Acid Resistance of Polyester-Impregnated Modified Cement Mortar

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ABSTRACT: The influence of distilled water and sulphuric acid solutions on the physico-mechanical properties of neat and modified cement mortar has been investigated. The samples were immersed in distilled water, and different concentrations of sulphuric acid ranged from 5–15% by vol for immersion times from 1 to 120 days. The effect on the loss of weight, compressive strength, apparent porosity, water absorption, IR, and SEM were studied. The results indicate that the compressive strength and loss of weight decrease, whereas the apparent porosity and water absorption increase with immersion time and acid concentration. These are probably due to partial dissolution of the set cement. IR spectra and SEM studies showed significant changes in some absorption bands and the appearances of new voids of the neat and composite mortars after being immersed in H_2SO_4 solutions. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 685–693, 1999

Key words: distilled water; sulphuric acid; modified cement mortar

INTRODUCTION

Solutions containing mineral acids are highly corrosive to Portland cement concrete. Studies were carried out to evaluate the relative chemical resistance of concrete containing styrene–butadiene latex or a silica fume admixture to different ratios of sulphuric acid and HCl. It was found that the concrete containing the silica fume showed a better resistance to chemical attack than other concrete types.[1] The loss of weight, compressive strength, and bonding strength of cement mortar impregnated with organic monomers and application of gamma-irradiation, which have been immersed in different concentrations of H_2SO_4 HCl, NaOH, and Na_2SO_4 solutions, were investigated.[2,3] The results indicated that the copolymerized impregnated is more effective in improvements of the chemical attack resistance than the unimpregnated specimens. Bhattacharga et al.[4] found that the durability of polystyrene mortar immersed in aqueous solutions of sulphuric acid and hydrochloric acids is lower than that of the polymethyl methacrylate composite because of the former being a nonpolar type of the polymer, which gives rise to a weaker cement–polymer interfacial bonding. Polymethyl methacrylate or polystyrene pre-formed polymer–cement mortar, whether polymerized by radiation or by thermal catalytic initiation, provides excellent protection against attack by sulphates at room temperature.[5] Polypropylene emulsions have been found to increase the durability of the concrete and decrease the shrinkage.[6] The purpose of this work is to study the influence of immersion time as well as different concentrations of sulphuric acid solutions on the physico-chemical and mechanical properties of neat and polyester-modified mortar.

EXPERIMENTAL

A fresh commercial ordinary (type 1) Portland cement sample, standard sand, and unsaturated

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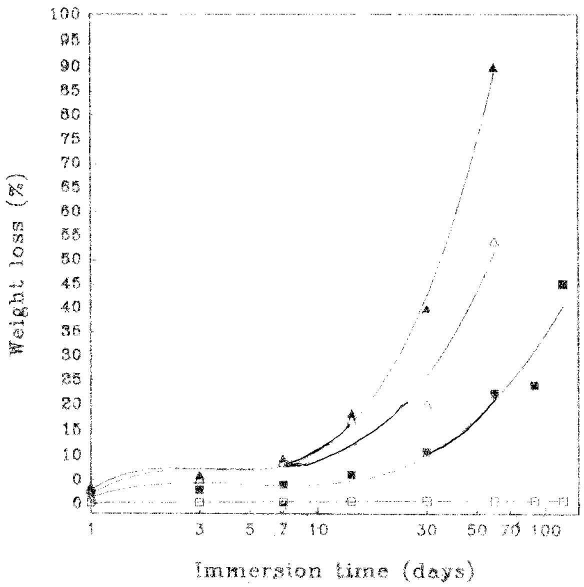

Figure 1 Weight loss of cement mortar as a function of immersion time in: (□) distilled water, (■) 5%, (△) 10%, and (▲) 15% H_2SO_4 solutions.

polyester resin were used. The chemical analysis and specific properties have been described elsewhere.[7] Mortar samples were prepared using cubic molds (edge 1 inch). These samples were made from cement and standard sand at a ratio of 1 : 3, respectively, and a 0.4 w/c ratio. These samples were demolded after the first 24 h and then cured under water for a further 6 days. The samples were then dried at 105°C for 24 h before testing.

A series of gamma-irradiation–induced polyester-modified mortar specimens were prepared by the impregnation of hardened mortar samples with unsaturated polyester resin. The impregnated samples were subjected to 50 kGy of gamma-irradiation in a ^{60}Co source of the gamma cell (dose rate 10 kGy/h). Two series of specimens, neat mortar (as blank) and polymer-modified mortar, were weighed and then immersed in different concentrations of sulphuric acid solutions, namely 5, 10, and 15% by volume, and distilled water for the periods of 1, 3, 7, 14, 30, 60, 90, and 120 days, respectively. At the end of each period, the samples were removed from the solutions and then weighted after drying at 105°C for 24 h. The measurements of weight loss, compressive strength, apparent porosity, and water absorption was carried out for the samples using standard procedures. IR spectra of some selected specimens were carried out using Waltson (Unicam). Fourier Transform Infrared (FTIR) spectrometer with wave number ranged from 400–4000 cm^{-1}. SEM was performed on some selected samples by using a JEOL-JSM 5400 scanning electron microscopy to reveal the structural changes due to the above-mentioned treatment.

RESULTS AND DISCUSSION

Loss of Weight

The effect of sulphuric acid solutions and distilled water on the loss of weight for both neat cement mortar and gamma-irradiated polyester-modified mortar samples as a function for immersion time and various concentrations of sulphuric acid solutions is shown in Figures 1 and 2, respectively. The results of Figure 1 showed that the weight loss values increase slowly for shorter immersion times followed by a relatively higher rate of weight loss for immersion times larger than 14 days. Moreover, there is a progressive increase in weight loss values with increasing the acid concentration for the same immersion time.

Waters that have acidic owing to the presence of uncombined cordon dioxide, organic, or inorganic acids are more aggressive in their action, the degree and rate of attack increasing as the acidity increases and the pH value of the solution falls.[8] In general, acid solutions that attack ce-

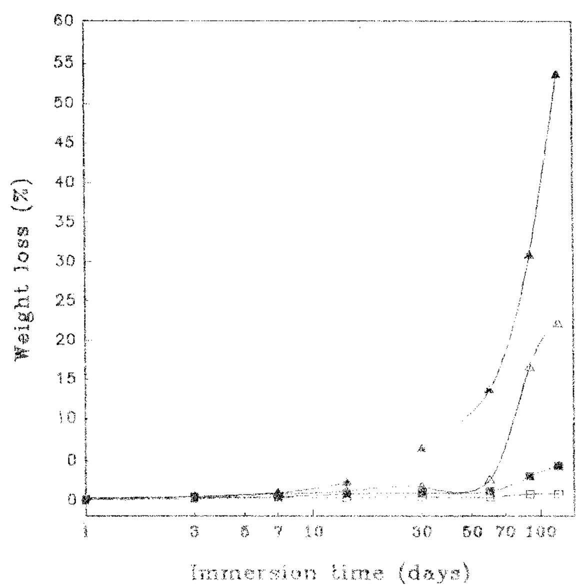

Figure 2 Weight loss of radiation-treated polyester-impregnated cement mortar as a function of immersion time in: (□) distilled water, (■) 5%, (△) 10%, and (▲) 15% H_2SO_4 solutions.

ment mortar or concrete, by dissolving part of the set cement, do not cause any expansion, but progressively weaken the material by removal of the cementing constituents. A soft and mushy mass is all that ultimately remains. In previous work[9] was found that sulphuric acid was less corrosive than that of hydrochloric acid, acetic acid, and lactic acid solutions. This was due to the formation of large amounts of gypsum, which were crystallized in the pores of the specimens near the surface. XRD analysis of the deteriorated concrete from the surface of specimens immersed in sulphuric acid or ammonium sulphate showed a large amount of gypsum present. In the present work, the reaction of sulphate ions with calcium hydroxide, calcium aluminate hydrate, and calcium silicate hydrates take place to form calcium sulphate and calcium sulphoaluminate; the formation of the reaction products within the pores of the samples is accompanied by dissolution of some particles of the cementious bending materials. This leads to a weakening of the bonding between the sand grains within the mortar structure, and some sand particles may easily leave the body; consequently, the weight of the sample is reduced.

Figure 2 shows the variation of weight loss of gamma-irradiation–impregnated polyester composites as a function of immersion time as well as distilled water and various concentrations of sulphuric acid solutions. No significant change in weight loss results has been achieved for the lower sulphuric acid concentration and shorter immersion times, whereas in distilled water for all immersion times there was no significant effect on the weight loss of the composite. At longer immersions and higher concentrations of sulphuric acid, the weight loss of the samples was relatively increased. It was found that the weight loss of the composite was 14% after being immersed in 15% H_2SO_4 solution for 60 days. This is due to lower pH values of the medium, which are the most important factor effects, and the dissolution of the hydrated cement. The chemical attack usually occurs at pH values below 6.5.[10] Also, the governing factor for dissolution of hydrated cement in the solution having a pH value between 3 to 6 is the diffusion rate through the residual layer of the low solubility products after calcium hydroxide has been dissolved. When the polyester mortar composite samples were immersed in acidic water (H_2SO_4 solution) having a lower pH value for longer immersion times (60 days), a part of the hydrated product that did not react with

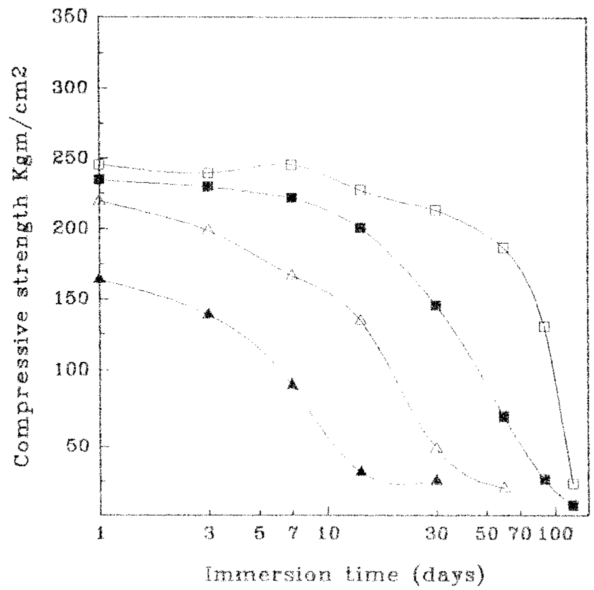

Figure 3 Compressive strength of cement mortar as a function of immersion time in: (□) distilled water, (■) 5%, (△) 10%, and (▲) 15% H_2SO_4 solutions.

the polyester during the copolymerization process was accordingly dissolved to stabilize the media. The magnitude of weight loss of the polyester composite mortar under the same experimental conditions is comparatively much less than the values obtained in the case of neat cement mortar, as shown in Figures 1 and 2, respectively. It was observed that the neat cement mortar specimens were found to be completely disintegrated after immersion in 10 and 15% sulphuric acid solutions for 90 days, whereas the weight loss values of polyester-impregnated mortar were 6.5 and 30% in the same conditions.

Compressive Strength

The compressive strength results for neat cement mortar and gamma-irradiated polyester composite exposed to distilled water and different concentrations of sulphuric acid solutions for various immersion times are given in Figures 3 and 4, respectively. The results in Figure 3 showed that the compressive strength values of neat cement mortar decreases with the increase immersion time in distilled water and sulphuric acid solutions. In the case of distilled water, the reasons of the reduction in the compressive strength with immersion time may be attributed to the fact that pure water decomposes the set cement compounds, dissolving the lime $[Ca(OH)_2]$ from them,

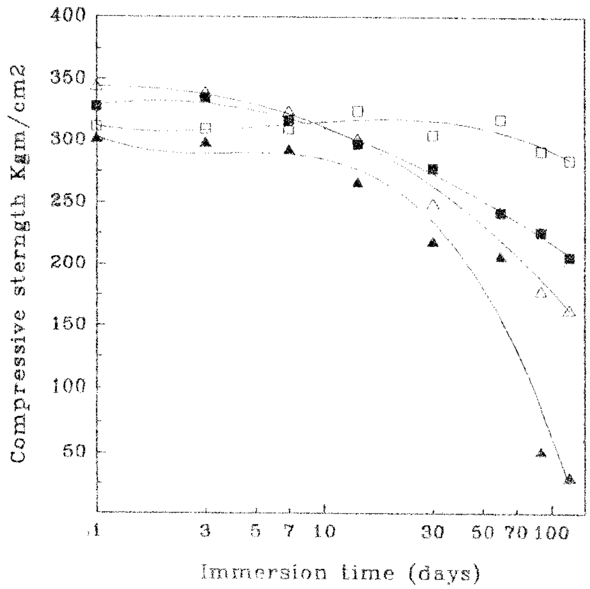

Figure 4 Compressive strength of polyester-impregnated cement mortar as a function as a function of immersion time in: (□) distilled water, (■) 5%, (△) 10%, and (▲) 15% H_2SO_4 solutions.

and to some extent, the alumina. Continued leaching eventually leaves a residue of incoherent hydrated silica, iron, and alumina. The leaching of lime from a set cement progressively reduces the strength of mortar or concrete.[8] Hence, increasing of immersion time leads to an increase of leaching of the lime from set cement in a mortar. Consequently, the compressive strength values were decreased. It was found that the compressive strength of neat cement mortar immersed 1 day in distilled water was 245 kg/cm^2, and become only 24 kg/cm^2 after 120 days. The reduction in the compressive strength of neat cement mortar with the increase of acid strength and immersion time is mainly due to the formation of calcium sulphoaluminate and gypsum, which have more than double the solid volume of the compounds replaced by them.[8] Accordingly, the expansion and disruption of the samples would occur. This is accompanied with a decrease in the compressive strength of the sample.

Upon examination of the results in Figure 4, it may be observed that the distilled water did not affect the compressive strength of the polyester-impregnated mortar, whereas the strength was decreased when immersed in sulphuric acid solutions for all the immersion times. The rate of reduction in the strength was considerably low at all sulphuric acid concentrations for shorter immersion times up to 7 days, but it was pronounced and increased at longer immersion times (Fig. 4). These behaviors are mainly attributed to a retardation of the chemical reaction between sulphuric acid, distilled water, and hydrated cement constituents; this leads to prevention of the dissolving of the set cement that has been reacted with these polyesters formed in the pores under the effect of gamma-induced copolymerization of the unsaturated polyester resin.[2,11,12] These conclusions showed that polyester-impregnated cement mortar has a higher resistance against that of sulphate and a distilled water attack compared to neat cement mortar, as shown in Figures 3 and 4.

Porosity and Water Absorption

The apparent porosity results obtained for neat cement mortar and polyester-impregnated mortar composite are given in Figures 5 and 6, respectively. It was found that the apparent porosity values of neat cement mortar and polyester-impregnated mortar immersed in distilled water increases relatively slowly with the increase of the immersion times due to continuous leaching of the lime from the set cement. This is accompanied by enlarging of the voids between the particles of sand in the samples. The apparent porosity values of the polyester mortar composite were much smaller than its corresponding values of

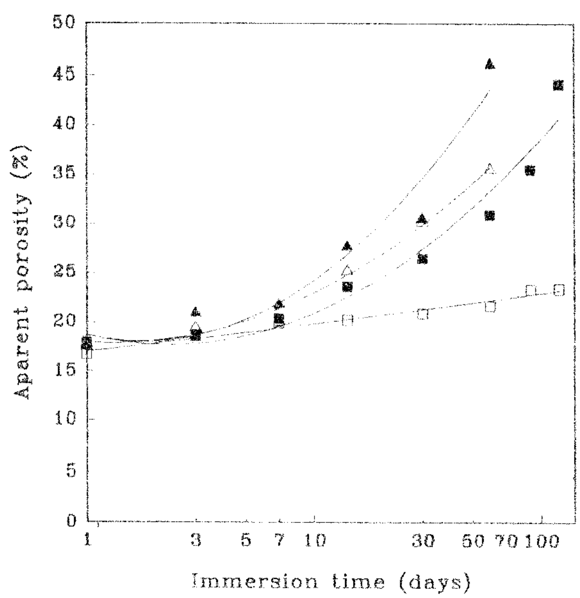

Figure 5 Apparent porosity of cement mortar as a function of immersion time in: (□) distilled water, (■) 5%, (△) 10%, and (▲) 15% H_2SO_4 solutions.

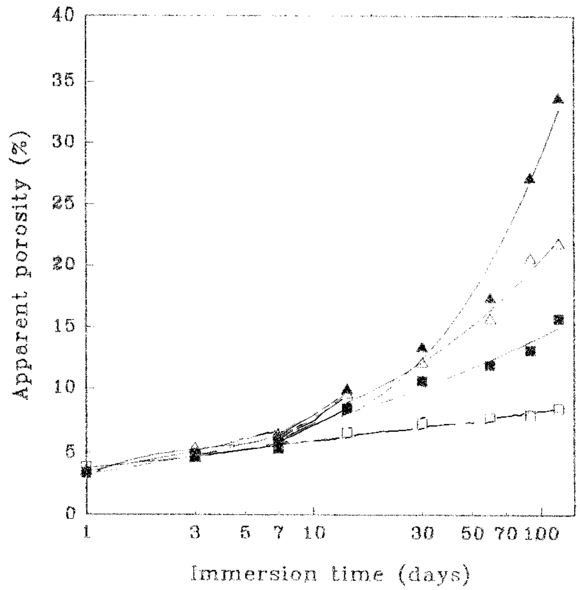

Figure 6 Apparent porosity of radiation-treated polyester-impregnated cement mortar as a function of immersion time in: (□) distilled water, (■) 5%, (△) 10%, and (▲) 15% H_2SO_4 solutions.

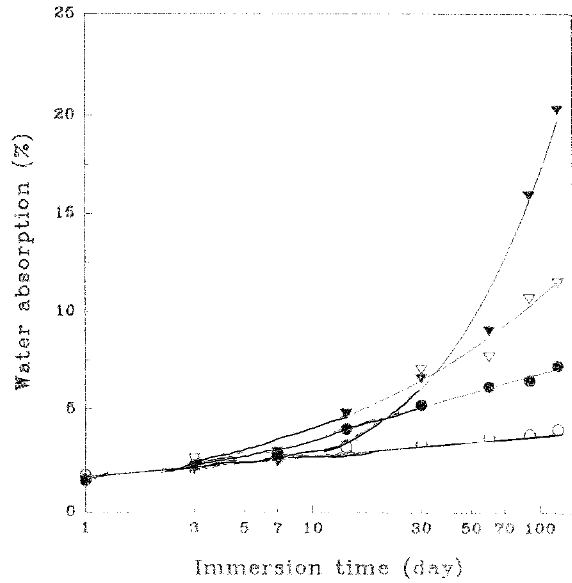

Figure 8 Water absorption of polyester-impregnated cement mortar as a function of immersion time in: (○) distilled water, (●) 5%, (▽) 10%, and (▼) 15% H_2SO_4 solutions.

neat cement mortar, as shown in Figures 5 and 6. The apparent porosity was found to be 16.76% for neat cement mortar and 3.8% for the polyester-modified mortar after immersion for 1 day in distilled water. These values become 23.3 and 8.4%, respectively, after 120 days of immersion. These are attributed to the presence of polymer in the pores of the specimens, which prevents the contact of water with the set cement of the specimens.

Figures 5 and 6 also showed that the apparent porosity values increase with the increase of sulphuric acid concentration as well as immersion time for both neat and polyester mortars. This is due to the formation of the sulphate products as a result of the chemical reaction between sulphate ions and hydrated cement constituents. The dissolving of the sulphate product leads to rapid enlarging of the voids between the particles of the specimens; consequently, the apparent porosity increased. The rate of the formation of the sulphate products of the neat cement mortar more than that of the polymer-modified mortar, results in the presence of the polyester in the pores of the samples immersed in different concentrations of sulphuric acid solutions for all immersion times, as shown in Figures 5 and 6.

The effect of distilled water and sulphuric acid solutions for immersion time on the water absorption of neat cement mortar and polyester-modified mortar are graphically presented in Figures 7 and 8, respectively. The results indicated that the water absorption values increase with the increase of the immersion time as well as the acid strength for neat cement mortar and polyester-

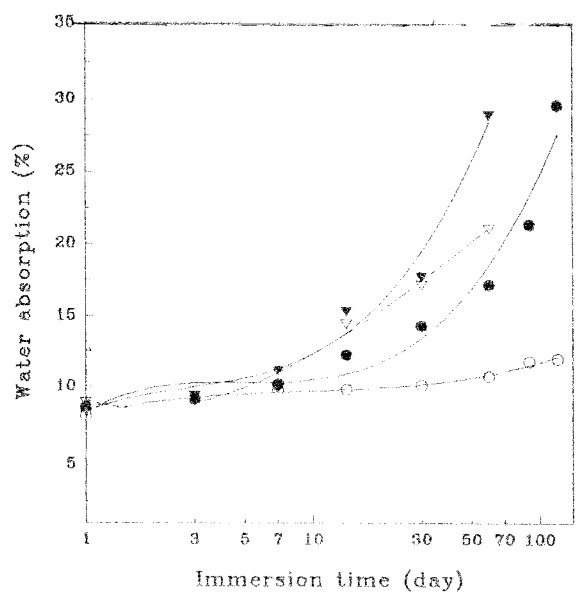

Figure 7 Water absorption of cement mortar as a function of immersion time in: (○) distilled water, (●) 5%, (▽) 10%, and (▼) 15% H_2SO_4 solutions.

modified mortars. It was also observed that the water absorption values of polyester-impregnated mortar were much smaller than that of the unimpregnated mortar, as shown in Figures 7 and 8. The water absorption values of the polyester composite mortar were 10.7 and 16% when immersed in 10 and 15% H_2SO_4 for 90 days, whereas the neat cement mortar samples were found to be completely disintegrated at the same conditions. These are attributed to the presence of the polyester in the pores of the specimens. These observations will receive further support from the IR and SEM studies.

Infrared Spectroscopy

IR spectra, which were applied to neat cement mortar and polyester-impregnated mortar before and after immersion in 10% H_2SO_4 for 3 days, are shown in Figure 9. The IR absorption spectra of hardened cement mortar sample are characterized by absorption bands at 3640, 3400, 1110, 940, and 1446 cm^{-1}, as shown in Figure 9(a).[13,14] The absorption band at 3640 cm^{-1}, which indicated the stretching vibration of OH complexes produced in the hydrated calcium silicate compounds, disappeared, as shown in Figure 9(b). The intensity of the absorption band at 1440 cm^{-1} as a result of the presence of $Ca(OH)_2$ was also reduced compared to the neat mortar before immersion [Fig. 9(a)]. These are associated with a small amount of calcium silicate hydrates and $Ca(OH)_2$ remaining after immersion in the H_2SO_4 solution as a result of the chemical reaction between sulphate and the set cement constituents.

Figure 9(c) and (d) illustrates the results of IR spectra of polyester-impregnated mortar together with the unimpressed sample (control) prepared under the same conditions. It was found that the intensity of the absorption band around 3000 cm^{-1} from the Si—C band vibration was slightly increased. In earlier studies[11,13] it was concluded that the Si—C bond formed as a result of the chemical reaction between the silicon atoms in the calcium silicate hydrate and (CH_2) groups in the unsaturated polyester during the copolymerization of the unsaturated polyester resin with application of gamma-irradiation. The presence of the absorption band that appears at 1530 cm^{-1} was found to be slightly decreased after immersion in 10% H_2SO_4. This band represents the stretching vibration of COO^- from the ester in the unsaturated polyester resin during the copolymerization. Also, the intensity of absorption band of —C═O at 1710 cm^{-1} tends to be slightly increased after immersion in H_2SO_4 compared to its intensity in Figure 9(c). These observations are indications to low dissolution of some hydrated cement constituents as a result the reaction between the sulphate ions and set cement. According to the that mentioned above, the polyester-impregnated mortar composite had a good resistance against the sulphuric acid attack compared to the neat mortar. These results are in a good agreement with the conclusion discussed before, and showed that loss of weight and the decrease of compressive strength of the polyester mortar composite were less than that of neat mortar.

SEM Studies

The SEM micrograph shown in Figure 10 (plates a and b) was taken for a hardened mortar before immersed in sulphuric acid solution. The micro-

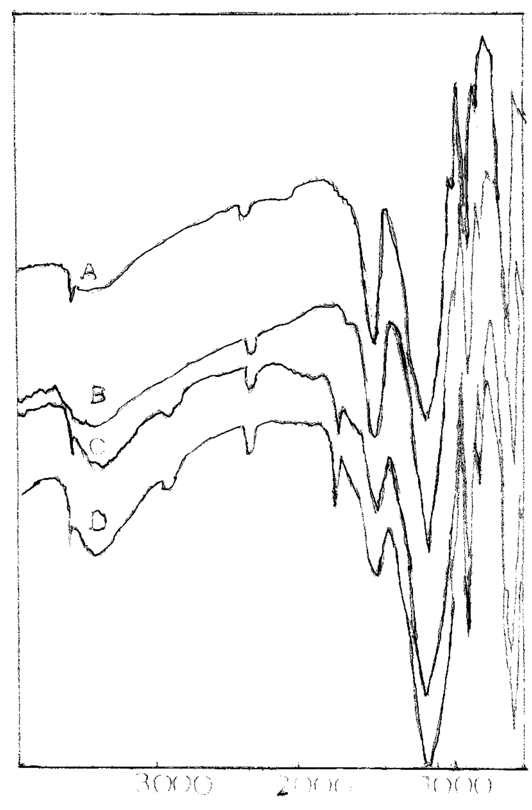

Figure 9 IR absorption spectra of (a) hardened cement mortar, (b) hardened cement mortar after immersed in 10% H_2SO_4 for 3 days, (c) polyester-modified cement mortar, and (d) polyester-modified cement mortar after immersed in 10% H_2SO_4 for 3 days.

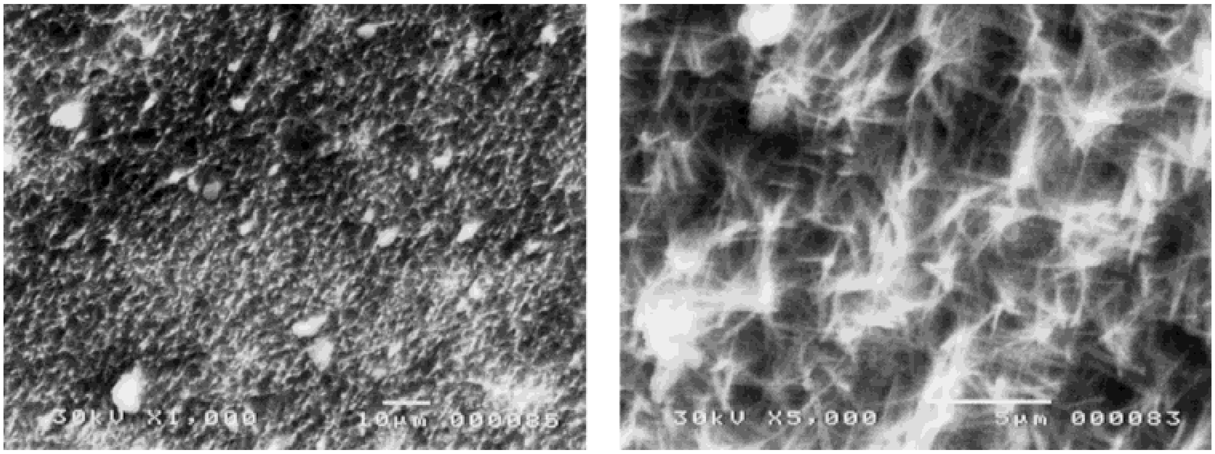

Figure 10 SEM micrograph of hardened mortar before being immersed in sulphuric acid solution.

structure displayed the existence of a large amount of hydration products within the voids of the solid sample. A higher magnification view of part of Figure 10(a) shows details of intersecting fibers of calcium silicate as well as cubic crystals of calcium aluminate, which are deposited on the surface of the sand particles [Fig. 10(b)]. Some hexagonal and irregular platy crystal of calcium hydroxide are also observed. The microstructural features seen in Figure 11(a) show an open structure, and the void volume between the particles are predominating and wide due to more disintegration of the hydrated products after immersed in 10% H_2SO_4 solution for 60 days. Also, it was observed that the presence of intersecting massive rods of calcium sulphoaluminate deposited in the pores of the samples result in the interaction of the sulphate ions with calcium aluminate [Fig. 11(b)]. An SEM micrograph of polyester mortar composite is shown in Figure 12 (plates a and b). Fibrous bundles of polyester coalesce to form a thin layer over the surface of the sand grains [Fig. 12(a)]. A higher magnification of a part of Figure 12(a) shows that a dense structure and fibrous bundle of polyester are filling the voids between the particles [Fig. 12(b)]. The morphologies of the polyester mortar composite after immersion in 10% H_2SO_4 solution for 60 days are shown in Figure 13(a) and (b). These figures show a low dense structure and appearance of the voids under the polyester layer. This open structure leads to high water absorption, apparent porosity, and lower strength of the composite samples. These are attributed to the same reasons mentioned

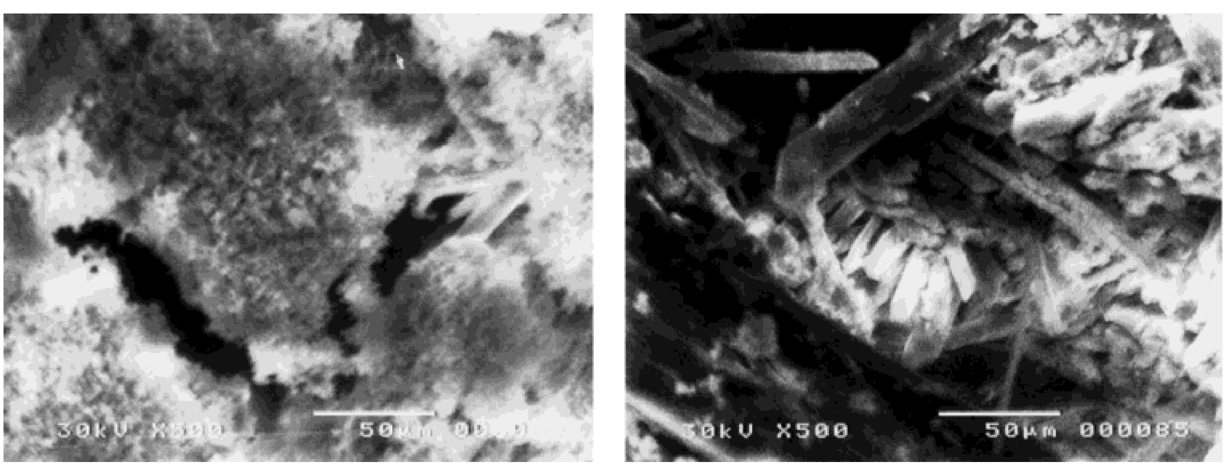

Figure 11 SEM micrograph of hardened cement mortar after being immersed in 10% sulphuric acid solution for 60 days.

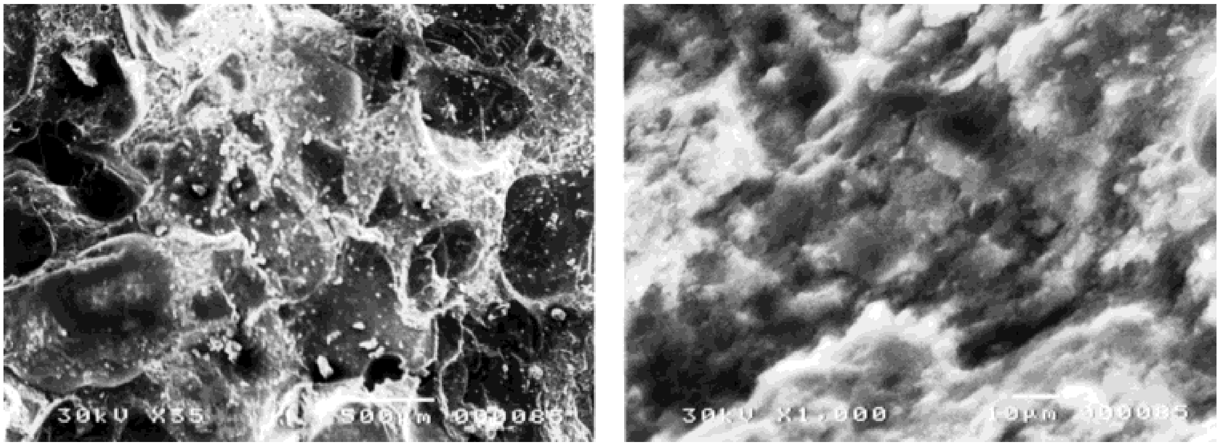

Figure 12 SEM micrograph of polyester mortar composite before being immersed in sulphuric acid solution.

before. These variations in the microstructural characteristics due to the effect of H_2SO_4 solutions on both cement mortar and polyester mortar composites are in good agreement with the variations in the compressive strength and loss of weight.

CONCLUSIONS

The weight loss percentage of both cement mortar and composite samples increase with the increase of concentration of H_2SO_4 for all immersion times. The weight loss of the composite is about 30%, whereas the cement mortar is completely deteriorated after immersed in 15% H_2SO_4 for 90 days.

The compressive strength of cement mortar and polyester–mortar composite samples decreases with increasing concentration and immersion time. The compressive strength of the composite samples is much higher than that of the cement mortar no results the interaction of the polyester and hydrated cement.

IR spectra showed that the intensity of absorption band at 1440 cm^{-1} was reduced, and the absorption band at 3640 cm^{-1} disappeared as a result of the chemical reaction between sulphate ions and the hydrated cement of cement mortar samples after immersion in the H_2SO_4 solution. The intensities of absorption bands around 1610 and 3000 cm^{-1} are slightly increased after immersion in H_2SO_4 solution compared to its intensities before the immersion in H_2SO_4 solution.

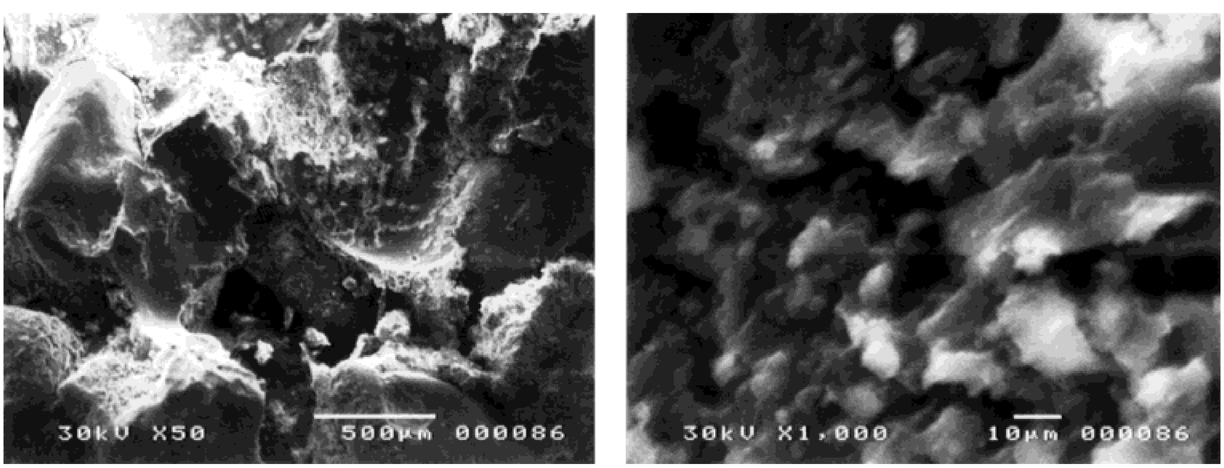

Figure 13 SEM micrograph of polyester mortar composite after being immersed in 10% sulphuric acid solution for 60 days.

This is attributed to low dissolution of some hydrated cement that did not react with polyester.

An SEM micrograph showed an open structure, and the voids between the particles predominated for the cement mortar samples compared to the polyester–mortar composite after immersion in the H_2SO_4 solution.

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