Evaluation of Properties of Unsaturated Polyester/ Acetylated Hydroxypropyl Guar Gum Composites

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ABSTRACT: Guar gum is a naturally occurring galactomannan, which is extremely hydrophilic in nature. Hydroxypropyl guar gum (HPG) was subjected to acetylation using acetic anhydride and pyridine. The effect of the reduction in the hydrophilic nature of the polymer on its filler properties was studied by using the derivatized guar gum as filler in an unsaturated polyester composite. The effect of degree of substitution and the concentration of filler on the rheological, chemical, and mechanical properties of the composites were studied. Results indicated that an increase in the acetate content in the HPG resulted in an increased polymer–filler interaction. However, the composites resulting from these derivatized HPGs showed reduced mechanical properties. This decrease in the mechanical properties were attributed to the decrease in the hydrogen bonding in the filler particles, thus reducing the cohesiveness and strength of the filler particles themselves. Thus, polysaccharides can be used as fillers but chemically modifying them results in a change in the basic nature of the filler itself and is not just restricted to surface modification as is the case of inorganic fillers and fibers. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 3204–3210, 2010

Key words: composites; fillers; mechanical properties; polysaccharides and thermosets

INTRODUCTION

Guar gum is a naturally occurring, hydrophilic galactomannan extracted from the endosperm of *Cyamopsis tetragonalobus*, which is commercially grown in the Indian subcontinent and to some extent in North Africa and South America. It and its derivatives are known to result in highly viscous solutions even at low concentrations, and hence, are commonly used in a variety of applications.[1–4]

Guar gum has also been used as a polymeric phase in the preparation of blends.[5,6] A limited number of studies using guar gum in thermoset composites have been investigated for its performance as reinforcing filler.[7,8] Other natural polymers, such as lignin,[9] starch,[10] and wood flour[11] are commonly used in polymeric composites and blends as reinforcing agents and to impart specific properties, such as enhanced biodegradability to the resultant composite. Apart from these natural polymers, natural fibers are widely used in polymer composites.[12–14] These fibers are usually surface treated to increase the wetting and adhesion of the polymeric phase on the fiber surface, which results in an increase in the mechanical properties of the resultant composites. The nature of the surface treatment varies and includes formaldehyde-dimethylomelamine,[15] silane,[16] sodium hydroxide, acetic anhydride, and formic acid[17] treatment. All these treatments have been found to be effective in increasing the adhesion between the polymer and the fiber resulting in an increase in the properties of the composites.

In this study, we propose to use hydroxypropyl guar gum (HPG) as a filler in an unsaturated polyester matrix. The effect of acetylation of HPG on the filler properties with respect to the mechanical properties of the resultant composites will be studied. The technique used to prepare cellulose reinforced unsaturated polyester composites with increased wetting of the fiber by acetylation of the cellulose was thought to be applicable in this case as well. We expect a similar increase in adhesion between the filler and the polymer matrix, resulting in an increase in the mechanical properties of the composites as compared with the unacetylated HPG, as was observed with the cellulose fibers. The difference between the studies is that such treatments have been conventionally used on fibers. The advantage of using polysaccharides as fillers would lie in the fact that they are a renewable resource, with low density, are nontoxic and biodegradable.

EXPERIMENTAL

Materials

The unsaturated polyester resin, cobalt octoate (accelerator), and methyl ethyl ketone peroxide

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(initiator) was obtained from M/s Mechamco, India. The unsaturated polyester was based on propylene glycol, maleic anhydride, and isophthalic acid and diluted with styrene (30% w/w). HPG was supplied by M/s Lucid Colloids, India and had a molar substitution of 0.8, moisture content of 4–5%, viscosity of 1200 cps, free propanol content <1%, and a particle size of 75–100 μ, as reported in the product's datasheet.

Esterification of HPG

HPG was acetylated using acetic anhydride as the esterifying agent in the presence of pyridine as solvent and catalyst. The reaction was carried out at 90°C and the reaction time varied to obtain different degrees of substitution. The degree of esterification was estimated from the ester value of the HPG derivatives. A weighed sample of HPG, as the blank, and the derivative were dissolved in an aqueous alkali solution and the ester allowed to hydrolyze completely. Unreacted alkali was then back titrated with hydrochloric acid, from which the degree of substitution (DS) of the HPG derivative was found out as given in eq. (1).

$$DS = \frac{162 \times (\text{ester value})}{56{,}100 - \{43 \times (\text{ester value})\}} \tag{1}$$

The rheology of the unsaturated polyester-HPG compositions, at 2.5 phr filler concentration, were studied on a RT10 Rheoviscometer (Haake, Germany) using a C35/2° cone and plate assembly. This particular concentration was used to negate effects of agglomeration on the viscosity of the composition. Further, we expect the trends observed at this concentration to be reflected in higher concentrations.

Preparation of composites

The fillers were uniformly dispersed in the unsaturated polyester resin along with the accelerator (0.5% w/w), following which the free radical initiator was added (2% w/w) and thoroughly mixed. The fillers were added on weight basis and reported in terms of parts per hundred of resin (phr), which means that 2.5 phr would refer to 2.5 g of filler for every 100 g of resin. A 0 phr concentration would refer to the pristine polymer, that is, without filler addition and coincides with the y-axis of the respective property graphs. This gives a comparison of the performance of the composite with reference to the pristine polymer. The composition was then deaerated to remove any entrapped air and poured in a metal mold maintained at 30°C. The cure cycle was 30°C/12 h and 100°C/2 h. The composites had a thickness of 3 mm ± 1%.
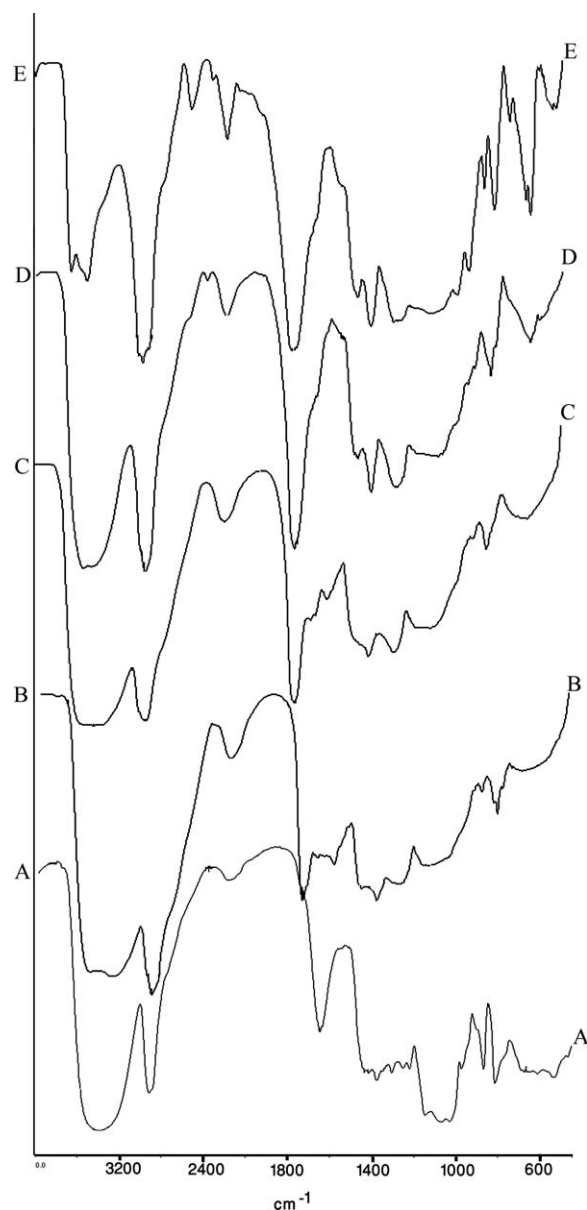

Figure 1 FT-IR of HPG and acetylated derivatives. (A) HPG, (B) Acetylated HPG (0.58), (C) Acetylated HPG (1.1), (D) Acetylated HPG (1.8), and (E) Acetylated HPG (3).

The composites were machine cut into the respective shapes for testing and the edges were uniformly ground to remove imperfections, which could lead to errors in the test results. Before testing, the samples were allowed to stabilize at 50% humidity and at 30°C for 7 days.

Testing of composites

The composites were tested for their tensile, flexural, and impact properties. The tensile strength and percentage elongation (Specimen Type IV[B]) and flexural strength (specimen dimensions 60 mm × 25 mm × 3 mm) were determined according to ASTM D638M and ASTM D790M, respectively, on a Universal

Tensile Testing Machine, Lloyd LR 50K, UK with a crosshead speed of 6 mm per minute for tensile measurement and 8 mm per minute for the three point bending test. Charpy impact was carried out on an Avery Denison Impact tester using 2.7 J striker with a striking velocity of 3.46 m/s in accordance with ASTM D256. Specimen dimensions were 127 mm × 12.7 mm × 3 mm. Tests were carried out on five samples and the averages have been reported as the test results.

Water and toluene absorption were studied using three 1 × 1 × 0.3 cm chips and suspending them separately for a period of 7 days in 100 mL solvent at 30°C. After the required amount of time, the samples were removed and gently dried using a filter paper to remove water or solvent adhering to its surface. The change in weight of the sample was then estimated, as shown in eq. (2).

$$\% \text{ Weight change} = \frac{(\text{Final weight} - \text{Initial weight})}{\text{Initial weight}} \times 100 \quad (2)$$

IR spectra

The IR spectra of HPG and its derivatives were taken with KBr pellets on a Perkin–Elmer System 2000 FT-IR spectrophotometer.

RESULTS AND DISCUSSION

Acetic anhydride treatment of cellulose fibers resulted in increased adhesion of unsaturated polyester on the fiber surface. The difference between the treatment of cellulose fibers and that of HPG lies in the fact that cellulose fiber treatment is primarily a surface treatment, whereas the reaction of acetic anhydride and HPG is not restricted to just the surface of the particle, but takes place in the entirety of the particle, as indicated by the DS of products. A completely substituted product with a DS of 3.0 was obtained indicating that although the HPG did not dissolve in the reaction medium, the acetylation was not restricted to the surface of the HPG particles. This has two effects, one, a change in the interaction between the polymer matrix and the filler particle, and the other, a change in the nature of the filler itself. The variation of the reaction time results in the formation of acetylated HPG derivatives with a DS of 0.58, 1.1, 1.8, and 3.0. The FTIR of the derivatized products, as shown in Figure 1, show an increase in the intensity of the carbonyl peak obtain in the region of 1735–1750 cm^{-1} with an increase in the DS as well as a decrease in the intensity of the peak at 1650 cm^{-1}, which was attributed to hydration of the HPG that was observed to decrease as
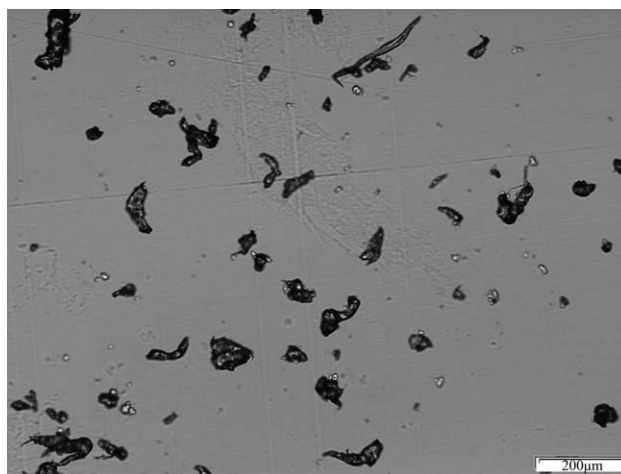

Figure 2 Image of HPG.

the esterification increased. Further, the intensity of the ─OH stretching peak observed at 3300–3400 cm^{-1} also decreased as the DS of the acetylated HPG increased, indicating reduction of hydroxyl groups due to its consumption in the esterification reaction.

The effect of acetylation of HPG on the filler–polymer interaction will be apparent from the viscosity of the formulations. The particle sizes and shapes of all the samples were found to be comparable irrespective of the degree of acetylation. Figure 2 shows a representative image of HPG, from which we see that the particles are highly irregular in nature. With an increase in the polymer–filler interaction there will be a corresponding increase in the viscosity of the formulation, which has been thoroughly studied.[18] The interaction between the polyester and filler results in an increased resistance to flow that is responsible for the increase in the viscosity of the composition. From Figure 3, we see that an increase in the extent of acetylation, as indicated by the DS, resulted in an increase in the viscosity of the compositions irrespective of shear rate. This shows that the acetylation does indeed increase the interaction between the filler particles and the polyester phase and these findings are corroborated by the results obtained from the acetylation of cellulose fibers.[15] Although the viscosity data only indicates that the interaction between the uncured polyester and the filler increases, we can expect a similar trend to be followed after curing of the polymer and in the composite. Thus, from rheology data, we can conclude that the acetylation of HPG results in an increase in the interaction between the polyester and filler, which has been proved to result in an increase in compatibility that in turn has a positive effect on the mechanical properties of the composite.[15–17]

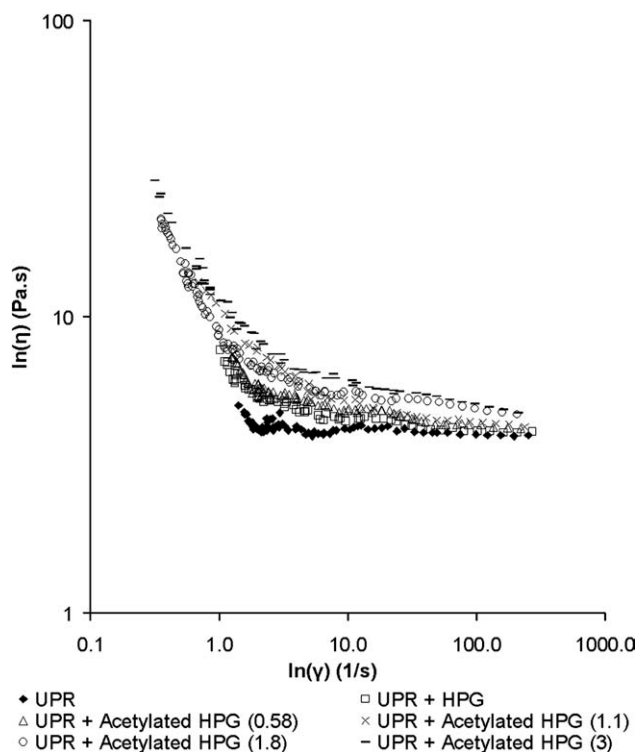The effect of toluene on the HPG and acetylated HPG-filled composites can be seen from Figure 4.

Figure 3 Rheology of unsaturated polyester compositions at 2.5 phr.

Figure 5 Variation of water absorption of composites.

The effect of solvent on the unsaturated polyester composites was studied to investigate the effect of filler addition on the crosslinking density of the composites. Toluene was chosen as the solvent because styrene-diluted unsaturated polyesters are notorious for their poor resistance to aromatic solvents. From the solvent absorption, we see that the addition of HPG to the composites results in a
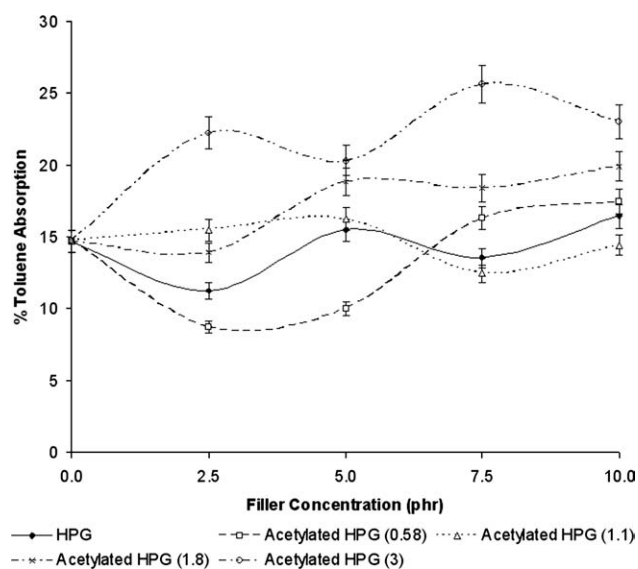
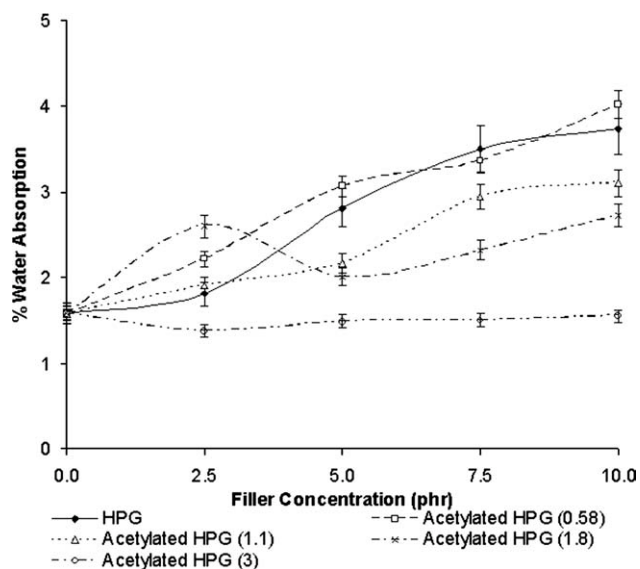decrease in the toluene absorption. This was due to the fact the HPG is hydrophilic and its inclusion in the composite made it more hydrophilic, and hence, decreased its affinity to toluene. Further addition of HPG did not result in a decrease in the crosslinking density of the composite as indicated by the toluene absorption, which remained almost steady. Addition of acetylated HPG (0.58) in the unsaturated polyester composite resulted in decreased toluene absorption, which was due to the increased interaction between the polymer matrix and the filler. Further addition of acetylated HPG with greater acetate content resulted in composites with increased toluene absorption. The acetylation of HPG results in the decrease in the hydrophilic nature of the polymer, thus, increasing its affinity for the polymer matrix and also organic solvents, which is responsible for the increased toluene absorption of the resultant composites.

Water absorption of the composites was studied and the results are graphically depicted in Figure 5. We can see that the addition of HPG and acetylated HPG (0.58) results in composites with comparative water absorption. The increase in filler content resulted in an increased water absorption of the composites because of the increased concentration of the hydrophilic filler. The addition of acetylated HPG with increased acetate content resulted in composites with reduced water absorption, because of the reduced hydrophilic nature of the acetylated HPG. Interestingly, acetylated HPG (3) showed the comparable water absorption as that of the pure unsaturated polyester and was independent of concentration of the filler added, in the range under study.

Figure 6 shows the variation of the tensile strength with composites based on acetylated HPG. From the
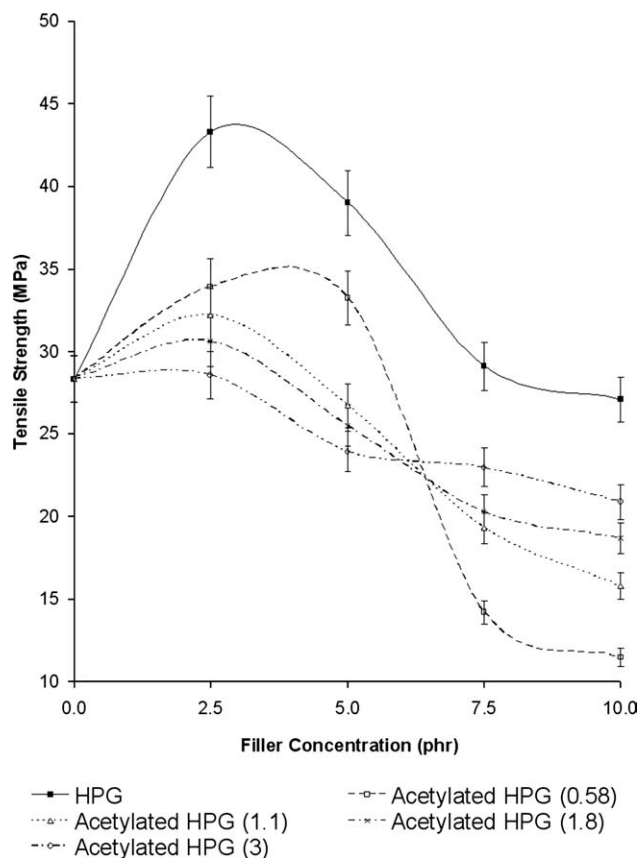

Figure 4 Variation of toluene absorption of composites.

Figure 6 Variation of tensile strength of composites.

graph, we can see that HPG-based composites showed the greatest tensile strength when compared with the acetylated HPGs. The rheological and chemical resistance of the composition and the composites showed that the interaction between the filler and polymer matrix increased with an increase in the acetate content. However, this was not reflected in the tensile strength of the composites. As mentioned earlier, the chemical modification of the HPG was not restricted to the surface of the particles, as is commonly observed in the treatment of fibers and mineral fillers, but occurs throughout the particle. The change in the chemical nature of the polymer itself impacts the properties of the particles. One change is the reduced hydrophilic nature of the polymer, which in turn would result in a reduction in the hydrogen bonding. The acetylated HPG particles are held together by chain entanglement, short range physical forces, such as Van der Waals forces as well as electrostatic forces, such as hydrogen bonding. With the esterification of the HPG polymer, the hydrophilic nature of the polymer reduces and this has a detrimental effect on the hydrogen bonding of the resultant particles. This would consequently results in filler particles with reduced integrity and cohesion. This could be a possible explanation for the reduction in the tensile strength

of the composites based on the acetylated HPG when compared with HPG. From the graph, it also becomes apparent that the tensile strength peaks at a concentration between 2.5 and 5 phr after which it reduces on further addition of filler. This reduction in the tensile strength of the composites above 5 phr could be attributed to the formation of agglomerates in the composites.

Figure 7 depicts the elongation at break of the composites. From the graph, we see that addition of the filler results in a decrease in the elongation at break of the composites irrespective of nature of the filler. The slight increase in the elongation at break above 2.5–5 phr could indicate the formation of agglomerates in the composite. Further, we see that the composites based on HPG showed the least elongation at break. Composites based on acetylated HPG showed a trend wherein the elongation at break was increased along with the extent of acetylation, which was because of the increased interfacial interaction between the polymer matrix and the filler particle. This shows that as the extent of acetylation of HPG increased it resulted in composites with increased elongation at break.

The influence of filler addition on the flexural strength of the composites can be seen from Figure 8. Similar to the tensile strength, the flexural
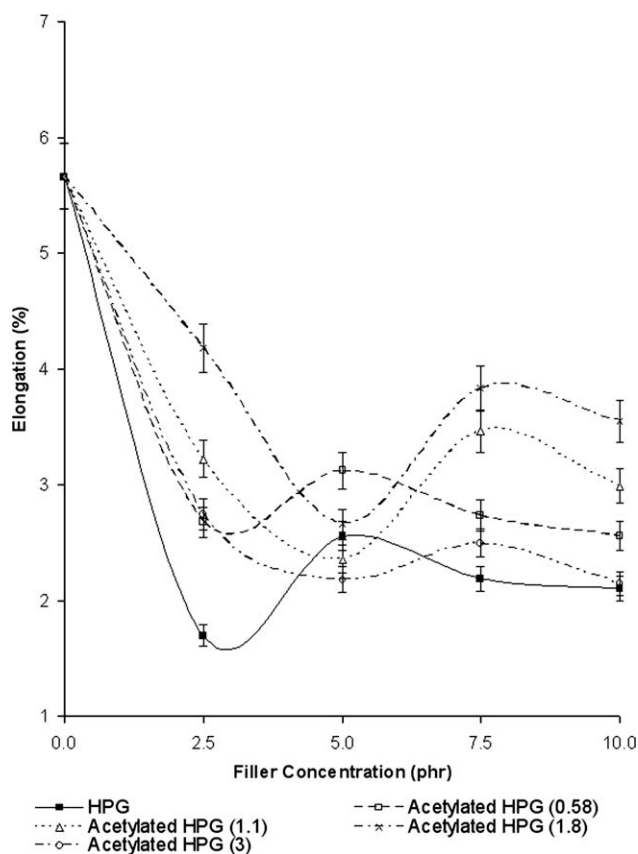

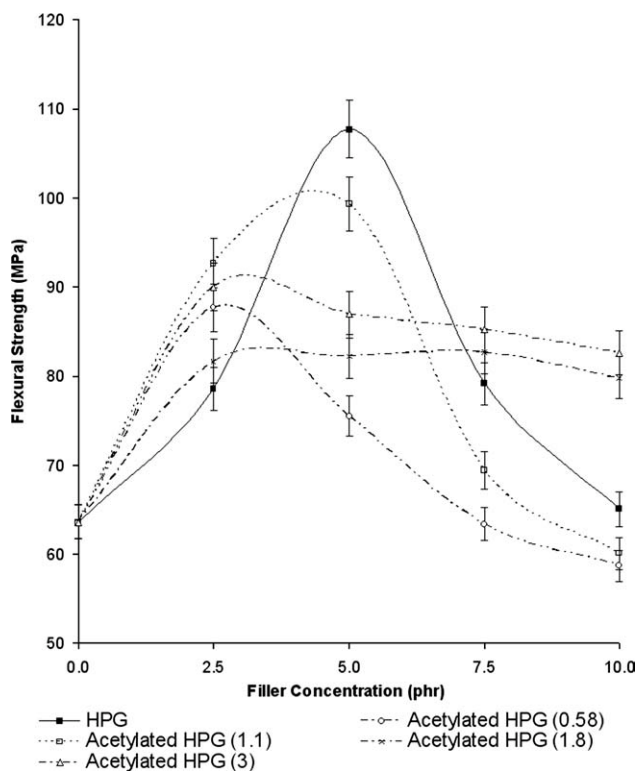**Figure 7** Variation of % elongation of the composites.

Figure 8 Variation of flexural strength of composites.

strength of HPG-based composites are found to be the greatest when compared with those of acetylated HPG. Again, as the extent of acetylation increases the flexural strength of the corresponding composites decreased. In this instance too, the reason could be the same as that cited for the lowering of the tensile strength. From the graph, it can be seen that the flexural strength peaks at 5 phr for HPG-based composites, whereas the peak is not as prominent for the acetylated HPG-based composites. In fact, HPG (1.8) and (3) based composites show a peak value at 2.5 phr after which there is a slight drop in the flexural strength followed by a steady state. This trend is not observed for the HPG-based composites as well as those based on HPG (0.58) and (1.1), which show a continuous decrease after the peak value is reached. At the higher concentrations where this trend is observed aggregates already form as indicated by tensile properties. Within an aggregate, the filler particles are held together by short range physical and electrostatic forces, such as hydrogen bonding. Another important point is that these fillers show a greater polymer–filler interaction, which could also contribute to the greater flexural strength after aggregate formation when compared with HPG. As explained earlier, hydrogen bonding becomes difficult in the case of acetylated HPG (1.8) and (3), thus, the formation of aggregates with these fillers becomes more difficult when compared with those based on the more hydrophilic fillers. Thus,

the composites based on acetylated HPG (1.8) and (3) would have aggregates to a lesser extent than the other fillers, which could explain the steady state after aggregate formation was observed in the other cases.

The flexural modulus of the composites is depicted in Figure 9. From the graph, we see that there is a maxima at 5 phr for almost all the composites, with the composite based on acetylated HPG (0.58) showing the greatest value followed by that incorporating HPG, acetylated HPG (1.1), (3), and (1.8). The flexural modulus indicates that addition of the HPG (0.58) and HPG fillers results in the most rigid composites, whereas acetylated HPG (1.8) and (3) resulted in the least rigid composites. Again the reduction in rigidity of the composites with the fillers with the highest acetate content can be explained by the reduction in the hydrogen bonding, which allows for more mobility, which is not available in those fillers with greater degrees of hydrogen bonding.

The impact properties of the composites are shown in Figure 10 from which we can see that hydrogen bonding plays a major role in dissipating the energy supplied to the composite during the impact. This explains why composites based on HPG show the greatest impact resistance, whereas the esterified HPG fillers result in composites with decreasing impact resistance. Although there may be more polymer–filler interaction in the case of acetylated HPG, which will result in more efficient energy transfer across this interface, once the energy is transferred to the filler particle the lack of cohesion
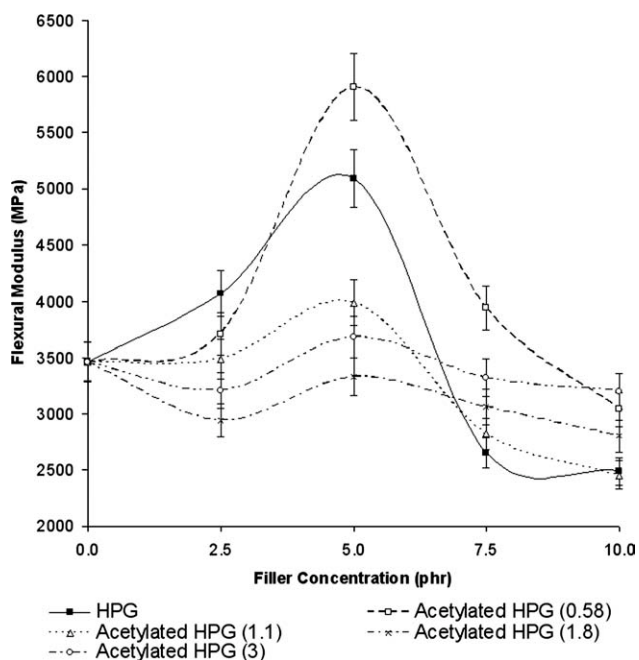

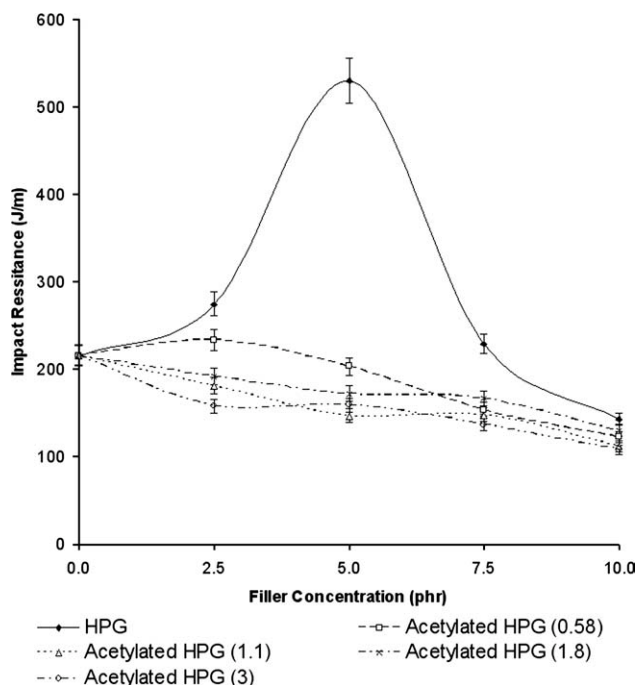**Figure 9** Variation of flexural modulus of composites.

Figure 10 Variation of impact properties of the composites.

in the filler itself can lead to the initiation of failure of the composite. In the case of HPG-based composites once the energy is transferred to the filler then it is dissipated by the breaking of temporary hydrogen bonds, lowering the energy available for fracture of the composite.

This study shows that although the hydrophobic modification of HPG results in increased polymer–filler interaction, it does not necessarily lead to an increase in the properties of the corresponding composites. The difference between using polysaccharides and other conventional fillers is that chemical modification of polysaccharides is not restricted to the particle surface but effects the nature of the filler itself as opposed to simple surface modification in the case of conventional fillers and fibers. Although polysaccharides can be used as fillers classical treatment methods do not apply as the nature of the polysaccharide particles themselves change. The highlight of this study is the possibility of using polysaccharides as fillers, which has the advantage in that they are renewable, nontoxic, and degradable. Thus, they could further be investigated as a replacement to mineral fillers. An improvement in properties could be obtained by using particles with a smaller particle size. Alternatively, restricting acetylation to the particle surface would increase polymer–filler interaction, whereas maintaining particle integrity would also lead to improved properties.

CONCLUSIONS

The acetylation of HPG led to an increase in the hydrophobic nature of the resultant polymer, which increased the polymer–filler interaction as indicated by the rheology of the unsaturated polyester–filler formulations. Composites based on the acetylated HPG showed decreased water absorption, whereas the toluene absorption increased, which was proportional to the extent of acetylation of the HPG. The mechanical properties of the composites were found to be inferior to those of unsaturated polyester and HPG. The decrease in the mechanical properties was attributed to the decrease in the cohesive strength of the filler particles themselves because of the reduction in hydrogen bonding on increased esterification. The chemical modification of polysaccharides for use as fillers with increased polymer–filler interaction leads to a change in the nature of the filler particle itself, as opposed to the simple surface modification of inorganic fillers and fibers. Thus, polysaccharides can be used as reinforcing fillers with chemical modification to improve polymer–filler interaction keeping in mind the nature of the filler itself is changed.

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