# Microstructural Studies of PMMA Impregnated Mortars

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**ABSTRACT:** Studies on cement concrete microstructures are carried out to explain experimentally observed phenomenon and for modeling of concrete at the macroscopic level. In this article, the preparation of polymer impregnated mortar (PIC) is carried out by partially or fully replacing the pores in the cement mortars (OPC) by PMMA. The effect of this polymer impregnation on density and morphology of the cement matrix is studied. The microstructural changes in the mortar, on exposure of these specimens to hydrochloric acid and sea water for 7 and 28 days, are also investigated in this article. The above studies indicated that the polymer addition decreased the voids in the mortar thereby preventing leaching of water soluble salts present in the OPC. It was observed that the polymer also prevented the external chemical media from permeating into the cement matrix and undergoing interactions with it. It is concluded that the durability and chemical resistance properties of the PIC are better compared with OPC. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 3534–3540, 2010

**Key words:** composites; microstructure; morphology; cement; cement mortar

## INTRODUCTION

Polymer cement composites are one of the most promising materials in current day construction engineering. They offer improved durability as well as flexibility to the cement concrete. Microstructural studies of cement concrete and its composites with polymers are carried out to gain insights into morphology of the cement matrix and the interactions between the cement and polymer phases. Such studies allow the creation of products or materials with superior properties viz. high chemical resistance and durability.[1–3]

Microcracks, pores, and voids form the three fundamental aspects that cause discontinuities in the cement matrix within the concrete microstructure.[4] However, a detailed study of the microstructure of the OPC and PIC and its changes on exposure to external chemical environments has not been investigated though these strongly affect the mechanical behavior and life span of concrete. Saccubai et al. have investigated the effect of chemical exposure on mechanical properties of PIC and reported that the polymethyl methacrylate (PMMA) impregnated concrete exhibits very good properties than many other polymers.[5] Liu et al. have reported that the rate of decrease of mechanical properties of crosslinked polymer in PIC at high temperatures is much less than that of uncrosslinked polymer.[6]

In this study, an attempt to envisage the possible changes in the OPC and PIC after exposure of these materials to chemical environments has been carried out. In this work, polymer impregnated mortars (PIC) were prepared by impregnating precast cement mortars with a mixture of methyl methacrylate (MMA) and 2, 2′-Azobisisobutyronitrile (AIBN) as initiator. The techniques employed to study polymer impregnated mortar at the microscopic level were scanning electron microscope (SEM), mercury porosimeter, and gel permeation chromatography (GPC).

## EXPERIMENTAL

### Materials

Ordinary Portland cement and sand used in the preparation of the precast cement mortar (OPC) specimens conformed to Korean standards KS L 5100. The amount of water to cement ratio was maintained at 0.48. The cement, sand, and water were mixed in the proportion of 1 : 2.45 : 0.48. The specimens were then cured for 28 days after mixing before carrying out the impregnation and

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polymerization. Samples for the microstructural studies were carried out using broken pieces obtained after determination of their mechanical properties.

### Impregnation and polymerization

The precast mortar specimens were dried in a hot air oven (Samwoo Science Company) at 80°C for 8 h. These were annealed to room temperature and weighed before impregnation. The MMA was mixed with 1 wt % of AIBN as an initiator. This mixture was impregnated into the mortar samples by placing the setup in a water bath inside an ultrasound vibration system for 4.5 h at room temperature. The samples were dried, weighed, and vacuum packed in PET packets to prevent the loss of monomer during polymerization.

Two sets of samples were thermally polymerized by conventional method and microwaves. In the conventional method, the impregnated mortar samples were packed in PET bags and immersed in hot water at 80°C for 3 h. This not only prevented evaporation of the monomer but also achieved uniform heating (HW-PIC). Polymerization of the specimens in the microwave reactor was carried out at a frequency of 2450 MHz (400 W) at 80°C for 2 h (MW-PIC). The samples were then removed from the PET packets, cooled to room temperature and weighed.

The samples of OPC and PIC were immersed separately in 2.5*M* hydrochloric acid and sea water for 7, 14, 21, and 28 days, respectively, at room temperature. The porosity and morphological changes during this exposure were analyzed and compared with those in OPC.

### Techniques employed

The techniques were performed to analyze the effect of the impregnation and subsequent polymerization of the monomer in the OPC mortar. The microstructure of OPC and PIC were studied using GPC (Waters) and SEM (Joel JSM 6390) and Mercury Porosimeter (Micromeritics, Auto Pore IV 9520).

#### SEM

The SEM studies revealed the changes in the porosity and development of micro cracks in the cement matrix of both OPC and PIC samples on exposure of specimens to sea water and hydrochloric acid. Samples of 1–2 mg weight were subjected to gold sputtering to make them conducting. They were analyzed by imaging the fractured surfaces under the SEM.

#### GPC

GPC was used to determine the molecular weight and the degree of polymerization of the PMMA in the composite. These parameters have direct influence on the strength parameters of PIC.[5] PMMA was extracted from 2–3 g of the PIC samples by dissolving it in Tetrahydro furan.

#### Mercury porosimeter

Porosity and average pore diameter are some of the important parameters determining the strength and permeability of the cement mortar samples.[7] In this study a Mercury Porosimeter was employed to ascertain these parameters before and after the impregnation and subsequent polymerization of the monomer in the OPC. The effect of porosity of the OPC and PIC samples when exposed to 2.5*M* hydrochloric acid was also determined in this study.

## RESULTS AND DISCUSSION

### Morphology of OPC and PIC

Investigations using SEM revealed porosity, micro cracks, and interactions in the cement in the OPC and PIC composites.

Figure 1 reveals the topography of the cement before and after impregnation and subsequent polymerization of the monomer. In Figure 1(a) the OPC surface shows minor cracks and voids developed because of the evolution of heat during the cement hydration in the mortar. In the PIC samples [Fig. 1(b,c)] the polymer seems to have sealed the cracks in the mortar to form a protective envelope around the cement particles. This resulted in a more compact and impenetrable structure.

In Figure 2 (a,b) the surfaces of PIC specimens prepared by microwaves and hot water are denser and more impermeable to external chemical environments than OPC [Fig. 2(c)]. This influences the resistance of these mortars when exposed to chemicals, such as acids and various salts present in sea water. Because of the porous surface of the OPC, the external chemicals penetrate into and undergo interactions with the cement matrix. This reduces the strength and durability of the OPC at an increasing rate than that of PIC specimens. This effect was also observed in the macroscopic properties of the mortars.[8]

OPC is very susceptible to attack by acids since the hydration products of Portland cement are alkaline.[9] Strong acids such as hydrochloric acid attacks the cement mortar by a dissolution reaction forming water soluble salts with the hydration products of cement. These salts leach out on exposure to water resulting in surface cracks and a permeable barrier to the external environments. Figure 3 shows the initial attack of hydrochloric acid below the surface of OPC and PIC specimens after 7 days immersion at

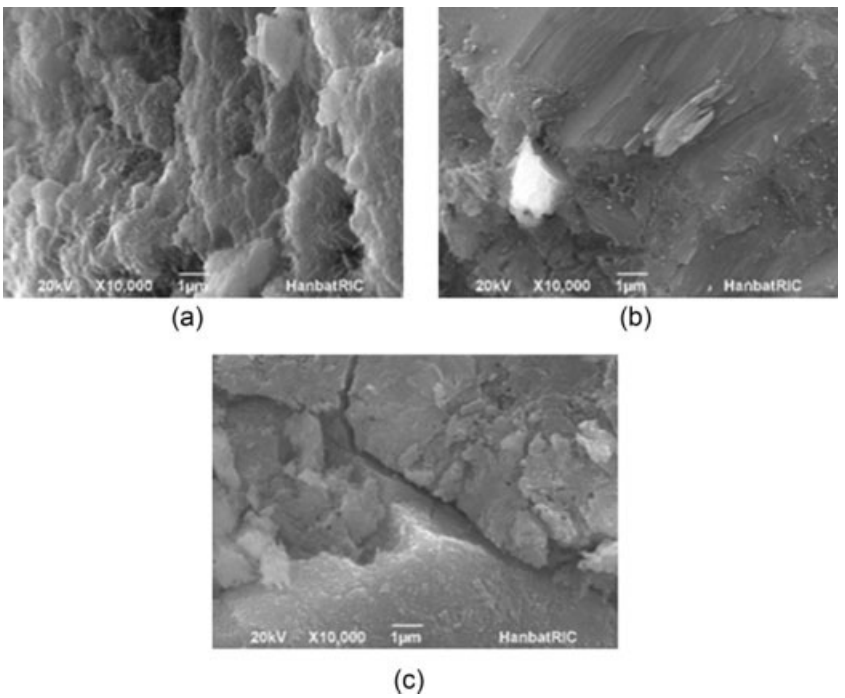


**Figure 1** Micrographs of below surfaces of (a) Hot water PIC, (b) Microwave PIC, and (c) OPC.

room temperature. On exposure to hydrochloric acid, a brown colouration was observed on the surface of the OPC. This was because of the reaction between hydrochloric acid and iron ions present in cement resulting in the formation of iron chloride.[10] The above reaction is comparatively slower in case of PIC. The polymer that forms a protective film around the cement in PIC samples prevents its reaction with hydrochloric acid.

From Figure 4(a), it is seen that on prolonged exposure to hydrochloric acid the OPC samples develop cracks. This increases porosity resulting in decrease of strength. The above phenomena may be due to the dissolution of the cement hydration

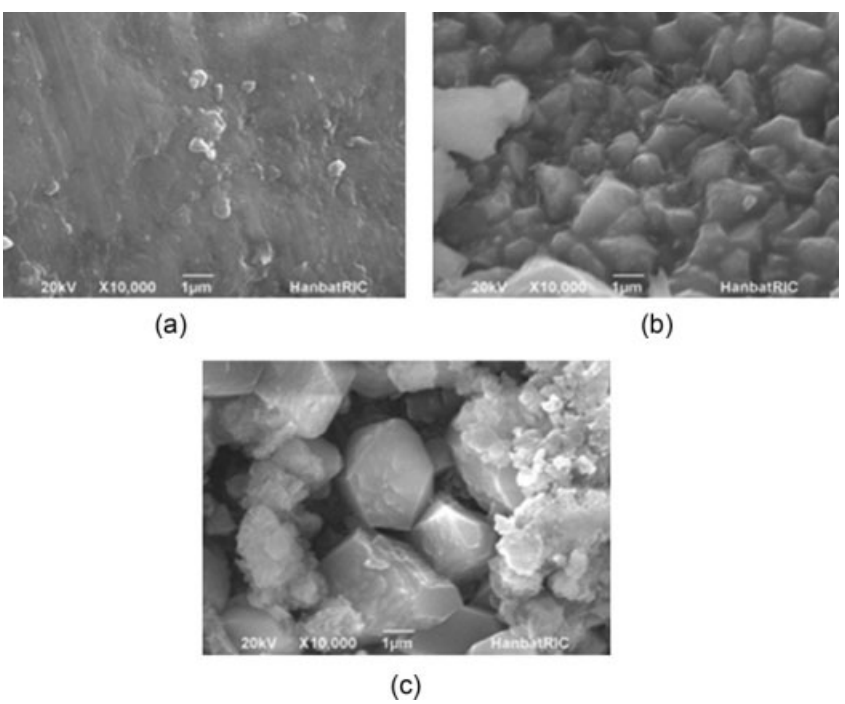


**Figure 2** Micrographs of surfaces of (a) Microwave PIC, (b) Hot water PIC, and (c) OPC.

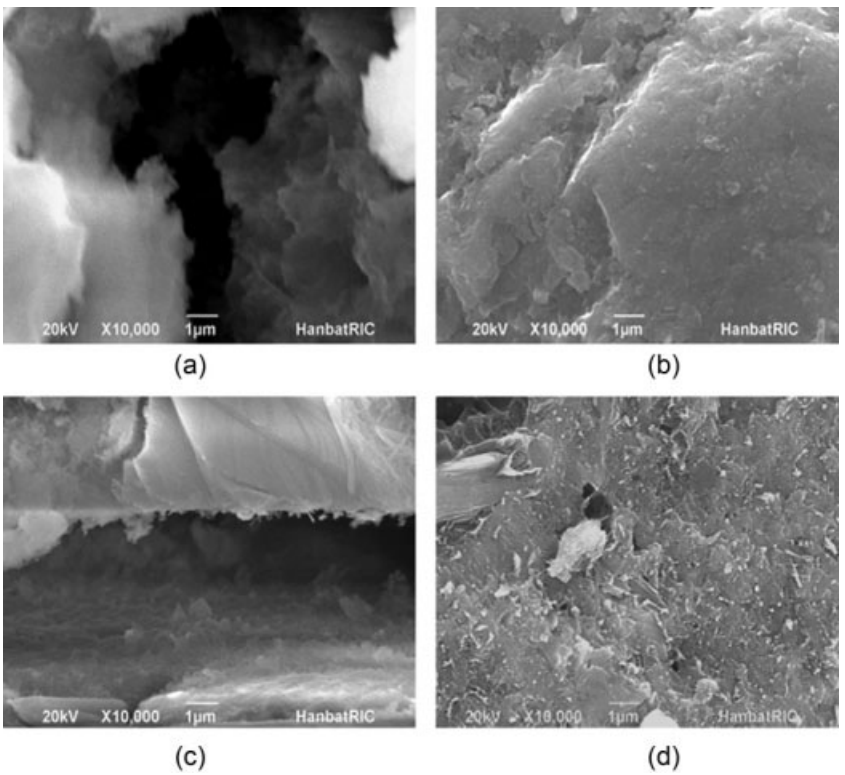


**Figure 3** Micrographs of (a) OPC surface, (b) PIC surface, (c) OPC below surface, and (d) PIC below surface after exposure to 2.5*M* HCl for 7 days.

products by the acid and destruction of the hydrosilicate complex in the cement matrix.[11] As the porosity increases, the permeability of external chemicals into the cement matrix increases causing a subsequent decrease in the effective surface area that can resist the load applied. The polymer forms a protective coating on the cement particles in PIC [Fig. 4(b,c)]. However, on prolonged exposure to strong acids some of this polymer undergoes degradation. This exposes some portions of the cement matrix to

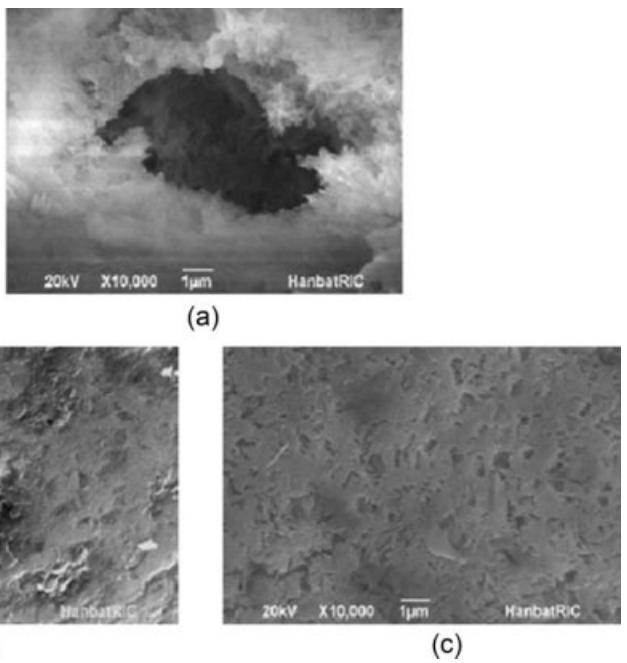


**Figure 4** Micrographs of (a) OPC, (b) PIC surface, and (c) PIC below surface after exposure to 2.5*M* HCl for 28 days.

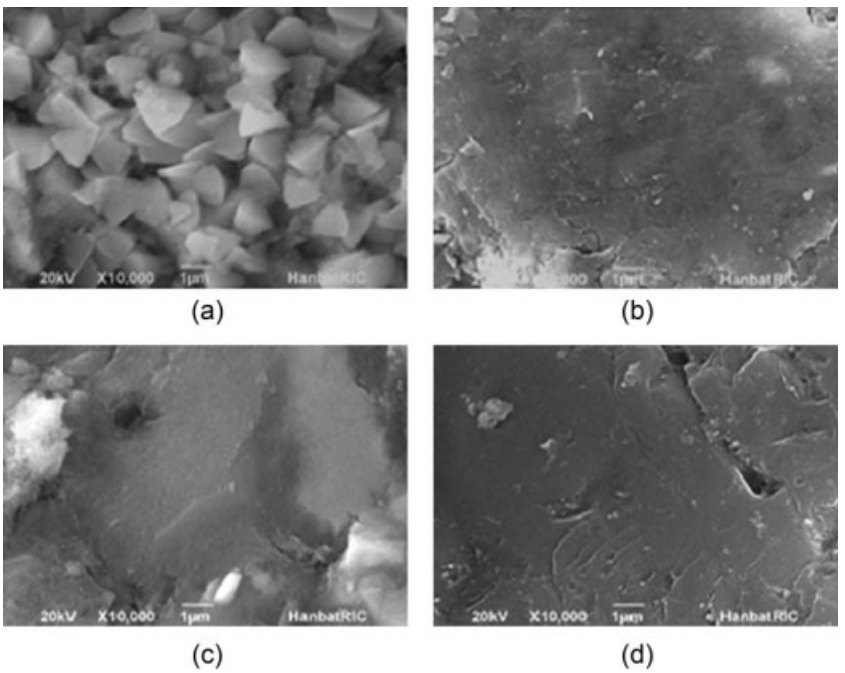


**Figure 5** Micrographs of (a) OPC surface (b) PIC surface (c) OPC below surface (d) PIC below surface after exposure to sea water for 7 days.

the hydrochloric acid. This results in a decrease in the degree of retention of strength properties.

The presence of plate like crystals on the surface of the OPC samples in Figure 5(a) indicates some interactions between the ions present in the sea water and the cement particles. Sea water contains chlorides, sulfates, and bicarbonates of sodium, magnesium, and calcium. These ions react with $Ca(OH)_2$, a by-product of cement hydration forming a porous reticular network.[12] Figure 5(b) revealed no effect on the cement matrix below the surface of the OPC after the exposure of the specimen to sea water for 7 days. It is also observed in Figure 5(c,d) that the cement matrix on the surface and below surface, respectively, of PIC specimens is not affected by sea water. This may be due to the protective sheath formed by the polymer over the cement particles in the PIC samples.

The micrographs of OPC as seen in Figure 6(a,b) reveal thick fan shaped crystals formed as a result of the reactions between magnesium sulfate in the sea water and aluminates present in the cement particles. These crystals eventually result in cracking of the concrete thus increasing its permeability. This results in the interactions between the chlorides, sulfates, and carbonates present in the sea water and calcium hydroxide present in cement to form bicarbonates that eventually leach out of the concrete structures. In Figure 6 (b and d) the protective hydrophobic coating of the polymer over cement particles in PIC seems to prevent contact with sea water.

### Molecular weight and degree of polymerization

From the GPC analysis the molecular weights (MP) of the polymer in PIC polymerized using microwaves and hot water were found to be 39,400 and 18,700, respectively. This indicates that the polymerization using microwaves for 2 h is more effective and economical than hot water polymerization for 3 h. This may be due to the fact that the thermal diffusivity in the samples is faster when heated by microwaves. As the degree of polymerization and molecular weight increases the strength and resistivity of the PIC to the external environments also increases.[13]

### Porosity of OPC and PIC samples

Porosity and pore structure of cement mortars and concrete have a direct control on the permeation of potentially deleterious substances into the cement matrix.[14] These substances undergo reactions with the ions present in the cement resulting decrease in the strength and durability of concrete structures.

In Table I porosity measurements reveal an initial decrease in porosity in OPC specimens after exposure to 2.5*M* HCl for 7 and 14 days after which there was a sharp increase on prolonged exposure. This reduction in the porosity may be attributed to the blocking of the pores in the cement matrix by the products of reaction between the cement particles and the hydrochloric acid. The interactions undergone by the cement matrix on exposure to hydrochloric acid are illustrated below.

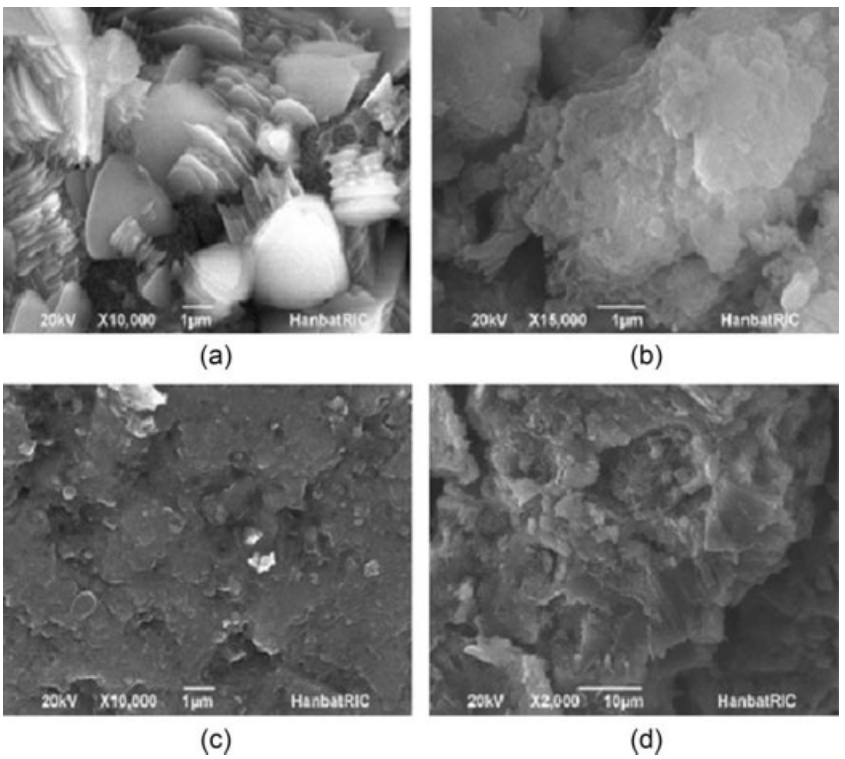


**Figure 6** Micrographs of (a) OPC surface, (b) PIC surface, (c) OPC below surface, and (d) PIC below surface after exposure to sea water for 28 days.

$$Ca(OH)_2 + HCl \longrightarrow CaCl_2 \quad (1)$$

$$CaCl_2 + Ca(OH)_2 \longrightarrow CaCl_{2x}3Ca(OH)_{2x} \cdot 12H_2O \quad (2)$$

$$CaCl_{2x} \cdot 3Ca(OH)_{2x} \cdot 12H_2O + 3CaO\ Al_2O_3 \longrightarrow Ca_3Al_2O_6 \cdot CaCl_2 \cdot 10H_2O \quad (3)$$

Some of the $CaCl_2$ formed during reaction (1) does not leach out of the cement matrix and forms a double salt with $Ca(OH)_{2x}$, namely $CaCl_{2x}$ $3Ca(OH)_{2x}$·12H2O. This salt reacts with 3CaO $Al_2O_3$, a product of cement hydration, forming Friedels salt, $Ca_3Al_2O_6.CaCl_2.10H_2O$.[15] Because of the above salt formation shown in reactions (2) and (3) there is a decrease in the porosity after 7 and 14 days of exposure of cement mortar to hydrochloric acid. The porosity values indicate that the breakpoint of deterioration of the OPC samples is after 14 days of exposure to 2.5*M* HCl. Beyond this their strength decreases because of the sharp increase in the porosity in the cement matrix.

In PIC, the porosity and average pore diameter remains almost constant till 21 days and then increases on prolonged exposure. This may be due to the sealing of the pores by the polymer and also partly due to the bond formation between the $Ca^{2+}$ ions in the cement and acrylate group present in the PMMA. After 28 days of exposure some of the cementitious binder undergoes reaction with the acid because of the degradation of the outer protective layer of the polymer as seen in the scanning electron micrographs (in Fig. 4). In case of PIC, breakpoint of deterioration on exposure to 2.5*M* HCl is more than

**TABLE I**
**Porosity Measurements of OPC and PIC Specimens**

| | OPC | | HW-PIC | | MW-PIC | |
|---|---|---|---|---|---|---|
| Days of exposure in 2.5*M* hydrochloric acid | Porosity (%) | Average pore diameter (μm) | Porosity (%) | Average pore diameter (μm) | Porosity (%) | Average pore diameter (μm) |
| 0 | 19 | 0.0878 | 10.5 | 0.0486 | 9.6 | 0.0318 |
| 7 | 14.8 | 0.0434 | 10.0 | 0.0537 | 12.0 | 0.0324 |
| 14 | 13.6 | 0.459 | 11.0 | 0.0678 | 12.0 | 0.0408 |
| 21 | 33 | 0.119 | 9.2 | 0.0682 | 10.0 | 0.0381 |
| 28 | 35.0 | 0.1356 | 22.0 | 0.0696 | 26.0 | 0.0420 |

21 days. This is evident from the increase of the porosity and average pore diameter of the PIC specimens on exposure to the acid for 28 days.

## CONCLUSIONS AND FUTURE WORK

From the above microstructural studies on PMMA impregnated mortar the following conclusions were arrived at. The polymer forms a protective sheath around the cement particles and fills in the voids in the cement mortar matrix thereby improving the durability of these composites when exposed to the external chemical environments. The cement particles in OPC undergo reactions with hydrochloric acid and sea water and increase the porosity by forming water soluble leachable salts. This decreases its strength and subsequently the durability of the building structures. The molecular weight of the polymer formed *in situ* in PIC by microwaves was found to be higher than that prepared using conventional thermal methods. Calcium ions in the cement form double salts with hydrochloric acid that initially decrease the porosity of the OPC. However, these salts leach out on prolonged exposure thereby increasing porosity. The widened pore size allows the movement of external chemicals in to the matrix degrading its performance.

The above studies on porosity and molecular weights of polymer in the PIC revealed that employing microwaves instead of the conventional hot water to polymerize the monomer is more efficient and economical. This is mainly because of the uniform temperature distribution and increased thermal diffusivity through out the specimen during the polymerization of the monomer. This methodology is being now applied for the production of polymer impregnated Hume pipes for the transportation of waste and sewage water. The uniform protective polymer coating in the interior of the pipes prevents contact between the cement particles and chemicals in waste water. This improves the durability and performance of the Hume pipes. The evaluation of chemical resistance of these polymer impregnated Hume pipes against deterioration in these environments is also underway.

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