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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Konar, B. B. and Pariya, T. K.(2009) 'Study of Polymer-Cement Composite Containing Portland Cement and Aqueous Poly (methyl methacrylate) Latex Polymer by Fourier-Transform Infrared (FT-IR) Spectroscopy', Journal of Macromolecular Science, Part A, 46: 8, 802 – 806

To link to this Article: DOI: 10.1080/10601320903004616

URL: <http://dx.doi.org/10.1080/10601320903004616>

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Study of Polymer-Cement Composite Containing Portland Cement and Aqueous Poly (methyl methacrylate) Latex Polymer by Fourier-Transform Infrared (FT-IR) Spectroscopy

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Received December 2008, Accepted February 2009

The polymer-cement composite is an immiscible band having modified morphology. Polymer phase improves the toughness of brittle cement and has a reinforcing effect, and interactions between cement components and polymers provide stability. In this study, polymer latex [poly(methyl methacrylate), PMMA] – cement paste was prepared with different weight proportions of polymer content. The main scientific objective of this report has been the analysis and the prediction of high strength with the aim of understanding the interactions of PMMA polymer with Portland cement after hydration reaction of cement pastes and curing the specimens for 28 days. The samples were studied by Fourier transform infrared (FT-IR) spectroscopy. The results are critically examined. It is shown that bands support the interaction of PMMA with cement in the composite.

Keywords: Polymer [poly(methyl methacrylate), PMMA], Portland cement, polymer-cement composite, infrared spectroscopy, mortar, hydration, stretching, bending

1 Introduction

A polymer is a substance composed of molecules characterized by the multiple repetition of one or more species of atoms or group of atoms (constitutional units). Cement, a powdery material, is a mixture of naturally occurring argillaceous (containing alumina) and calcareous (containing calcium carbonate or lime) materials to a partial fusion at high temperature (about 1450°C).

Polymer cement composite (PCC) consists of cement with an aggregate and a polymer. The polymer may be a thermoplastic, but more frequently it is a thermosetting type (1). The amount of polymer binder used is generally small. It is usually determined by the size of base material. Polymer binder improves adhesion and flexibility of PCC. Many polymers like poly(methyl methacrylate), styrene butadiene polymer, polyester, epoxy, furan-based polymer etc. are well developed in polymer cement composite for different applications. But the mechanism by which polymer

reinforced cement is not well understood. Adhesion in polymer cement composite refers to the bonding between the phases (2). van der Waal force of attraction, diffusion of polymer chains in layers of the cement and filler surface interaction affinity is essential for a strong bond in such immiscible blends. van der Waal attraction force is very low in compared to chemical bond. Thus, surface chemical bond could be utilized effectively to promote adhesion. Reactive functional groups have been found to promote adhesion at the surface of different phases. Generally, hydrogen bonding, acid/bases, charge transfer complexes, ionic groups etc. have been found to be very effective adhesion promoters. Cement, a powder, forms a solid, cohesive and adhesive mass by hydraulic reaction. Portland cement clinker is the result by the reaction of calcium oxide with acidic components C₃S, C₂S, C₃A and a ferrite phase C₃AF. A hypotheses (3) is proposed that latex polymer particles coalesce around each cement grain and aggregate particles to form and interpenetrating network throughout the structure. The challenging group of micro defect free (MDF) cement materials/composites has been identified by some workers (4–6). Existence of a crosslinking of the polymer chains by Al or Ca ions coming from the hydration reactions of the cement were reported by Bonapasta et al.

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(4). Popoola et al. (5) reported MDF cement consists of CaAl_2O_4 and CaAl_4O_7 grains randomly distributed in a polymer matrix. The polymer phase preferably crosslink with Al. Common acrylic polymer poly(methyl methacrylate), PMMA, $-\text{[CH}_2-\text{C(CH}_3\text{)(COOCH}_3\text{)]}_n-$, is a versatile material used as a cement binder. Many investigators (7–9) reported their views. The objective of the present work is to evaluate the effect of PMMA latex on the cement hydration process and to elucidate specific interactions of the interpenetrating network of PMMA film throughout the composite. Infrared spectroscopy, not frequently used in cement industry, was used in this characterization.

(*cement chemistry notation: C = CaO, A = Al_2O_3 ,
F = Fe_2O_3 , S = SiO_2)

2 Experimental

Materials were used in their normal commercial forms without preparatory treatment. Ordinary Portland cement was used in this study. Cement was obtained from Ultratake, India. The potential composition were supplied as: clinker 67, Blast furnace slag 30, Mineral gypsum 30. Acrylic (PMMA) latex, appearing as a milky white liquid, was obtained from Shika, India. Latex on analysis gives 51% solid content, 9 pH, 65cps Brook Field viscosity at 20°C, 1.01 specific gravity, about 0.2 micron particle size, nonionic stabilization and minimum 4°C minimum film forming temperature. Adequate amounts of cement were hydrated with a W/C ratio 0.4 in the reference sample. A mortar batch was prepared with three parts of sand and one part of cement.

Composites were prepared like mortar with the addition of acrylic latex. In this study, water was substituted for latex. Wright ratio of polymer in the composites is shown in Table 1. The denomination given to each sample is also mentioned. The minimum quantity of water was added to achieve a reasonable consistency in accordance with good working ability. All the samples were kept in a sealed condition. Grinding the product mixing with acetone stopped the hydration process. Powder was dried at 40°C under reduced pressure. Solid, finely powdered samples were analyzed by IR techniques with a Perkin-Elmer 1330 infrared

Table 1. Composition of the composites

Composite sample Name	Cement (gm)	Sand (gm)	PMMA latex, solid content by weight of cement (%)
C ₀ (Pure cement)	50	0	0
S ₀ (Mortar)	50	150	0
S ₁ (PMMA composite)	50	150	10
S ₂ (PMMA composite)	50	150	15
S ₃ (PMMA composite)	50	150	20

Table 2. IR frequencies of the principle bands of the hydrated Portland cement

Frequencies cm^2	Assignment
3645	Stretching O-H of Ca(OH)_2
3430	O-H band in the water stretching region of chemically bonded water or water of crystallization.
3400–3100	Symmetric and asymmetric stretching of O-H
1630–1615	Deformation mode H-O-H of the molecular water absorbed.
1450	Carbonate ion (CO_3^{2-}), v3.
923	Si-O, asymmetrical stretching frequency (v3)
872	Carbonate ion (CO_3^{2-}), v2.
712	Carbonate ion (CO_3^{2-}), v4.
1100–900	Free inorganic silicate ion (SiO_4^{4-}).
522	Stretching Si-O (v4)
452	Stretching Si-O (v2)

Spectrophotometer at a resolution of 4 cm^{-1} and 16 scans using KBr pellets.

3 Results and Discussion

The characteristic IR bands of Portland cement paste and poly (methyl methacrylate) are shown in Tables 2 and 3. Figure 1(a, b, c, d, e and f) shows FT-IR spectrum of cement, mortar, composites and PMMA studied for the present work.

The spectrum of cement paste (C₀) exhibits a peak at 3645 cm^{-1} in the high zone. It is combined and absorbed water of C-S-H, O-H stretching of Ca(OH)_2 formed (10, 11). Intensity of the peak decreases in mortar (S₀) and in cement polymer composites. A decrease of portlandite formation by addition of cement modifier (PMMA) is in line with those shown by studies of Afrid et al. (12).

It is reported (2) that in spite of an initial retardation of hydration reaction, a higher degree of hydration is found after 90 days for the polymer modified mortars. In the present work, such a result was not observed after 28 days

Table 3. IR frequencies of the principle bands of PMMA polymer

Frequencies cm^2	Assignment
3440	Adsorbed bound water
2924	O-CH ₃ , C-H stretching vibration
2948	C-CH ₃ C-H stretching vibration
1728	C=O stretching vibration
1630 – 1600	Deformation mode H-O-H of molecular water absorbed
1453	O-CH ₃ , C-H bending vibration
1358	C-CH ₃ , C-H bending vibration
1164	C-O-C, stretching vibration

of hydration. PMMA latex film has no peak (3645 cm^{-1}) in this region.

Cement (C_0) exhibits a peak at 3430 cm^{-1} . Corresponding peak 3434 cm^{-1} in mortar (S_0), 3468 cm^{-1} in composite S_1 , 3440 cm^{-1} in composite S_2 and in composite S_3 are observed. For cement, it is a discrete OH band in a water stretching region of chemically bonded water or water of crystallization. Dry PMMA film from latex also shows a

peak at 3440 cm^{-1} . This may be a result of a H-O-H vibrator of bound water molecules present in the polymer film after repeated drying under reduced pressure. It is expected from the hydrogen bonded water molecule with C=O group (13).

Deformation mode H-O-H (ν_2) at $1630\text{--}1600\text{ cm}^{-1}$ of molecular water adsorbed is also present in this study. But intensity of peak increases in mortar (S_0). Intensity of peak

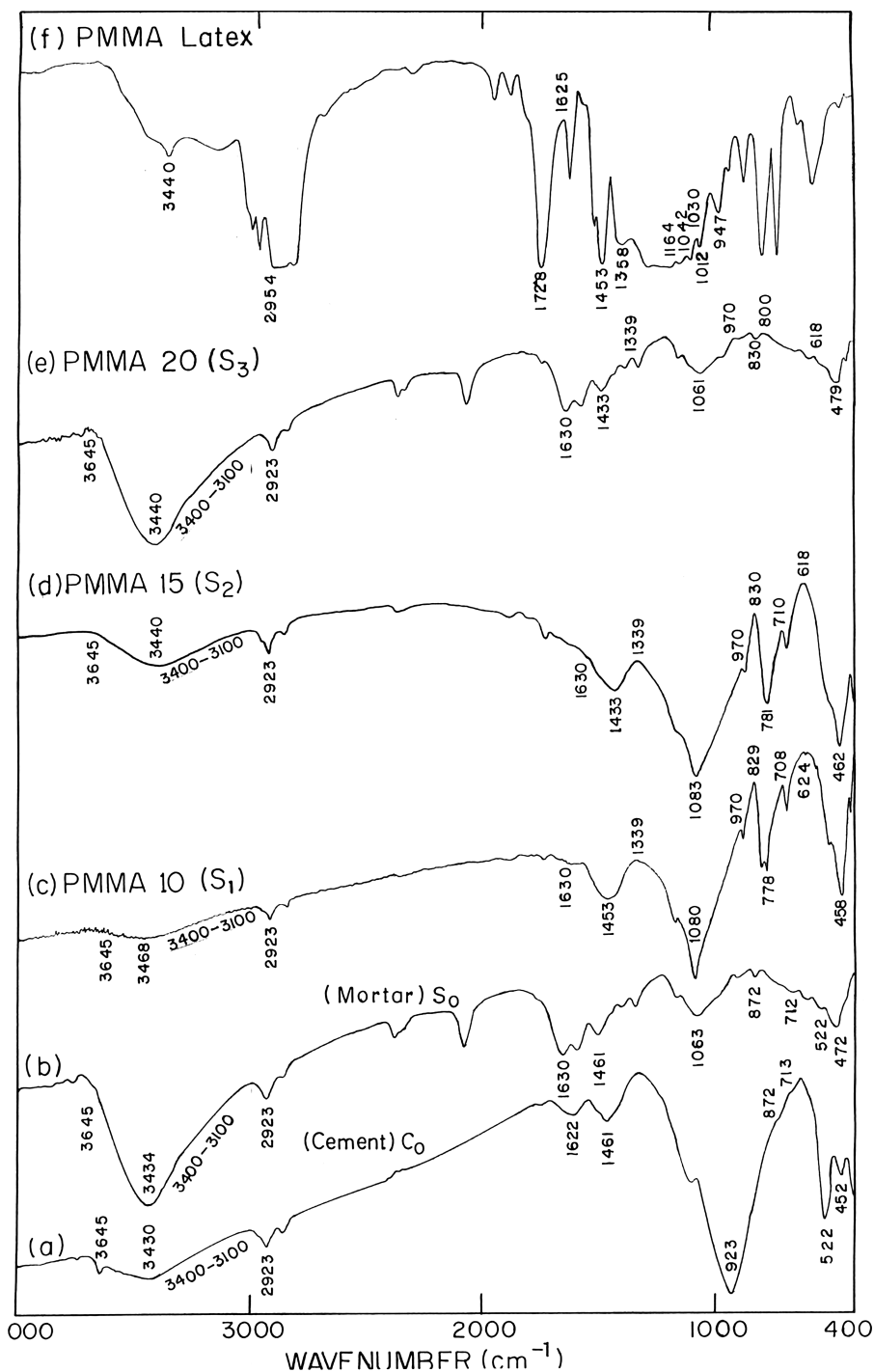


Fig. 1.

decreases in composites S_1 and in S_2 , and similar results like mortar in composite S_3 . A probable cause may be the increased amount of bound water in the polymer. A wide band is found in the region $3100\text{--}3400\text{ cm}^{-1}$ in cement, mortar and also in composites. It is due to symmetric and asymmetric stretching (ν_1 and ν_3) of H-O-H vibrator of water molecules. A deformation mode H-O-H (ν_2) of molecular water absorbed (14, 15) is also present in all the samples.

A characteristic wide band at 2954 cm^{-1} of spectrum of PMMA corresponds to an alkane functional group (16). Peaks are at $2975\text{--}2950\text{ cm}^{-1}$ as part of a residual saturated hydrocarbon portion of the molecule (C-CH₃, C-H stretching vibration) and $2995\text{--}2955\text{ cm}^{-1}$ correspond to alkane attached to an oxygen atom (O-CH₃, symmetric C-H stretching vibration). These are displaced to a lower wave number (2923 cm^{-1}) in composites. Strong deformation vibration at 1453 cm^{-1} (O-CH₃) and weak deformation vibration at 1358 cm^{-1} (C-CH₃) of PMMA are also shifted to 1433 cm^{-1} and 1339 cm^{-1} in composites. Cement and mortar show a strong peak at 2923 cm^{-1} . These displacements indicate a strong interaction between cement/mortar and particular groups of polymer material.

A band at 1728 cm^{-1} (very strong peak) of PMMA corresponds to an ester carbonyl (>C=O) group. The band disappears in composites, which means the carbonyl bond is shielded by the constituent present in cement/mortar. Stretching vibration frequency of C=O bond is lowered due to its coordination to a metal atom/ion through the oxygen (17). Bonapasta and others (4) reported the interaction between Ca ions and poly(acrylic acid) chains in MDF cements. The result shows that a stable CaO₄ complex can be formed by a Ca ion and the atoms belonging to the -COO-groups of two polymer chains. The present results show that a strong coordination bond appears in composites for carbonyl group and metal atom/ion of cement.

The band at 1164 cm^{-1} is a stretching vibration of the C-O-C group. Peak intensity increases in all composites, it is shifted to 1080 cm^{-1} in S_1 , to 1083 cm^{-1} in S_2 and to 1061 cm^{-1} in S_3 . A shift to a lower wave number indicates an interaction between cement/mortar and C-O-C group of PMMA.

Bands for Carbonate ion (CO₃²⁻) (18) are at 1450 cm^{-1} , 872 cm^{-1} , and 712 cm^{-1} , respectively. In the present study, 1461 cm^{-1} and 872 cm^{-1} for cement; 1461 cm^{-1} , 872 cm^{-1} and 712 cm^{-1} for mortar; 1453 cm^{-1} , 829 cm^{-1} and 708 cm^{-1} for composite S_1 ; 1433 cm^{-1} , 830 cm^{-1} and 710 cm^{-1} for composite S_2 ; 1433 cm^{-1} , 872 cm^{-1} and 618 cm^{-1} for composite S_3 are observed. The most important reaction product of Portland cement is calcium silicate hydrate (C-S-H) and the reaction of calcium silicate hydrate (C-S-H) with atmospheric CO₂ takes place during the hydration reaction to form carbonate or carbonate-like phases (19). Low peaks intensity indicates less carbonate formation in composites. In this study, an important peak for hydrated Portland cement is found at 923 cm^{-1} . It is 1063 cm^{-1} for mortar and 1080 cm^{-1} for S_1 , 1083 cm^{-1}

for S_2 and 1061 cm^{-1} for S_3 . This peak accounts for the polymerization of SiO₄⁴⁻ present in C₃S and C₂S. The peak region of free inorganic silicate ion is $1100\text{--}900\text{ cm}^{-1}$. Hassaan et al. (19) reported that 915 cm^{-1} is assigned to the asymmetrical stretching frequency ν_3 SiO₄²⁻ and 910 cm^{-1} for the out-of-plane bending frequency ν_4 SiO₄²⁻. Mortar and polymer composites show higher values in this study; this may be due to ring strain (20). Cyclic siloxane trimers absorb at $1020\text{--}1010\text{ cm}^{-1}$, whereas tetramers (which have less ring strain) absorb at $1090\text{--}1070\text{ cm}^{-1}$. Another report (21) shows linear small chain siloxanes tend to absorb at about 1050 cm^{-1} and with an increase in molecular weight, this band gradually broadens to occupy the region $1100\text{--}1000\text{ cm}^{-1}$. In this study, it is observed that PMMA provides bands at 1012 cm^{-1} , 1030 cm^{-1} and 1047 cm^{-1} , so strong interaction is expected for PMMA and silicate in composites.

The spectrum of cement generally exhibits a strong band at 522 cm^{-1} and a weak one at 452 cm^{-1} . Bensted et al. (22) reports C₂S is characterized by a very strong band at 525 cm^{-1} and a band of medium intensity at 450 cm^{-1} . In this study, only bands at 474 cm^{-1} for mortar, 458 cm^{-1} for S_1 , 462 for S_2 and 479 cm^{-1} for S_3 are observed. This result reflects a decrease in the freedom of movement. It is for polymerization of ortosilicate (23).

4 Conclusions

FT-IR curves obtained show typical interaction aspects of Portland cement mortar modified by poly(methyl methacrylate). In the high zone, cement presents a good peak at 3645 cm^{-1} . Peak intensity decreases in mortar and composites; the result was attributed to lower hydration. The addition of 15% latex (S_2) strongly reduces portlandite [Ca (OH)₂] formation and this is attributed to very low cement hydration. Dry PMMA film obtained from latex shows O-H stretching and deformation vibration. The result indicates some bound water molecules (hydrogen bonded C=O group) present in the film. The hydration process in composites varies with the variation of bound water. A shift of PMMA peaks (C-CH₃, C-H stretching and deformation vibration; O-CH₃, symmetric C-H stretching and deformation vibration; and C-O-C stretching vibration) in the composites indicate a strong interaction with cement and of the particular groups of PMMA. Carbonyl bond shielding in composite suggests a strong coordination bond between the C=O group of polymer and metal atom/ion of cement.

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