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DIFFERENTIAL THERMAL STUDIES OF POLYMETHYL METHACRYLATE-IMPREGNATED CEMENT PASTES

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ABSTRACT

Differential thermal curves have been obtained for two polymethyl methacrylate-impregnated cement pastes prepared at a water/cement ratio of 0.37 and 0.70. Complex thermal effects, including a substantial decrease in the endothermal peak for $Ca(OH)_2$ decomposition, were observed in samples heated in air. These effects originate in the portland cement paste, in the polymer, and from interactions between the polymer and the hydrated cement during heating. Less complex effects resulted when DTA was carried out in N_2. There was no evidence of a reaction between the hydrated cement and PMMA during impregnation.

INTRODUCTION

Polymer-impregnated concretes have received considerable attention in recent years. In addition to exhibiting more than a three-fold increase in compressive and tensile strengths, these composites manifest better durability characteristics than conventional concrete. Concrete impregnated with acrylic-type polymer exhibits much better improvement in mechanical properties than most others[1].

The exact mechanism of the strength development in polymer-impregnated concrete is not clear. Decrease in porosity by impregnation may be an important factor, but it is not the only one that determines strength development, as is clear from the following illustration[2]. In a normally cured cement at 28 days 78.7 per cent of the pores may be filled by the methyl methacrylate monomer, and in a steam-cured specimen it may be as high as 99+ per cent. In spite of the significant differences in the monomer loading no appreciable increase in the strength of the steam-cured paste is apparent. It is difficult to explain the wide variation in the strengths developed by different types of polymers in terms of the changes in porosity. It appears that additional factors such as a surface interaction between the polymer/monomer and the hydrated cement, and healing in the microcracks play an important role.

The Differential Thermal Analysis (DTA) technique has been used in many instances to detect the chemical compounds formed in cement pastes[3,4]. This method has also been used with some success to explain the low strength development in polymer–cements obtained by the premixing method. Gebauer and Coughlin[5] and Auskern *et al.*[6] have used DTA to seek evidence of the possible interaction between hydrated cement and methyl methacrylate. Gebauer found that in a polymethyl methacrylate (PMMA)-impregnated cement the endothermal effect from the decomposition of $Ca(OH)_2$ was almost completely absent. It was inferred that an interaction occurred between the MMA/PMMA and hydrated cement. Auskern made a careful study of the PMMA-impregnated cement but could not confirm these results. He, however, reported that polymerization of an intimate mixture of $Ca(OH)_2$ and MMA resulted in a new peak at about 430°C that could be attributed to the calcium salt of methacrylic acid. From this it was concluded that $Ca(OH)_2$ in cement paste reacts with PMMA. Neither study gave direct evidence that a compound had formed between MMA/PMMA and hydrated cement. Both investigators used a low water/cement ratio for the preparation of the cement pastes and based their conclusions on the thermograms obtained in an inert atmosphere in which oxidation effects of the polymer were suppressed.

It is thought that evidence of a possible reaction between MMA/PMMA and hydrated cement requires a more completely hydrated cement. In the present study, therefore, an almost completely hydrated portland cement was chosen for impregnation. In addition, DTA investigation was carried out in N_2 as well as in air in order to pick up all possible oxidation effects. By these means it was thought that the apparent discrepancy in the previously reported data could be resolved.

EXPERIMENTAL

Materials

Seven samples were used for the present investigation:

1. *Portland cement paste I:* A high early-strength portland cement was hydrated for 271 days at a water/cement ratio (w/c) of 0.37. The sample had hydrated to an extent of 83 per cent and had a porosity of 19.9 per cent as measured by methanol.

2. *Portland cement paste II:* This was obtained by hydrating a high early-strength portland cement for 268 days at a w/c of 0.70. The degree of hydration was 97.2 per cent and the porosity was 42.2 per cent as determined by methanol.

3. *Polymer-impregnated cement I:* Portland cement paste I was dried to a constant weight at 110°C, evacuated for 4 hours and soaked in methyl methacrylate monomer containing 0.5 per cent azobisisobutyronitrile as an initiator for 24 hours. Samples were polymerized for 48 hours at 80°C under a pressure of 170 lb/sq in., followed by a further 48 hours at 110°C. The volume fractions of monomer and polymer calculated from weight changes by assuming bulk densities were 17.8 per cent and 14.0 per cent, respectively.

4. *Polymer-impregnated cement II:* Portland cement paste II was impregnated with PMMA, as described above. The monomer loading for this sample was 41.0 per cent and the polymer loading 31.1 per cent by volume.

5. *Polymethyl methacrylate:* This was obtained by the polymerization of the MMA monomer. The material was obtained in a powdered form by filing of the solid piece of the polymer.
6. *Portland cement paste I–PMMA mixture:* Portland cement paste I was ground to pass through 100-mesh sieve and mixed with PMMA in the ratio 4:1 using a Wig-l-bug vibrator.
7. *Portland cement paste II–PMMA mixture:* Portland cement paste II was mixed with PMMA as described above.

Method

Differential thermal analysis was carried out using a DuPont 900 Thermal Analyser. The unit utilizes platinum holders and platinum versus platinum–rhodium (13 per cent) thermocouples. The reference material was ignited α-Al_2O_3.

In each run 50 mg of sample passing a 100-mesh sieve was packed with moderate pressure. Thermograms were obtained in air or in a continuous flow of N_2 at 1.2 cu ft/hr. The rate of heating was maintained at 10°C/min. The sensitivity of ΔT plotted on the Y-axis was 0.02 mV/in. Each sample was run in duplicate.

RESULTS AND DISCUSSION

Curve A-1 in Figs. 1 and 2 represents the thermal behaviour of portland cement hydrated at a water/cement ratio of 0.37 or 0.70. The low temperature endothermal effects in the range 215 to 225°C are the result of expulsion of water from the hydrated cement. The large endothermal effect in the range 490 to 505°C denotes the dehydration of $Ca(OH)_2$. The endothermal peak for the portland cement paste obtained at a w/c of 0.37 is less intense than that for the cement prepared at a w/c of 0.70. Less cement is hydrated in the sample prepared at a w/c of 0.37. In addition, it is known that more lime is bound in the C–S–H phase in cements prepared at low w/c.

PMMA-impregnated cement pastes (B) exhibit several complex endo- and exothermal effects when heated in air (curve B-1, Figs. 1 and 2). In fact, the distinction between the endo- or exothermal character of the effects becomes less obvious, especially in the temperature interval 400 to 500°C. The PMMA-impregnated sample prepared at a w/c of 0.70 showed endothermal effects at about 200, 315, 340, 460, 480, 500, 525 and 820°C. The polymer-impregnated sample prepared at a w/c of 0.37 showed a similar thermogram (curve B-1), Fig. 1. The PMMA-impregnated samples in Figs. 1 and 2 are not identical, however, because they differ in the polymer loading, in the nature of the hydrated product, and in the amount of calcium hydroxide. One of the obvious distinctions between the portland cement and the impregnated samples is the decreased intensity of the $Ca(OH)_2$ decomposition peak occurring around 525°C. This does not necessarily mean that a large proportion of $Ca(OH)_2$ in the impregnated cement has reacted with the polymer. The decrease may be due to the masking effect of an exothermal effect occurring at about the temperature of

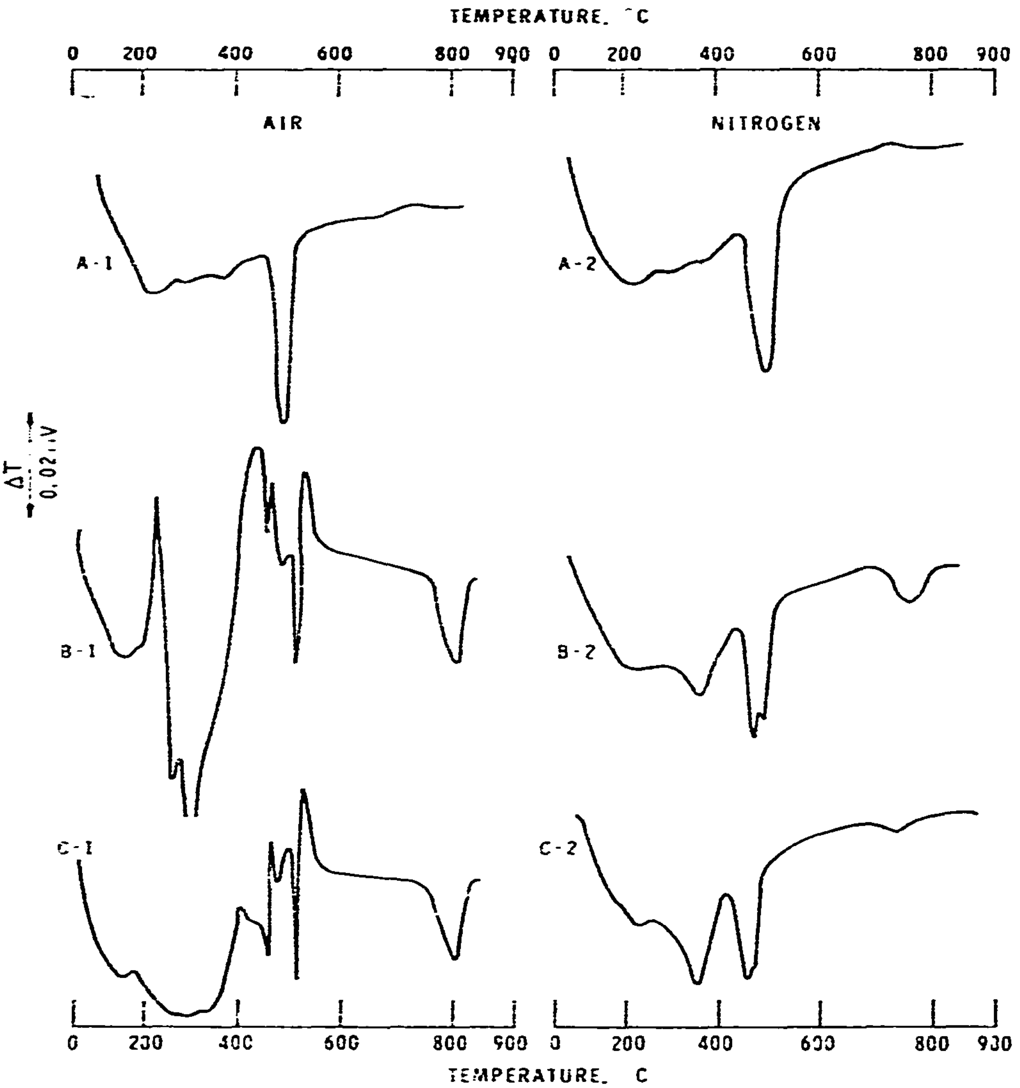

Fig. 1. Thermograms of polymethyl methacrylate-impregnated portland cement paste (w/c = 0.37).

decomposition of $Ca(OH)_2$. It should also be noted that the cement is diluted with the polymer in the polymer-impregnated sample.

In many instances the thermogram of a mixture of two or more compounds is a superimposition of the thermograms of the individual components of the mixture. If this were so, the PMMA-impregnated paste would exhibit thermal curves reflecting those of portland cement and PMMA (curve A-1, Figs. 1 and 2 and curve D-1, Fig. 3). On the contrary, several new inflections emerge in the polymer-impregnated sample (curve B-1, Figs. 1 and 2). Some of the new effects include: a decrease in the intensity of the $Ca(OH)_2$ peak, evolution of an endothermal effect just before the onset of the $Ca(OH)_2$ decomposition effect, an exothermal hump immediately following $Ca(OH)_2$ decomposition, and a large endothermal effect at about 800 to

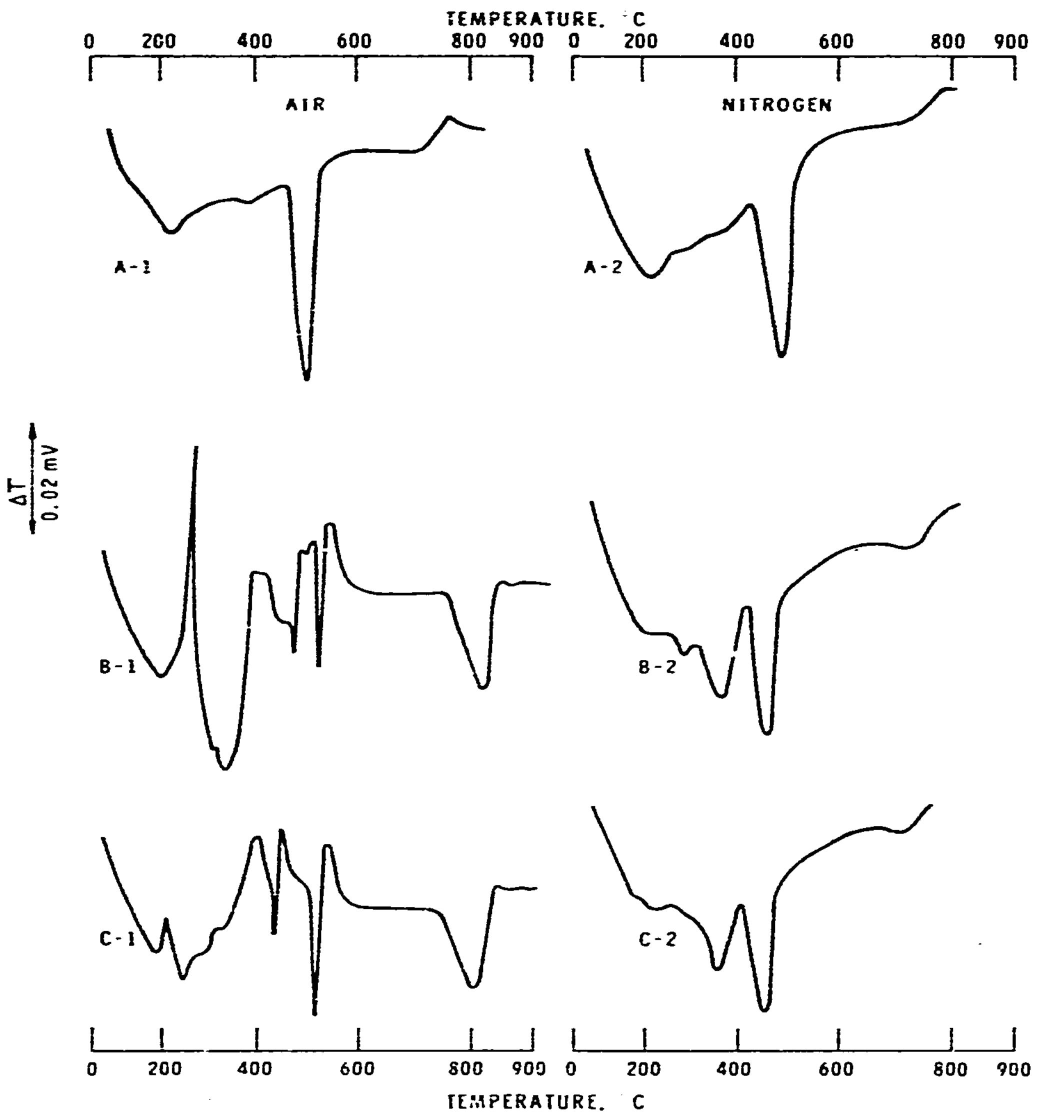

Fig. 2. Thermograms of polymethyl methacrylate-impregnated portland cement paste (w/c = 0.70).

830°C. That these new effects do not imply an interaction between PMMA and the hydrated cement phase during impregnation can be demonstrated.

In order to check whether the new thermal effects revealed in sample B represent reactions occurring during the course of heating in the DTA furnace, two mixtures containing portland cement and PMMA were prepared (samples 6 and 7). Curve C-1 in Figs. 1 and 2 denotes the thermograms of the PMMA–cement mixtures. A close study of thermograms B-1 and C-1 shows that they are very similar in terms of exo- and endothermal effects, except that the sharp exothermal effect from 230 to 270°C and two endothermal effects in the range 250 to 350°C are not very apparent in sample C-1. This could be attributed to the masking effect of the endotherm of the

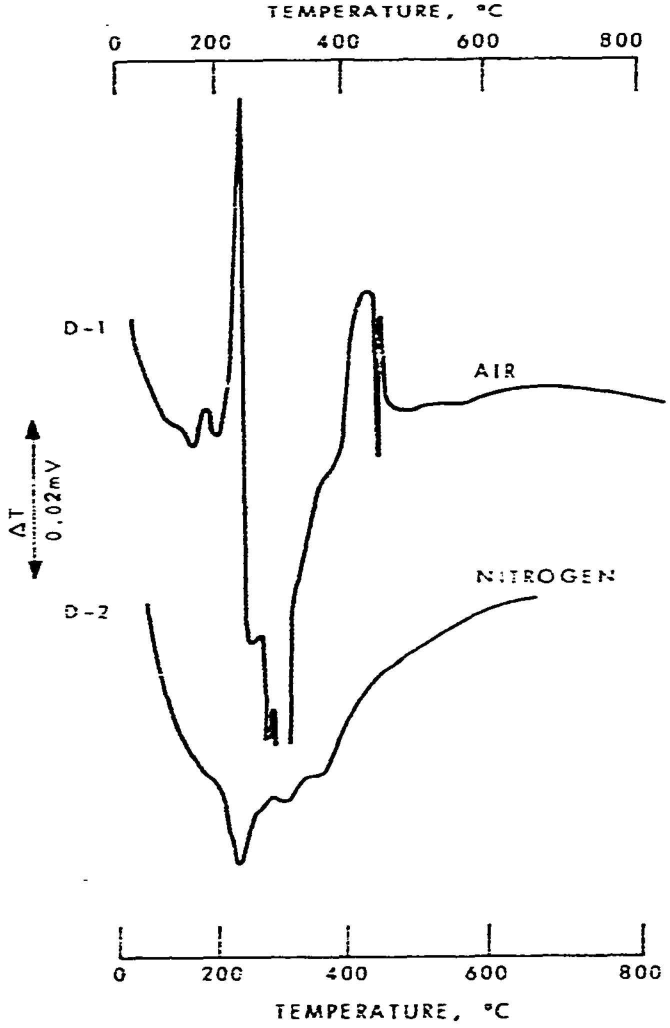

Fig. 3. Thermograms of polymethyl methacrylate.

portland cement paste. The portland cement used for impregnation was much better dried than that used in making mixtures. Thus when sample C-1 was prepared by preheating portland cement paste I or II at 110°C for four days prior to mixing with PMMA, the resulting thermogram resembled curve B-1. It appears, therefore, that the emergence of many of the new thermal effects in the polymer-impregnated cement is not due to compound formed during impregnation. The inflections seem to demonstrate that complex reactions occur between the hydrated cement and the decomposition products of PMMA during heating in the DTA apparatus. Auskern obtained similar results[6].

Thermograms obtained in air yielded complex thermal effects resulting from oxidation and mutual interactions. Thermograms of the same sample carried out in N_2 are expected to show simpler patterns. All the samples were therefore run in DTA in a flow of N_2 and the thermograms again examined for evidence of the formation of a reaction product between the PMMA and the hydrated cement by impregnation.

Thermal curves for the portland cement paste in a flow of N_2 show characteristics similar to those obtained in air (curve A-2, Figs. 1 and 2). The endothermal peak for the cement prepared at a w/c of 0.37 is less intense than that at a w/c of 0.7. The PMMA-impregnated sample (curve B-2, Fig. 2) indicates only endothermal effects at about 210, 295, 360, 465, 435 and 760°C. The sample prepared at a w/c of 0.37 shows peak effects at about 215, 295, 375, 470 and 730°C. The main difference between the two samples is the existence of an endothermal doublet in the sample prepared at a w/c of 0.37.

PMMA shows four endothermal effects at about 190, 240, 300 and 360°C in an N_2 atmosphere (sample D-2, Fig. 3). In the polymer-impregnated samples the first three endothermal effects may be due to the effects of PMMA.

The curve of PMMA-impregnated cement is not just a combined effect of portland cement paste and PMMA. The $Ca(OH)_2$ peak is reduced in intensity, an endothermal doublet occurs in one of the samples, and enhanced endothermal effects result at 360 to 375°C and again at about 730 to 760°C. A well-mixed cement-PMMA sample shows a thermogram very similar to that of the impregnated samples (compare curves B-2 and C-2 in Figs. 1 and 2). Hence the differences observed in sample B-2 may be linked to an interaction between PMMA and hydrated cement during heating in the DTA apparatus.

The doublet occurring in sample B-2 in Fig. 1 was confirmed by repeated experiments. In N_2 the onset of the endothermal effect for the polymer-impregnated sample occurs at a slightly lower temperature than that for the cement paste. In the doublet the first peak may represent the interaction between PMMA and $Ca(OH)_2$, the second peak, the dehydration of the residual $Ca(OH)_2$. The absence of a doublet in the impregnated cement at a w/c of 0.7 may be explained as follows: the amount of $Ca(OH)_2$ being larger, more $Ca(OH)_2$ reacts with the PMMA during DTA heating and the resulting effect may mask the endothermal effect of the residual $Ca(OH)_2$.

The almost complete disappearance of the $Ca(OH)_2$ endothermal effect in the PMMA-impregnated sample reported by Gebauer and Coughlin[5] appears to be due to the masking effect of the large exothermal hump exhibited by PMMA in their samples.

It is possible that some interaction does take place at the interface between the polymer and the $Ca(OH)_2$ of the cement paste, but it would represent a small part of the total polymer and DTA analysis would not detect it. The present work confirms that no reaction occurs between the bulk polymer and cement paste during the impregnation and polymerization of the PMMA, contrary to what has been suggested.

CONCLUSIONS

There is no indication in differential thermal curves that hydrated cement interacts with PMMA during impregnation and polymerization. Decrease in the intensity of the $Ca(OH)_2$ peak in impregnated specimens is mainly attributable to a reaction between PMMA and $Ca(OH)_2$ during heating in the DTA furnace. The evolution of endo- or exothermal peaks in the thermograms obtained in air may be ascribed to the reaction between hydrated cement and decomposition products of PMMA. Evidence presented at this time, however, does not rule out the possibility of some reaction at the interface between polymer and cement paste, but the amount so reacted would be small and would be undetected by this method.

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