Poly (methacrylic acid) Sodium Salt Interaction with Hydrating Portland Cement

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Abstract

Portland cement is the most important hydraulic binder in the construction industry. The addition of a small amount of polymer to a cement mix changes the hydraulic properties of the cement significantly. When poly (methacrylic acid) sodium salt - a polymer - is added in small amounts, the properties of the hydrating cement paste are changed considerably. The polymer increases the workability of the cement paste. The heat evolution profile has shown that the polymer retards the hydration and that the retardation increases with polymer concentration. Total heat evolved during hydration decreased with polymer concentration. The polymer improved the pore structure by decreasing the porosity and as a result the compressive strength was increased. Differential scanning calorimetric and IR spectroscopic studies have shown that a chemical and physical interaction occurs between the polymer and hydrating cement. The mechanism of hydration of the cement in the presence of poly (methacrylic acid) sodium salt is discussed.

1 Introduction

Portland cement (OPC) based materials are dominant in the construction industry. The addition of a small amount of polymer to a cement mix can change the properties of the resulting materials significantly [1-3]. Increase in aggregate-cement bond strength increases the strength of the concrete and the polymers are known to increase the bond strength [4,5]. Apart from bond strengths, many other properties such as workability, porosity and mechanical properties are changed in the presence of polymers [6-9]. In order to understand the role of polymer in cement based materials, it is essential to know the nature of the interaction between the cement and the polymer. According to other investigations, there are controversies regarding the nature of interaction. Some think that only physical interactions occur in the system and the others think that chemical interactions also occur [10-12]. However different polymers may interact in different ways.
Therefore the purpose of this article is to investigate the role of poly (methacrylic acid) sodium salt during the hydration of OPC.

2 Experimental

2.1 Materials

A commercial OPC Typ CEM I 32.5 R acc. DIN EN 197-1 [18] was used for the hydration studies (SiO_2 = 22.28 wt%; Al_2O_3 = 3.78 wt%; Fe_2O_3 = 1.35 wt%; CaO = 65.60 wt%; MgO = 0.82 wt%; K_2O = 0.61 wt%; Na_2O = 0.16 wt%; SO_3 = 3.16 wt%; LOI = 1.80 wt%; Blaine surface area = 2,615 cm²/g). Poly (methacrylic acid) sodium salt (Sigma-Aldrich) (molecular weight M_w = 6500 g/mol, M_n = 4000) in 30 wt% water solution was used as a polymer. The basic structural unit of the polymer is given in Fig. 1. Different amounts of the 30 wt% solution of the polymer added to cement were used during the hydration studies as shown in Table 1.

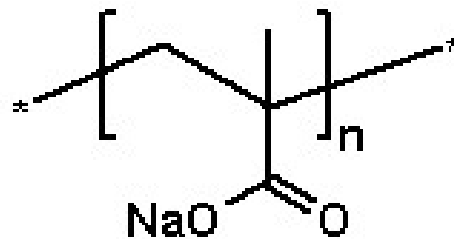In this article the word "polymer" refers to the poly (methacrylic acid) sodium salt.

Fig. 1 Structural unit of poly (methacrylic acid) sodium salt

Table 1 Concentration of used polymer

conc. of polymer [wt%]	water/solid = 1.0 [wt%] of solid polymer per 100 g of OPC	water/solid = 0.5 [wt%] of solid polymer per 100 g of OPC
0.30	0.30	0.150
0.75	0.75	0.375
1.50	1.50	0.750
3.00	3.00	1.500

2.2 Methods

2.2.1 Heat evolution measurements

In order to determine the heat evolution profile and the total heat evolved during the hydration of OPC in the presence of polymer an isothermal heat flow calorimeter (C3, type TAM Air) was used. The instrument consists of 8 measuring cells contained in an aluminum block in which glass vials of a given specification can be placed. OPC was weighed in each glass vial

and mixed with water or polymer solution to have a water/solid ratio of one (w/s = 1.0) and vibrated for 30 s to produce a homogeneous mixing. This prepared sample was immediately placed into the calorimeter chamber (< 30 s). Quartz powder mixed with water (quartz/water = 1.0) in a glass vial was used to establish the baseline. The experiments were performed at $20^{o}C$ for 7 days, i.e. till the heat evolution became very low. Experiments were performed in the presence of 0, 0.3, 0.75 and 1.5 wt% polymer (Table 1) with reference to OPC.

2.2.2 Preparation of hydrated samples

In order to get information about the interaction between the polymer and the hydrating OPC, hydration was allowed to occur in the presence of higher concentrations of the polymer (3.0 wt%). OPC was weighed and mixed in polythene bags and water or 3.0 wt% polymer solution was added (w/s = 0.5). The air from inside the bags was removed; the bags were sealed and kept at $20^{o}C$. The hydration was stopped at different time intervals by using isopropyl alcohol and afterwards heating at $105^{o}C$ for 24 h. The samples were stored in airtight glass vials.

2.2.3 Powder X-ray diffraction studies of the hydrated samples

Powder X-ray diffraction studies of the hydrated samples were measured (2θ = 5 - 65 ^{o}) with a Philips X-ray powder diffractometer using CuK_{α} radiation.

2.2.4 IR spectroscopic studies of the hydrated samples

IR spectra of the hydrated samples were recorded between 400 - 4000 cm^{-1} in KBr phase by using a Bruker Vertex 70 spectrometer.

2.2.5 DSC studies of the hydrated samples

DSC studies of the hydrated samples were carried out in N_2 atmosphere from ambient to $1000^{o}C$ by using a Netzsch STA 409 PG/PC using Al_2O_3 as reference. The heating rate was $10^{o}C$ min^{-1}.

2.2.6 Strength measurements

Compressive strengths of the cement mortar (cement/sand = 1/3) with water/cement ratio equal to 0.5, in the presence of 0, 0.75 and 1.5 wt% polymer, were determined in accordance with DIN EN 196-1 [19] at 28 days of hydration in a relative humidity of 100%.

2.2.7 Porosity measurements

The porosity and the pore size distribution in the pore range of 0.0037 – 300 µm of the hydrated samples (28 days) were measured by using a Mercury Intrusion Porosimeter (MIP), ThermoQuest, Typ Pascal 140/240.

3 Results

Fig. 2 shows the evolution of heat flow as a function of time in pastes containing from 0 to 1.5 wt% polymer. In the absence of polymer, the characteristics of the heat flow curve can be viewed as consisting of five different stages:

1. the stage in which a short but rapid reaction takes place immediately after the OPC comes in contact with water (not measured by the calorimeter),
2. the stage which corresponds to the so called dormant or induction period where the reaction rate is very slow,
3. the stage in which the reaction is most active and accelerates with time,
4. the stage where the reaction rate decreases after the end of most active reaction period,
5. the stage in which the rate of reaction is very slow.

Heat flow studies have also been made in the presence of 0.3, 0.75 and 1.5 wt% polymer. With the increase in concentration of the polymer, the following changes occur in the heat evolution profile:

1. the induction period increases,
2. the maximum heat flow decreases,
3. the time of maximum heat evolution increases.

Total heat evolved during the hydration is shown in Fig. 3. The results show that the total heat increases with time and decreases with polymer concentration.
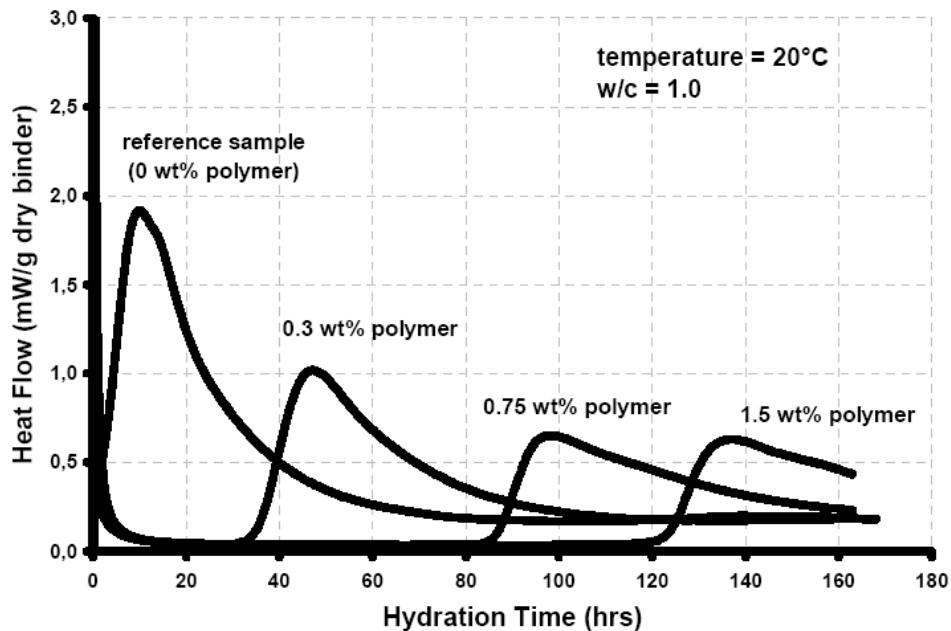

Fig. 2 Heat flow as a function of time in the presence of different concentration of polymer
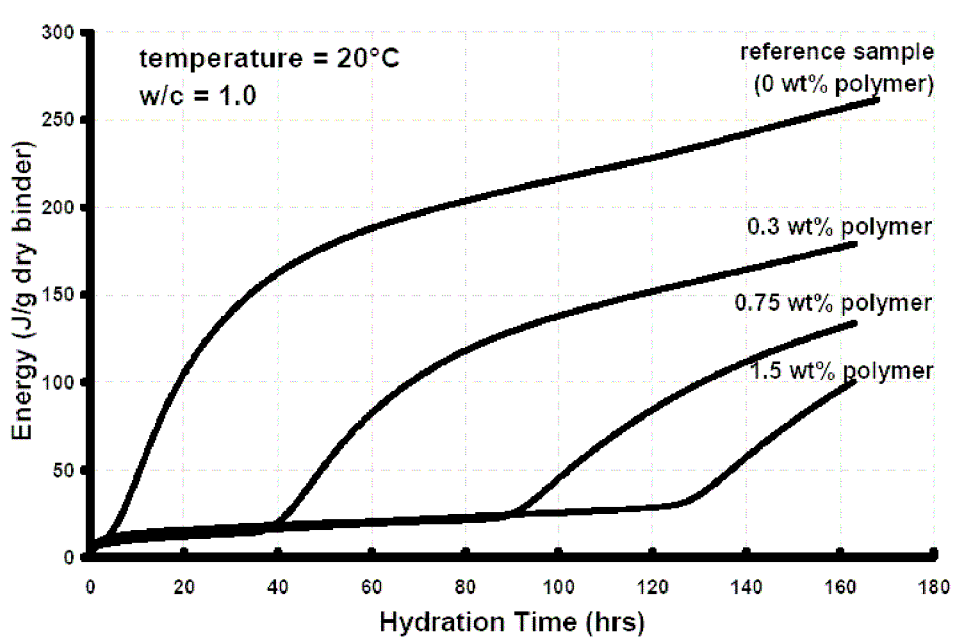
Fig. 3 Total heat evolved as a function of time in the presence of different concentrations of polymer

Powder X-ray diffraction patterns of anhydrous cement and paste hydrated for 7 days in the absence and presence of 3.0 wt% polymer were recorded. The results show that the polymer retards the hydration of cement and no new diffraction lines are obtained due to the presence of polymer. This indicates that either there is no interaction between the polymer or the hydrating cement or some amorphous (gelatinous) compounds are formed which do not give diffraction lines.

DSC curves of OPC hydrated for one day in the absence and presence of 3.0 wt% polymer are shown in Fig. 4. In the case of OPC hydrated for one day, three endothermic peaks appear at 70.4, 98.5 and 455.1°C. The first two peaks are due to the removal of adsorbed water and decomposition of C-S-H/ettringite respectively, whereas the third peak is due to the decomposition of calcium hydroxide formed as a result of hydration. In the presence of 3.0 wt% polymer, a broad endothermic peak appears at 99.2°C. This may be due to removal of adsorbed water molecules only since practically no hydration has taken place as indicated by the absence of calcium hydroxide peak. In addition to one endothermic peak two exothermic peaks at 384.8 and 426.1°C also appear (these peaks are not shown by the pure polymer). These peaks may be due to decomposition of some compound formed by the interaction of the polymer and the hydrating cement. As X-ray diffraction studies do not give any information regarding the formation of new compound, it appears that the compound formed is amorphous in nature.
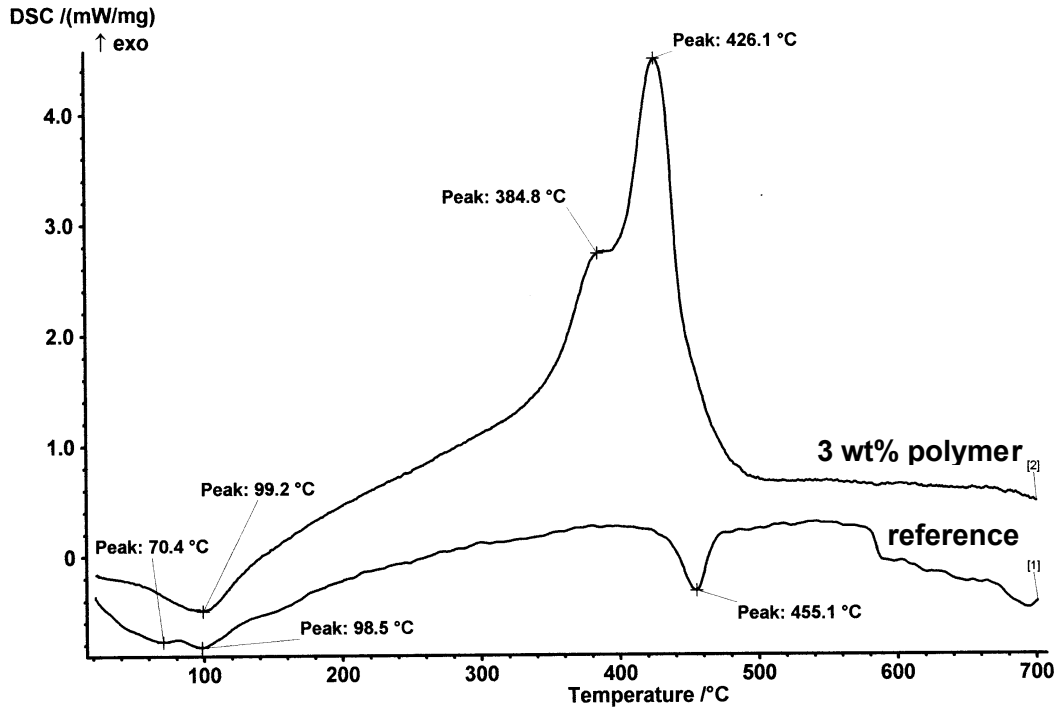
Fig. 4 DSC curves of OPC hydrated for one day in the absence (reference) and presence of 3 wt% polymer (3 wt% polymer)

The IR spectra of anhydrous and hydrated OPC are given in Fig. 5. The bands at 917.27, 509.56 and 457.75 cm^{-1} respectively are due to Si-O asymmetric stretching vibration (v_3), Si-O out-of-plane bending vibration (v_4) and Si-O in-plane bending vibration (v_2) of silicate phase in the case of anhydrous cement. SO_4^{2-} group of gypsum gives weak bands due to S-O stretching vibration (v_3) between 1000-1150 cm^{-1} and at 674.51 and 597.41 cm^{-1} due to bending vibrations. Bands at 3641.88 and 1622 cm^{-1} are due to trace amount of adsorbed water, which could not be avoided. Carbonate group present in the cement shows a band at 1429.39 cm^{-1}. The carbonate phase in the unhydrated cement appears as a result of added lime stone powder in the plant. In the hydrated samples it is both: (i) added lime stone powder and (ii) a reaction of atmospheric CO_2 with $Ca(OH)_2$ present in the cement.

When the cement was allowed to hydrate without polymer for 7 days, the bands due to Si-O vibrations underwent changes both in position and intensity. The shifting of the Si-O asymmetric stretching vibration (v_3) to higher wave number (981.18 cm^{-1}) indicates the polymerization of the silicate unit $[SiO_4^{4-}]$ with the formation of C-S-H phase. On the other hand the cement hydrated for 7 days in the presence of 3 wt% polymer, shows band due to Si-O asymmetric stretching vibration at 975.70 cm^{-1} which is

a

b

c

Fig. 5 IR Spectra of hydrated OPC with 3 wt% polymer (a), hydrated OPC without polymer (b) and anhydrous OPC (c)

very sharp and the intensities of the bands due to Si-O out-of-plane and Si-O in-plane bending vibrations are decreased considerably indicating some interaction between the polymer and the silicate phase.

The weak bands due to bending vibrations of SO_4 groups are shifted to higher wave numbers (682.49 and 607.30 cm^{-1}) in case of cement hydrated for 7 days. However in the presence of 3 wt% polymer the bending vibrations of SO_4 groups almost disappear, indicating some sort of interaction of polymer either with the gypsum or ettringite (AFt) or monosulphate (AFm).

The band appearing at 3642.12 cm^{-1} in the case of cement hydrated for 7 days, is due to metal bonded hydroxides [14], whereas the band at 3427.86 cm^{-1} is attributed to hydrogen bonded OH species associated with C-S-H, AFm and AFt phases. In the presence of the polymer these two bands are almost unaffected. However the bending vibrational band of water in the presence of polymer is shifted from 1628.7 to 1646.05 cm^{-1}. This indicates that the polymer plays some role in improving the water interaction with the cement system.

During hydration in the absence of polymer, the band associated with the carbonate groups remains unaffected. However in the presence of polymer this band splits into two parts (1419.71 and 1477.44 cm^{-1}). One peak may be due to carbonate group and the other peak due to polymer or interaction product of polymer with the cement system. The band assignments are in good agreement with those reported in the literature [15]. The overall results of IR spectra show that there is some sort of interaction between the polymer and the cement or its hydration products.

With the addition of polymer the compressive strength of the mortars at 28 days increased (Fig. 6). This is due to a decrease in porosity (Fig. 7). It appears that the polymer interacts with the hydrating cement forming some amorphous compound(s) of unknown composition: these compounds decrease the total porosity of the paste.
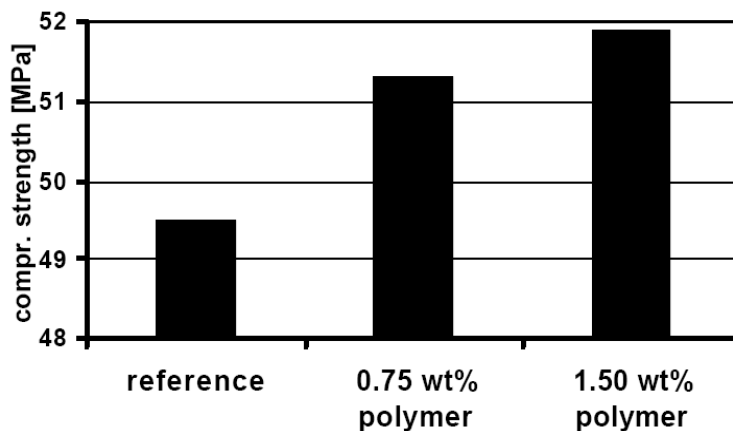

Fig. 6 Change in compressive strength with polymer concentration of mortars at 28 days of hydration.
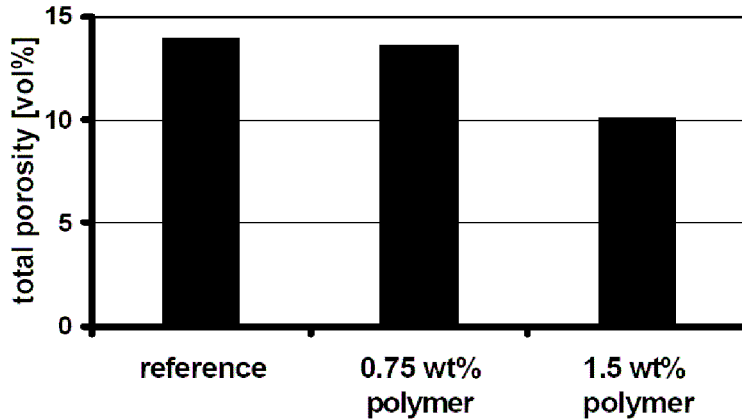
Fig. 7 Change in total porosity with polymer concentration of mortars at 28 days of hydration

4 Discussions

As soon as the OPC comes in contact with water, rapid heat evolution occurs as a result of cement wetting, dissolution of alkalis and hydrations of hemihydrate and free lime. The hydration of C_3A also contributes to the rapid heat evolution. It is well known [13] that in the presence of gypsum, C_3A forms an insoluble calcium sulphoaluminate (ettringite). Apart from ettringite, various other hydrates are formed. These hydrates act as nuclei for further hydration. For nucleation to occur, the growing nuclei should have a critical size. During the induction period, the growing nuclei acquire the critical size. As soon as the critical size is reached, the nucleation and crystal growth start and accelerate with time and reach a maximum value. This is the third stage of hydration and in this stage mainly C_3S (alite) hydration occurs. With the increase of hydration, the amount of hydration products increases and covers non-hydrated grains. This is the fourth stage of hydration, where the reaction becomes diffusion controlled. In the fifth stage, large amounts of hydration products are formed which cover almost completely the remaining non hydrated cement grains and the hydration becomes very slow.

The overall results of heat evolution clearly indicate that the polymer retards the hydration of OPC and the retardation increases with polymer concentration. It appears that polymers are adsorbed at the surface of cement grains forming a type of semi permeable membrane and hinders the approach of water molecules to the fresh surface of the cement. As a result, the solution concentration of the polymer decreases and fewer ions are available to form the nuclei of critical size, resulting in an increase of induction period. In due course, water diffuses through the so-called membrane and when the internal pressure is increased due to accumulation of water molecules, rupturing of the membrane takes place and hydration accelerates with time. Since only a part of the fresh surface of the cement is available the heat evolution and the maximum heat

evolved are lower as compared to the reference. The adsorption of polymer onto the cement surface may be physical or chemical or both. Thus there might be some interaction of polymer with the cement or with its hydration product.

When cement get in contact with water, Ca^{2+} ions go into solution, leaving negatively charged silica tetrahedral $[SiO_4^{4+}]$. The positive Ca^{2+} ions are then adsorbed at the negatively charged surface, forming an electrical double layer. This has been confirmed by positive zeta potential [16]. The polymer, which is a sodium salt gets ionized in the water giving Na^+ and negatively charged polymethacrylate ions. The negative end of the polymer ion is then adsorbed on the surface. This may form a semi permeable membrane and hinder the diffusion of water and ions towards the cement grain surfaces causing a shielding or screening effect [17]. This causes two effects: (i) dispersion and (ii) retardation of hydration. As a result of this the water requirement is reduced and the workability is increased. The extent of adsorption will depend on a number of factors such as: chemical structure of the polymer, concentration of the polymer, nature of adsorption (physical and/or chemical), chemical composition of the cement, presence of soluble salts such as sulphates, etc. Different mineral phases of the cement adsorb the polymer to different extent.

The rate of diffusion of water molecules and other ions through the semi permeable membrane will then depend on the above factors. However the process of diffusion will continue and when large numbers of water molecules and ions accumulate inside the membrane, the rupturing of the membrane takes place due to internal pressure and the hydration accelerates with time. The rate of diffusion depends mainly on the thickness of the membrane and the type of adsorption. If there is a chemical interaction (chemisorption) between the polymer and cement grains/hydrated cement, it will take a longer time to rupture the membrane. Thus the period up to the rupturing of the membrane is a dormant period of hydration. During this period critical size nuclei are formed. After the rupturing of the membrane, hydration accelerates. When large amounts of hydration products are formed they cover the surface and hydration reaction becomes purely diffusion controlled and hence very slow. In the presence of the polymer, even after the rupturing of the membrane, a reduced surface is available for hydration and hence the extent of hydration is low. The higher the concentration of the polymer, the higher will be the adsorption, so the dormant period is longer and the extent of hydration less at any given time.

IR spectral studies have shown the interaction between the hydrating cement and the polymer. DSC studies have indicated the formation of a new chemical compound in the presence of the polymer, which has been shown to be amorphous in nature by X-ray diffraction studies. It appears

that this amorphous compound precipitates and fills the pores, decreasing the pore size and increasing the compressive strength.

5 Conclusions

The overall results have shown that poly (methacrylic acid) sodium salt interacts with hydrating OPC to form some amorphous compound, which retards the hydration. The compound formed fills the pores and the compressive strengths are thus increased.

6 Acknowledgments

7 References

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