

Mechanical properties and durability of PMMA impregnated mortar

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Abstract—Polymer impregnated concrete (PIC) is known to exhibit better strength and durability characteristics than the other classes of polymer cement composites. In the work described herein the monomer was impregnated into cement mortar and polymerized by two methods - the conventional thermal method and using microwaves. The mechanical properties and durability characteristics of the samples and on exposure to chemical environments were then evaluated. The above studies revealed that the strengths of PIC specimens were almost 2-3 times better than those of conventional cement mortars. The chemical resistance was also found to be superior even on prolonged exposure to the chemical media. This may be attributed to the protective layer formed by the polymer on the cement mortar, which prevents the external chemical media from interacting with the cement particles. The properties of the PIC specimens prepared by both methods have also been compared and discussed in this paper.

Key words: Durability, Cement Mortar, Composite, Polymer, Strength

INTRODUCTION

Concrete is a versatile and widely used construction material in civil engineering. Its record of durability has been remarkable especially when exposed to extreme environments [1,2]. However, there are phenomena that can produce considerable damage to concrete if proper precautions are not taken. The advent of industrialization has led to early deterioration due to corrosion of embedded reinforcement and spalling of the concrete cover exposing the reinforcement bars within and resulting in structural instability of the concrete structures [3,4].

Durability is the ability of the cement concrete to resist weathering actions, chemical attacks, abrasion or any other process of deterioration. Causes for deterioration of a concrete structure may be physical, mechanical or chemical. External chemical attacks occur through the action of chlorides, sulfates, carbon dioxide and many natural or industrial liquids [5] and gases [6]. Most processes that can cause deterioration in concrete produce an ultimate excessive expansion resulting in cracking. In certain situations, these problems can be solved by using materials that contain an organic polymer or resin [7] instead of Portland cement or in conjunction with it. These relatively new materials offer higher strength, improved durability and good resistance to corrosion, reduced water permeability and greater resistance to damage from freeze-thaw cycles.

The use of polymers in cement concrete and mortar to enhance its durability and performance is not entirely new. In polymer impregnated concrete (PIC) the water and air filled pores of conventional concretes are impregnated partially or completely by polymers, thereby increasing the strength and durability of the cement concrete or mortar [8,9]. The microstructure of the PIC reveals an impermeable matrix in which the cement hydrate phase, aggregate

phase and the continuous polymer phase interpenetrate each other [10,11].

In this work, PIC samples were prepared by impregnating methyl methacrylate (MMA) into precast cement mortars and polymerized by using two different techniques. The mechanical properties and the resistance of PIC against deterioration when exposed to acid and sea water were evaluated to assess the performance of these composites. These properties were compared to precast cement mortars (OPC) without impregnation of the monomer.

EXPERIMENTAL PART

1. Materials

Ordinary Portland cement and sand conforming to Korean standard KS L 5100 were used in the preparation of these specimens. The water to cement ratio (w/c) was 0.48, while the cement, sand and water were mixed in the proportion of 1 : 2.45 : 0.48. Cubical specimens of OPC mortars of dimensions 5 cm×5 cm×5 cm weighing around 250 g were used to determine compressive strength. The flexural strength was determined using specimens of dimensions 4 cm×4 cm×16 cm weighing 530 g approximately. All the specimens were cured for 28 days after mixing of the cement, sand and water before carrying out the impregnation and polymerization.

2. Impregnation and Polymerization

The precast mortar specimens were dried in a hot air oven (Samwoo Science Company) at 80 °C for 8 hours. These were annealed to room temperature and weighed before impregnation. The MMA was mixed with 1% by weight of 2,2'-Azobisisobutyronitrile (AIBN). The mortar samples were immersed into this mixture and impregnated by placing the setup in a water bath with an inside ultrasound vibration system for 4.5 hrs at room temperature. The samples were dried, weighed and vacuum packed in poly polyethylene terephthalate (PET) packets to prevent the loss of monomer during polymerization.

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The samples were thermally polymerized by two different procedures, i.e., using conventional method and microwaves.

(i) In the conventional method, the impregnated mortar samples were packed in PET bags and immersed in hot water at 80 °C for 3 hrs so as to achieve uniform heating (HW-PIC).

(ii) Polymerization of the specimens in the microwave reactor was done at a frequency of 2,450 MHz (400W) at 80 °C for 2 hours (MW-PIC). After polymerization the samples were removed from the PET packets, cooled to room temperature and weighed.

3. Mechanical Properties

The properties studied in this section include the uniformity of the matrix in the mortar samples, its load bearing capacity and the stress at point of rupture of the PIC and OPC specimens.

3-1. Pulse Velocity Measurements

The pulse velocity measurements help to establish uniformity and detect cracks in the concrete samples. The velocity of an ultrasonic pulse travelling in a solid material depends on the density and the elastic properties of that material [12]. Specimens were tested according to ASTM D2845: 2005 [13], and the pulse velocities were determined for fresh samples and for samples immersed separately in acid and sea water.

The travel time of an ultrasonic pulse through the test specimen under direct transmission was recorded and pulse velocity was calculated by dividing the length of the specimen by the travel time.

3-2. Compressive Strength

Compressive strength is the capacity of a material to withstand axially directed pushing forces and is calculated by dividing the maximum load applied when the cubical specimen breaks by its cross sectional area resisting the load. This property was evaluated in accordance to KS L 5105 standards [14] and the maximum load needed to break the conventional cement mortar and PIC samples was determined using a Universal testing machine, Servo UTM US-200.

3-3. Flexural Strength

The highest stress experienced within the material at its moment of rupture is defined as the flexural strength. In a bending test, the highest stress is reached on the surface of the sample. The flexural strengths of conventional cement mortar and PIC specimens made were evaluated according to KS F 2476:2007 [15]. A Digital Flexure Tensile Tester HJ-1171 was employed to calculate the flexural strengths of the conventional cement mortar and PIC specimens.

4. Durability Tests

These tests are of prime importance in assessing overall concrete performance during service conditions. Water absorption properties and resistance of OPC and PIC samples against deterioration after exposure to 2.5 M hydrochloric acid and sea water have been portrayed in the later sections of this paper.

4-1. Water Absorption

This was also evaluated by computing the percentage weight gain of the PIC and OPC at regular intervals of time and was done according to ASTM C1585-04 [16].

4-2. Chemical Resistance to Hydrochloric Acid and Sea Water

The percentage weight loss and percentage retention of the compressive and flexural strength were calculated to assess the performance of the mortars after 7, 14, 21 and 28 days of immersion in the respective media.

Hydrochloric acid was used for this study since the damage of the cement concrete is higher than other acids like nitric and sulphu-

ric acids [17]. It attacks the concrete by a dissolution reaction resulting in the formation of soluble salts which eventually gets leached out on exposure to water.

Exposure to sea water was studied to evaluate the performance of samples in marine environments. Sea water contains many salts, and these undergo reactions with the hydration products of the cement particles. These are very detrimental to any concrete structure.

4-3. Freeze Thaw Resistance

Freeze thaw test was performed according to KS F 2456 [18]. Samples of conventional cement mortar and PIC specimens of dimensions 4 cm×4 cm×16 cm were employed in this test. The OPC and PIC samples were subjected to rapid freeze and thaw temperatures of -18 °C to 4 °C.

RESULTS AND DISCUSSION

1. Preparation

The OPC samples were weighed before and after impregnation of the MMA and subsequently after the polymerization to ascertain the weight of monomer and polymer in the OPC. It was found that there was an increase of around 5% in the weight of the specimens after impregnation of the MMA for 4.5 hours and 0.3% decrease after polymerization. The initial increase in the weight is due to the permeation of the monomer into the cement mortar matrix. The above observation has also been made and cited by A.Auskern and W.Horn, the reason being that the polymer occupies only 80% of pores in the cement matrix. This is due to the evaporation of the monomer and water during the thermal polymerization of the monomer [19].

2. Mechanical Properties

2-1. Pulse Velocity Measurements

As seen in Table 1 the values obtained from the pulse velocity measurements reveal the presence of a compact and dense microstructure after the impregnation and polymerization of the monomer in the PIC samples. When the OPC is exposed to sea water the values increase marginally due to the permeation of salts into the cement matrix. The presence of polymer seems to prevent the creation of voids and cracks when exposed to 2.5 M hydrochloric acid.

2-2. Strength Parameters

Fig. 1 reveals superior mechanical properties of the PIC samples compared to those of the OPC. The values of compressive and flexural strengths obtained for the PIC samples are observed to be twice that of OPC samples. The compressive and flexural strengths of PIC specimens prepared from hot water are marginally better the

Table 1. Ultrasonic pulse velocity measurements of OPC and PIC specimens before and after the exposure to acid and sea water

Sample	Pulse velocity (km/sec)	
	Before immersion in chemical media	After immersion in Sea water 2.5 M HCl
OPC-1	3.75	4.11 3.78
Microwave PIC	4.34	4.39 4.34
Hot water PIC	4.33	4.36 4.33

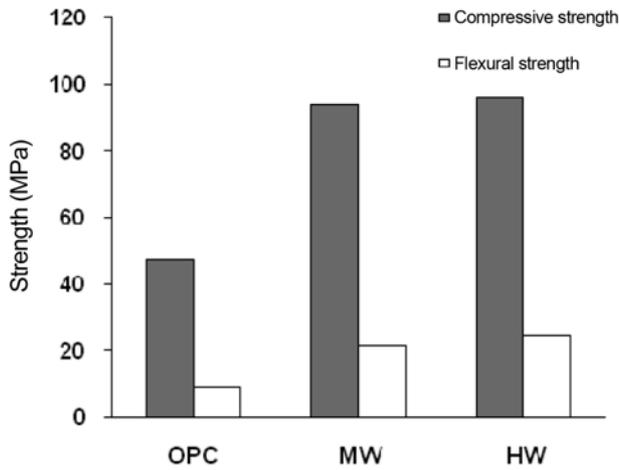


Fig. 1. Mechanical properties of PIC and OPC specimens.

specimens polymerized by microwaves.

In case of PIC specimens the enhancement of strengths both compressive and flexural could be attributed to the increase in effective area to resist the stress applied on the specimen due to the presence

of the polymer in the cracks and micro voids within the matrix.

2-3. Durability of OPC and PIC Specimens

a. Water absorption of OPC and PIC mortars

The water absorption of the OPC and PIC specimens were calculated in terms of weight change at various intervals of time and the results are presented in Fig. 2.

Water dissolves $Ca(OH)_2$, a by-product of cement hydration in the cement mortar. This solution leaches out of the concrete structures, thereby reducing its durability. As shown in Fig. 2, OPC specimens show around 4-5% increase in weight. The increase is greater in the initial stages and becomes almost a constant after 7 days of immersion in water. The percentage of weight gain in case of PIC specimens was around 0.3% initially and increased to 0.8% after 16 days. This may be attributed to presence of the polymer envelope around the cement mortar that prevents the contact between water and the cement particles. The polymer is hydrophobic and thus does not undergo any interactions with water [20]. The PIC specimens prepared by the two techniques, i.e., conventional hot water and microwaves exhibited similar water absorption behavior.

b. Resistance to hydrochloric acid and sea water

The following paragraphs describe the evaluation of the OPC and PIC specimens that were exposed separately to 2.5 M hydro-

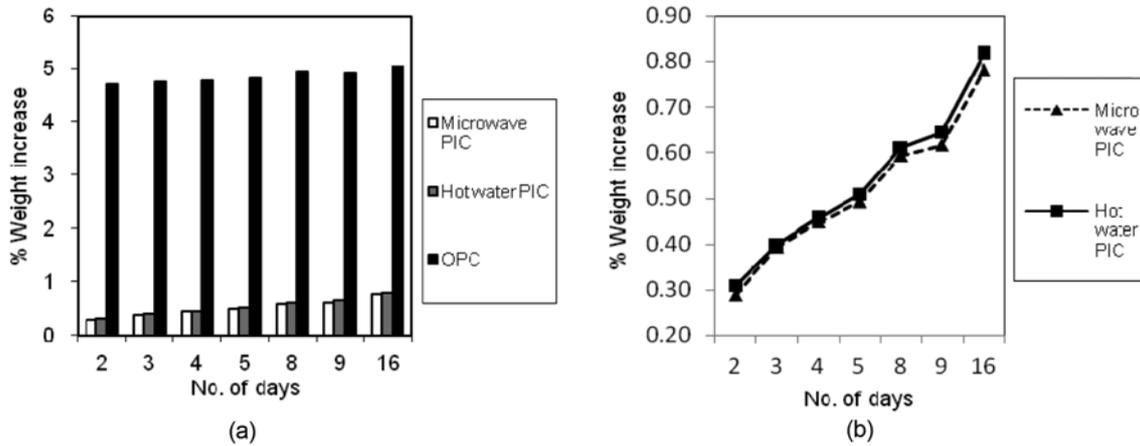


Fig. 2. Water absorption of (a) MW-PIC, HW-PIC and OPC specimens (b) MW-PIC and HW-PIC.

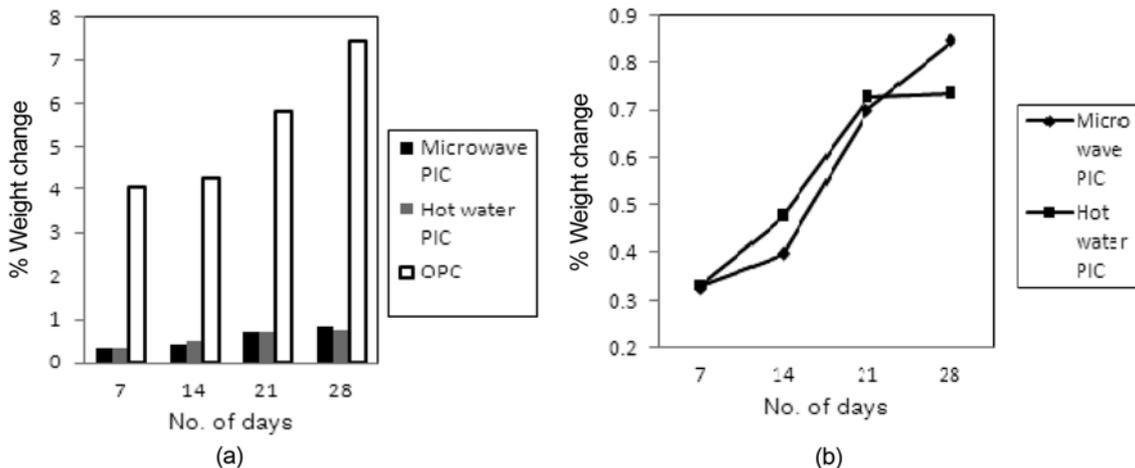


Fig. 3. Percentage weight gain of (a) MW-PIC, HW-PIC and OPC (b) Microwave and hot water PIC specimens on exposure to sea water.

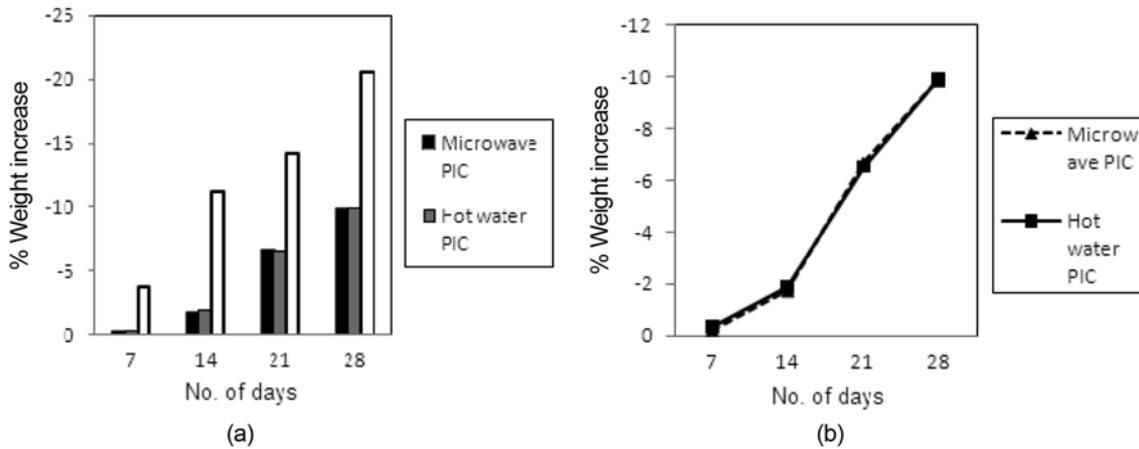


Fig. 4. Percentage weight gain of (a) MW-PIC, HW-PIC and OPC (b) MW-PIC AND HW-PIC specimens on exposure to 2.5 M HCl.

chloric acid and sea water for various periods of time.

Fig. 3 shows that the PIC samples prepared by both the techniques underwent minimum percentage weight gain (0.7% in 28 days) on exposure to sea water as compared to OPC (7.5% in 28 days). This possibly is due to the sealing of the pores and voids by the polymer, which possibly prevents the entry of external chemicals into the cement matrix, thereby inhibiting deposition of metal salts from sea water. These results indicate that PIC has resistivity against deterioration when exposed to polluted environments.

As shown in the Fig. 4, the percentage weight loss for OPC is higher than PIC and is almost similar for PIC specimens prepared by microwaves and hot water. The cement particles in OPC undergo interactions with the hydrochloric acid, resulting in cracks and voids on the surface which becomes porous on prolonged exposure. The effective load area to resist stress applied on the specimen becomes less since cement forms leachable salts with hydrochloric acid which removed on exposure to the aqueous solution of the acid.

The percentage degree of retention of the flexural strength was calculated for OPC and PIC samples immersed separately in hydrochloric acid and sea water for 15 days.

As shown in Fig. 5, the OPC specimens gave less than 75% retention of flexural strength (Fig. 5) as compared to the 90% in case of PIC specimens. The compact structure of the PIC composites seems to have prevented the cracking and rupture of the specimens. From the graph it is seen that the PIC samples that were polymerized by

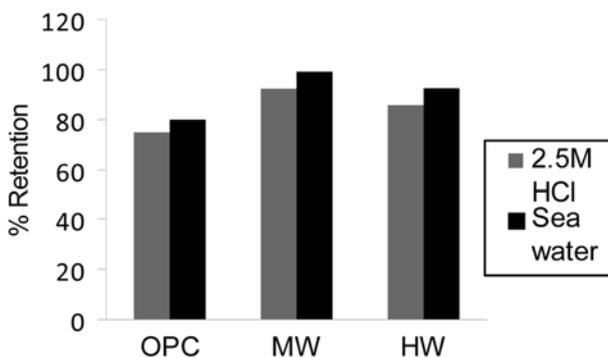


Fig. 5. Percentage degree of retention of flexural strength of OPC and PIC specimens.

microwaves gave around 99% and 91% retention of flexural strength when dipped in hydrochloric acid and sea water, respectively, than 92% and 80% retention by composites prepared by hot water.

Hydrochloric acid undergoes dissolution reaction with hardened concrete forming soluble salts which leach out of the cement matrix. This results in destruction of the hydrosilicate matrix in the cement, thereby resulting in loss of strength [21,22].

Fig. 6 illustrates the retention of the original load bearing capacity of the specimens after exposure to 2.5 M hydrochloric acid and reveals that this property is almost identical at around 90% for all the samples for the first 7 days. A sharp decrease of retention of compressive strength was then observed in case of the OPC samples for a longer immersion time in the media. The rate of decrease of this property is gradual for PIC specimens due to the presence of the polymers in the voids and micro cracks. This prevents reaction between hydrochloric acid and the cement particles in the cement mortar matrix. On exposure for 28 days the percentage degrees of retention of compressive strength were found to be 34% and 27% for PIC samples prepared by microwaves and hot water, respectively. This is perhaps due to the degradation of the polymer when the PIC was immersed for 28 days in 2.5 M hydrochloric acid. PIC specimens prepared by microwaves exhibited better chemical resistant than that of hot water polymerised specimens.

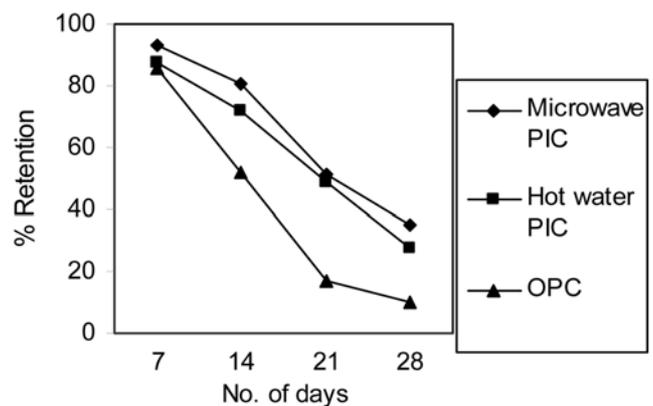


Fig. 6. Percentage degree of retention of compressive strength of OPC and PIC specimens on exposure to 2.5 M HCl.

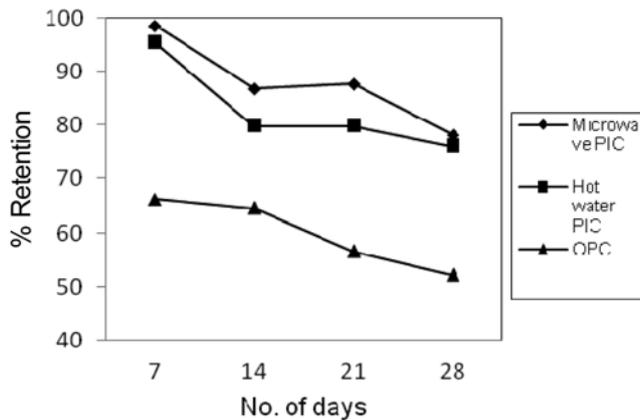


Fig. 7. Percentage degree of retention of compressive strength of OPC and PIC specimens on exposure to sea water.

Sea water contains chlorides, bicarbonates and sulphates of many metal ions such as Na^+ , Mg^{2+} and Ca^{2+} . Among these the presence of magnesium sulfate ions is the most detrimental for the durability of cement mortars. It undergoes interactions with the cement hydration products, which in turn results in cracks in the concrete structure [22].

The percentage degree of retention of compressive strength as cited in Fig. 7 gradually decreases in all cases, though it is much lower in case of OPC specimens. Among the PIC specimens, the ones in which the monomer was polymerized by microwaves exhibited much higher degree of retention of compressive strength, i.e., 88% after 21 days as compared to 79% in case of hot water polymerized specimens. This could be attributed to the higher degree of polymerization of the monomer when the monomer was uniformly heated by the microwaves. This has resulted in more enhanced properties of the impregnated polymer present in the precast OPC.

These results indicate high resistivity of the composite to deterioration when exposed to polluted environments.

c. Freeze thaw resistance

The resistance to freeze and thaw cycles of OPC and PIC was evaluated in terms of relative dynamic modulus of elasticity and change in compressive strengths before and after the test. The compressive strengths before and after subjecting the OPC and PIC specimens to rapid cycles of freeze and thawing from temperatures -18°C and 4°C are indicated in Fig. 8.

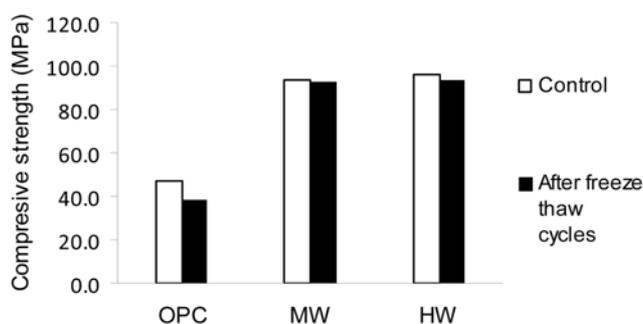


Fig. 8. Compressive strength of OPC and PIC specimens before and after subjecting to freeze thaw cycles.

Table 2. Values obtained after Freeze thaw cycles

Sample	% Retention of compressive strength	Relative dynamic modulus of elasticity, %
OPC	80.5	85
MW-PIC	98.78	97
HW-PIC	97.29	88

Table 2 indicates the relative dynamic modulus of elasticity and percentage retention of original compressive strength after the freeze thaw cycles of PIC and OPC specimens. These values signify that the PIC specimens prepared from microwaves are superior in terms of durability after exposure to extreme variations of temperature compared to those of OPC and PIC specimens prepared by conventional methods. When the monomer is polymerized by microwaves the thermal diffusivity inside the specimens is better. This results in an increase in the degree of polymerization of the monomer throughout the PIC specimen than the same when conventional thermal methods are used.

CONCLUSIONS

Polymer fills the voids and microcracks in the OPC, thereby increasing its mechanical and chemical resistant properties. The percentage degree of retention of mechanical properties of the PIC after exposure to chemical environment is better than OPC, and rate of decrease on prolonged exposure is faster for prepared from microwaves exhibit better durability characteristics compared to ones prepared from hot water, probably due to increased degree of polymerization of the monomer by the microwaves. At prolonged periods of exposure of the PIC specimens to 2.5, M hydrochloric acid represents better resistance to degradation than OPC. The resistance to water absorption of the PIC specimens is superior compared to OPC specimens.

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