Physico-chemical changes in polymer impregnated mortars on exposure to sea water

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Abstract−This paper highlights the results and interpretations of experiments conducted to analyze the effect of sea water on conventional precast cement mortar (OPC) and polymer impregnated mortars (PIC). The precast cement mortars were impregnated with a mixture of methyl methacrylate and 2, 2′-Azobisisobutyronitrile (AIBN) initiator and polymerized using two different procedures: by microwaves and by conventional hot water method. The OPC and PIC specimens were immersed in sea water separately for 7, 14, 21 and 28 days and their strength parameters were calculated. The changes in the microstructure indicated movement of ions into the cement matrix and the presence of fan-like crystals on the surface of cement mortar. The protective polymer coating in the PIC prevented contact of sea water with cement concrete, thereby increasing the durability of the composite.

Key words: Polymer, Cement Mortar, Strength, Microstructure, Interactions

INTRODUCTION

In marine environments, the penetration of water, chloride and other aggressive ions into concrete is the most important factor contributing to the physical and chemical processes of deterioration. The microstructure of concrete controls the physical/chemical phenomena associated with water movements and the transport of ions in concrete. Chlorides and sulfate ions from seawater penetrate into the concrete and cause deterioration of reinforced concrete structures and corrosion of metal reinforcements [1]. The sulfate attack in marine environment gives rise to expansive ettringite, gypsum and brucite and is associated with calcite formation [2]. Among all the salts present in the sea water $MgSO_4$ is the most detrimental to cement concrete. It displaces the calcium present in the hydrated silicate C-S-H in cement forming hydrated calcium magnesium silicate C-M--S-H. It also reacts with calcium hydroxide in the cement forming secondary gypsum and brucite [3]. These reactions lead to the formation of cracks in the cement concrete structure. The other problems of exposure of concrete to sea water include freeze thaw attack, salt weathering and abrasion by sand and ice. The intensity of these attacks depends on the location of the concrete with respect to the sea level and the thermal gradients to which the concrete and sea water is exposed [4] The rate at which the hardened cement paste is deteriorated due to the exposure to harmful chemicals depends mainly on the concentration of the chemicals, the duration of exposure, and the chemical resistance of concrete [5].

Polymer-impregnated concrete (PIC) has been used as a potential construction material for desalination plants since the 1970s [6]. PIC is one of the oldest polymer cement composites used and is prepared by impregnating a mixture of monomer and initiator into the precast cement concrete. The monomer is subsequently polymerized *in situ* in the concrete by thermal or radiation methods. This serves not only to fills the pores and voids in the concrete structure but also to enhance its strength, freeze thaw resistance and durability when exposed to chemical environments [7].

In this paper, precast cement mortar specimens were impregnated separately with two monomers, methyl methacrylate and styrene, and the monomers were separately polymerized both by conventional thermal method and by microwaves. The durability of PIC and OPC in sea water was assessed by calculating the variation in compressive and flexural strengths for different periods of time. The morphological changes were studied by a scanning electron microscope and the movement of ions into the cement concrete was monitored by inductively coupled plasma.

EXPERIMENTAL METHODS AND TECHNIQUES

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 was maintained at 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 the compressive strength. The flexural strength specimens were of dimensions 4 cm× 4 cm×16 cm weighing 530 g approximately.

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/ styrene was mixed with 1 wt% of AIBN as an initiator. The mortar samples were immersed into this mixture and impregnated by placing the setup in a water bath inside an ultrasound vibration system for 4.5 hours at room temperature. The samples were dried, weighed and vacuum packed in PET packets to prevent the loss of monomer during polymerization.

The samples were thermally polymerized by two different pro-

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cedures: conventional methods and microwaves. In the conventional method, the impregnated mortar samples were packed in PET bags and immersed in hot water at 80 °C for three hours so as to achieve uniform heating (HW-PIC). Polymerization of the specimens in the microwave reactor was carried out at a frequency of 2,450 MHz (400 W) at 80 °C for two hours in case of MMA and 3 hours in case of styrene. After polymerization the samples were removed from the PET packets, cooled to room temperature and weighed.

3. Mechanical Properties

In this work, the cubical specimens of precast mortars and PIC samples of dimension 5 cm×5 cm×5 cm were employed to determine the above value. The evaluation of this property was performed in accordance to KS L 5105 standards [8] and the maximum load needed to break the conventional cement mortar and PIC samples was determined using a Servo UTM US-200.

In a bending test, the highest stress is reached on the surface of the sample. In this part of the study, the flexural strengths of conventional cement mortar and PIC specimens of dimensions 4 cm×4 cm×16 cm were evaluated according to KS F 2476:2007 [9]. A digital flexural tensile tester (HJ-1171) was employed to calculate the flexural strengths of the conventional cement mortar and the PIC specimens.

Freeze thaw experiments were performed according to KS F 2456 [10] and 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 300 rapid freeze and thaw cycles of temperatures from −18 °C to 4 °C.

4. Chemical Resistant Properties

Durability is of prime importance in assessing overall concrete performance during service conditions. The mechanical and water absorption properties and resistance of OPC and PIC samples against deterioration after exposure to 2.5 M hydrochloric acid and sea water are reported in this paper. The percentage weight loss and percentage retention of the compressive strength were calculated to assess the performance of the mortars after 7, 14, 21 and 28 days of immersion in the respective media [11].

The decrease of flexural strength of the test specimens after 15 days of exposure to sea water was also determined.

5. Microstructural Studies

These studies were performed to analyze the effect of the impregnation and polymerization of the monomer in the OPC mortar. The microstructure of OPC and PIC was studied using gel permeation chromatography (GPC, Waters Model) and scanning electron microscope (SEM, Joel JSM 6390).

The SEM studies revealed the porosity and micro cracks in the cement matrix in the samples. Samples of 1-2 mg weight were subjected to gold sputtering to make them conducting. These samples were analyzed by imaging the fractured surface under the SEM.

GPC was used to determine the molecular weight and the degree of polymerization of the poly methyl methacrylate (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.

$MgSO_4$, present in sea water, is the most detrimental to the durability of cement mortars. The movement and concentration of magnesium ions permeating into the cement mortar was studied using inductively coupled plasma (ICP-OES, Perkin Elmer Model: 5300DV).

The concentration of Mg^{2+} ions in sea water was initially determined before immersion of the cement mortar. The samples were dipped in sea water for 28 days at room temperature after which the concentration of Mg^{2+} ions was again evaluated.

RESULTS AND DISCUSSIONS

1. Polymer Loading

The OPC samples were weighed before and after impregnation of the MMA/styrene 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% and 4% in the weight of the specimens after impregnation of the MMA and styrene, respectively. The decrease in the weight after polymerization was found to be 0.3% and 0.5% for MMA and styrene, respectively. The initial increase in the weight is due to the penetration of the monomer into the cement mortar matrix. The above observation has also been made and cited by Auskern and Horn [12], 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.

2. Strength Parameters on Exposure to Sea Water

In Fig. 1 illustrates the compressive strengths of the OPC and PIC samples after 7, 14, 21 and 28 days of exposure to sea water.

From Fig. 1 it was found that the compressive strength of OPC samples decreased on prolonged exposure to sea water from 47.7 MPa to around 36 MPa after 7 days and to 24 MPa on prolonged
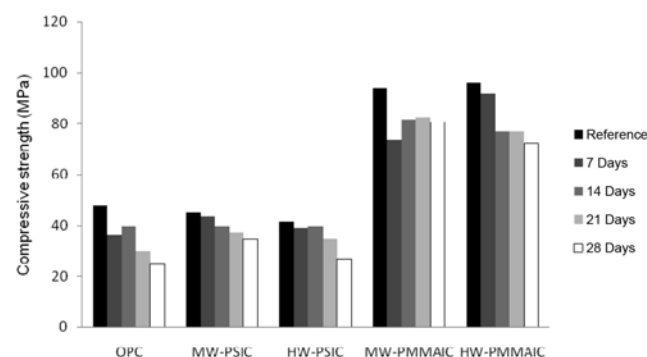

Fig. 1. Strength of OPC and PIC specimens on exposure to sea water. OPC, Ordinary cement mortar; MW-PSIC, Microwave PS impregnated cement mortar; HW-PSIC, Hot water PS impregnated cement mortar; MW-PMMAIC, Microwave PMMA impregnated cement mortar; HW-PMMAIC, Hot water PMMA impregnated cement mortar.

Table 1. Percentage degree of retention of original compressive strength of OPC and PIC specimens

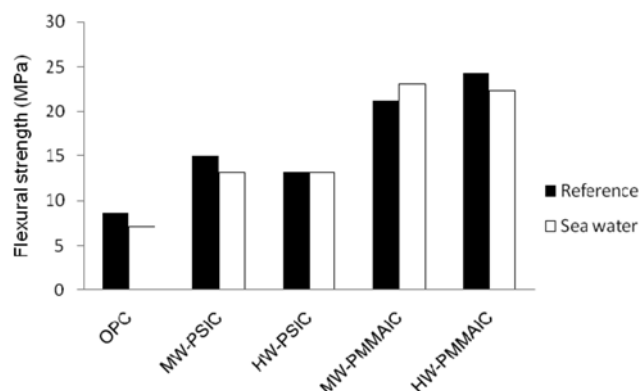| No. of days	% Retention of compressive strength				
	OPC	PSIC		PMMAIC	
		Microwave	Hot water	Microwave	Hot water
7	66.19	86.17	85.9	98.57	95.36
14	64.52	84.2	84	86.9	79.87
21	56.56	83.13	83.6	87.68	79.91
28	52.16	76.75	65.33	78.24	76.12

Fig. 2. Flexural strength of OPC and PIC before and after exposure to sea water. OPC, Ordinary cement mortar; MW-PSIC, Microwave PS impregnated cement mortar; HW-PSIC, Hot water PS impregnated cement mortar; MW-PMMAIC, Microwave PMMA impregnated cement mortar; HW-PMMAIC, Hot water PMMA impregnated cement mortar.

Fig. 3. Freeze thaw resistance of OPC and PMMAIC polymerized by conventional method and microwaves. MW, Microwave PMMAIC; HW, Hot water PMMAIC.

exposure for 28 days. This could be attributed to the interactions between the hydration products of the cement and salts present in the sea water. In the PIC samples, the protective layer formed by the polymer is hydrophobic. It, therefore, prevents contact of sea water with the cement particles.

Among the PIC samples, the compressive strength parameters of those that were impregnated with PMMA (PMMAIC) exhibited higher values of compressive strength (96 MPa) and flexural strength (25 MPa) than the ones prepared from PS (PSIC) (45 MPa and 15 MPa of compressive and flexural strength, respectively). From Table 1 it is seen that the percentage degree of retention of original compressive strength of PIC is better than that of OPC.

The viscosity of MMA (0.6 CPa at 20 °C) is less than that of styrene (0.762 CPa at 20 °C). Thus the effective area of its impregnation into the cement mortar and subsequent polymerization is more than that of styrene [13]. This not only fills up the pores and voids in the cement mortar, but also increases the effective area that can resist the load applied on the specimen. Moreover, the presence of the polymer in the brittle cement mortar matrix has increased the ductility and chemical resistance of the cement mortar. The impermeable barrier formed by the polymer prevents the cement particles from undergoing interactions with sea water. This contributes to the superior flexural strength of the specimens against cracking and rupture even on exposure to sea water.

Off-shore cement concrete structures and bridges, built in the sea, are subjected to severe freeze thaw conditions [14]. The freezing point of water decreases in the presence of salt. Thus the ice is formed at different times in different layers in the cement concrete matrix. This results in differential stresses in the concrete structure due to hydraulic and osmotic pressure development.

The resistance to freeze and thaw cycles of OPC and PIC was evaluated in terms of the 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. 3.
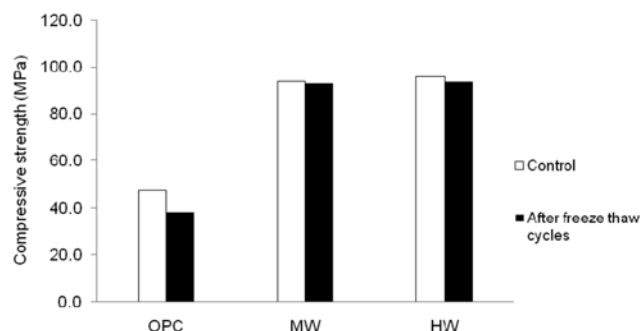
These values signify that the PIC specimens prepared from microwaves are superior in terms of durability after exposure to extreme variations of temperature compared to those of OPC and PIC specimens prepared by conventional methods. When the polymerization of the monomer is carried out by microwaves, the uniform temperature distribution and increased thermal diffusivity inside the specimens is better. This results in an increase in the molecular weight of the monomer throughout the PIC specimen than that when conventional thermal methods are used.

3. Studies on Microstructure

In view of the above changes of the mechanical properties in OPC and PIC, the molecular weight of the polymer formed in situ the precast cement mortar and the variations in morphology were also investigated using scanning electron microscope. The penetration of magnesium ions into the cement matrix in OPC and PIC was also explored since these ions caused maximum damage to the cement concrete.

From the GPC analysis in Table 2 the molecular weights (MP) of the polymer in PIC polymerized using microwaves were found to be more than the conventional hot water method. This indicates that the polymerization using microwaves is more effective and economical than hot water polymerization. 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.

Fig. 4 reveals the topography of the cement before and after impregnation and subsequent polymerization of the monomer. In Fig. 4(a) the OPC surface shows minor cracks and voids developed due to the evolution of heat during the cement hydration in the mortar. In the PIC samples (Fig. 4(b) and (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 imperme-

Table 2. Molecular weight of polymers formed in situ in the precast cement mortars

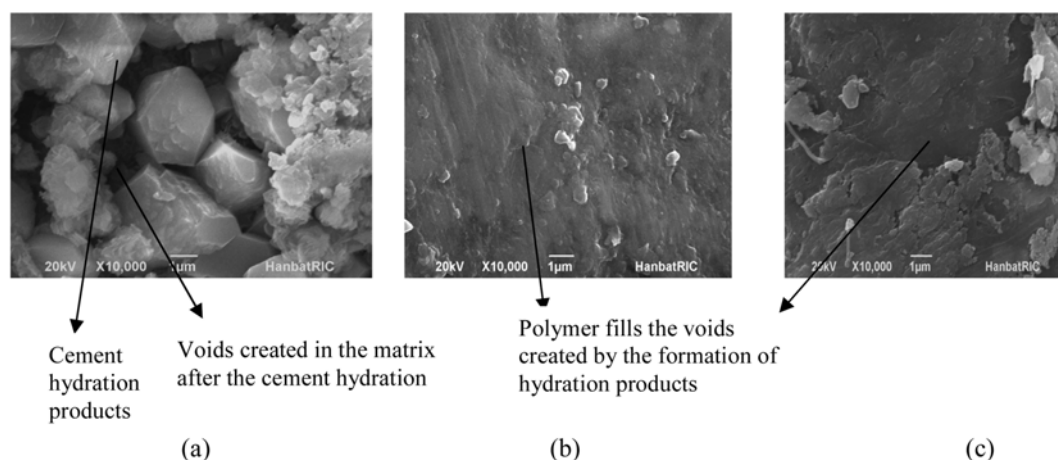| Sample	Molecular weight	
	Microwave PIC	Hot water PIC
PMMA	39400	18700
PSIC	59457	43482

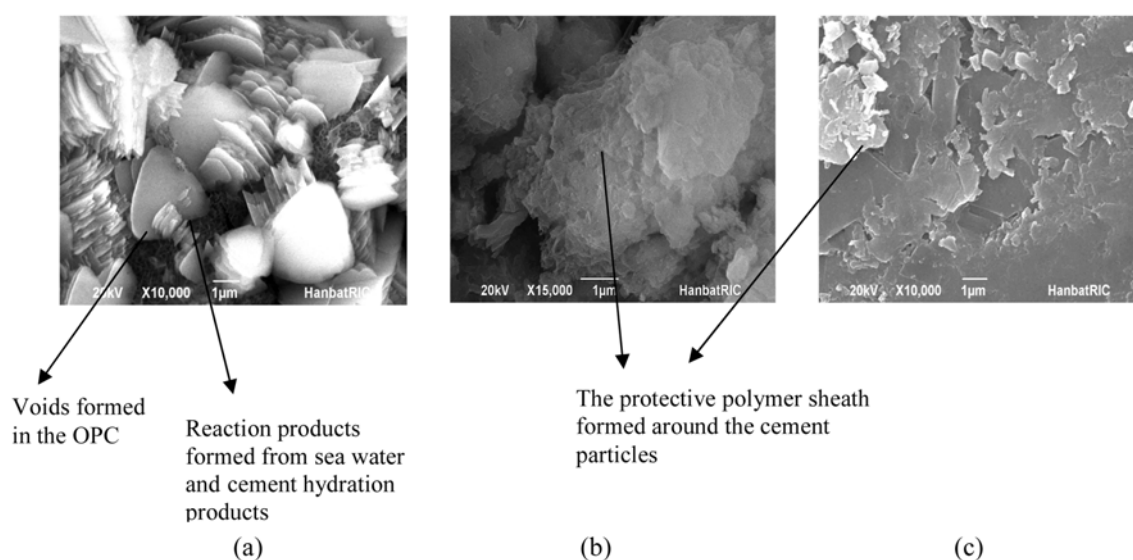Fig. 4. Microstructure of cement mortar before and after impregnation of polymer (a) OPC, (b) PMMAIC, (c) PSIC.

Fig. 5. Microstructure of (a) OPC, (b) PMMAIC, (c) PSIC on exposure to sea water for 28 days.
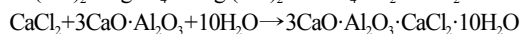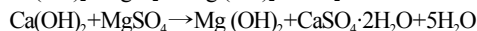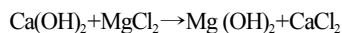
able structure.

The micrographs of OPC as seen in Fig. 5(a) reveal thick fan-shaped crystals formed as a result of the reactions between magnesium sulphate 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 formation of secondary gypsum, brucite and magnesium salts of aluminates in the cement matrix has been proved by Regourd [15]. 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 [16]. In Fig. 5(b) and (c) the protective hydrophobic coating of the polymer over cement particles in PIC seems to prevent contact with sea water.

Table 3 shows the initial and final concentration of Mg^{2+} ions in sea water and after immersion of OPC and PIC for 28 days, respectively. The above data gives an idea of the movement of Mg^{2+} ions into the OPC and PIC specimens. When OPC is immersed in sea water for 28 days the concentration of Mg^{2+} ions decreases, indicating that the ions have permeated into the cement matrix. These

Table 3. Concentration of Mg^{2+} ions in sea water before and after immersion of OPC and PIC specimens for 28 days

	Concentration of Mg^{2+} ions in ppm
Sea water	1091
OPC	327.2
PSIC	814.1
PMMAIC	965.3

ions undergo reactions with aluminates present in the cement particles [17] forming crystals that eventually result in cracking of the concrete. Furthermore, the interactions between the chlorides, sulphates and carbonates present in the sea water and calcium hydroxide present in cement result in the formation of bicarbonates that leach out of the concrete structures. The above cracking and leaching of the salts increases the permeability of the concrete. The following reactions illustrate some of the interactions that take place between the Ca^{2+} ions in the cement and the Mg^{2+} ions present in the sea water.

$$Ca(OH)_2 + MgCl_2 \rightarrow Mg(OH)_2 + CaCl_2$$
$$Ca(OH)_2 + MgSO_4 \rightarrow Mg(OH)_2 + CaSO_4 \cdot 2H_2O + 5H_2O$$
$$CaCl_2 + 3CaO \cdot Al_2O_3 + 10H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$$

When the PIC specimens were exposed to sea water for 28 days the concentration of Mg^{2+} ions in the sea water was much more than OPC samples. This suggests that the impermeable and hydrophobic barrier formed by the polymer restricted the movement of Mg^{2+} ions into the matrix. This not only improved the durability of the composite but also its performance.

CONCLUSIONS

From the above studies the following conclusions were drawn.

Cement concrete undergoes chemical reactions with ions in the sea water that affect its strength, durability and performance. These interactions result in an increase in the porosity of the concrete structure, thereby making it very vulnerable to damage. Impregnation and subsequent in situ polymerization of the monomer into the cement matrix increases the strength and durability of the concrete structure. The polymer forms a protective coating and fills the pores and voids present in the cement matrix, resulting in a compact and dense microstructure. The movement of ions into the cement structure is far less in the PIC than in the OPC.

This technique is being now applied for the preparation 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. Off-shore and other marine applications are the other areas where PIC could be employed.

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