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Evaluation of mechanical properties of acrylated guar gum - unsaturated polyester composites

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Summary

Guar gum (GG) and its derivatives are commonly used in aqueous solutions as rheology modifiers. The use of polysaccharides as fillers in thermoset polymer composites has as yet not received that attention attributed to other materials. In the present study GG and the effect of acrylation on its filler properties were evaluated. Unsaturated polyester composites were evaluated for their mechanical properties as well as solvent resistance and water absorption. It was observed that the acrylate derivatives with the highest degree of substitution resulted in composites with the best mechanical properties as well as increased toluene and water resistance. Thus, polysaccharides could be used as reinforcing fillers in thermoset composites.

Keywords

Composites, Natural Polymers, Mechanical Properties

Introduction

Guar gum (GG) is a non-ionic polysaccharide extracted from the endosperm of *Cyamopsis tetragonalobus*. Chemically it is a galactomannan with a galactose to mannose ratio of 1:2, where the galactose is randomly distributed on the mannose backbone in galactose rich and deficient regions [1-3]. Guar gum and its derivatives are water soluble hydrophilic polymers whose solutions are highly viscous in nature. This property resulted in these polymers to be commercialized in various applications where a high viscosity is required [4-7]. When incorporating the polysaccharide in a polymer matrix, its hydrophobic modification is required to increase its compatibility. Cellulosics, lignins and starches have been used as fillers in thermoplastic polymers as reinforcing materials and to impart special properties such as biodegradability [8-11]. These materials have evidenced interest over micro-silicate fillers such as clays, mica and fly ash because they are obtained from renewable resources and are eco-friendly. Further, composites based on these materials score over mineral fillers in that they have a lower density and result in reduced tool wear while being economical.

In reinforced composites coupling agents are conventionally used to increase interaction between the polymer and the filler, resulting in increased adhesion between the two phases. This increased adhesion leads to an increased energy transfer across the polymer-filler interface, resulting in increased mechanical properties [12-14]. Our previous investigations on the effect of increasing the hydrophobic nature of GG resulted in composites with increased properties [15,16]. The hydrophobic nature of the polymer was increased through hydroxypropylation, which resulted in an increased compatibility. In this study guar gum was functionalized through acrylation leaving the terminal unsaturation free. This was thought to be analogous to vinyl silane treatment of fibers and fillers [17-19] which has proved to be highly effective. These acrylated guar gum derivatives were incorporated in unsaturated polyester resins and the resultant composites evaluated for their mechanical properties. The study is important because it explores an avenue for the use of natural, eco-friendly, renewable resources as fillers.

Experimental

Materials

The unsaturated polyester resin, cobalt octoate (accelerator) and methyl ethyl ketone peroxide (initiator) was obtained from M/s Mechamco Ltd. India. The unsaturated polyester used was based on isophthalic acid, maleic anhydride and 1,3 propane diol and had a solid content of 70%, acid value of 18-20 mg KOH/g resin, hydroxyl value of 30-35 mg KOH/g resin and styrene was used as the reactive diluent. Guar gum (GG) was supplied by M/s Lucid Colloids Ltd., India and had a moisture content of 5-6%, 1% solution viscosity of 1800cps and ash content of 0.8-1.0%. Acrylic acid and benzoyl chloride was obtained from M/s S.D. Fine Chemicals, India, was of analytical reagent grade and was used without any purification. Hydroquinone, sodium hydroxide, solvents like methyl ethyl ketone, toluene and acetone were also procured from M/s S.D. Fine Chemicals, India, were of laboratory reagent grade and were used without any further purification.

Synthesis of acryloyl chloride

Acryloyl chloride was prepared just before use by the reaction of acrylic acid and benzoyl chloride. 1.0 mole of acrylic acid was heated with 2.0 moles of benzoyl chloride in the presence of hydroquinone and the fraction distilling out between 65-75°C was collected in a flask containing hydroquinone. This crude acryloyl chloride was then redistilled and the fraction distilling out at 70-73°C was isolated and used for the esterification of guar gum. the schematic representation of the reaction is given in Figure 1.

Acrylation of guar gum

A solution was prepared by dissolving 5.0g guar gum, 0.5g hydroquinone and sodium hydroxide in 50ml distilled water and 50ml methyl ethyl ketone. The solution was maintained at a temperature between 0-5°C, to which a solution of 50ml toluene, 10ml methyl ethyl ketone and a stiochiometric amount of acryloyl chloride was added dropwise over a time span of 10 minutes. The initial addition of acryloyl chloride solution to the reaction mixture was taken as the start of the reaction. The reaction was carried out at 0-5°C for varying time periods after which the derivatised product was precipitated in acetone. The precipitate was then filtered, washed with acetone and

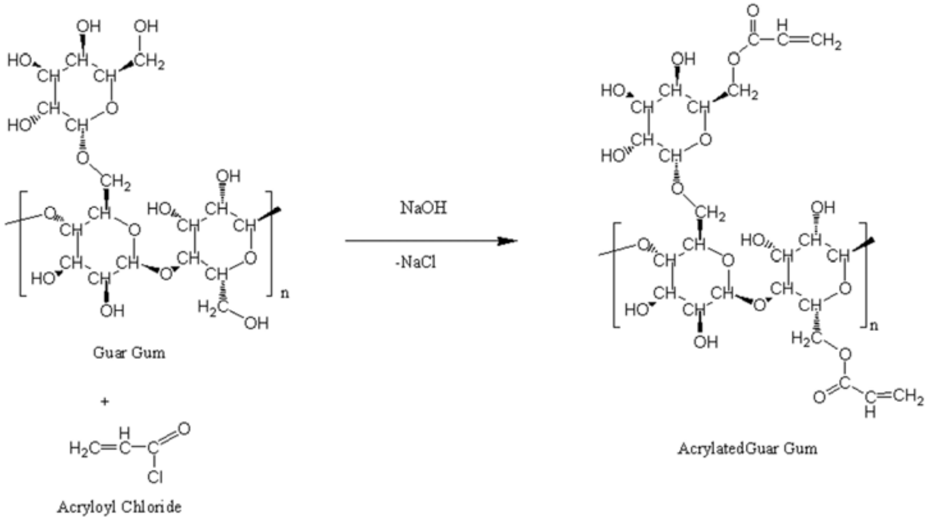

Figure 1. Schematic representation of acryloylation of guar gum.

dried at 50°C under reduced pressure for 12 hours to obtain a dry acryloylated guar gum. The derivatives prepared along with their properties are given in Table 1.

Table 1. Properties of acrylated guar gum.

Sample Name	Time of reaction (hr)	Ester value (mg KOH/g)	DS	Intrinsic Viscosity (dL/g)
GG	-	-	-	14.54
AGG1	1	154	0.50	0.87
AGG3	3	170	0.56	0.97
AGG5	5	122	0.39	4.03
AGG7	7	56	0.17	8.4
AGG11	11	21	0.06	14.19

Estimation of DS

The DS of the derivatised products were estimated by evaluating the ester value of the samples. Weighed quantities of the derivatised guar gum and a blank of native guar gum were dissolved in 25ml aqueous solution of 0.2N KOH and allowed to stand for 24 hours at room temperature, to affect hydrolysis. The samples were then titrated against a solution of 0.2N HCl to estimate the amount of unreacted potassium hydroxide. The ester value thus obtained was then used to calculate the DS of the samples [20,21].

$$\text{Ester value} = \frac{56100 \text{ x functionality}}{\text{Molecular weight}} \tag{1}$$

The functionality in this case is the same as the DS and the molecular weight is the weight of the repeat unit of guar gum and the weight of the added acrylate moiety.

The weight of the added acrylate moiety per repeat unit will be 41 x DS, where 41 is the molecular weight of the acrylate moiety. Thus the equation becomes

$$\text{Ester value} = \frac{56100 \times \text{D.S.}}{(162 + 41 \times \text{DS})} \tag{2}$$

Rearranging Eq. 2 we get.

$$\text{D.S.} = \frac{162 \times (\text{ester value})}{56100 - \{41 \times (\text{ester value})\}} \tag{3}$$

Spectral analysis

FTIR of the samples were carried out on films of the samples. Films were cast on a Teflon mold from an aqueous solution and dried at 80°C in an air circulating oven. The films thus obtained were than analysed using a Perkin Elmer 781 spectrophotometer.

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 filler was added on weight basis, on parts per hundred grams of resin (phr), i.e. 2.5 phr would refer to 2.5 grams of filler per 100 grams of UPR. The composition was then de-aerated to remove any entrapped air and poured in a metal mold maintained at 30°C. The cure cycle was 30°C/12 hours and 100°C/ 2 hours. The composites had a thickness of 3mm +/- 1%.

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. Prior to 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 60mmx25mmx3mm) were determined according to ASTM D638 and ASTM D790 respectively on a Universal Tensile Testing Machine, Lloyd LR 50K, UK with a crosshead speed of 6 mm per minute for tensile and 8 mm per minute for the three point bending test. Charpy impact was carried out on an Avery Dension Impact tester using 2.7J striker with a striking velocity of 3.46m/s in accordance with ASTM D256. Specimen dimensions were 127mmx12.7mmx3mm. 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 1x1x0.3cm 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 was then estimated.

Results and discussion

GG as mentioned earlier is a hydrophilic polymer, the acrylation of GG would have two effects. One would be to increase the hydrophobic nature of the resultant acrylated guar gum derivatives (AGG) by the consumption of hydroxyl groups and the other would be the formation of derivatives with free terminal double bonds which would help in reactive compatibilisation of the filler with the polymer matrix. From Table 1 it was observed that after 3 hours of acrylation the DS was 0.56, on further reaction it was observed that the DS decreased. The decrease was caused due to the hydrolysis of the ester group during the course of the reaction, since the reaction was carried out in an aqueous medium. Thus, as the time of reaction increased, above 3 hours, it was observed that the hydrolysis of the acrylate group also progressed to almost yield the initial GG after 11 hours. Further, it was observed that as expected the water binding capacity, and hence the hydrophilic nature, of the GG decreased as the DS of the AGG increased, as indicated by the intrinsic viscosity. Figure 2 shows the FTIR spectrum of the AGG derivatives. As could be seen GG and AGG showed a peak at 1640 - 1650cm^{-1} which was attributed to hydration [22]. On acrylation the spectra showed an additional peak at 1720-1730 cm^{-1} which was caused due to the carbonyl stretching vibrations, indicating the presence of ester group in AGG. Further, it was observed that the intensity of the peak attributed to the carbonyl stretching decreased as the time of reaction increased, further indicating a reduction in the DS of the AGG derivatives.

For the study derivatives AGG3, AGG5 and AGG7 were chosen as they represented a range of DS. This would allow for the investigation into the effect of acrylate content on the AGG derivative on the properties of the resultant composites as compared to the control composite containing the unmodified GG.

Unsaturated polyesters have been known to have poor resistance to aromatic solvents, because of the use of styrene as a reactive diluent, the solvent absorption was carried out using toluene as the solvent. Figure 3 illustrates the effect of AGG on the toluene absorption of the composites. It was observed that the addition of GG to the composites decreased the toluene absorption. This was due to the inclusion of a hydrophilic component in the composites, thus increasing the hydrophilic nature of the composite as a whole. This also explains the decrease in the toluene absorption with increasing GG concentrations. Following this explanation the inclusion of an AGG derivative with reduced hydrophilic nature should result in composites with increased toluene absorption. However, this was not observed. The acrylated GG derivatives would posses a terminal reactive unsaturation through the inclusion of the acryloyl moiety. Since the curing of the unsaturated polyester resin is accomplished through free radical polymerisation of the double bonds present on the maleate esters on the polyester backbone the presence of the unsaturation on the AGG would allow for their participation in this curing reaction. It was thought that this would be analogous to the use of vinyl silanes as coupling agents [17-19]. This possible interaction between the AGG and the polymer matrix would result in an increase in the interaction between the AGG and polymer, which would reduce the permeation of toluene into the composite via capillary action at the polymer-filler interface. Further it was observed that AGG derivatives with lower DS resulted in composites with increased toluene absorption, with AGG7 based composites being comparable to GG based composites. This observation was also satisfactorily explained by the reduced interaction as the acrylate content in the AGG decreased. On the whole the addition of GG or AGG resulted in composites with reduced toluene absorption.

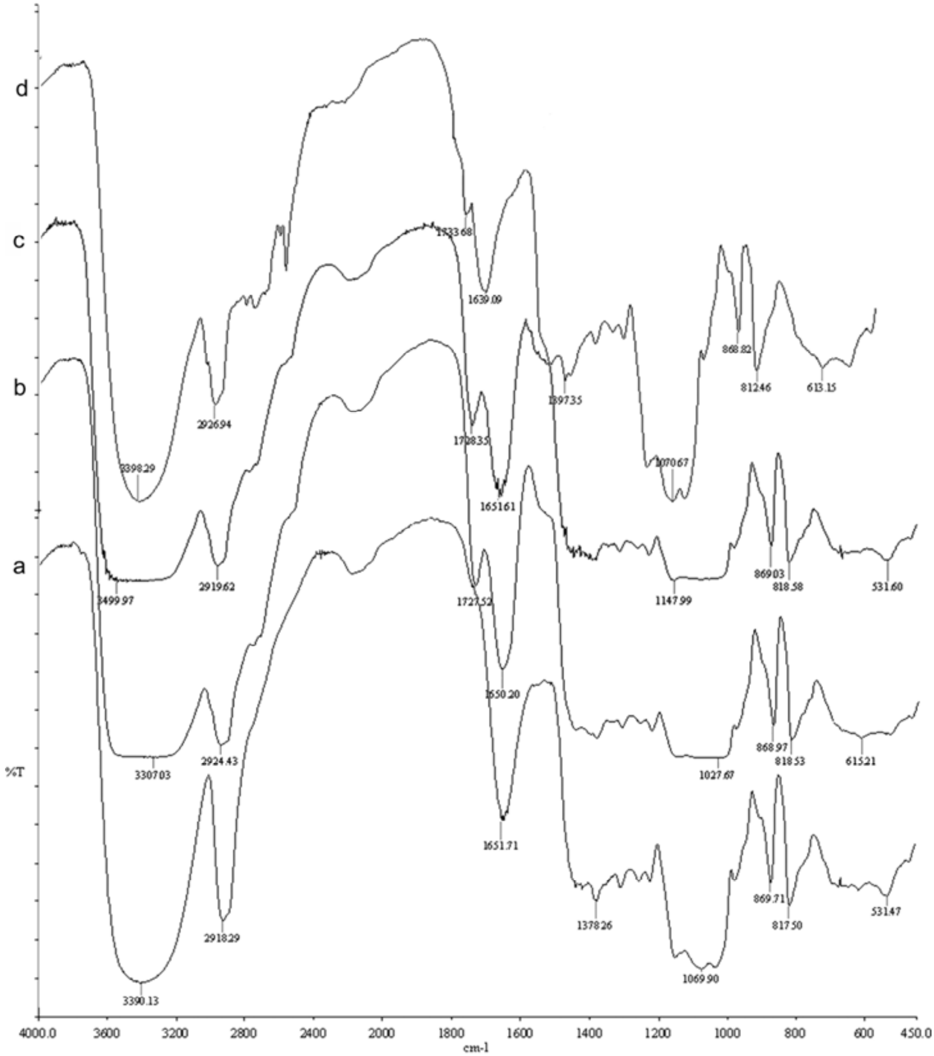

Figure 2. FTIR spectra of a: GG, b: AGG3, c: AGG5 and d: AGG7.

The inclusion of a hydrophilic, water soluble filler in the composite makes the evaluation of the water absorption behaviour of the composites important. The effect of inclusion of GG/AGG in the composite can be seen in Figure 4. The addition of GG in the composites resulted in an increase in its water absorption, which was found to be proportional to the concentration of the filler. On the other hand the use of AGG3 resulted in a reduction in the water absorption of the resultant composites. This was due to the fact that on acrylation the hydrophilic nature of the derivatives decreased coupled with the increase in the filler-polymer interaction. This reduced the hydrophilic nature of the composite as a whole as well as reduced the absorption of water through capillary action as in the case of the toluene absorption explained above. Thus, it was expected that the water absorption of the composites be inversely proportionate to the DS of the AGG used, which was in fact observed.

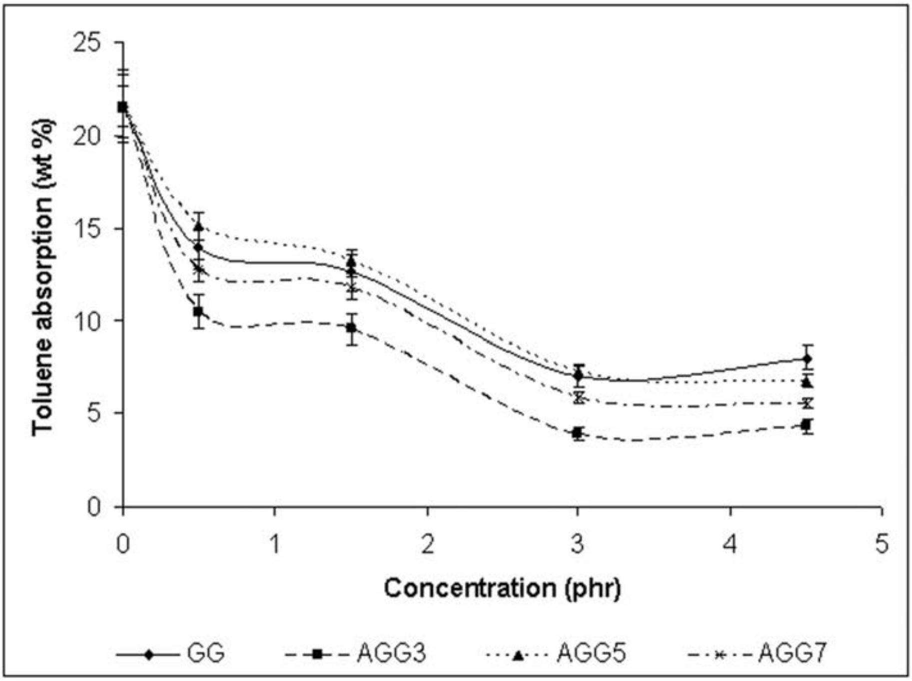

Figure 3. Toluene absorption of AGG based composites.

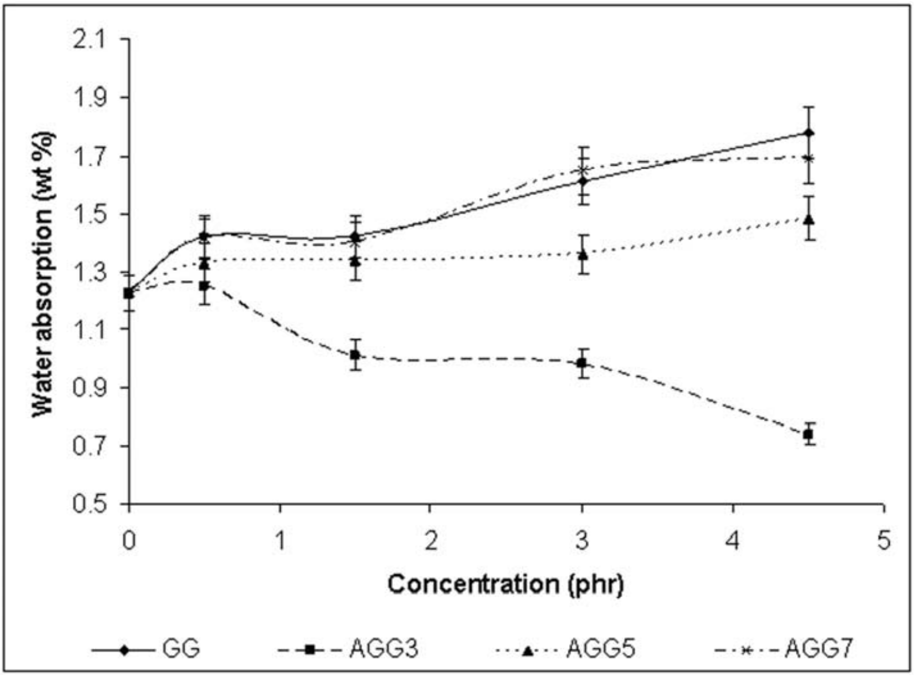

Figure 4. Water absorption behavior of GG and AGG based composites.

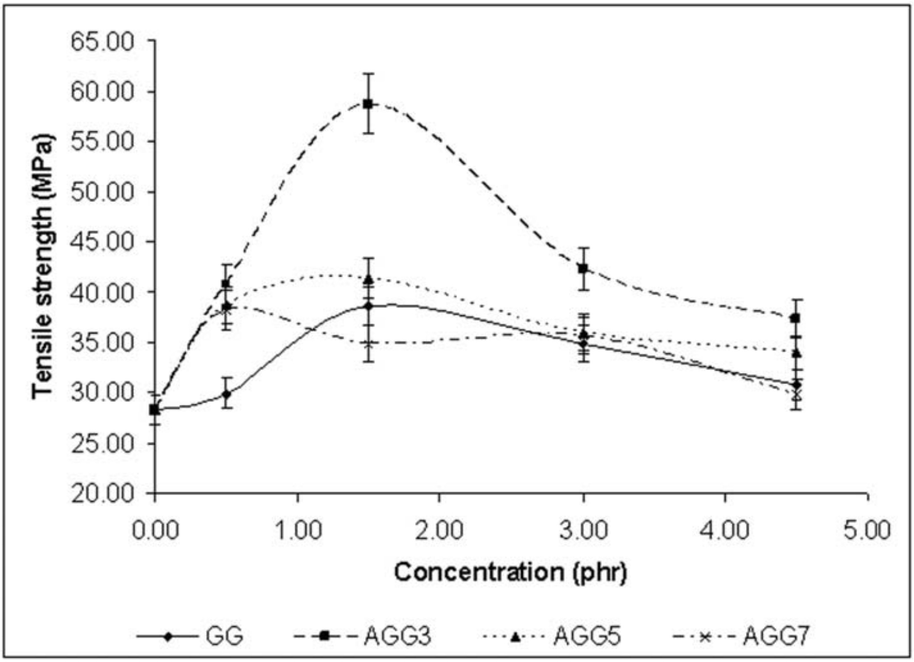

Figure 5. Variation of tensile strength of GG/AGG based composites.

The effect of AGG derivatives on the tensile strength of the composites could be seen in Figure 5. The addition of GG in the composites were seen to increase its tensile strength and reached a peak value at approximately 1.5 phr. The incorporation of AGG resulted in composites with increased tensile strength as compared to GG and the pure unsaturated polyester. Composites based on AGG with lower DS exhibited lower tensile strengths as compared to AGG3, while AGG7 based composites, as in the case of toluene and water absorption, were seen to be comparable to those based on GG. The observed increase in the tensile strength in the case of AGG3 and AGG5 was due to the increased filler-polymer interaction due to reaction via the acrylate groups. The decrease in the tensile strength of the composites proportional to the DS was explained on the basis of reduced filler-polymer interaction with reduced acrylate content in the AGG derivatives. As the concentration of AGG and GG in the composites increased the formation of agglomerates lead to the observed decrease in the tensile strength of the composites, which has been well documented as a cause of reduction of tensile strength [15,16]. Further, in the case of AGG based composites an increase in the concentration of AGG would also result in the increased possibility of reaction between AGG particles through the double bonds. This would lead to the formation of agglomerates with strong inter-particulate chemical bonding as opposed to the weaker inter-particulate bonding in the case of GG. As the tensile strength of the composites increased it was observed that the elongation at break of the composites decreased, as seen from Figure 6. In the case of reinforcing fillers, the resultant composites show a trend wherein the tensile strength and the elongation at break are antagonistic in nature, as has been observed in a number of instances [23,24]. All the composites showed an initial reduction in the elongation at break at

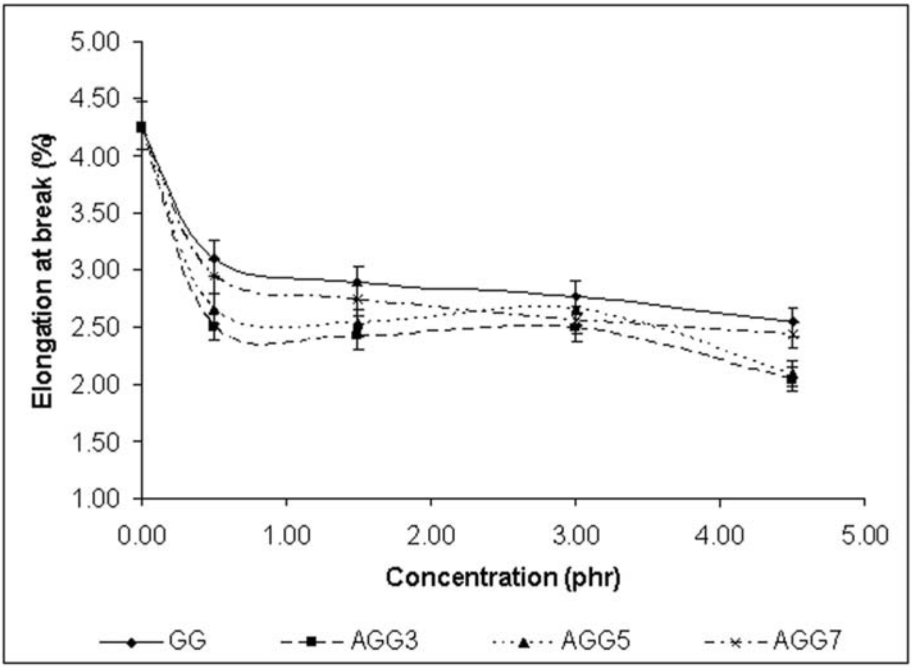

Figure 6. Variation of elongation at break for GG / AGG based composites.

0.5phr filler concentration, after which it seemed to stabilize. This change in the nature of the composites could indicate the formation of agglomerates, as inferred by the tensile strength at similar concentrations. Further, it was observed that the elongation at break was inversely proportional to the acrylate content of the AGG indicating the increased reinforcing action in these instances. The increased reinforcing action of AGG in the composites was due to the increased polymer-filler interaction, brought about by the inclusion of the acrylate moiety in the filler as explained earlier. As the acrylate content decreased the polymer-filler interaction also decreased, leading to a decrease in the reinforcing interaction, which was reflected in the decreased tensile strengths and increased elongation at break values.

Figure 7 depicts the variation in the flexural strength of the composites based on GG and AGG. As in the instance of tensile strength, the composites showed a peak value at approximately 1.5phr followed by a reduction, which was due to the formation of agglomerates at higher GG/AGG concentrations. As in the case of the tensile properties the flexural properties of the composites were found to be inversely proportionate to the acrylate content of the AGG used. The increased polymer-filler interaction was responsible for the increased performance of AGG based composites, as in the case of tensile properites.

The impact strength of the composites could be seen in Figure 8. The impact resistance of a composite can be improved by the use of coupling agents and by surface treatment of the filler particles [25,26], which results in an increase in the polymer-filler interaction. This in turn translates to increased energy transfer across the polymer-filler interface allowing the energy to be dissipated, leading to an increase in the impact strength of the composites on the whole. This was in fact observed in

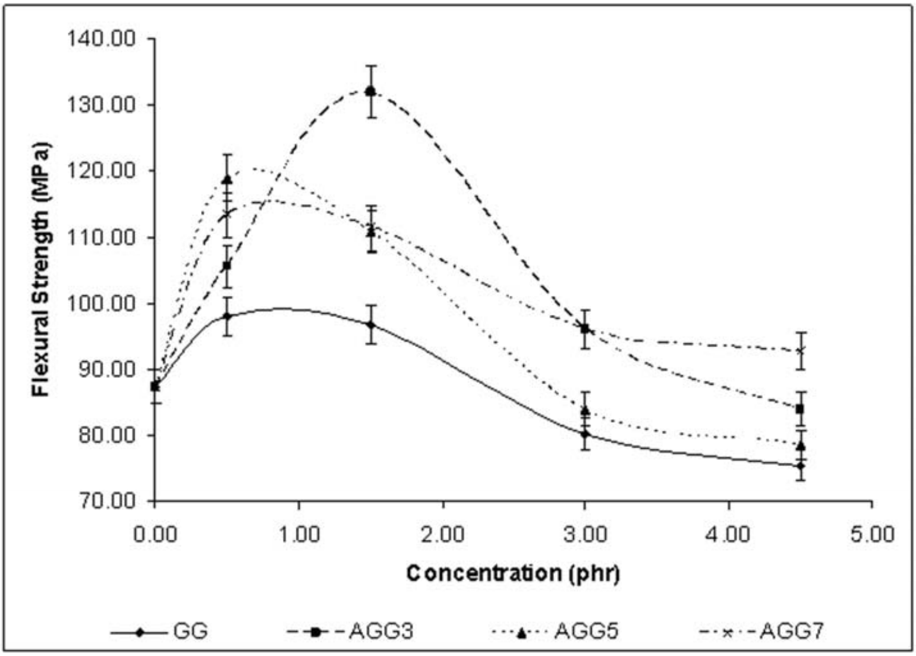

Figure 7. Variation of flexural strength of GG / AGG based composites.

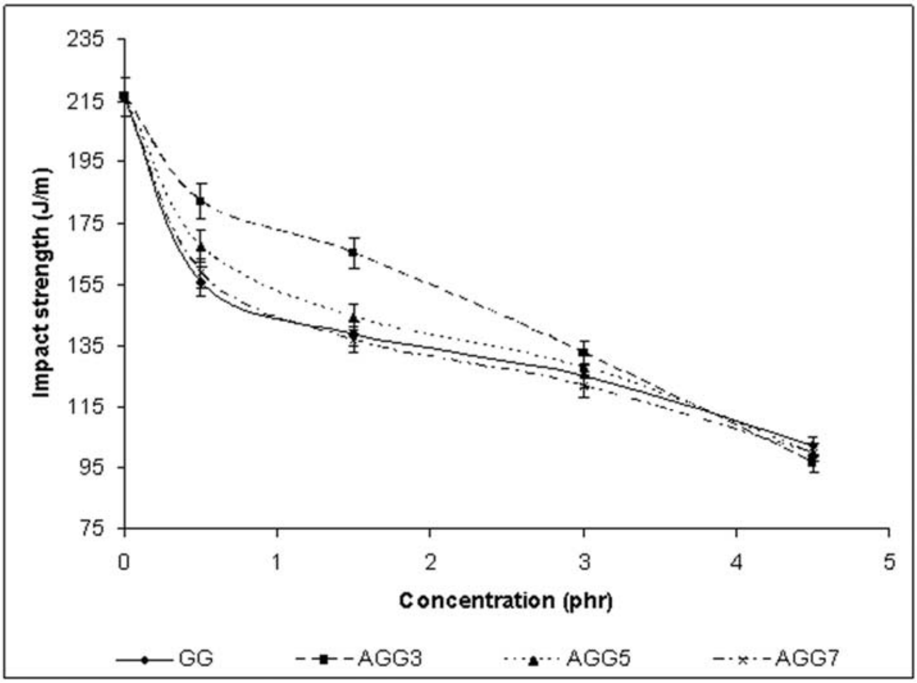

Figure 8. Variation of impact resistance of GG / AGG based composites.

previous studies incorporating derivatives of GG in unsaturated polyesters [15]. It was observed that the incorporation of GG in the unsaturated polyester lead to a decrease in the impact strength of the resultant composites. The inclusion of AGG3 resulted in increased impact strengths of the composites as compared to GG based composites, though lower than the neat unsaturated polyester. The acrylation of GG would lead to consumption of hydroxyl groups and hence a reduction in the hydrophilic character of the polymer leading to a reduced energy dissipation. However, this reduction in energy dissipation character of the composites seems to have been balanced by the increased energy transfer across the polymer – filler interface caused by the acrylation of GG. The composites were seen to exhibit an impact strength proportional to the acrylate content of the AGG used. As in the case of the tensile and flexural properties the formation of agglomerates at higher filler concentrations would result in the observed reduction of impact strength as the filler concentration increased.

From the results it could be said that the use of polysaccharides was feasible as fillers with chemical modification resulting in an increase in the properties through increased polymer-filler interaction. The analogy between the vinyl silane treatment of fillers and the acrylate of GG seems to hold true. This allows for the use of natural polymers in composites as reinforcing fillers as another option to the use of less eco-friendly mineral fillers. Further studies into the biodegradability of the composites are currently being carried out.

Conclusions

The incorporation of acrylated guar gum in unsaturated polyester composites resulted in increased mechanical properties as well as toluene and water resistance, as compared to those based on guar gum and the pure unsaturated polyester. Derivatives with higher acrylate content resulted in composites with superior properties. Thus, composites based on polysaccharides as well as modified polysaccharides show promise as another option to mineral filler based composites, with respect to performance as well as environmental impact.

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