

Evaluation of Biodegradability of Epoxy-Guar Gum Composites

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Received 24 August 2008; accepted 4 January 2009

DOI 10.1002/app.29996

Published online 14 April 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Epoxy composites incorporating natural components have been mainly limited to the use of natural fibers. However, there have been a few instances where polysaccharides have been used as particulate fillers in thermoset compositions. The present study investigated the effect of guar gum/hydroxypropyl guar gum as a filler on the degradative properties of epoxy composites at various filler concentrations, with reference to fungal degradation and soil burial tests. It was found that at higher filler concentrations, the degradation increased. Composites

based on hydroxypropyl guar gum showed increased degradation initially but on prolonged exposure to the fungal environment, the difference between guar gum and the hydroxypropyl guar gum-based composites was found to be marginal. Microscopic evaluation of the composites showed that the degradation occurred at both the composite surface and in the bulk. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1494–1500, 2009

Key words: composites; polysaccharides; biodegradable

INTRODUCTION

Environmental concerns and legislation have highlighted the need for eco-friendly plastics and polymers. There are various methods by which a composite or polymer can be rendered biodegradable; one is by using an inherently biodegradable polymer^{1–3} and the other is by blending or incorporating biodegradable components.^{4–6} It has also been observed that the incorporation of biodegradable material in an already degradable polymer matrix increased the degradation of the resultant blends and composites. The routes of degradation of these polymeric compositions have also been studied.⁷

To date, the incorporation of natural materials in thermoset composites has been limited to fibers and agro-waste such as lignin and wood flour, in which natural fibers have successfully replaced inorganic fibers such as glass fibers, with no loss in mechanical properties.⁸ However, compatibilization or surface treatment of the fibers was required to increase adhesion between the hydrophilic fibers and the hydrophobic polymer matrix.⁹ The increase in polymer-fiber adhesion also resulted in a reduction in the moisture absorption in the composites, which, if not checked, would lead to a reduction in the performance and life of the composites.^{10,11} There have

been a limited number of studies investigating the incorporation of particulate fillers obtained from natural sources, especially polysaccharides, in thermoset composites.^{12,13} On the other hand, starches, lignin, and wood flour among other natural materials have been used in thermoplastic blends and composites for the chief purpose of imparting biodegradability.^{14–17} In the case of starch, the resultant composition was a blend, since the starch was treated prior to incorporation in the polymer matrix to remove existing hydrogen bonds, causing it to behave as a dispersed polymer phase.

The mechanical and chemical properties of epoxy-guar gum composites were evaluated in a prior study.¹⁸ The mechanical properties, with reference to tensile, flexural, and impact strength, of the epoxy-guar gum (GG)/hydroxypropyl (HPG)-based composites showed an optimum value at 5–10 per hundred grams of resin (phr) filler concentration. The increase in performance, most notably the tensile and flexural properties, indicated the behavior of the fillers as reinforcing fillers with HPG-based composites showing improved mechanical properties as compared with those based on GG. At higher concentrations of filler, the formation of agglomerates leads to a decrease in the mechanical and solvent resistance properties of the respective composites. The increase in performance was also proportional to the hydroxypropyl content of the hydroxypropyl guar gum filler, which led to an increased wetting of the filler by the polymer matrix due to the increase

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TABLE I
Properties of Guar Gum and Hydroxypropyl Guar Gum

	GG	HPG4	HPG8
Viscosity (1% solution)	1,800 cps	1,400 cps	1,200 cps
% Moisture	5–6	6–7	5–6
Ash content (%)	0.8–1.0	1.1–1.3	0.9–1.1
Free propanol (%)	–	<0.1%	<0.1%

in the hydrophobic nature of the hydroxypropyl guar gum as compared with pure guar gum. The study showed that the use of natural fillers as reinforcing materials was possible and resulted in composites with improved mechanical properties.

In the present study, the degradability of epoxy composites with GG and HPG was evaluated with respect to fungal degradation and aerobic degradation in soil. This could open an avenue for the formulation of thermoset composites using polysaccharides as particulate fillers. This would lead to the use of renewable resources as fillers and result in composites with enhanced degradability. Further, composites based on natural materials have been reported to show a reduced density and tool wear as compared with inorganic fillers-based composites.¹⁹

EXPERIMENTAL

Materials

The epoxy resin DER331, with an epoxy value of 180–190, and the curing agent Polyetheramine D 230, with an amine value of 476 mg KOH/g, was obtained from M/s BASF India Limited (Mumbai, India). The curing agent has a chemical structure represented as follows: $\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2-(\text{OCH}_2\text{CH}(\text{CH}_3))_x-\text{NH}_2$. GG and hydroxypropyl guar gum with a molar substitution of 0.4 and 0.8, referred to as HPG4 and HPG8, was supplied by M/s Lucid Colloids Ltd. (Mumbai, India). The properties of guar gum and derivitized guar gum are listed in Table I and have been obtained from the data sheet provided by M/s Lucid Colloids, India. *Saccharomyces cerevisiae* was obtained from M/s S.D. Fine Chemicals Ltd. (Mumbai, India).

Preparation of composites

The fillers were uniformly dispersed in the epoxy resin, following which a stoichiometric amount of curing agent was added and thoroughly mixed. The filler was added on a weight basis per hundred grams of resin, i.e., 2.5 phr would refer to 2.5 g of filler per 100 g of epoxy resin. The composition was then de-aerated to remove any entrapped air and then poured into a preheated metal mold at 60°C.

The cure cycle was 60°C/3 h, 80°C/5 h, and 120°C/3 h. The composites had a thickness of 3 mm ± 1%. Prior to testing, the specimens were allowed to stabilize at 50% humidity and at 30°C for 7 days. The dimensions of specimens used for the degradation tests were 30 mm × 30 mm × 3 mm.

Solvent extraction

Specimens were subjected to extraction with water in a Soxhlet condenser that had a capacity of 200 mL water for each cycle, and extraction was carried out for a total of 50 cycles. After the specimens were subjected to the extraction procedure, they were dried at 80°C in a vacuum oven. Three specimens of each epoxy-guar gum/hydroxypropyl guar gum composition were subjected to the extraction procedure. The results of the extraction were reported in terms of percentage weight loss of the weight of specimens. The reported results are the average of the three specimens tested for each composition.

Fungal degradation

The specimens of each composition were immersed in 100 mL of a 100 ppm aqueous solution of *Saccharomyces cerevisiae* maintained at 30°C in a humidity chamber at 50% relative humidity. After the specified time period, the specimens were removed from the solution, washed with water, and dried at 80°C in a vacuum oven. The change in weight was determined with an accuracy of 1 mg. The extent of degradation was evaluated by the weight loss of the composite specimens reported as the percentage weight loss. Three specimens were used to evaluate the effect of fungus on the composites at varying filler concentrations and time periods.

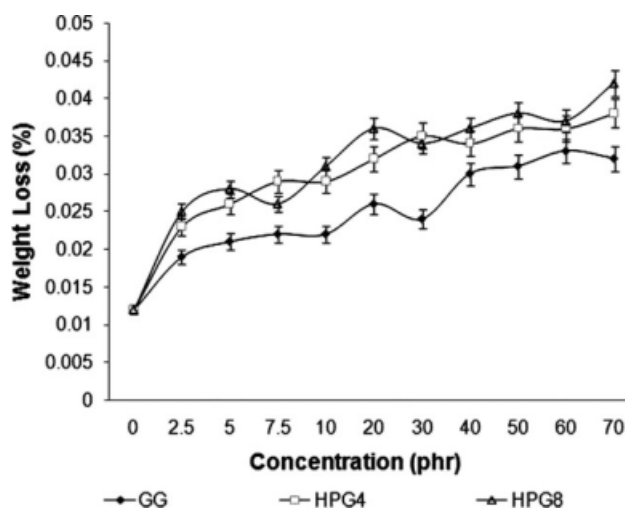


Figure 1 Variation in weight loss on solvent extraction.

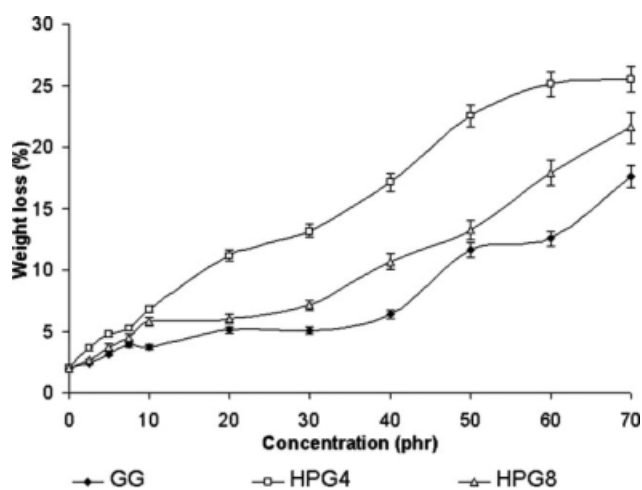


Figure 2 Variation in weight loss with filler concentration after 14 days.

Soil burial

A glass tank with a porous base and a depth of 1 m was filled with common garden soil in which the specimens were buried at a depth of 30 cm. The soil was sieved using a coarse metallic net with square perforations with dimensions of 3 mm × 3 mm; this eliminated the presence of stones in the soil mixture. Each specimen was buried such that there was no other specimen within 5 cm. The moisture content of the soil was maintained at 15%. The specimens were left buried for 1 year, after which the loss in weight was determined and reported as the percentage weight loss. Three specimens of each concentration were used for the test.

Microscopic evaluation

The micrographs were estimated using an optical microscope, Olympus BX41. The surfaces of the

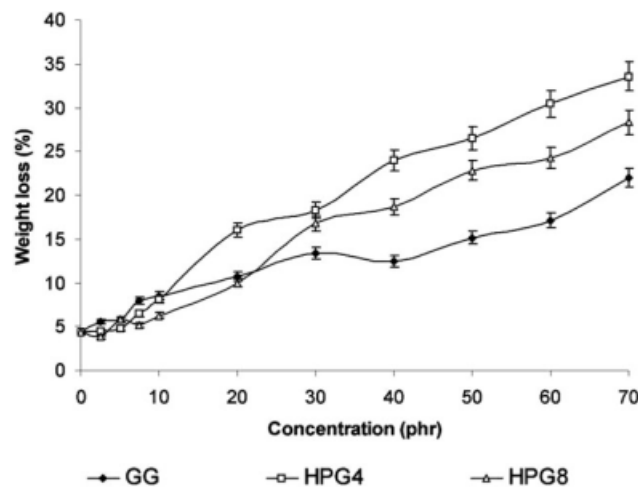


Figure 3 Variation in weight loss with filler concentration after 28 days.

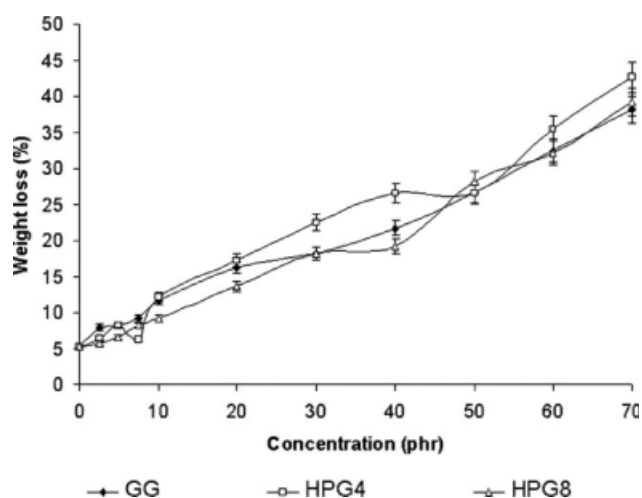


Figure 4 Variation in weight loss with filler concentration after 42 days.

specimens were examined to evaluate the effect of soil burial. Further, the effects of soil burial within the composites were examined by examining the fractured surface of the composites at a thickness of approximately 1.5 mm (± 0.2 mm), i.e., midpoint, in the composites.

RESULTS AND DISCUSSION

The solvent extraction of the epoxy composites was carried out to ascertain the extent of water extraction of GG and HPG. Water was used in the extraction process because it is the solvent for GG and HPG. Figure 1 shows the effectiveness of the water extraction process. It could be seen that as the concentration of the filler, i.e., GG or HPG, increased the percentage weight loss, i.e., the amount extracted also increased. However, it was observed that the actual quantity of material lost was extremely low. It could be that the loss was restricted to the surface of the specimens; however, this could not be confirmed. It was also observed that the composites based on HPG showed a greater weight loss as compared with GG, which could be attributed to the greater solubility of the HPG as compared with GG due to its lower molecular weight, as reflected by their lower viscosities at similar concentrations.

Figures 2–4 show the variation in weight of the specimens at various time intervals. It could be observed that the weight loss of the specimens increased with filler concentration. This was expected because the filler itself was degradable and would be attacked by the fungus, resulting in the observed weight loss of the composite specimens. Further, it was observed that the pure epoxy composites themselves showed a minor reduction in weight. This degradation was attributed to the use of the polyetheramine curing agent, which would be

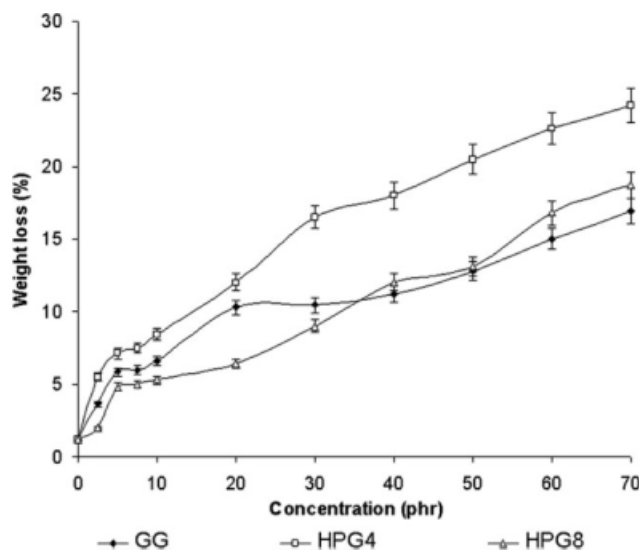


Figure 5 Variation in weight loss with filler concentration after burial in soil for 1 year.

susceptible to some extent to fungal attack due to the presence of ether groups via an oxidative cleavage mechanism.²⁰ It was observed that the weight loss in the case of HPG4-based composites was the greatest, whereas those based on GG was the least. However, after 42 days, the weight loss between the composites based on HPG8 and GG was comparable, whereas HPG4 showed only a marginal increase in weight loss over the other composites. Thus, the initial degradation of HPG-based composites was seen to be greater than that of GG-based composites, after which they equalized, as observed from the time period carried out. The process of hydroxypropylation involves the addition of propylene oxide on GG in the presence of an alkali in an aqueous medium. The reaction conditions led to a reduction in the molecular weight of the polymer molecules, as reflected by the reduced solution viscosity of the HPGs in Table I. It has been shown that as the molecular weight of a polymer is decreased, its degradability increased.^{21,22} The propoxylation of GG has the effect of increasing the hydrophobic character of the polymer; alkoxylation has been reported to alter degradation characteristics of various compounds.²³ In the case of guar gums, specifically, its etherification with propylene oxide or ethylene oxide resulted in derivatives with improved solution stability.²⁴ The increase in solution stability indicates that these derivatives are more resistant to degradation than that of the pure GG. Thus the combined effects of these factors results in the observed degradation trends. The fastest degradation was observed for HPG4-based composites because it could have resulted in the most balanced form, wherein the reduction in molecular weight was countered by the increase in stability. On the other hand, although

GG was more prone to degradation, its high molecular weight resulted in its composites having a lower degradation rate initially, though over time the degradation of GG resulted in it being comparable to that of HPG-based composites. HPG8-based composites showed a lower degradation rate than HPG4 because of its increased stability, which was not effectively countered by the reduction in molecular weight.

Figure 5 shows the effect of burial of the respective composites in soil for 1 year. It could be seen that the composites followed a similar trend, as in the case of fungal degradation, with HPG4-based composites showing the greatest degradability. Whereas GG- and HPG8-based composites were comparable at higher filler concentrations, at lower filler concentrations GG-based composites showed a slight improvement in degradability over HPG8-based composites. The reasons for the observed trends would be the same as that cited in the case of fungal degradation. As in the case of fungal degradation, the pure epoxy showed some weight loss; however, the weight loss only amounted to $\sim 1\%$. With the addition of pure GG at 2.5 phr, the weight loss was 3.6%, and in the case of HPG4 and HPG8, it was 5% and 2%, respectively. This showed that even a small addition of the filler resulted in at the least a 100% increase in the weight loss, viz., in the case of HPG8. At 5 phr, it was observed that the weight loss for GG-, HPG4-, and HPG8-based composites were 5.8%, 7.1%, and 4.8%, respectively, which increased to 6.6%, 8.4%, and 5.3% at 10 phr. Thus, at the concentrations showing optimal mechanical properties, the increases in degradability of the composites were seen to increase by 400% at the least and 740% at the most. Further addition of filler resulted in composites with as much as 17%, 24%, and 18.5% weight loss at 70 phr after 1 year. This

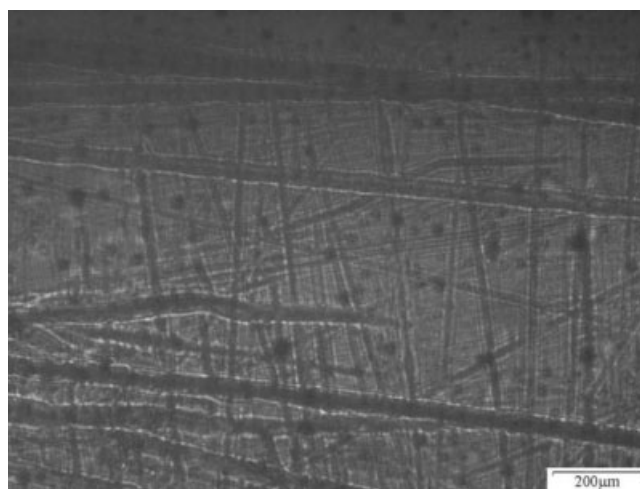


Figure 6 Surface of pure epoxy.

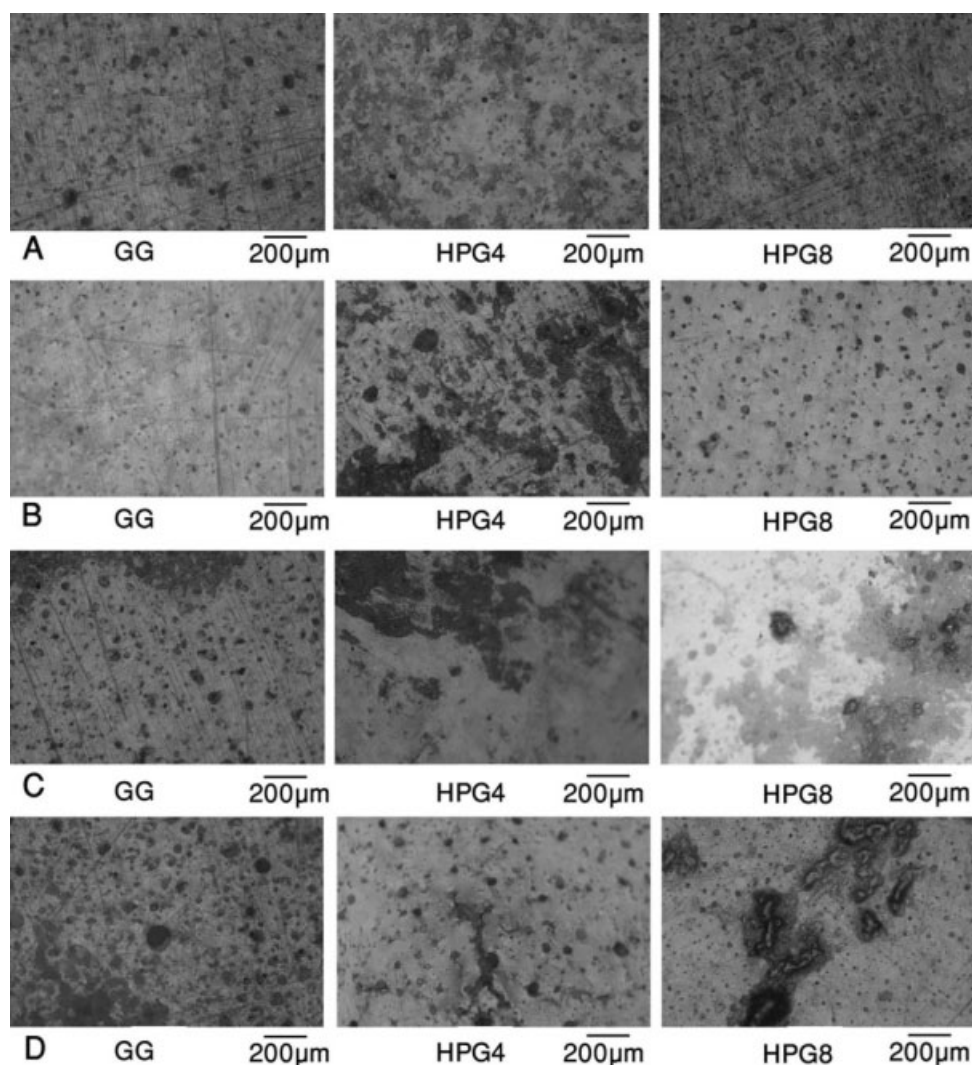


Figure 7 Comparison of surface of composites before and after soil burial for 1 year at (A) 5 phr; (B) 10 phr; (C) 30 phr; (D) 50 phr.

indicates the efficiency of the use of polysaccharide fillers as a means to impart biodegradability to the resultant composites.

The exterior surface of the composites and the fractured surfaces were evaluated to ascertain the effect, if any, of soil burial. Figure 6 shows that the exterior surface of the epoxy composite was not affected to a great extent on burial. On the other hand, composites with the GG and HPG filler showed signs of degradation, as shown in Figure 7. In the micrographs, dark portions or “blemishes” could be observed; these were in fact areas where the filler was present prior to the burial test but had since degraded or partially degraded. It could be observed that those composites based on HPG4 seemed to show the greatest discoloration or blemishes, at all concentrations, indicating that degradation was greater in its case. Further, as the filler concentration increased, the degradation at the com-

posite surfaces also increased. At higher concentrations, there was the formation of a crack, viz., 50 phr HPG4. This indicated that the degradation had progressed to such an extent that it compromised the structural integrity of the composite. In HPG8-based and to a lesser extent GG-based composites, at 50 phr, deep pitting was observed on the surfaces. These micrographs support the weight loss data, which show that the composites based on HPG4 showed the greatest degradation.

Figure 8. depicts the interior of the composites, as observed from the fractured surfaces. The GG and HPG particles were not easily noticeable after soil burial. Figure 10 shows the change in the composite bulk after soil burial for 1 year. Before burial, there were a number of particles of GG at the fracture surface; however, after burial there were a reduced number of particles. Similar observations were made for HPG4- and HPG8-based composites. The

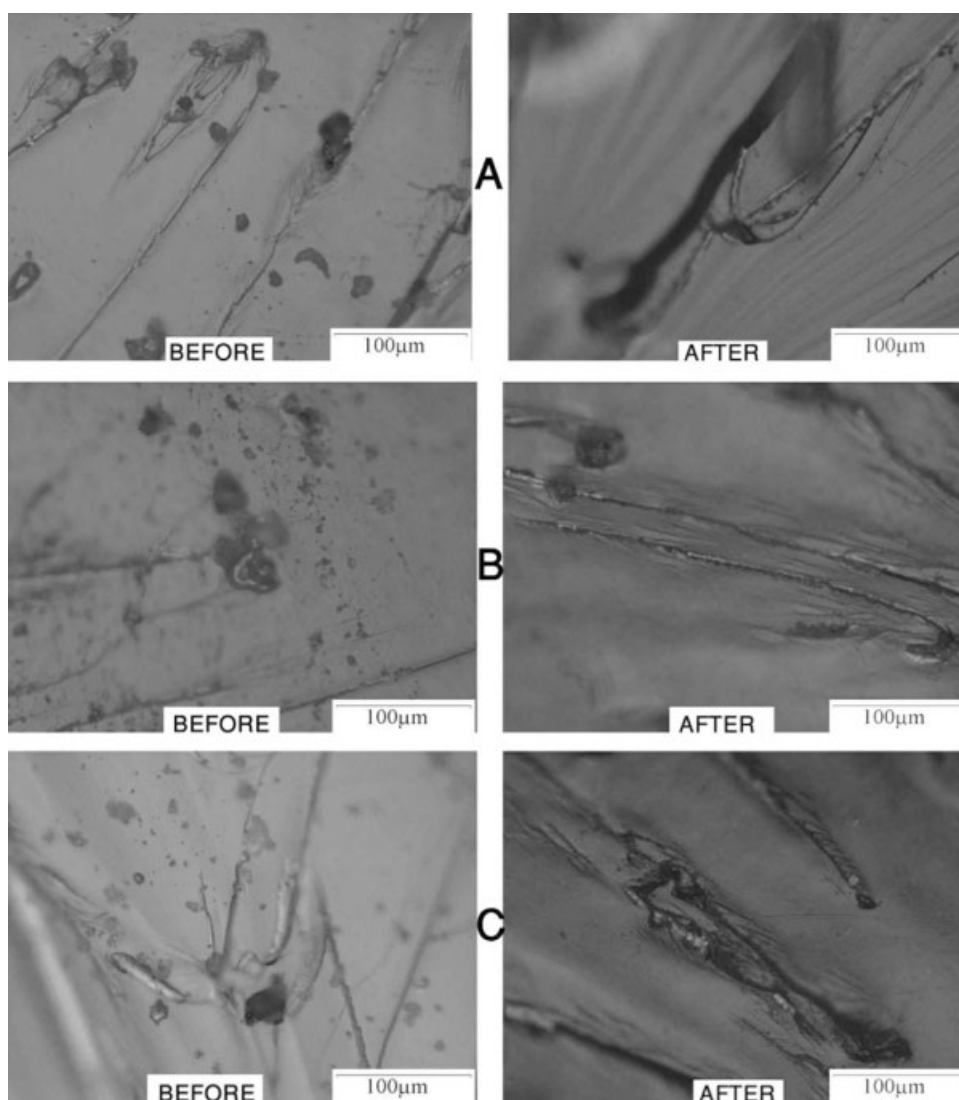


Figure 8 Comparison of fracture surface of composites before and after soil burial for 1 year at 5 phr based on (A) GG; (B) HPG4; (C) HPG8.

reduction in the instance of the filler particles in the composite bulk could be attributed to the degradation of the filler. Any particles in the composites after burial could be partially degraded, which could not be ascertained from the microscopic examination of the composites. The nature of the fractures in the specimens remained constant. The fractures originated from the interface of the filler–polymer matrix before soil burial, as is apparent from the images in Figure 7. After soil burial, although as mentioned earlier the filler particles were not prominently observed, the fractures appeared to originate from seeming voids or partially degraded particles. There was no observable change in the epoxy matrix.

Thus, degradation occurred throughout the composite and not just at the surface. The degradation of the filler led to an increase in the degradation rate of the polymer matrix as well, as proved in the case of

starch-filled polyethylene.²⁵ This was because the degradation of the filler, whether at the surface or the bulk of the composite, resulted in an increase in the surface area, temperature, microbial concentration, and humidity, all of which lead to an increase in the rate of degradation of the polymer matrix itself. The use of polysaccharides as fillers was observed to increase the degradability of the resultant composites. Although an increase in the concentration of the filler did increase, the weight loss it was observed that the optimum concentration with reference to the mechanical performance of the composites was between 5 and 10 phr. The effect of propoxylation was studied; however, the advantage of using polysaccharides lies in the innumerable reactions, and hence modifications, possibly resulting in composites with varying properties.

CONCLUSIONS

The addition of polysaccharides, specifically guar gum, as particulate fillers in an epoxy composite resulted in an increase in the degradability of the composite. It was also observed that the propoxylation of the guar gum resulted in an increase in the degradability of the resultant composites to a certain hydroxypropyl content, after which it decreased. Microscopic evaluation of the composites showed that the degradation was not limited to the surface of the composites but also occurred in the bulk. Thus the study highlights the possibility of using polysaccharides and modified polysaccharides as particulate fillers in the formation of more eco-friendly composites.

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