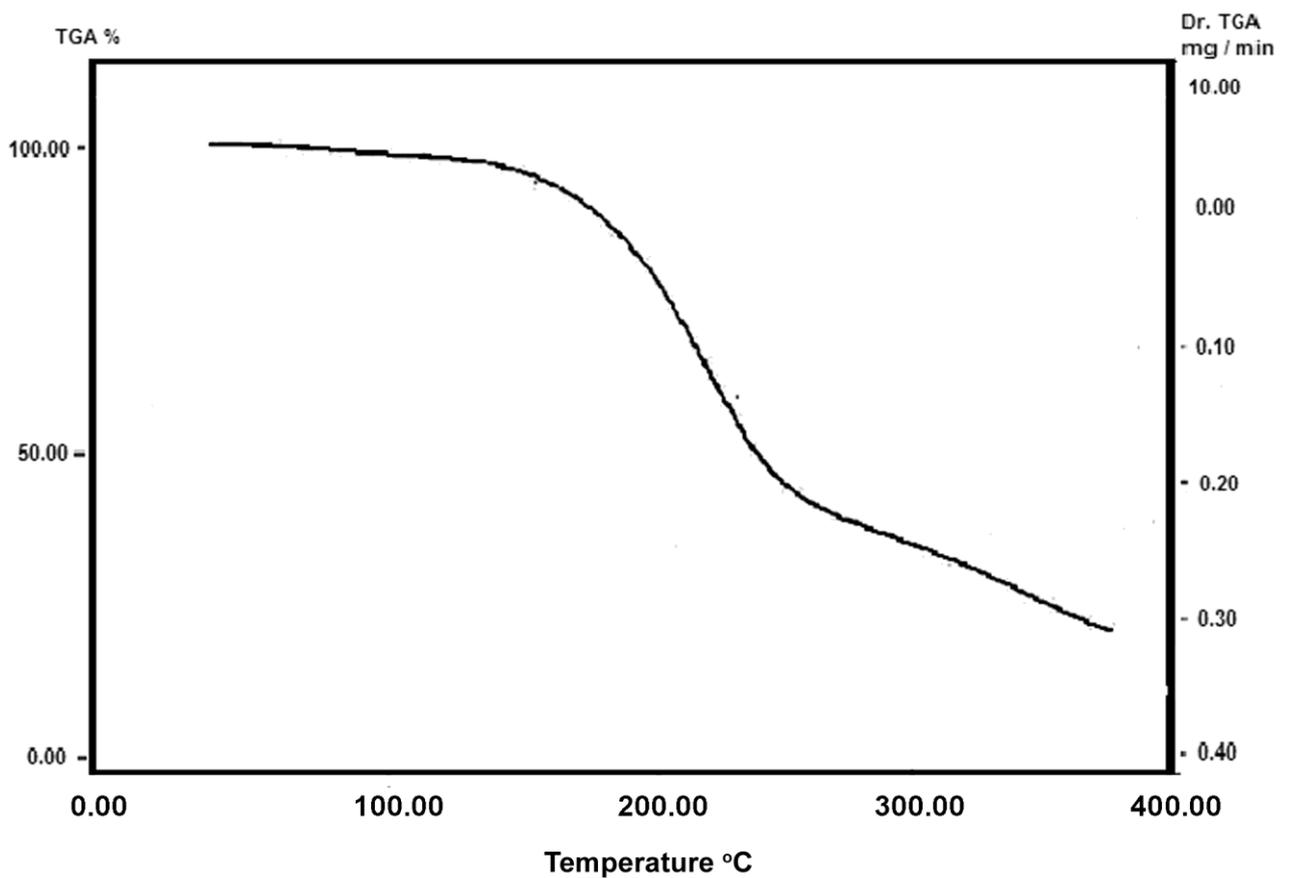


Figure 3: TGA of HBPAE

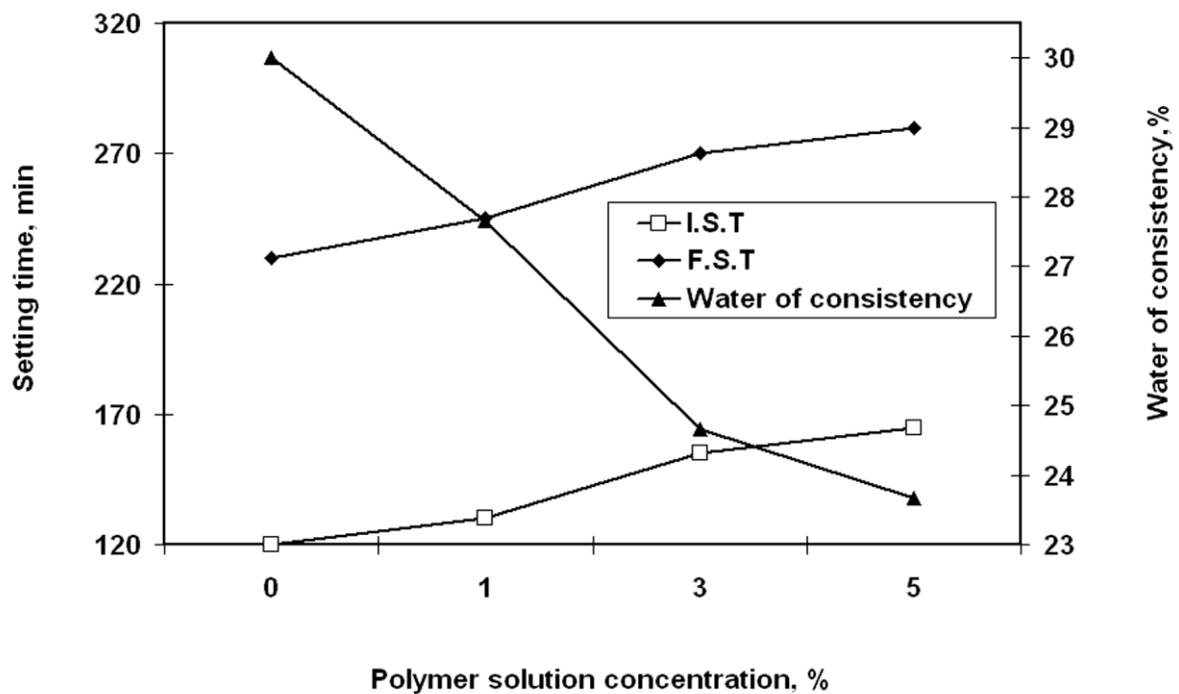


Figure 4: Water of consistency and setting times (initial and final) measurements of OPC premixed with 1, 3, and 5% of HBPAE.

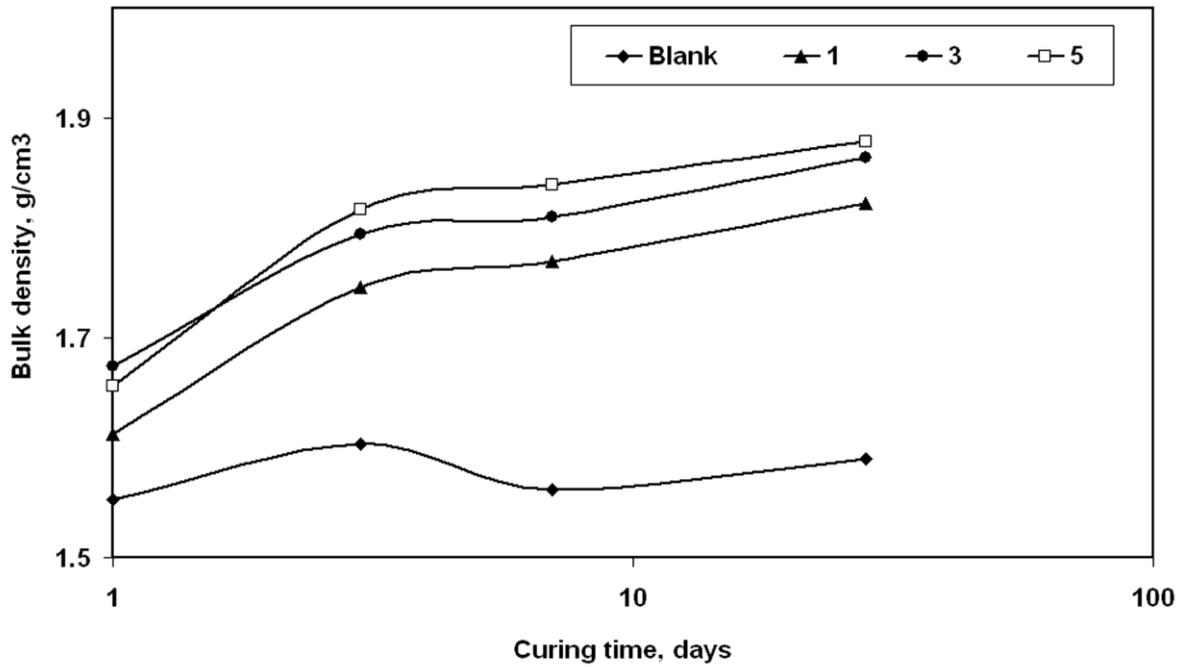


Figure 5: Bulk density of OPC cement pastes premixed with 1, 3 and 5 % HBPAE.

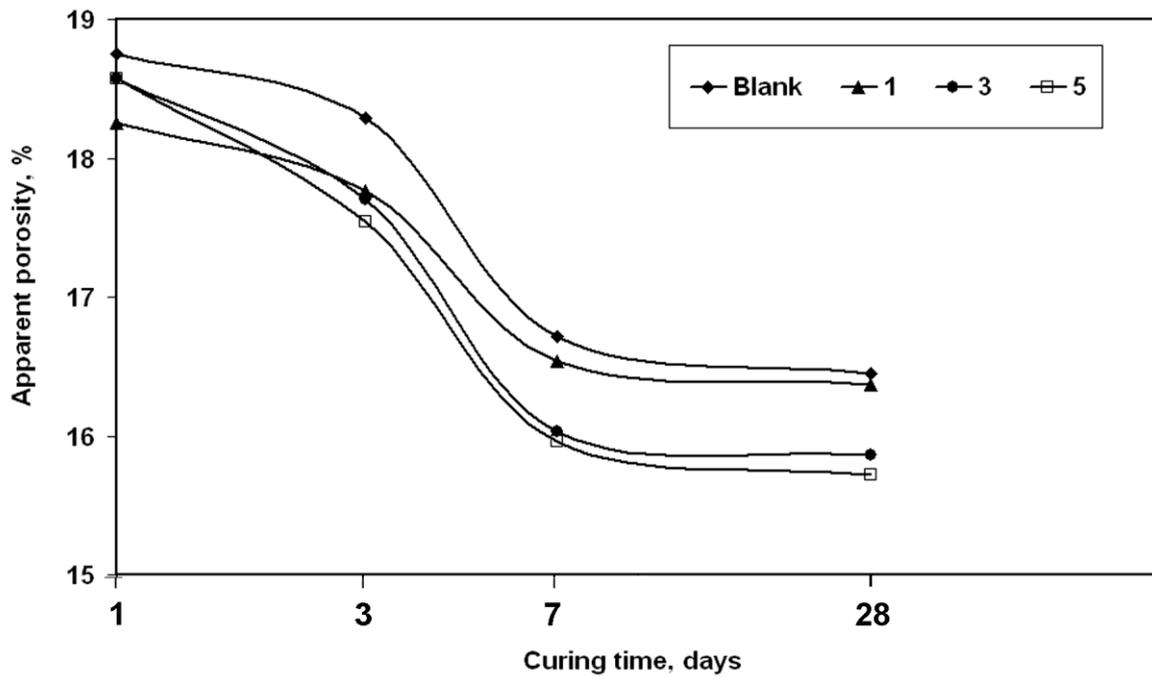


Figure 6: Apparent porosity of OPC cement pastes premixed with 1, 3 and 5 % HBPAE.

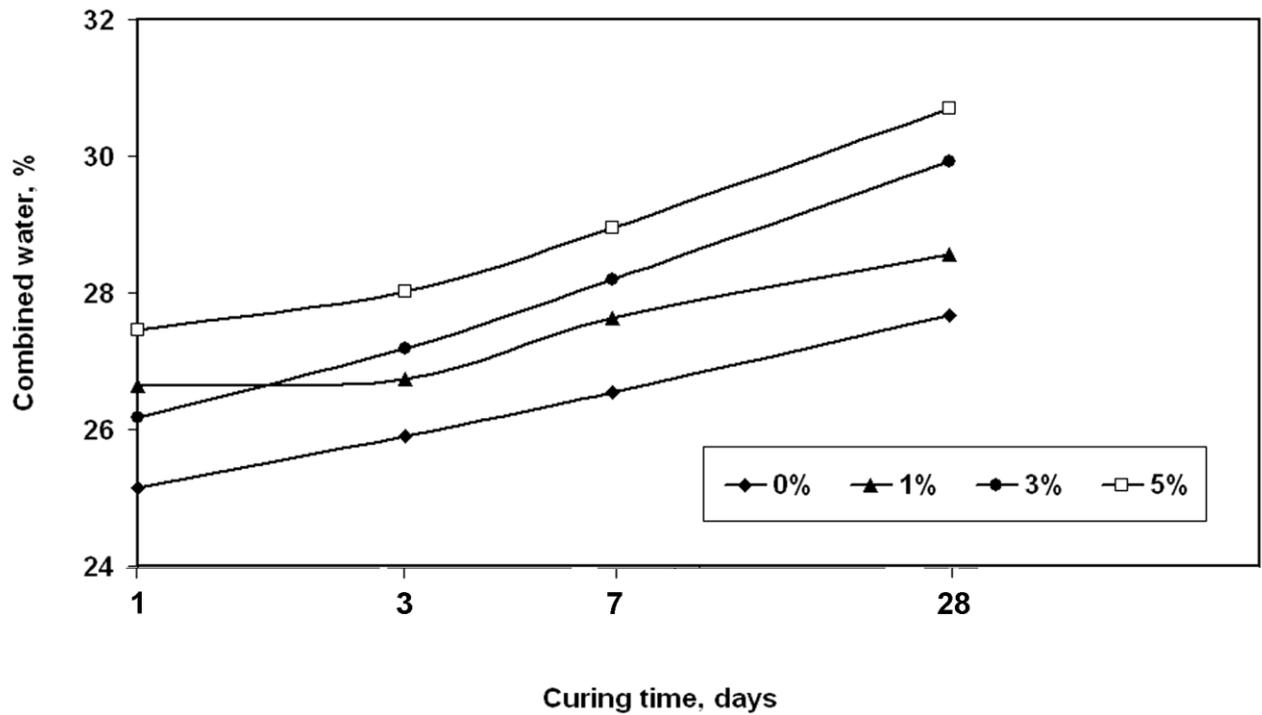


Figure 7: Chemically-combined water contents of OPC cement pastes premixed with 1, 3 and 5 % HBPAE.

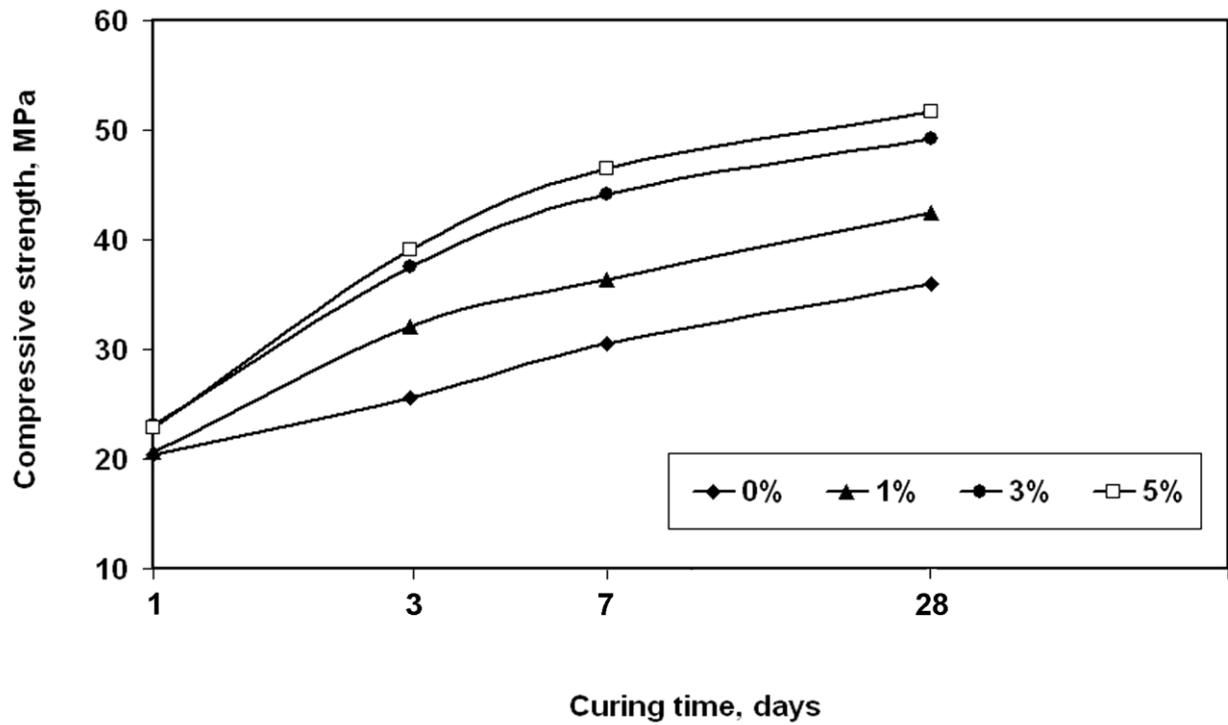


Figure 8: Compressive strength measurements of OPC pastes and those premixed with 1, 3, and 5% of HBPAE up to 28 days.