



Influence of Some Soluble Polymer Admixtures on the Hydration and Strength Development of Portland Cement Pastes

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Abstract: Hardening of cement pastes modified with 1 % polymers as methyl cellulose (MC), hydroxyl ethyl cellulose (HEC) and polyvinyl alcohol acetate (PVAA) comprises cement hydration and polymer effect on physicochemical and mechanical features of the modified cement pastes. Results showed that the water/cement ratio and setting times largely declined with polymers, where the values of water of consistency are 28.55, 25.69, 25.12 and 24.95 %, respectively. The initial setting times are 142, 134, 133 and 132, while the final setting times are 190, 185, 183 and 181 min., respectively. The incorporating of these polymers improves and enhances the bound water contents, bulk density, and compressive strength at 90 days curing, where the bound water contents are 13.26, 14.55, 14.73 and 15.29 %, the bulk density are 2.0369, 2.0413, 2.0421 and 2.0563 g/cm³ and the compressive strength are 62.23, 64.13, 65.25 and 68.71 MPa, respectively. The apparent porosity gradually declined as 22.12, 21.36, 20.84, and 18.82 %, respectively. The free lime contents are also diminished as 7.55, 6.18, 6.65 and 4.61 %, respectively. The rate of hydration was retarded at early ages of hydrating, while was improved and enhanced at the later ages. The obtained results are confirmed with Isothermal Calorimetry, thermal analysis, and FT-IR spectra. Despite the early reduction of the hydration reactions, a higher grade of hydration is observed after 90 days of hydration for the modified cement pastes according to the better dispersion of the cement grains during mixing and casting.

Keywords: Cement, polymer, admixture, setting, density, strength, microstructure, FTIR, SEM

1. Introduction

Sustainable binders and environmental protection are the key items having various ways to diminish the emission of CO₂↑. Ordinary Portland Cement (OPC) participates the energy consumption through all sectors of industry all over the world. Therefore, it is a threat to the worldwide sustainable growing targets [1]. The fresh mixtures properties could be improved by water-soluble polymers addition. Mortars modified with those polymers showed a higher level of water retention than Portland cement cements. Water molecules in the fresh mixtures could be fixed by the polymeric hydrophilic parts to eliminate its drying by evaporation into the surrounding porous material [2-11]. Water retaining capacity always creates a thickening and viscosity increasing behavior. Due to the excellent viscosity of cement pastes, lower free water is existed for bleeding as the segregation tendency diminishes. So, the suitable mortar homogeneity is obtained [12–20]. Therefore, the superior dispersion of carbon and steel fibers in the cement paste is occurred [21-29]. Despite the reduction of consistency of cement pastes or mortars in existence of soluble polymers, the facility to apply these fresh composites is markedly improved on account of the plasticizing, lubricating and air-entraining effects of the polymers. The dispersion action of polymers on the morphology and microstructure was extremely investigated [27-37], few knowledge is available on the influence of polymer dispersions. On contrary, polymers are being added in mixing water on a molecular scale and no surfactants are desired. Thereby, adding of little ratios of polymers, i.e., < 2 % affects

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all features of the hardened product [35-42]. On hardening, two operations could be happened, i.e., cement hydration and formation of polymer films. Though the concentrations of polymer are too low, these polymer films are formed in modified mortars with 1% of polyvinyl alcohol acetate (PVAA) and methylcellulose (MC). Large contribution of those films to the mechanical properties of mortars was illustrated [36-42]. Moreover, the hydration reactions could be affected with the incorporation of the polymers.

In the current research article, the influence of three various sorts of soluble polymers on the rate and degree of hydration, water consistency and setting times, density, porosity, and strength development was studied. These are polyvinyl alcohol acetate (PVAA), methylcellulose (MC) and hydroxyethyl cellulose (HEC). The obtained results were confirmed by Isothermal Calorimetry (ITC), Thermogravimetry (TGA) and Fourier Transform Infrared Spectroscopy (FTIR).

2. Experimental Methodology

2.1 Materials

Starting raw materials in the present article are Ordinary Portland cement (OPC Type I- CEM I 42,5R) with blaine surface area 3400 cm²/g. The OPC specimen was supplied by Sakkara cement factory, Giza, Egypt. Its commercial name is “Asmant El-Momtaz”, and its oxide composition as determined by X-ray fluorescence technique (XRF) is recorded in Table 1, while its mineralogical phase constitution [2,3] is shown in Table 2. Three various kinds of polymers are gradually added to the fresh mixtures: a polyvinyl alcohol-acetate (PVAA, Celvol 805 of Celanese Chemicals), which is a 87–89% hydrolyzed polyvinyl acetate, and two cellulose ethers, methyl cellulose (MC, Methocel A15-LV of the Dow Chemical Company) and hydroxyethyl cellulose (HEC, Cellosize QP40 of the Dow Chemical Company).

Table 1 - Composition of the used raw materials (mass %)

Material	Oxide										LOI	Total (%)
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	MnO	SO ₃	Na ₂ O	P ₂ O ₅	K ₂ O		
OPC	22.21	4.38	1.95	63.12	1.86	0.43	2.51	0.57	0.14	0.27	2.56	100

Table 2 - Mineralogical composition of the used OPC sample (mass %)

Material	Phase				Total (%)
	C ₃ S	β-C ₂ S	C ₃ A	C ₄ AF	
OPC	44.74	28.68	5.69	11.85	90.97

2.2 Preparation

The used polymers are soluble in water and its solubility is essentially conducted with its solution viscosity. The polymers are firstly dissolved in water before pouring onto the cement powder in the mixer based on the standard specifications using the concentrations that are proposed by the producer. All these polymer concentrations are transparent at room temperature. Cement pastes are placed in tapped containers till the time of testing. Specimens are taken from the center of the pastes. The free water must be eliminated by drying. Then, it is being crushed and well ground to fine or nanoparticles. The cement pastes are dried for two hours. Specimens are then put in an Alpha 1-2 LD Martin Christ type freeze-dryer without pre-freezing. Samples were placed inside round bottom flasks and then are connected to a vacuum system consisting of a vacuum room that permits the use of a vacuum of 2.5×10⁻² mbar. Water extracted is gathered in an ice condenser at a temperature of -62 °C. The exposure to a high vacuum, made the drying process to begin instantly at a high temperature. A big quantity of heat is always required for water evaporation, and then it is extracted from the environment. Consequently, the samples are quickly cooled followed by the freezing of water. Then, the hydration is ceased in few minutes.

Before casting, all molds were oiled with a thin film of motor engine oil to simplify the cubes release from the molds during its demolding. A certain percentage of 1 % methyl cellulose (MC), hydroxyl Ethyl cellulose (HEC) and polyvinyl alcohol acetate (PVAA) admixtures (Fig. 1) must be added to the cement with the mixing water during casting of cement pastes to improve the various cement pastes and to prevent the collection of the fine particles of cement.

To obtain homogenous powders, a suitable laboratory mixer was used for bending the cement batches. Standard water of consistency [43] and setting time [44] of cement pastes firstly were directly determined using Vicat Apparatus (Fig. 2).

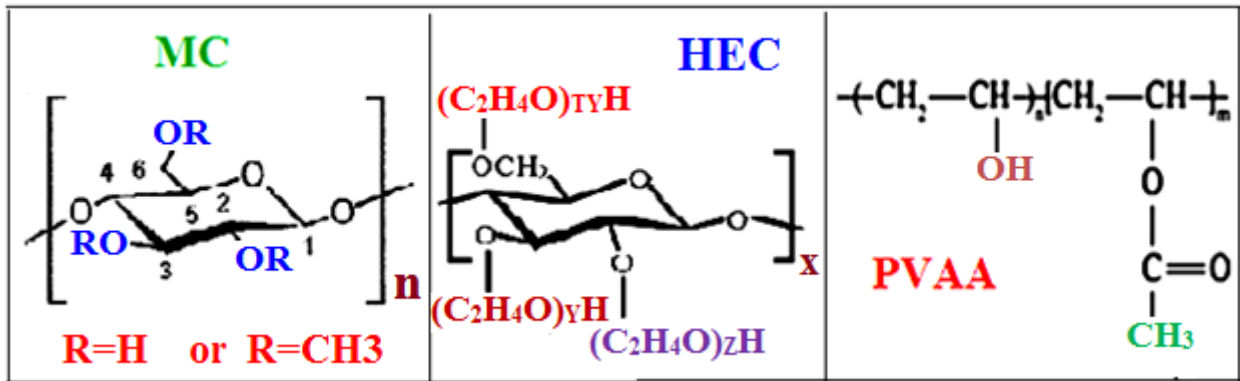


Fig. 1 - Chemical formula of MC, HEC and PVAA polymers

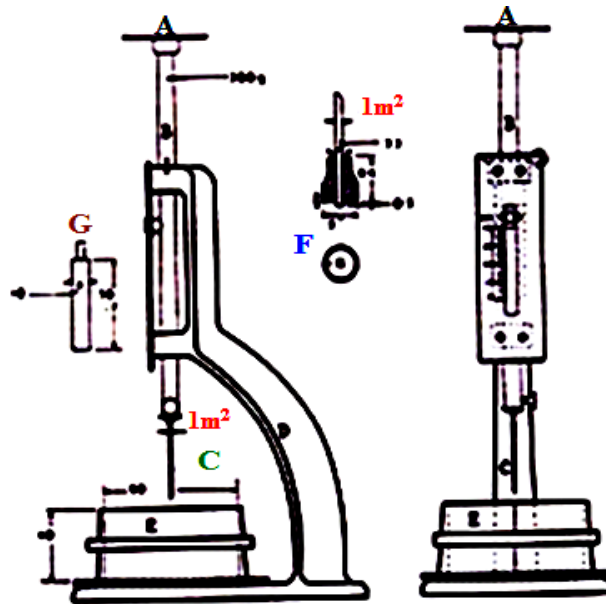


Fig. 2 - Vicat Apparatus for water consistency and setting times

During casting, the correct w/c-ratio was added to the dry cement powder inside the mixer. The mixture was let to run for five minutes to obtain homogenous pastes. One-inch stainless steel cube molds (2.5 x 2.5 x 2.5 cm³) was used. The molds were filled with the premixed cement pastes to the top hesitating the molds for five minutes to eliminate all air bubbles from the cement pastes, Surfaces of moulds were smoothed using a suitable spatula. After casting, they were covered with a wet sheet for 24 hours to avoid moisture loss. The molds were kept in a humidity cabinet for 24 hours under 100 % RH and room temperature 23 ± 1 °C. In the next day, it demolded and soon cured under water till the time of testing at 1, 3, 7, 28 and 90 days.

At each hydrating interval, the bulk density (BD), apparent porosity (AP) and compressive strength (CS) [2-5,7-10,14,18] of the hardened cement pastes were measured.

Then, about 10 grams of the broken specimens from measuring of compressive strength were first well ground, dried at 105°C for 30 min. and then were placed in a solution mixture of 1:1 methanol: acetone to stop the hydration [47-51]. The chemically combined water content was performed based on ignition loss at 1000 °C for 30 minutes. One gram of the sample was placed inside a crucible and first dried at 105°C for 24 hours, and then the crucibles were placed into a furnace [51-54]. The free lime content (FLn) of the hydrated samples pre-dried at 105°C for 24 hours was also determined. 0.5 gram sample + 40 ml ethylene glycol → heating to about 20 minutes without boiling, and 1–2 drops of pH indicator were added to the filtrate. Then, titrated against freshly prepared 0.1N HCl until the pink colour disappeared. 0.1 N HCl was prepared. The heating and titration were repeated several times until the pink colour did not appear on heating [4,55-57].

To study the thermal analysis, isothermal calorimetry (IC) was carried out on a TA Instruments TAM Air Calorimeter at 20 °C. Thermogravimetry (TGA) for some selected samples was performed using a Netzsch STA 409 PC. Samples were fired from the room temperature to 1000 °C with a heating rate of 10 °C/min in a N₂ atmosphere (60 ml/min). Infrared Spectroscopy (FT-IR) was carried out by Perkin Elmer 1725× spectrometer. Powdered samples are mixed with KBr and pressed into pellets, where the analysis was done in the frequency range of 400–4000 cm⁻¹.

3. Results and Discussion

3.1 Water of Consistency and Setting Times

The water of consistency (WC) as well as initial and final setting times (IST and FST) of the pure OPC (P0) and polymer modified cement pastes with 1 % MC, 1 % HEC and 1 % PVAA was presented versus polymer modified cement in Fig. 3. The WC of the pure OPC (P0) is 28.55 %, which is sharply decreased with the polymer modified cement. The sharply lower amount of WC for the polymer modified pastes than for the unmodified OPC pastes is mainly due to the adsorption of the polymers on the nucleation sites, that stops the absorption of excess water [4,56,58-63]. Also, the IST and FST diminished with polymer modified cement pastes if compared with those of the blank (P0). This is principally due to the same factor as in WC, and this hinders or stops the absorption of excess water as mentioned above [4,7,59-63].

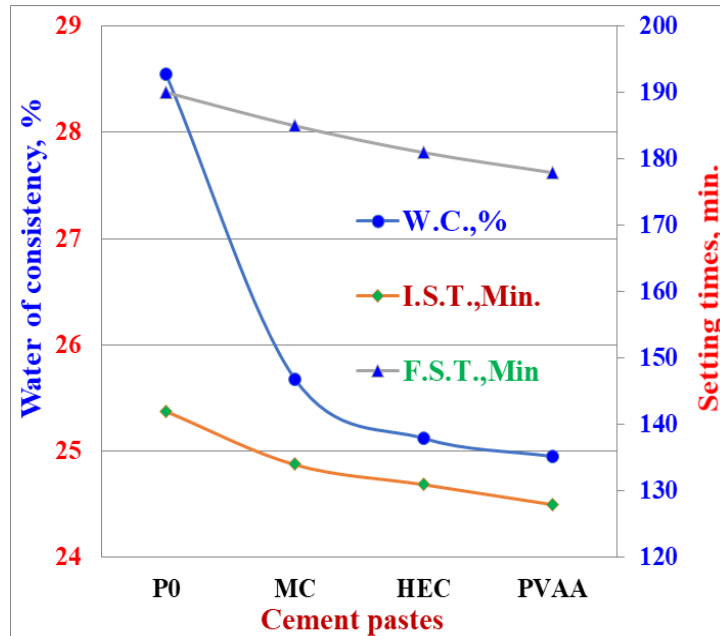


Fig. 3 - Water of consistency and setting times of the unmodified (P0) and polymer modified cement pastes with 1 % MC, 1 % HEC and 1 % PVAA

3.2 Chemically-bound Water Contents

As the bound water content is a very important indicator for the degree of hydration, the chemically-bound water contents of the unmodified pure OPC (P0) and polymer modified cement pastes with 1 % MC, 1 % HEC and 1 % PVAA cement pastes, respectively which are hydrated from 6 hours up to 90 days are graphically drawn versus the hydration times in Fig. 4. Thus, the bound water contents of all cement pastes improved and enhanced as the hydration time progressed from 6 hours up to 90 days. It is mainly contributed to the normal hydration of the major cement phases, particularly C_3S , C_3A and C_4AF at early ages up to 7 days, except that of $\beta-C_2S$ which always hydrates at older stages from 28 days up to 90 days [2,3,47,50,55]. The bound water contents slightly decreased with the existence of polymers at the early hours of hydration compared to the pure OPC pastes (P0), but during older periods, the bound water contents increased and are being over the blank one, i.e., the bound water contents of the polymer modified cement pastes are larger at 90 days than those of the blank cement pastes (P0). It is primarily due to the activation effect by the polymers and the rate of high dispersion [48-50].

The initial retardation of hydration at the first hours up to 24 hours is evidently clear by the formation of the bound water (Fig. 4). Hence, at 90 days, a slight large quantity of bound water was obtained for cement pastes modified with polymer. It could be contributed to a suitable level of particles dispersion of the cement during mixing [6,8,16,19-21,23,24], that produces a higher rate of hydration, i.e., the water-soluble polymers were also reported to enhance the rate of hydration according to its water retaining characteristics [20,25,26]. The bound water contents at 90 days of the OPC modified with PVAA polymer achieved the highest when compared with those of other polymers, or even the blank.

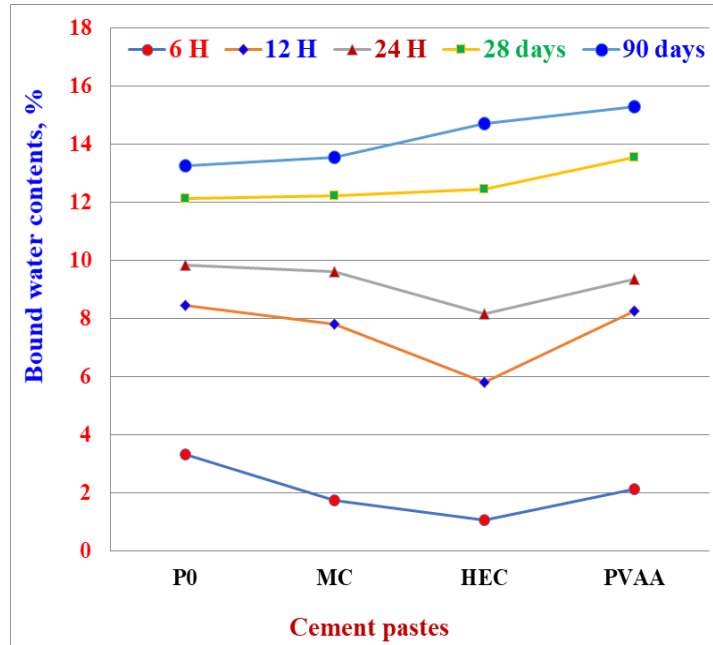


Fig. 4 - Chemically-bound water contents of unmodified (P0) and polymer modified cement pastes with 1 % MC, 1 % HEC and 1 % PVAA hydrated from 6 hours up to 90 days

3.3 Free Lime Content

Free lime contents of the unmodified pure OPC (P0) and polymer modified cement pastes with 1 % MC, 1 % HEC and 1 % PVAA cement pastes, respectively which are hydrated from 6 hours up to 90 days are graphically drawn versus the hydration times in Fig. 5. On this basis, the free lime contents of the blank (P0) and other cements modified with polymer were gradually improved and enhanced with the hydration times up to 90 days [2,3] due to the normal hydration of the major calcium silicate phases (C_3S and $\beta-C_2S$) of the cement.

But, with the polymer modified cements, the free lime contents little declined when compared with the blank (P0). Continual increase of free lime content is principally contributed to the normal hydration of the main silicate phases of the cement (C_3S and $\beta-C_2S$), while the decrease is contributed to the activation effect of the polymers [48-51, 59-65]. The slight decrease of free lime contents for the polymer modified pastes if compared with the unmodified pastes at all stages (Fig. 5) is mainly due to the adsorption of the polymers on the nucleation sites of $Ca(OH)_2$. This stops the growing of crystals [59-63].

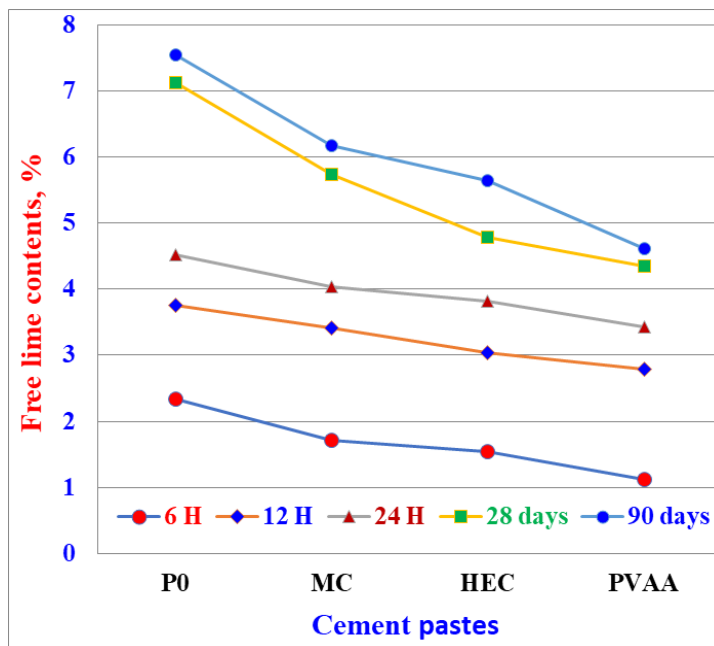


Fig. 5 - Free lime contents of unmodified (P0) and polymer modified cement pastes with 1 % MC, 1 % HEC and 1 % PVAA hydrated from 6 hours up to 90 days

3.4 Bulk Density and Apparent Porosity

Fig. 6 and Fig. 7 show the results of bulk density (BD) and apparent porosity (AP) of the unmodified pure OPC (P0) and polymer modified cement pastes with 1 % MC, 1 % HEC and 1 % PVAA cement pastes, respectively which are hydrated from 6 hours up to 90 days. The BD of cement pastes improved and enhanced as the hydration time proceeded up to 90 days, whereas the AP declined. It is essentially attributed to as soon as the dry cement powder becomes in contact with water, the hydration process starts to produce CSH and/or CAH, which at once precipitated and collected in the pore volume of the specimens. This decreased the AP and a slight increase in the BD [2,3]. When the hydration time progresses till 90 days, the formed hydration products increased too according to the activation effect of the modified polymers [47,50].

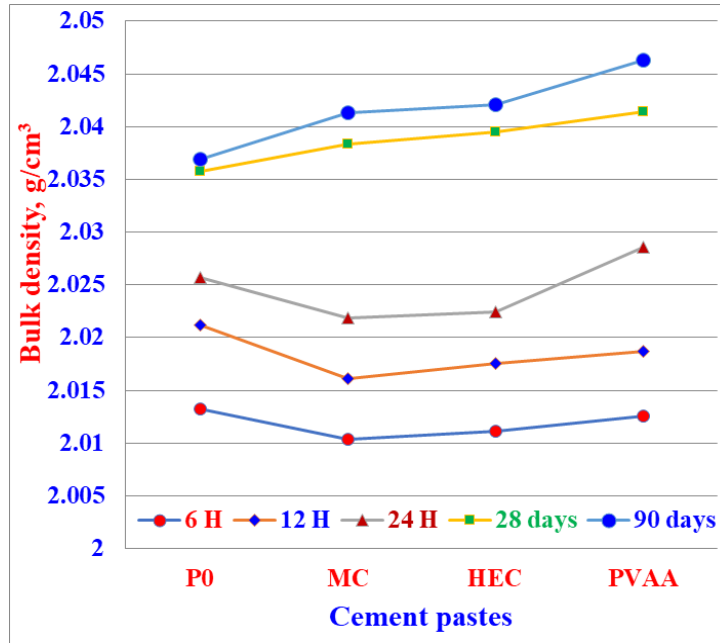


Fig. 6 - Bulk density of unmodified (P0) and polymer modified cement pastes with 1 % MC, 1 % HEC and 1 % PVAA hydrated from 6 hours up to 90 days

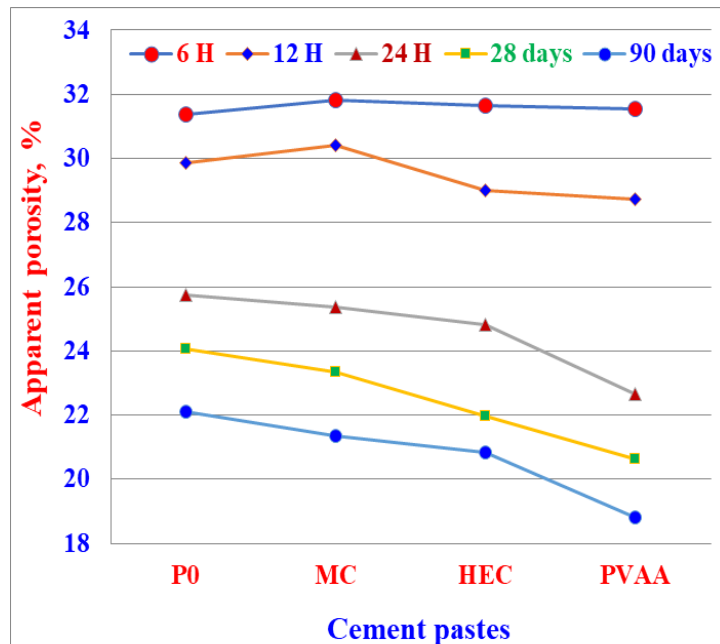


Fig. 7 - Apparent porosity of unmodified (P0) and polymer modified cement pastes with 1 % MC, 1 % HEC and 1 % PVAA hydrated from 6 hours up to 90 days

The BD of the modified cements with MC or HEC slightly decreased only during the first 24 hours of hydration, but then improved and enhanced at 28 up to 90 days, while the opposite was occurred with the AP, i.e., the bulk density is

little lowered, whereas the apparent porosity becomes higher than those of the of the blank (P0). The bulk density of the modified cement premixed with PVAA was higher than those mixed with MC and HEC, or even the control (P0). This is evidently attributed to that PVAA improves the workability of cement pastes faster and more than MC or HEC due to the degree of dispersion and workability by the polymers [2,3,50]. Hence, the incorporation of these modified polymers improves the dispersibility and workability of cement pastes, i.e., they are so beneficial to cement that it helps the hydration process to a large extent. The cement pastes modified by PVAA achieved the highest BD values at the older times of hydration, while the AP was the lowest (Fig. 6 and Fig. 7).

3.5 Compressive Strength

Water/cement ratio of cement pastes, mortars or concretes influences the workability to a large extent. It is in turn affects the strength developments at all hydrating times, i.e., the lower w/c-ratio is the higher degree of workability which often followed by increasing the mechanical properties of the hardened cement pastes, while the higher level of the w/c rate is the lower indication for of workability [2,3]. The compressive strength (CS) of the unmodified pure OPC (P0) and polymer modified cement pastes with 1 % MC, 1 % HEC and 1 % PVAA cement pastes, respectively which are hydrated from 6 hours up to 90 days is represented as function of hydration times in Fig. 8. As the hydration periods proceeded from 6 hours onwards, the CS gradually improved and increased. It is essentially due to the production of hydration products like CSH and/or CASH which deposited into the pore structure of the hardened cement samples leading to the decrease of the pore volume (matrix) and the improving of the bulk density. This raised the degree of compaction of specimens. Good dispersion by polymers and good compaction during casting also increased the level of compaction. In turn, it is positively reflected on the CS. Therefore, the values of compressive strength improved and enhanced [11,66]. The CS also improved and enhanced with the premixing by the modified polymers. This is essentially contributed to the dispersibility action of the used polymers which improves the workability of the fresh cement pastes [2,3,50]. The cement pastes modified by PVAA exhibited the highest results of CS at the older times of hydration (28-90 days), while the other two polymers recorded lower CS values than blank (P0) particularly during the first times of hydration (Fig. 8). The gradual precipitation of hydration products (CSH) due to the hydration of the major phases of the cement strengthened the cement structures. The cement pastes modified with 1 % PVAA achieved the highest values of CS, whereas those premixed with 1 % MC exhibited the lowest CS values. Hence, not only did the modified polymers enhance the properties of the OPC, but also it is very important for the building construction [63-66].

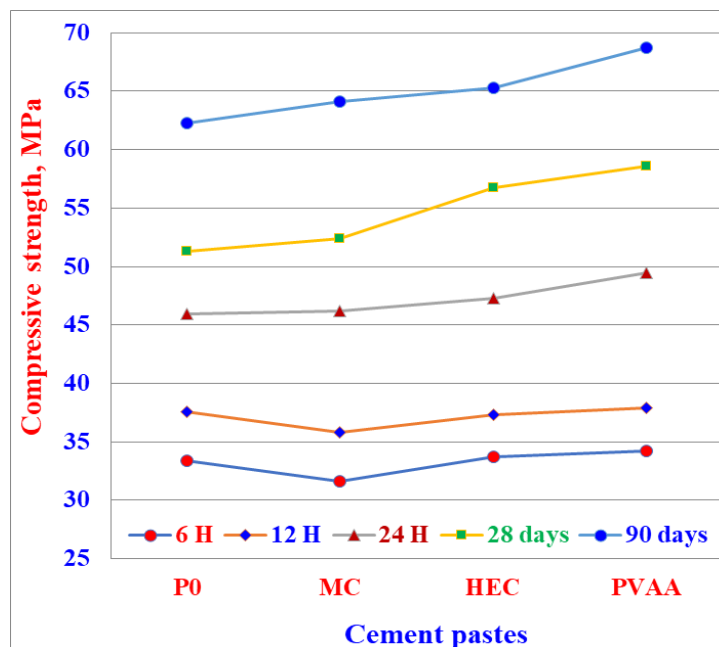


Fig. 8 - Compressive strength of unmodified (P0) and polymer modified cement pastes with 1 % MC, 1 % HEC and 1 % PVAA hydrated from 6 hours up to 90 days

3.6 Isothermal Calorimetry

The heat evolution of the unmodified pure OPC (P0) and polymer modified cement pastes with 1 % MC, 1 % HEC and 1 % PVAA cement pastes, respectively which are hydrated from 6 hours up to 90 days, which was performed with the Isothermal Calorimetry Apparatus (ITCA) is shown in Fig. 9. The beginning acceleration rate of hydration was delayed with ~30 min in the PVAA and MC modified cements, but with > 5 hours in the HEC modified cement pastes. Where the creation or motionless interval was continued, the rate of the accompanied hydration reactions was slowed

down. It could be demonstrated with the lower data of the highest liberation of heat, whereas in the isothermal calorimetric curves of polymer modified cements, wider exothermal peaks are occurred [67].

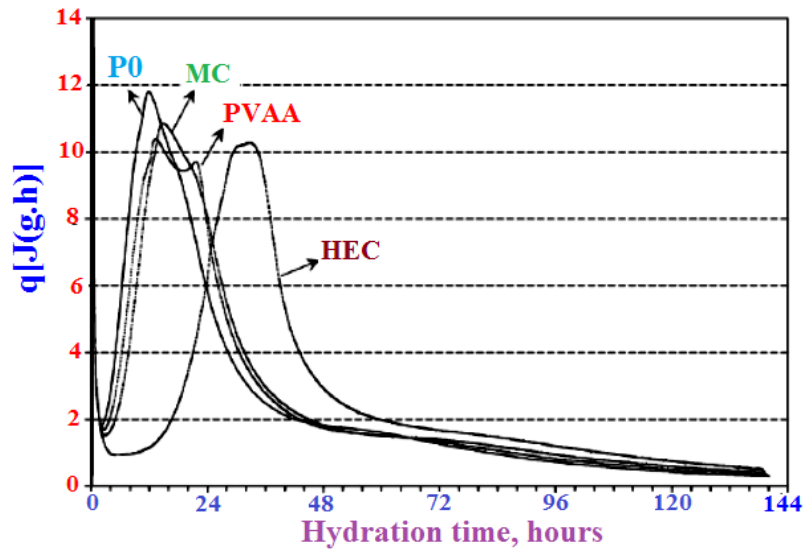


Fig. 9 - Rate of heat evolution at 20 °C for unmodified and 1 % MC, 1 % HEC and 1 % PVAA cement pastes

3.7 Thermal Gravimetry Analysis (TGA)

Graphs of the thermal gravimetry analyses (TGA) at the first day of hydration for the pure cement (A), 1 % PVAA (B), 1 % MC (C) and 1 % HEC (D) are represented in Figures 10-13, respectively. At the temperature ~125 °C, gypsum plaster often dehydrates to generate a slightly bloc loss in the DTG curves of the unhydrate early age cement. At ~400 °C, a small bloc loss was detected [Ca (OH)₂]. At ~700 °C, another mass loss (CaCO₃) was observed. This is mainly due to that the hydration and carbonation were partially occurred on storage. At early times of hydration, the DTG curves nearly remained without any change. At ~100 °C, a large peak was formed after six hours of hydration. It is due to the dehydration of CSH and it increased as the hydration time proceeded. Similarly, gypsum was exploited in the formation of ettringite, accompanying by a decrease in the intensity of the peak at ~125 °C. Ettringite phase did not clearly identify. This may be attributed to the overlapping with the CSH peak [11]. The free lime, Ca (OH)₂ started to produce. The temperature where the decomposition of the smaller crystals of Ca (OH)₂ formed on storing are much lower than those of the relatively large crystals that formed from the hydration of cement phases [9]. The formed carbonate phases could be decomposed at the temperature range ~ 600-800 °C (Fig. 10 and Fig. 11).

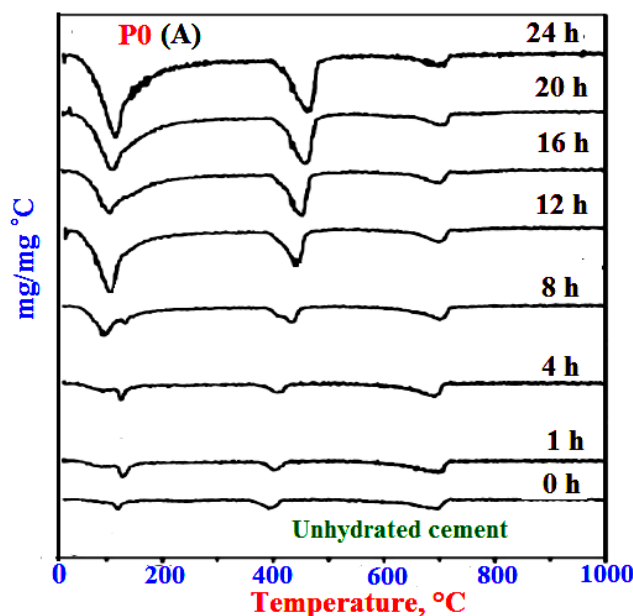


Fig. 10 - TGA analysis of the unhydrated cement (A) during the first 24 hours of hydration

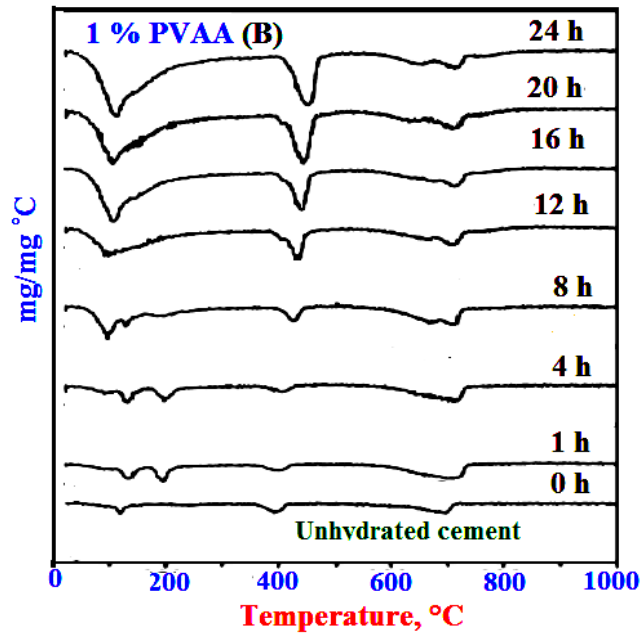


Fig. 11 - TGA analysis of the modified cement pastes with 1 % of PVAA (B) polymer during the first 24 hours of hydration

With the cement pastes modified by MC polymer (Fig. 12), the hydration products tended to be formed quickly after 8 hours, whereas with HEC polymer (Figure 13), nearly there is no any hydration products were produced, However, the formation of CSH and Ca (OH)₂ was also rather slow. At the temperature range ~600–800 °C, a double peak was detected in the DTG curves of the modified cements with polymers, when carbonates (or carbonate-like phases) decomposed. At high temperatures, the DTG curves of the unmodified cement only show a single peak.

At early ages of hydration, extra peaks are occurred at ~200 °C (PVAA), ~300 °C (MC) and ~260 °C (HEC). This temperature is not match to the temperature at which the neat polymer solutions (320 °C (PVAA), 355 °C (MC) and 305 °C (HEC)) were decomposed. Extra peaks started to hide completely when the hydration was quickly happened and the CSH and Ca (OH)₂ began to appear. After six hours, a slight peak of CSH is only existed in the DTG curves of the PVAA cement modified with polymers.

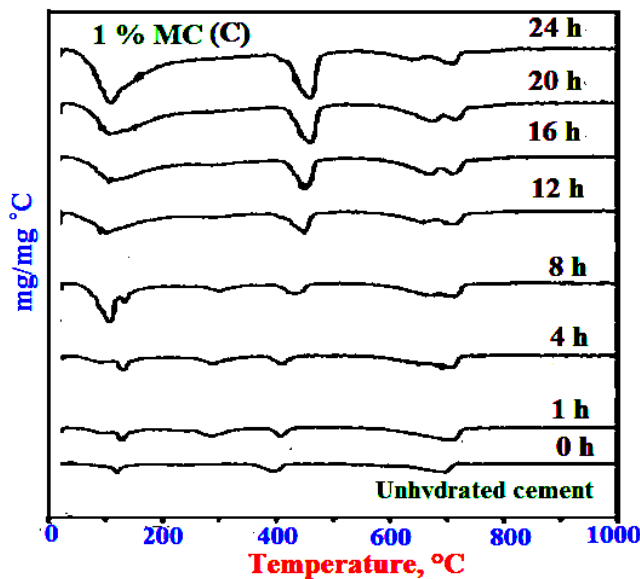


Fig. 12 - TGA analysis of the modified cement pastes with 1 % MC (C) polymer during the first 24 hours of hydration

At older ages, the analysis did not reveal any new products. The quantity of combined water and the Ca (OH)₂ contents of pure and modified cements after 4, 12 and 24 hours, and 90 days of hydration are graphically plotted in Fig. 13. At the first times, smaller amounts of combined water contents were occurred for all cement modified with polymers.

At the end of the first day, the combined water contents for blank and PVAA and MC (Fig. 11 and Fig. 12) modified cement pastes respectively were exactly 56.78 %, 50.65 % and 47.81 % of the combined water after 90 days, whilst a smaller value (16.69 %) was determined for the HEC modified cement pastes. However, after 90 days, cements modified with polymers produce higher quantities of combined water contents. It could be finally concluded that the free lime content is always the highest for the unmodified cements, while the polymer-modified cement pastes exhibited lower values.

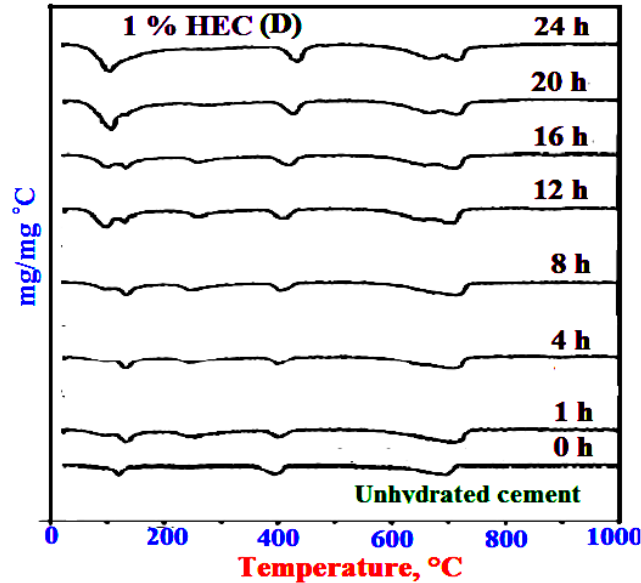


Fig. 13 - TGA analysis of the modified cement pastes with 1 % HEC (D) polymer during the first 24 hours of hydration

3.8 FT-IR Spectroscopy

FT-IR spectra of the plain unhydrated OPC (A), pure hydrated OPC (B) and polymer modified OPC pastes with 1 % PVAA (C), 1 % MC (D) and 1 % HEC (E) after 8 hours of hydration is shown in Fig. 14. During the wave number between 3100–3700 cm^{-1} , the stretching vibration bands of water, H_2O and free lime, $\text{Ca}(\text{OH})_2$ could be obtained. The characterized spectrum of H_2O is also existed in the unhydrated pastes due to the high hygroscopic and free water contents. The intensity of the peak related to the OH^- band, associated with the Ca^{2+} (Free lime) at 3642 cm^{-1} is slightly increased if it is compared with the unhydrated pastes. The stretching vibration bands of S–O are formed in the range 1100 and 1170 cm^{-1} .

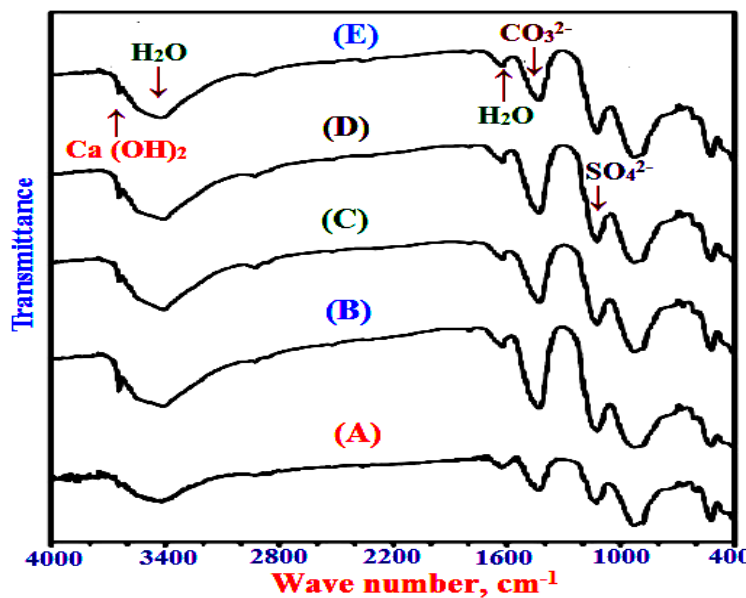


Fig. 14 - FT-IR spectra of the pure unhydrated OPC (A), hydrated OPC (B), 1 % PVAA (C), 1 % MC (D) and 1 % HEC (E) after 8 hours of hydration

In the unhydrated cement powders, some bands are exhibited between 1106 and 1152 cm^{-1} . After 6 hours of hydration, the ettringite phase, $\text{C}_3\text{A}\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$ is early formed at 1121-1124 cm^{-1} . A slight increase in the intensity of this peak is shown in the unmodified paste. As the hydration progressed, a shift of the Si-O asymmetric stretching vibration (ν_3) is also characterized at 926 to 970 cm^{-1} . This may be due to the polymerization of the SiO_4^{2-} units during the formation of CSH. So, after 6 hours, no silicate phases resulting from were occurred. At 1428 cm^{-1} , 878 cm^{-1} and 736 cm^{-1} , CO_3^{2-} were described by a $\nu_2 + \nu_3$ band, a ν_4 band and a ν_4 shoulder, respectively Bands, supported with the same polymer could not be noted due not only to the very little contents of polymer, but also to the partial overlapping with the bands of both hydrated and unhydrated phases.

3.9 General Discussion

Incorporation of polymers in cement pastes or concretes affects the rate, degree, nature, composition, and quantity of hydration products of the hydrated cement phases. In addition, the microstructure and morphology of the formed crystals are different. Measuring the w/c ratio, initial and final setting times, isothermal calorimetry (Fig. 9), thermal analysis (Fig. 10 to Fig. 13) and FT-IR (Fig. 14) showed a retardation action of the hydration process (Fig. 3). The reactions due to hydration of the cements modified with HEC are significantly reduced. Soluble polymers prolong the creation interval and could be interfered into the early reactions during hydration process. This retardation action in the existence of some organic compounds could be interpreted as adsorption [13,68], nucleation sites [14], controlling rate of complex alkalis [15,16, 69,70], interfering into the protective membrane surrounding the cement grains [17,26] and decreasing of ion mobility [18,69], i.e. may be, not one mechanism is sufficient to elucidate all points of retardation, but a complex of interactions could be occurred [15,70]. Polymers favored and tended to adsorb on the lateral surfaces of the unhydrated cement grains to prevent the attack by water [13,36]. Soluble polymers contain many (OH^-) ions to enable them to form (H^+) bonds with (O^{2-}) ions on the lateral edges of the anhydrous compounds [17,20]. A reduced polyvinyl alcohol (PVA) and polyethylene oxide (PEO) adsorption on SiO_2 is however noted at higher pH values. It is due to the lower surface hydroxyl groups (OH^-) decreasing the number of specific (H^+) bonding sites [21-23]. Cellulose ethers were strongly adsorbed on C_3S and supported with the delayed hydration of this phase [23,71].

In addition, the adsorption on both hydrating compounds and unhydrated particles could be formed. Adsorption of polymers on the $\text{Ca}(\text{OH})_2$ and CSH nucleation sites can delay and hinder the growing of those phases [15,23]. In Fig. 12, the bridges of MC in between the layers of $\text{Ca}(\text{OH})_2$ crystals were noticed indicating the strong affinity of the polymers. Metal ions are too complex in the pore structure by soluble polymers is another assumption, where the ion solubility enhances the early deposition of CSH which was illuminated. So, much more cement compounds could be dissolved before hydration barriers are set up [15,23,72]. Due to the high Ca^{2+} ions concentration, the quantity of polymers should be high to have an important action on the Ca^{2+} equilibrium. Complex aluminate, ferrite or silicate ions may have a high effect due to its much lower concentration in the solution [15,73]. Retardation of the hydration process could be attributed to the lower ion mobility in the pore water [18,73]. Soluble polymers raised the viscosity of mixing water and restricted the movement of ions, whereas the rate of dissolving of the unhydrated phases and the deposition of CSH decreased. Polymer solution having the highest viscosity (HEC solution) has the strongest influence on the degree of hydration, while MC and PVAA having the lower viscosity solutions. It is finally concluded that these polymers could be strengthened the cement matrix and improved the internal cohesion between the various particles.

4. Conclusion

The following conclusions can be made:

- 1- The water/cement ratio, initial and final setting times are decreased with the incorporation of polymers, where PVAA polymer recorded the lowest values.
- 2- The contents of chemically-combined water, bulk density and compressive strength are lower at early times of hydration, but are higher at older ages, where PVAA achieved the best results at all hydration times when compared with other polymers or even the blank.
- 3- The apparent porosity is decreased with the curing times, while the free lime contents increased.
- 4- Existence of 1 % polymers affects the hydration reactions of the cement. A little reduction in the level of hydration of cements modified with PVAA and MC is noted at the early times of hydration, whereas the hydration of the modified cement by HEC is largely reduced. In spite of the reduction effect at early times, the bound water content of the polymer modified cements is more than the blank (P0) after 90 days. This is essentially contributed to the good dispersion of the cement grains during mixing.
- 5- Measured $\text{Ca}(\text{OH})_2$ content is slightly lower after mixing with polymer. On account of the reactions among polymers and hydration products, the true content of $\text{Ca}(\text{OH})_2$ could be underestimated in presence of polymers.
- 6- The FT-IR analysis showed that there are no new phases are formed, but at early times new phases are noted in the DTG thermographs of cements modified with polymers.
- 7- The intensity of the $\text{Ca}(\text{OH})_2$ crystals was influenced by water-soluble polymers. The increment of MC produces a layer of $\text{Ca}(\text{OH})_2$ deposited which arranged in stack without distortion.

- 8- Bridges-based polymer are existed among Ca (OH)₂ crystals, which are doing as a sort of a bonding factor among the various layers. Moreover, it improves and enhances the interparticle bonding forming a better structure.
- 9- The internal cohesion of bulk cements was enhanced and increased due to the incorporation of water-soluble polymers. This was reflected positively on the mechanical properties of the bulk pastes resulting in a noticeable lower creation of lower cracks.

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