Studies on Sand/Clay Unsaturated Polyester Composite Materials

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ABSTRACT: The effect of a radiation-initiated polyester on the physicomechanical properties of a sand/clay-polyester composite has been investigated. The unsaturated polyester resins containing various styrene contents were used at different sand/clay composites from 10 to 70 wt % with respect to the weight of sand and clay together; polymerization was conducted using γ -irradiation at 50 kGy. Also, different particle sizes of clay (namely 1.25–0.80, 0.80–0.50, and <0.50) were used. The compressive strength, apparent porosity, and water absorption—in addition to infrared spectroscopy of the composite samples—were studied. Results indicate that the compressive strength decreases with an increase in sand/clay, as well as the styrene content in the unsaturated polyester resin, whereas the apparent porosity and water absorption of the composite samples increase. Infrared spectra showed the appearance of new bands, which indicated a chemical reaction between polyester and clay constituents. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1031–1038, 1999

Key words: clay particle sizes; composite; gamma irradiation; compressive strength; infrared spectroscopy

INTRODUCTION

An industrial material of clay plastic composite for the substitutes of ceramic material has been investigated and developed by Wing.¹ It was found that the clay components and their amorphous state were the two fundamental factors to govern the copolymerization rate of the copolymer onto clay. The majority of grafting was confirmed to occur on the silicon atoms in the amorphous silicates in the clay from the silicon Si—C bond. Beeson and Mayhan² stated that two types of polymers were formed in the radiation-initiated polymerization of the methyl methacrylate–kaolin clay complex. It was found that the addition

Journal of Applied Polymer Science, Vol. 72, 1031–1038 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/081031-08 of clay to the polymer system did not result in a decrease in compressive strength-a small increase in strength was actually noted. Hirano³ reported impregnated polymer in porous ceramics of fired clay tile or brick. The mechanical strength of the product at elevated temperatures was twice as great, even at the glass transition temperature of the polymer used, as those of unimpregnated material. The investigators^{4,5} studied the process of impregnation of completely dried raw dust clay and autoclaved lime-rich clay composite specimens in unsaturated polyester and vinyl monomers, followed by exposure to Co^{60} γ -radiation. The system of unsaturated polyester and vinyl compounds was an ideal impregnation system for the preparation of this composite, and an improvement in the mechanical strength was observed. It was concluded that some interesting facts of graft copolymerization and crosslinking

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Figure 1 Compressive strength of sand/clay-polyester composites as a function of the clay-to-sand ratio (polyester resin contains 40 vol % styrene) for the different particle sizes of clay: (\Box) 1.25–0.8 mm, (\blacksquare) 0.8–0.5 mm, and (\triangle) <0.5 mm.

occurred in the preparation of clay plastic. The silicate contents on surface structure in clay were found to be effective in the radiation of the site graft.^{6,7} This work aims to provide some conclusions on the effectiveness of different percentages of clay particle sizes and exposure doses of γ -irradiation on the physicochemical and mechanical properties of composites.

EXPERIMENTAL

Materials

Clay

A representative clay sample was brought from the Aswan area and provided by the General Company for Ceramics (Cairo). Chemical analysis of the clay was: SiO₂, 51.20%; Al₂O₃, 26.56%; Fe₂O₃, 8.24%; CaO, 2.89%; MgO, 1.08%; SO₃, 0.36%; alkali, 0.83% and 0.83%; and LOI, 9.50%. Clay samples were separately crushed to the required grain size by screening a certain batch through standard sieves (namely 1.25, 0.85, and 0.50 mm).

Specific properties of sand, styrene, and unsaturated polyester—as well as the preparation of sand/clay-polyester composite samples with the application of γ -irradiation—have been described elsewhere.⁸ Clay ratios varied from 10 to 70 wt %, with respect to the weight of sand and clay together. The amount of added unsaturated polyester resin, having different styrene content, was kept constant at 20%.

Measurements of compressive strength, porosity, and water absorption were conducted for the samples using standard procedures. Infrared (IR) spectra of some selected samples were conducted using Mattson (Unicam) and Fourier Transform IR (FTIR) spectrometers, with wavenumbers ranging from 400 to 4000 cm⁻¹. Scanning electron microscopy was performed on some selected samples by using a JEOL JSM-5400 to reveal structure changes as a result of the presence of different particle sizes of clay in the composite.

RESULTS AND DISCUSSION

Compressive Strength

Variation of compressive strength of sand/claypolyester composites as a function of clay/sand ratios for different particle sizes of clay—as well as concentrations of styrene content in the unsaturated polyester resin—are given in Figures 1–3. Results indicated that the compressive strength of sand/clay-polyester composite decreases with



Figure 2 Compressive strength of sand/clay-polyester composites as a function of the clay-to-sand ratio (polyester resin contains 50 vol % styrene) for the different particle sizes of clay: (\Box) 1.25–0.8 mm, (\blacksquare) 0.8–0.5 mm, and (\triangle) <0.5 mm.



Figure 3 Compressive strength of sand/clay-polyester composites as a function of the clay-to-sand ratio (polyester resin contains 60 vol % styrene) for the different particle sizes of clay: (\Box) 1.25–0.8 mm, (\blacksquare) 0.8–0.5 mm, and (\triangle) <0.5 mm.

the increase of clay/sand ratios, as well as the monomer concentrations of styrene in the unsaturated polyester resins for particle sizes of clay (1.25–0.8 mm and 0.8–0.5 mm selectively), whereas it was increased by using a particle size <0.5 mm of clay.

The effect of particle sizes of clay on the compressive strength of sand/clay-polyester composites may arise from the catalytic effect of aluminosilicate on the copolymerization rate of the unsaturated polyester/styrene mixture.^{1,9} The catalytic effect of clay, its amorphous state, and its inorganic oxides were investigated by several authors. Beeson and Mayhan² reported that the presence of the inorganic kaolin clay, either in air or inert gas, was found to have a catalytic influence on the polymerization reaction of methyl methacrylate at a constant dose. Also, a small concentration of inorganic materials belonging to group IIA metal oxides or hydroxides [such as MgO, Mg(OH)₂, CaO, and Ca(OH)₂ (present in clay)] react with the acidic groups of unsaturated polyester resin. After this reaction took place, the unsaturated sites of the polyester reacted with styrene monomer via free radical copolymerization to form a dense network structure.¹¹ Theng¹² observed that the amorphous minerals in clay, particularly those of aluminosilicate, were found

to be effective to radiation in situ graft copolymerization of the vinyl monomer system and crosslinking of their graft copolymer. These effects resulted in the enhancement of the mechanical strength of the clay-polymer composite. The surface area of a certain amount of material will decrease with increasing particle size. Accordingly, when particle size of clay decreases its surface area, as well as its ability to retain unsaturated polyester/styrene mixture on its surface to be increased, consequently the copolymerization rate of the unsaturated polyester/styrene mixture using γ -irradiation was also improved with an increasing clay-to-sand ratio particle size <0.5 mm. The compressive strength of the composites was increased. This attributed to a greater amount of copolymerized polyester/styrene that is associated with a large number of crosslinking formed during the γ -irradiation process in the presence of fine particle clay sizes. The copolymerized polyester/styrene products act as strong and durable binders, which hold the grains of sand and clay together into one solid mass. On the other hand, the compressive strength depends on the magnitude of interfacial adhesion forces that will develop between the particles and the matrix on curing by γ -irradiation. These forces are a function of the magnitude on the contact area between the constituents of the composite. For the composite containing clay having particle size <0.5 mm, the interfacial adhesion forces between the constituents of the composite increases with the increase of contact area between the composite components as a result of the distribution of fine grains of clay between the sand particles.

The compressive strength of the sand/claypolyester composite, prepared with using clay that had particle sizes of 1.25-0.80 and 0.8-0.5mm, decreased with an increase of clay content in the composite (Figs. 1–3). This was attributed to the presence of larger clay particles that were bigger than the sand particles in the matrix, which was accompanied with a lower catalytic effect of aluminosilicate on the copolymerization rate of the unsaturated polyester/styrene mixture. As a result, a partial reaction occurred between the polyester and clay constituents on the outer surface of the larger clay particles under the effect of γ -irradiation. This was associated with more voids between the particle sand decrease of the interfacial adhesion between particles of the composite. This lead to a decrease of the compressive strength of the composite. This observation



Figure 4 Porosity of sand/clay-polyester composites as a function of the clay-to-sand ratio (polyester resin contains 40 vol % styrene) for the different particle sizes of clay: (\Box) 1.25–0.8 mm, (\blacksquare) 0.8–0.5 mm, and (\triangle) <0.5 mm.

will receive further support with results from scanning electron microscopic studies.

In comparison with the results obtained in Figures 1–3, it can be observed that the compressive strength of the composite decreased with increasing styrene content in the unsaturated polyester from 40 to 60%. This may be due to the supposition that a higher concentration of styrene monomer lead to a lower degree of unsaturation in the polyester and a lower magnitude of crosslinking reactions on curing with γ irradiation.¹³ Therefore, a lower degree of curing was attained; (the lower the magnitude of adhesion), as well as compressive strength values of sand/clay-polyester composites.

Total Porosity

The total porosity of sand/clay-polyester composites as a function of sand/clay ratio for different particles size of clay at various concentrations of styrene contents is graphically represented in Figures (4–6). Results indicated that the total porosity increases with the increase of the clay/ sand ratios for particle sizes 1.25-0.80 and 0.80-0.5 mm, whereas it decreases with using particle sizes of clay <0.5 mm up to 40% clay in the mixture; then it was increased. Moreover, it was observed that the total porosity values increased



Figure 5 Porosity of sand/clay-polyester composites as a function of the clay-to-sand ratio (polyester resin contains 50 vol % styrene) for the different particle sizes of clay: (\Box) 1.25–0.8 mm, (\blacksquare) 0.8–0.5 mm, and (\triangle) <0.5 mm.

with the increase of styrene content in the polyester resin. The porosity of such particulate composites would be expected to be a function of the



Figure 6 Porosity of sand/clay-polyester composites as a function of the clay-to-sand ratio (polyester resin contains 60 vol % styrene) for the different particle sizes of clay: (\Box) 1.25–0.5 mm, (\blacksquare) 0.8–0.5 mm, and (\triangle) <0.5 mm.



Figure 7 Water absorption of sand/clay-polyester composites as a function of the clay-to-sand ratio (polyester resin contains 40 vol % styrene) for the different particle sizes of clay: (\Box) 1.25–0.8 mm, (\blacksquare) 0.8–0.5 mm, and (\triangle) <0.5 mm.

specific properties of individual components, particles size, shape, and state of aggregation of the particles, as well as the degree of adhesion between them. Accordingly, total porosity increased with using 1.25-0.80 and 0.80-0.50 mm, whereas it decreased for < 0.50 mm clay particles, as previously described. Another property that should be considered when determining the porosity of the composite is the retention property of the constituent particles with respect to water. As previously described, the surface of clay particles possessed a catalytic activity and hence its ability to absorb water molecules; consequently, its retention to water was considerably higher with respect to sand, which possessed a glassy type of surface. Therefore, it was expected that water retention will increase with clay content ratio; this lead to a corresponding increase in the magnitude of retained porosity. Also, it was found that the total porosity % increases with an increase of styrene content in the unsaturated polyester resin, thus causing a decrease in the relative degree of unsaturation in the polyester/styrene monomer mixture. This lead to a decrease in the magnitude of cured polyester and the degree of crosslinking reaction that occurred by γ -irradiation. The magnitude of adhesion forces between the particulate constituents (sand and clay particles) and polyester will be decreased, and the voids between sand and clay particles will be enlarged. The retention ability of clay particles (<0.5 mm) decreased despite a size smaller than sand particles. This could be attributed to the possibility that the fine clay particles filled the voids between the sand particles up to 40 wt % of clay content. This was associated with a decrease in the magnitude of retained porosity %. Beyond a 40 wt % of clay, porosity may develop as a result of the retention of water by clay particles; thus, total porosity slightly increased. Finally, it was concluded that clay with particle sizes <0.5 mm and 40 wt % were optimum conditions to get a composite with minimum porosity.

Water Absorption

Figures 7–9 illustrate variation of water absorption (%) of the composite specimens as a function of clay ratio for different particles size of clay at various styrene contents in unsaturated polyester resin. Results showed that the water absorption values increase with increasing clay ratio in the specimens; as a result, catalytic activity of the clay particles and its ability to retain and absorb water molecules occurred. Water absorption values increased with increases in styrene content in the mixture when comparing samples having the



Figure 8 Water absorption of sand/clay-polyester composites as a function of the clay-to-sand ratio (polyester resin contains 50 vol % styrene) for the different particle sizes of clay: (\Box) 1.25–0.8 mm, (\blacksquare) 0.8–0.5 mm, and (\triangle) <0.5 mm.



Figure 9 Water absorption of sand/clay-polyester composites as a function of the clay-to-sand ratio (polyester resin contains 60 vol % styrene) for the different particle sizes of clay: (\Box) 1.25–0.8 mm, (\blacksquare) 0.8–0.5 mm, and (\triangle) <0.5 mm.

same clay content. This was attributed to a reduction in the cured polyester and the degree of crosslinking reaction, which diminished the void spaces between sand and clay particles. Water absorption values of the samples contained a <0.5 mm particles size, which was the lowest value for all styrene concentrations and different clay ratios, as previously described.

IR Spectroscopy

The IR spectra of clay with sand, unsaturated polyester resin (containing 40% styrene) before irradiation, and the sand/clay-polyester composite after irradiation at 50 kGy are shown in Figure 10(a, b, and c, respectively). Characteristic bands of the clay/sand mixture, as shown in Fig. 10(a), appear at 1100, 3450, 3625, and 3695 cm⁻¹ (see refs. 4, 14, and 15). Figure 10(b) showed the IR absorption bands of unsaturated polyester resin containing 40% styrene before irradiation. The absorption bands appeared at 750, 1138, 1294, 1600, 1575, 1740, 1379, and 3400–3600 cm⁻¹ (see refs. 16–19).

Figure 10(c) illustrates the IR absorption bands of the radiation-treated sand/clay-polyester composite. The absorption band at 1100 cm^{-1} , which is characteristic of the amorphous silicate in clay, becomes more intense, apparently because of its polarization after irradiation. It was noted that both bands at 1070 and 1138 cm⁻¹ (polymerized phthalic anhydride and C—O—C linkages) of the unsaturated polyester disappeared [Fig. 10(b)] due to overlapping with the previous band of silicate [Fig. 10(c)]. Also, the absorption band at 1294 cm⁻¹ from C—O of maleic anhydride in the polyester mixed with the amorphous silicate bands and a new band appears near 1265 cm⁻¹. It was also observed that the band at 2940 cm⁻¹ from the —CH₋₂



Figure 10 IR absorption spectra of: (a) sand and clay together; (b) unsaturated polyester resin containing 40 vol % styrene; and (c) irradiation-treated sand/clay-polyester composites.

methylenic group of glycol in the polyester [Fig. 10(b)] becomes less intense at the same wavenumber in the composite spectra [Fig. 10(c)]. This weak absorption band at 2940 cm^{-1} is assigned to the methylenic radical attached to the silicon atom as a result of replacing the hydroxyl groups on the silicate surface by methylenic radicals (-CH₂-) of glycols in the polyester under the effect of γ -irradiation. A similar conclusion has been obtained by the authors.^{1,4,20} They found that the clay components and their amorphous state were the two fundamental factors to govern the copolymerization rate of the copolymer onto clay. The majority of grafting was confirmed to occur on the silicon atoms in the amorphous silicate, which gave the absorption band region at $900-1100 \text{ cm}^{-1}$ to form the C-Si-C- bond that is seen at the absorption band at 2940 and 1265 cm^{-1} . The amorphous aluminosilicate in clay was also recognized as affecting an increase in the number of crosslinks to form a three-dimensional copolymer network, thus resulting in the enhancement of the mechanical strength of the sand/ clay-polyester composite.^{1,4}

On the other hand, the intensity of the absorption band at 1740 cm^{-1} of the composite [Fig. 10(c)], which corresponds to the stretching vibration of -C=O of ester, is less than its intensity in the unsaturated polyester spectra [Fig. 10(b)]. The intensity of $Mg(OH)_2$ and $Ca(OH)_2$ bands at 3695 and 3625 cm⁻¹, respectively, of the composite is less than its intensity in the clay/sand mix spectra as a result of the concentrations of acidic groups of the polyester and concentrations of both $Mg(OH)_2$ and $Ca(OH)_2$ (which present in clay) are lower when mixing with each other. This predicts that a reaction takes place between $Mg(OH)_2$ and Ca(OH)₂ in clay and the acidic groups of the polyester. Rodriguez²¹ stated that the absorption band at 3695 cm^{-1} corresponds to the O—H stretch intermolecular hydrogen bonding assigned to water formed during the thickening reaction between $Mg(OH)_2$ with the acidic groups of the polyester. Two bands were also observed: one sharp band at 3700 cm^{-1} and the other band at 3570 cm^{-1} . This region suggests the presence of unbounded OH radicals in clay. These conclusions are in good agreement with those of previous sections in the present work.

Scanning Electron Microscopy

The morphologies of sand/clay-polyester composites prepared using clay, which have particle sizes 1.25–

0.8, 0.8-0.5, and < 0.5 mm, are represented in Figure 11 (a, b, and c, respectively). The microstructural features seen in Figure 11(a) showed a dense structure as a result of the distribution of the fine clay particles (<0.5 mm) between the sand particles. This lead to a higher adhesion between the sand and clay particles as a result of the copolymerization of unsaturated polyester, which reacted with clay under the effect of γ -irradiation. This is associated with improving the strength of the composite. Micrographs of the composite prepared by particle sizes of clay of 0.8-0.5 and 1.25-0.8 mm [shown in Fig. 11(b and c)] displayed a mixture of coarse sand and clay particles, and the voids between the particles were predominating. This open structure was due to a low amount of polyester deposited on the outer surface of larger clay particles. This lead to lower adhesion between the particles; consequently, the compressive strength of the composite was decreased. These variations in the microstructural characteristics due to the effect of different particle sizes of clay on the composite were in good agreement with the variation in compressive strength.

CONCLUSIONS

- For a given unsaturated polyester resin/styrene mixture, the clay constituents and its particle size had an effective influence on the compressive strength of the sand/clay-polyester composites. The compressive strength was decreased with an increase in size of clay (1.25–0.8 and 0.8–0.5 mm). It was found to be increased when using clay having a particle size <0.5 mm as result of the catalytic effect of clay constituents.
- Total porosity and water absorption % increased with increasing clay content when using clay having particle sizes of 1.25–0.8 and 0.8–0.5 mm. Whereas the composite prepared using clay <0.5 mm, total porosity and water absorption values decreased with an increase of clay content up to 40% in the composite, after which the values increased with an increasing clay-to-sand ratio. The results indicated that the porosity and water absorption values increased with an increase in styrene in the unsaturated polyester resin/ styrene mixture.
- IR spectra showed a reduction of the intensities of the absorption bands at 1740 and 2940 $\rm cm^{-1}$ and disappearance of the absorp-



(a)







(c)

Figure 11 Scanning electron microscopic micrograph of the sand/clay-polyester composite.

tion bands at 1070 and 1138 $\rm cm^{-1}$ of the sand/ clay-polyester composite as a result of the reaction between polyester and clay constituents.

• Scanning electron microscopic morphology of the sand/clay-polyester composite showed a dense structure of the composite due to the distribution of the fine particles of clay, whereas it approved an open structure. Voids between the particles were predominated by using a coarse clay particle.

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