

# Durability Properties of $\gamma$ -Radiation-Induced Polymer-Modified Mortar. I. Effect of Sodium Sulfate

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## SYNOPSIS

The influence of sodium sulfate solutions on the physicochemical properties of neat and modified cement mortar has been investigated. The samples were immersed in sodium sulfate solutions having different concentrations between 0.5 and 2.5% and immersion times from 20 to 100 days. The effect on the compressive strength, weight loss, bulk, density, and water absorption and the microstructure (scanning electron microscopy) were studied. The results indicate that the compressive strength and loss in weight decrease with the increase in sodium sulfate concentration and immersion time. The bulk density increases and then decreases as a result of the increase in sodium sulfate concentration and the time of storage, whereas water absorption behaves in an opposite direction, probably due to partial dissolution of the hydrated products. SEM study showed the formation of new products and voids between the particles were pronounced.

## INTRODUCTION

Studies on polymer-cement paste and polymer-mortar composites have been conducted to contribute to the understanding of the remarkable structural changes of properties and durability of such materials. The mechanical properties and chemical durability of polymer-concrete (PC) are far superior to those of conventional Portland cement concretes at ambient temperatures.<sup>1,2</sup> Poly(methyl methacrylate) or polystyrene preformed polymer-cement mortar whether polymerized by irradiation or by thermal-catalytic initiation provides excellent protection against attack by sulfates at room temperature.<sup>3</sup> As a result, polymer-impregnated concrete effectively resists penetration by water and salt solutions. Several research programs<sup>3-8</sup> have been initiated to apply polymer impregnated concrete technology to highways, and, in particular, to bridge decks, in which the corrosion of steel reinforcing rods by deicing salt is a pressing problem. Latex has been used commercially to modify portland cement

mortar, e.g., vinylidene chloride copolymer latex when added to the mortar mix, gives a two- to four-fold increase in the strength of brick masonry wall.<sup>9</sup> Styrene-butadiene copolymer latex imparts superior durability and structure properties to the mortar used to resurface highways and bridge decks.<sup>10</sup>

The purpose of this work is to study the effect of different concentrations of sodium sulfate on the physicochemical properties of neat and polymer-modified mortars.

## EXPERIMENTAL

### Materials

A fresh commercial ordinary (Type 1) Portland cement sample, standard sand, and two organic monomers, methyl methacrylate (MMA) and divinyl benzene (DVB), were used. The chemical analysis, specific properties, preparation of hardened mortar, and polymer-impregnated mortar sample with application of  $\gamma$ -radiation have been described elsewhere.<sup>11</sup> Mortar samples had been prepared using cylindrical molds (25 mm dia and 25 mm height). These samples made from cement and standard sand at a ratio of 1 : 3, respectively, and 0.4 W/C ratio. Demolding of samples was performed after the first

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24 h and then cured under water for further 6 days. The samples were then dried at 105°C for 24 h before testing.

A series of  $\gamma$ -radiation-induced polymer-modified mortar specimens was prepared by the impregnation of hardened mortar samples into a mixture of MMA and DVB with the ratio 94 : 6, respectively. The impregnated samples were subjected to 20 kGy of  $\gamma$ -radiation in a cobalt-60 source of the gamma cell. J.6500 type, manufactured by the Atomic Energy of Canada (dose rate 10 kGy/h). After the polymerization, the samples were dried at 50°C for 24 h to remove excess monomer which did not polymerize.

Two series of specimens, neat mortar (as blank) and polymer-modified mortar, were weighed and then immersed in various solutions of sodium sulfate having different concentrations between 0.5 and 2.5% for immersion periods from 20 to 100 days. At the end of each period, the samples were removed from the solutions and then weighed after drying at 105°C for 24 h.

The weight loss of the specimens was determined by

$$\frac{W_1 - W_2}{W_1} \times 100$$

where  $W_1$  is the weight of dried sample before immersion and  $W_2$  its dried weight after soaking. Measurements of compressive strength, bulk density,

and water absorption were carried out for the samples using standard procedures.

Scanning electron microscopy was performed on some selected samples by using a JEOL 7 SM-25 scanning electron microscope, to reveal the structural changes due to the above-mentioned treatments.

## RESULTS AND DISCUSSION

### Weight Loss

The influence of sodium sulfate solutions on the weight loss of both neat and polymer-modified mortar as a function of immersion time is shown in Figures 1 and 2, respectively. In general, the weight loss increases with concentration of sodium sulfate solution and with storage time. It is also seen that the increase of weight loss for neat mortar is more than that for polymer-modified mortar samples.

When hardened concrete is immersed in sodium sulfate solution, the reaction of sodium sulfate with both calcium hydroxide and calcium aluminate hydrate takes place<sup>12</sup> to form calcium sulfoaluminate. In addition, sodium hydroxide and gypsum are precipitated within the pores of the sample, and this is accompanied by an expansion and disruption of the concrete. In the present study, it can be concluded that the formation of the reaction products (as a result of the reaction between sodium sulfate and

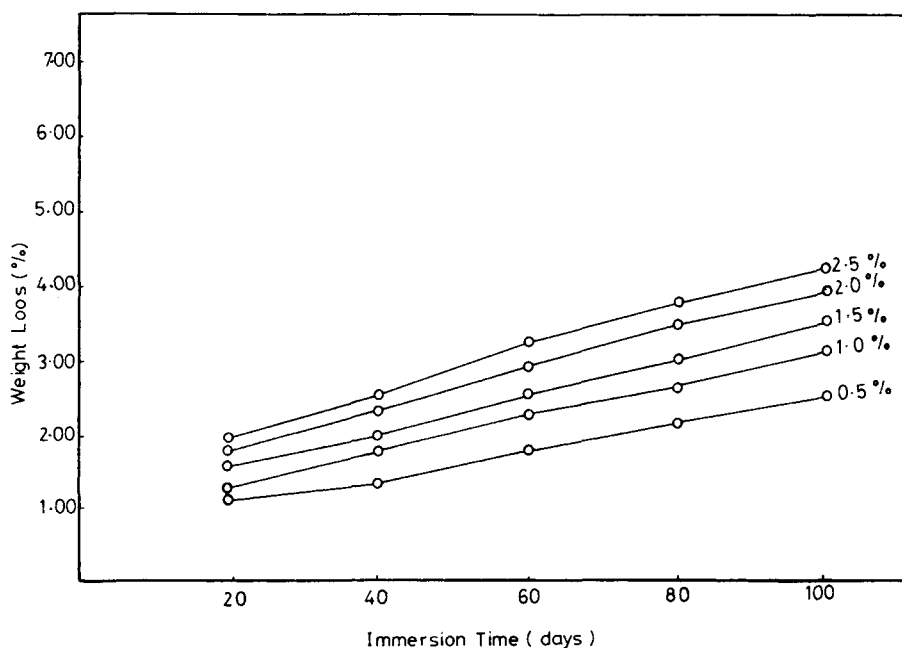
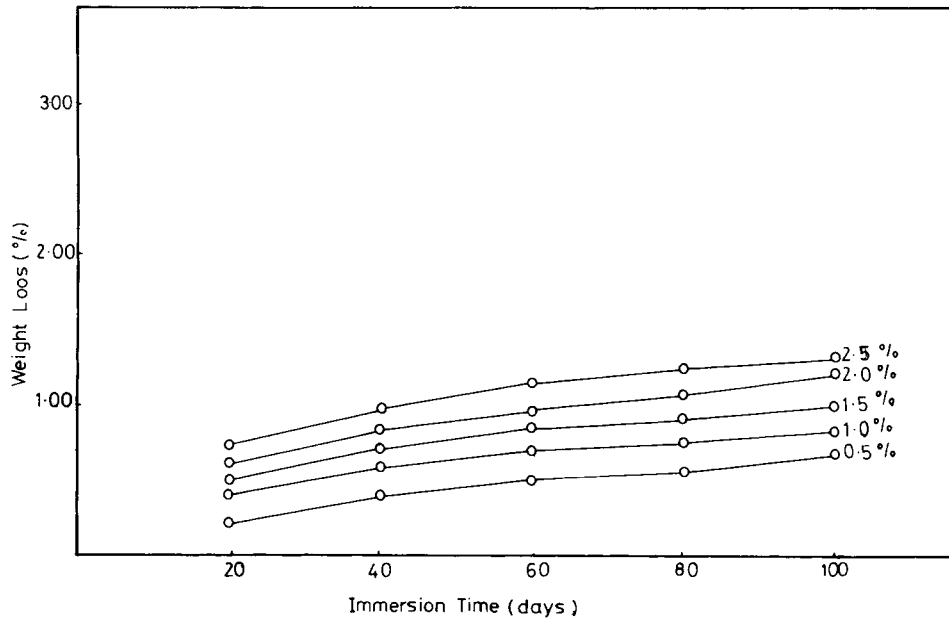


Figure 1 Effect of sodium sulfate solutions on the loss of weight of neat mortar.



**Figure 2** Effect of sodium sulfate solutions on the loss of weight of polymer-modified mortar.

hydrated cement) is accompanied by partial dissolution of some particles of cementitious binding materials. This leads to a weaker bonding between the sand grains within the mortar structure and some sand particles easily leave the body; consequently, the weight of the sample is reduced. The magnitude of weight loss is continuously increased as the concentration of sulfate solution rises and periods of storage are increased (Fig. 1).

On the other hand, Figure 2 shows the weight loss of induced polymer-modified mortar immersed in various concentrations of sodium sulfate as a function of soaking time. No change can be seen for the lower concentration and shorter immersion time; however, at longer times and higher concentrations of sodium sulfate, the weight of samples are reduced. This behavior is mainly attributed to a retardation of chemical reaction between sodium sulfate and hydrated cement products as a result of the presence of polymer in the pores of the samples. In previous work<sup>11,13</sup> using the DTA, IR spectra, and SEM techniques, it was found that calcium silicate hydrate reacts with the polymer present in pore structure during  $\gamma$ -induced polymerization of monomers and forms a sort of chemical bond between the silicon atoms and  $-\text{CH}_2$  groups in the polymer. In the present study, the presence of polymer within the pores retards the diffusion of sulfate ions into the specimen, so that the reaction of these ions with the hydrated cement is also retarded. On the other hand, for high concentration and longer times of immer-

sions, sulfate ions can be diffused into the specimens to react with the hydrated cement. This leads to dissolution of a part of the hydrated products and the weight of the specimens is accordingly decreased as shown in Figure 2. From these observations, it is concluded that  $\gamma$ -radiated polymer-modified mortar has a higher resistance towards the sodium sulfate attack as compared with neat mortar.

### Compressive Strength

The compressive strength results for neat and polymer-modified mortars exposed to different concentrations of sodium sulfate for various storage times are given in Figures 3 and 4. The results of Figure 3 show an initial increase of the strength, and they then are followed by a decrease for high concentrations and longer soaking times. At the beginning of immersing the sample, the initial increase of strength is probably due to filling of the voids by the reaction products between the hydrated cement and sodium sulfate, whereas, with longer time of exposure of high concentrations of sulfate solutions, it is expected that a large amount of the products are precipitated within the pores. Calcium sulfoaluminate and gypsum produced as mentioned in Ref. 12 (cf. Introduction of this paper) have more than double the solid volume; accordingly, the expansion and disruption of the mortar occurred. This leads to a weaker bonding between the particles and con-

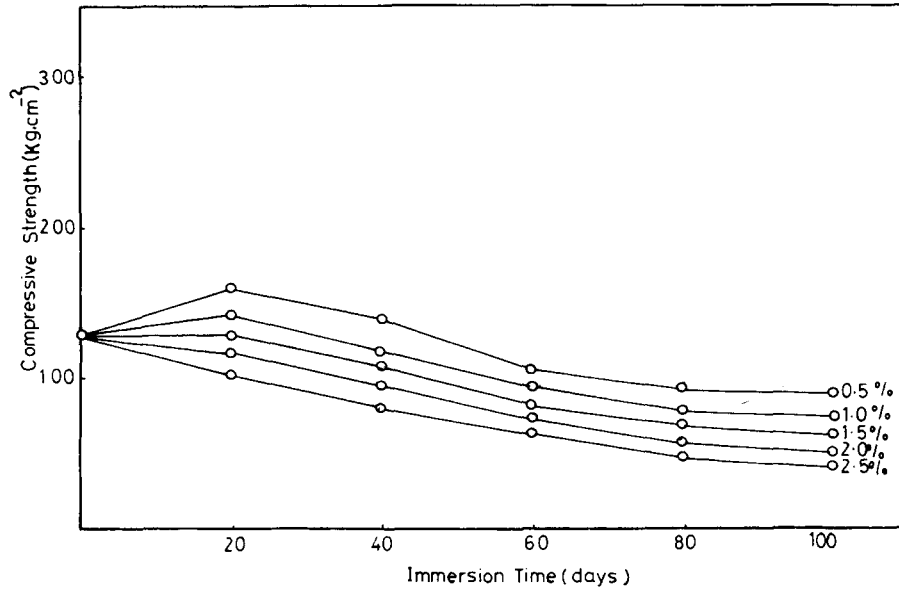


Figure 3 Effect of sodium sulfate solutions on the compressive strength of neat mortar.

sequently the compressive strength of the samples is also reduced.

The data of Figure 4 show that the  $\gamma$ -induced polymer mortar has a good resistance against sodium sulfate attack. At high concentration of sulfate and longer time of exposure, a partial reaction between hydrated cement and sodium sulfate was carried out. This is accompanied with a small expansion as a result the deposition of reaction products, so that the compressive strength is slightly reduced. These

observations are related to the presence of polymer in the pores which prevents the contact of sulfate with the hydrated cement.

#### Bulk Density and Water Absorption

The results of the effect of sodium sulfate solutions on the bulk density and water absorption on both neat and modified mortars are given in Tables I and II, respectively. The data of Table I indicate that

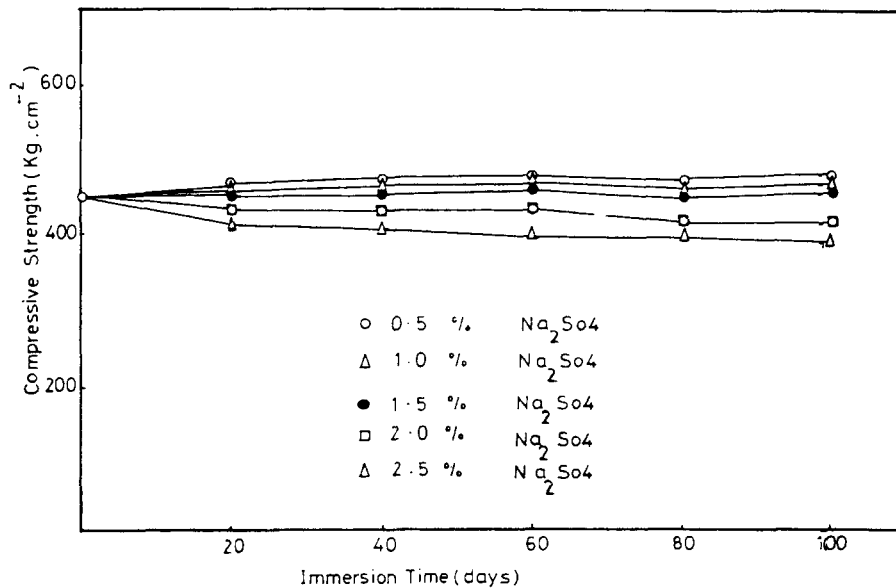


Figure 4 Effect of sodium sulfate solutions on the compressive strength of polymer-modified mortar.  $\text{Na}_2\text{SO}_4$  (%): (O) 0.5; ( $\Delta$ ) 1.0; ( $\bullet$ ) 1.5; ( $\square$ ) 2.0; ( $\Delta$ ) 2.5.

**Table I Bulk Density of Samples after Exposure to Na<sub>2</sub>SO<sub>4</sub> Solutions**

Time of Immersions (Days)	Na <sub>2</sub> SO <sub>4</sub> (%)									
	Neat Mortar					Polymer-modified Mortar				
	0.5%	1.0%	1.5%	2.0%	2.5%	0.5%	1.0%	1.5%	2.0%	2.5%
20	2.011	2.018	2.029	2.032	2.137	2.131	2.138	2.146	2.150	2.167
40	2.009	1.997	1.893	1.972	1.972	2.142	2.149	2.161	2.169	2.172
60	1.995	1.980	1.971	1.967	1.959	2.148	2.150	2.168	2.188	2.201
80	1.973	1.962	1.955	1.955	1.973	2.132	2.140	2.151	2.147	2.133
100	1.967	1.950	1.941	1.933	1.927	2.111	2.093	2.005	1.998	1.991
Standard deviation	0.0200	0.027	0.049	0.037	0.082	0.014	0.023	0.068	0.076	0.083

\* Bulk density of neat mortar and polymer modified mortars before exposure to Na<sub>2</sub>SO<sub>4</sub> solutions are 1.962 and 2.128 g/cm<sup>3</sup>, respectively.

the bulk density increases with increasing the sulfate concentration and periods of storage up to 60 and 80 days for neat and polymer-modified mortars, respectively; then it behaves in an opposite manner. This behavior is mainly due to the accumulation of the reaction products within the pores of the specimens; however, at higher concentration of sulfate and longer time of storage, a large amounts of the products are deposited in the pores to the extent that expansion and cracks of the samples have occurred. As a result of these, some of hydrated cements are disintegrated in the medium. This is accompanied with a reduction of the bulk density. The change of bulk density is more pronounced for neat mortar than for those of the composite mortars due to the presence of polymer.

The results of Table II indicate that the water absorption of neat and modified mortars are running opposite to those of bulk density, i.e., water absorption values decrease as a result of the deposition of reaction products calcium of sulfate and sulfoaluminates. This leads to diminishing of the voids between the particles, whereas, absorption increases at higher concentration of sulfate solutions due to the expansion effect. This observation will receive further supports with the result of the SEM studies.

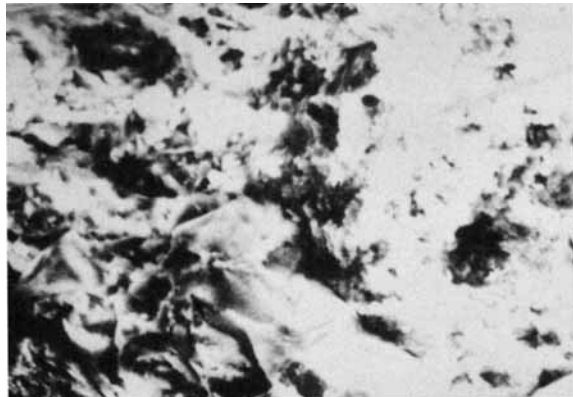
#### Scanning Electron Microscopy

The results of SEM studies of selected samples for neat and polymer-modified mortars are shown in Figures 5–10. Figure 5 shows the microstructural

**Table II Absorption (%) of Samples after Exposure to Na<sub>2</sub>SO<sub>4</sub> Solutions**

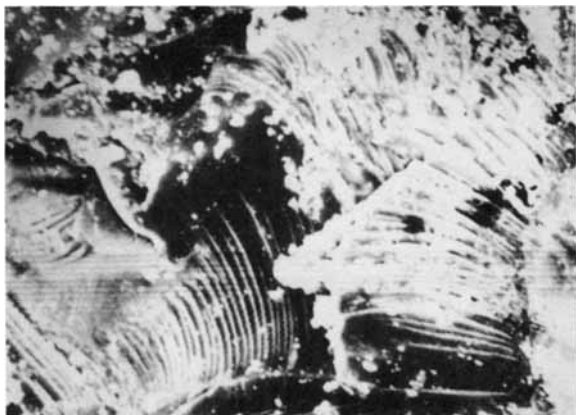
Time of Immersions (Days)	Na <sub>2</sub> SO <sub>4</sub> (%)									
	Neat Mortar					Modified Mortar				
	0.5%	1.0%	1.5%	2.0%	2.5%	0.5%	1.0%	1.5%	2.0%	2.5%
20	9.94	9.63	9.43	9.37	9.01	2.65	2.31	2.07	1.91	1.70
40	9.69	9.27	9.00	8.88	8.51	2.33	2.01	1.88	1.61	1.61
60	9.73	9.95	10.06	10.33	10.67	2.03	1.79	1.96	2.11	2.41
80	10.00	10.38	10.73	10.89	11.00	2.41	2.73	2.89	3.00	3.00
100	10.39	10.66	11.00	11.41	11.79	2.96	3.07	3.55	3.81	4.01
Standard deviation	0.279	0.417	0.563	0.686	1.384	0.349	0.522	0.721	0.902	0.993

\* Water absorption of neat mortar and polymer modified mortars before exposure to Na<sub>2</sub>SO<sub>4</sub> solution are 10.00 and 2.71% respectively.



**Figure 5** SEM micrograph of neat mortar before immersion ( $\times 2500$ ).

features of neat mortar samples before immersion in sodium sulfate solutions. It is found that the microstructure of the sample displays a mixture of ill-crystallized intersecting fibers of calcium silicate hydrate as well as cubic crystals of calcium aluminate hydrate which are deposited on the surface of sand particles. Some hexagonal and irregular platy crystals of calcium hydroxide are also observed. SEM micrograph of polymer mortar is shown in Figure 6. Bundles fibrous material are deposited on the surface of unreacted grains. Sand particles fill the voids of the structure of the mortar, resulting in improving the strength of the composite as compared with a blank specimen as described in previous work.<sup>11</sup> Figures 7–10 show the microstructural features of some representative samples of neat and composite mortar after immersing in 2.5% sodium sulfate solutions for 60 and 100 days, respectively. Figure 7 reflects the effect of sodium sulfate on the mor-



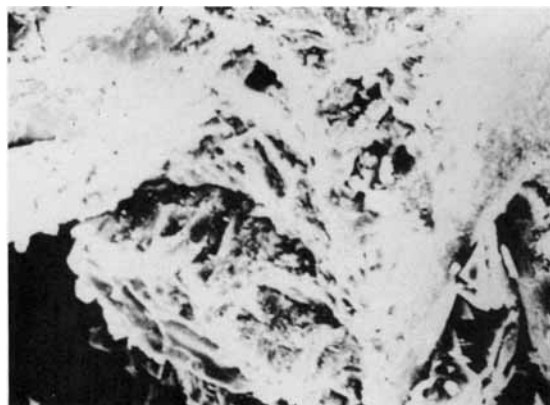
**Figure 6** SEM micrograph of polymer-modified mortar before immersion ( $\times 2500$ ).



**Figure 7** SEM micrograph of neat mortar immersed in 2.5%  $\text{Na}_2\text{SO}_4$  for 60 days ( $\times 2500$ ).

phology of neat mortar, immersed in 2.5% sodium sulfate solution for 60 days; it shows the effect of increasing the voids between the particles as a result of disintegration of hydrated cement products during the reaction with sulfate solution. It is also observed that the deposition of products having a large volume in the pores caused a widening of the spaces. It can be also seen the decrease of the hexagonal or irregular crystals of  $\text{Ca}(\text{OH})_2$  and the cubic crystals of calcium aluminate hydrate. On the contrary, the SEM micrographs obtained for the composite mortar show a dense structure of fibrous polymer intersecting with a needle crystals of calcium sulfoaluminate (Fig. 8). This micrograph also shows a further reduction in the porosity.

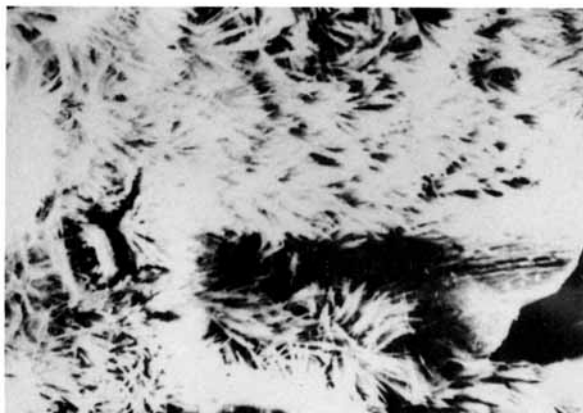
The morphologies of neat and composite mortars soaked in 2.5% of sodium sulfate for 100 days are represented by Figures 9 and 10, respectively. The microstructural feature seen in Figure 9(A) shows



**Figure 8** SEM micrograph of polymer-modified mortar immersed in 2.5%  $\text{Na}_2\text{SO}_4$  for 60 days ( $\times 2500$ ).

an open texture and more reduction of crumpled foil crystal of various calcium silicate hydrates; therefore, the voids volume between the particles are predominating and wide due to more disintegration of the hydrated products. On the other hand, it was found that in Figure 9(B) a mixture of intersecting massive plates, fibrous and large amounts of needle crystals of calcium sulfoaluminate deposited on the sand particles. These micrographs also show a further reduction of bulk density.

The SEM micrographs shown in Figures 10(A) and (B) show a low dense structure, and appearance of the voids under polymer fibers and needle crystals of the products in Figure 10 are observed. This open structure leads to a low bulk density and high water absorption of the samples. This is due to the same reasons mentioned before. The rate of change for neat mortar is more than that for the composite material. Finally, these variations in the microstructural characteristics due to the effect of sodium sulfate solutions on both neat and composite mortars are in good agreement with the variation in the



**Figure 9** SEM micrographs of neat mortar immersed in 2.5%  $\text{Na}_2\text{SO}_4$  for 100 days ( $\times 2500$ ).



**Figure 10** SEM micrographs of polymer-modified mortar immersed in 2.5%  $\text{Na}_2\text{SO}_4$  for 100 days ( $\times 2500$ ).

compressive strength, loss of weight, bulk density, and water absorption.

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