

Preparation of Acetylated Guar Gum – Unsaturated Polyester Composites & Effect of Water on Their Properties

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ARTICLE INFO

Article history:

Received June 25, 2012
Received in Revised form
September 21, 2012
Accepted 21 September 2012
Available online
22 September 2012

Keywords:

Composites
Fillers
Mechanical Properties
Polysaccharides
Thermosets

ABSTRACT

Guar gum has seen extensive use in blends, however, its application as a filler in thermoset composites has as yet not been investigated. The effect of the addition of guar gum and its acetyl derivatives on the kinetics of water diffusion in unsaturated polyester composites was studied. The effect of water on the mechanical properties of the composites was studied with respect to the nature of filler, filler concentration and time of immersion. All the mechanical properties were observed to decrease on exposure to water. Further, it was observed that acetylated guar gum, with a degree of substitution of 0.21, showed the best mechanical properties, surpassing the other filled composites and that of the pure unsaturated polyester. Thus, acetylated guar gum showed promise as eco-friendly filler in composite formulation.

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1. Introduction

Guar gum (GG) is a non-ionic, hydrophilic polygalactomannan, with a galactose to mannose ratio of approximately 1:2, in which the galactose units are randomly distributed on the polymannose backbone¹⁻³. GG is extracted from the endosperm of *Cyamopsis tetragonolobus*, commercially grown in the Indian subcontinent, North Africa and South America. GG and acetylated GG (AGG) were incorporated as particulate fillers in an unsaturated polymer matrix (UPR) to study the effect of acetylation on the mechanical properties of the resultant composite. It was found that AGG based composites showed increased mechanical properties as compared to those based on GG. This increase in mechanical properties was attributed to the increase in polymer-filler interaction brought about by the reduction in hydrophilic nature of the filler. However, it was seen that although acetylation increased the polymer-filler interaction the composites resulting from high DS GG did not perform as

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expected. This was due to the intrinsic change in the nature of the filler itself and not just a surface treatment, which is a common procedure for conventional inorganic fillers and fibers⁴⁻⁶.

Composites, whether based on fibers or fillers have an inherent drawback arising out of their inherent heterogeneous nature in that they absorb moisture. The moisture is absorbed by three basic mechanisms, permeation through the polymer matrix, through capillary action at the polymer-filler interface and via capillary action of micro-cracks and faults caused during processing or curing of the articles⁷⁻⁸. This absorption of water has a profound negative impact on the mechanical properties of the composites, caused by the de-bonding occurring at the polymer-filler interface, degradation of the filler, if cellulosic in nature and it can act as a plasticiser when entrapped in the composite⁹⁻¹⁰. These effects result in reduced stress transfer across the polymer-filler interface. This problem has been alleviated, to some extent, by the chemical or physical treatment of fillers and fibers¹¹⁻¹². The kinetics of water absorption are seen to follow Fickian, non-Fickian or anomalous behaviour¹³. The nature of diffusion can be determined by analysing the nature of the curve obtained from the plot of mass gained versus the square root of the time of immersion. The diffusion of water in the composite depends on the nature of the filler, its volume fraction, void content, temperature and humidity among other factors¹⁴.

Composites based on glass, inorganic fillers and related materials are coming under environmental and legislative pressure because of their adverse effects on the environment and human health, during their incorporation, life-cycle and during disposal. The use of hard inorganic fillers and fibers also have a disadvantage in that they result in heavier composites with increased wear and tear on machine components during their processing. Current research is focussed on identifying replacements for such fillers, which do not have these related disadvantages while showing comparable or superior performance. This has been most apparent in the field of fiber-reinforced composites, where glass and inorganic fibers have been replaced with natural fibers with no loss to their mechanical properties¹⁵⁻¹⁶.

Previously we have reported preparation of hydroxypropyl derivatives of guar gum and their composites with unsaturated polyesters. The rheological, chemical and mechanical properties of these composites were investigated along with the effect of water on overall properties¹⁷⁻¹⁹. In addition we have also reported synthesis and characterization of acryloyloxy guar gum²⁰ and epoxy- guar gum composites²¹. In the same line of work, we had synthesized acrylated guar gum and thereby unsaturated polyester composites and studied their properties²².

The aim of the current study was to investigate the behaviour of GG and AGG filled UPR composites when subjected to water. The absorption behaviour of the composites was also studied with an aim of analysing the diffusion kinetics of water in these composites. The effect of acetylation on the diffusion kinetics and the mechanical properties of the composites as a function of time of immersion were also studied.

2. Results and discussion

The FTIR spectra of the acetylated GG shown in Fig. 1 indicated esterification by the emergence of a peak at 1735-1750 cm^{-1} attributed to C=O stretching, indicating the presence of the acetyl group. The peak observed for GG at 1650 cm^{-1} has been attributed to the hydration of the GG molecule²⁵. On acetylation this peak was seen to decrease and in the case of AGG (0.56) the peak was not resolved from that of the C=O group. The peak at 3300-3400 cm^{-1} caused by -OH stretching was also seen to decrease with an increase in acetyl content. Thus, the FTIR spectrum confirms the acetylation of the GG. Further, the decrease in the hydration and hydroxyl peaks indicated a reduction in the hydrophilic nature and hydrogen bonding in AGG derivatives.

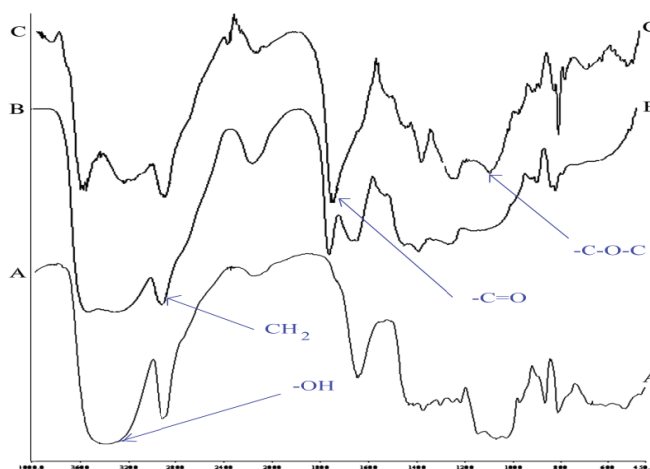


Fig. 1. FTIR spectra of GG and AGG; A - GG; B - AGG(0.21); C - AGG(0.56)

The ^{13}C -NMR analysis of the AGG (0.56) sample showed that the acetylation took place at the primary hydroxyl groups in preference to the secondary groups. Table-I shows the peaks observed in the NMR analysis along with their peak assignments, which could be compared to the structure in Fig. 2. Fig. 3 showed the actual NMR spectra obtained. The peaks obtained at 129, 132 and 160 ppm indicate the presence of the acrylate moiety in the AGG3 derivative. Further, the shift of the peaks of the M6 and G6 carbon atoms to 61.18 ppm from 60.44 and 60.92 ppm indicated the position on the carbohydrate ring where substitution occurred. However, the peaks were not sufficiently resolved to show separate peaks for the acetylation at positions M6 and G6.

Table 1. ^{13}C NMR analysis of AGG (0.56)

M1	100.14	G1	98.67	X	161.1
M2	69.77	G2	68.34	Y	129.9
M3	71.22	G3	68.34	Z	130.2
M4	74.48	G4	68.34		
M5	73.18	G5	71.22		
M6	60.44	G6	60.92		
M6-G	66.31	G6-Acetate	61.18		
M6-Acetate	61.18				

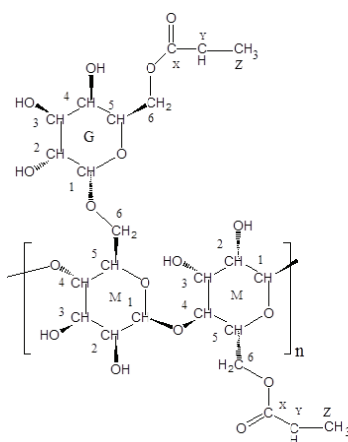


Fig. 2. Schematic representation of AGG (0.56)

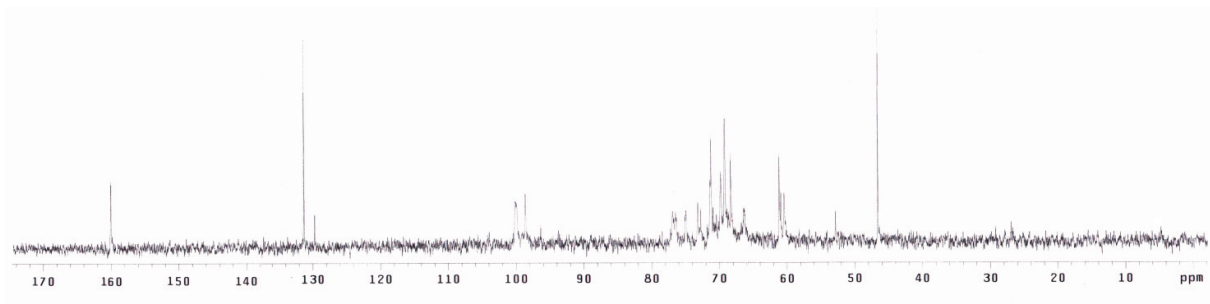


Fig. 3. ^{13}C NMR spectra for AGG (0.56) sample

The study can be divided into two parts, one dealing with the absorption behaviour of the composites when immersed in water and the other the effect of water immersion on the mechanical properties of the composites.

3.1 Absorption behavior

There have been a number of studies proposing models to predict the absorption behaviour in composites²⁶⁻²⁷. In a one-dimensional moisture absorption system both sides of the sample are exposed to the same environment and the total moisture content, denoted as G , can be expressed as shown in Eq. 1.²⁸⁻²⁹

$$G = \frac{m - m_i}{m_f - m_i} \left[1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} \exp\left[-\frac{(2j+1)^2 \pi^2 D_x t}{h^2}\right] \right], \quad (1)$$

where,

m_i – initial weight of the moisture in the material

m_f – weight of moisture at saturation, at equilibrium

D – mass diffusivity in the composite

h – specimen thickness

t – time of immersion

j – summation index

For the analysis to ascertain whether a material follows Fick's law the diffusion coefficient, D , and the nature of the graph of % absorption versus $t^{1/2}$ is important. On solving the above equation the diffusion coefficient can be calculated using Eq. 2.^[29]

$$D = \pi \left(\frac{kh}{4M_m} \right)^2 \quad (2)$$

where,

k – initial slope of the graph of mass gain (%) versus $t^{1/2}$

M_m – maximum weight gain or weight gain at saturation / steady state.

The absorption behaviour of the composites can be seen in Fig. 4-6. It was observed that the initial portion of the plots was linear after which there was no change in water uptake, which corresponded to the saturation of the composites i.e. a steady state where absorption of water was equal to the desorption of water from the composite. The nature of the plots indicated that the water absorption behaviour of the composites followed Fick's law, irrespective of the concentration of the filler or the

nature of the filler, i.e. GG or AGG. It could also be seen that as the filler concentration increased the saturation moisture level also increased, indicating greater water absorption. Similar trends were observed with natural fibers based unsaturated polyester composites [30].

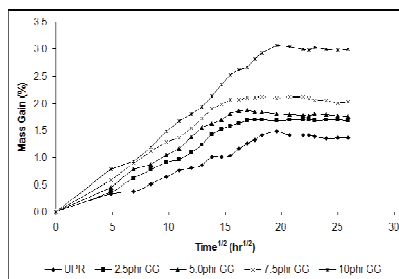


Fig. 4. Absorption behaviour of GG-UPR composites

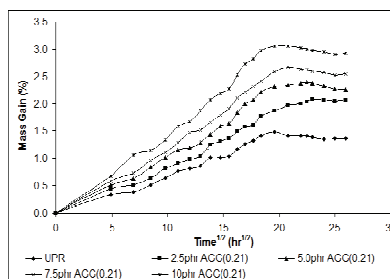


Fig. 5. Absorption behaviour of AGG (0.21)-UPR composites

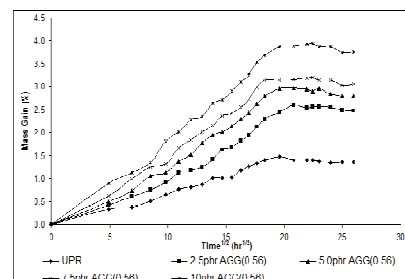


Fig. 6. Absorption behavior of AGG (0.56)-UPR composites

Table 2 lists the saturation moisture content, slopes of the linear portions of the individual absorption curves and diffusion coefficients of the composites. It could be seen that on addition of fillers, GG and AGGs, the saturation moisture content increased with concentration of the filler. The saturation moisture content in UPR composites also increased with acetyl content in AGG. This was against expectations, on acetylation the hydrophilic nature of AGG decreased with an increase in the acetyl content as reflected by the FTIR. It was expected that with an increase in the hydrophobic character of the AGG the resultant composite should have had an increased water resistance. GG particles are held together by hydrogen bonds, Van der Waal's forces and chain entanglements. On acetylation hydrogen bonding decreased³¹, thus resulting in particles with reduced cohesion. This could explain the increased water absorption. Although the water binding capacity of the filler (AGG) would decrease, water could nevertheless physically penetrate into the filler aided by the decrease in the hydrogen bonding. This physical penetration of water could explain the observed phenomenon of increased water absorption with acetyl content, though it could not be experimentally verified.

Table 2

Diffusion coefficients of water absorption of composites

Composites	Saturation Moisture Content M_m (%)	Slope of linear portion of M_m versus $t^{1/2}$ plot, ($\text{hr}^{-0.5}$)	Diffusion Coefficient, D $\times 10^{-3}$, (m^2/s)
Unsaturated polyester	1.67	0.0694	2.12
2.5phr GG	1.71	0.0979	1.86
5.0phr GG	1.99	0.1134	2.07
7.5phr GG	2.37	0.1301	2.14
10phr GG	3.01	0.1553	2.31
2.5phr AGG(0.21)	1.81	0.085	1.73
5.0phr AGG(0.21)	2.28	0.1033	1.86
7.5phr AGG(0.21)	3.21	0.1191	1.97
10phr AGG(0.21)	3.34	0.1449	2.13
2.5phr AGG(0.56)	2.14	0.105	1.71
5.0phr AGG(0.56)	3.14	0.135	1.76
7.5phr AGG(0.56)	3.44	0.155	1.93
10phr AGG(0.56)	3.87	0.1861	2.20

The diffusion coefficients of the composites decreased with the addition of the fillers, similar observations were made with natural fiber reinforced unsaturated polyester³⁰. Further, the diffusion coefficient of the composites decreased with an increase in the acetyl content in the AGG. It was observed that GG based composites had the highest diffusion coefficients compared to the other filled composites. In the case of AGG the increase in the polymer-filler interaction resulted in a decrease in the de-bonding, leading to a reduced rate of water penetration, this phenomenon is similar to surface

treatment of fibers and fillers, which had a similar effect on the water absorption properties^{11-12,30}. The diffusion coefficient increased with concentration of filler. At higher concentrations the diffusion coefficients were found to be greater than that of the pure unsaturated polyester, 7.5phr and above for GG and at 10 phr for AGGs. At higher filler concentrations aggregate formation leads to an increase in the voids in the composites, these voids were responsible for the increase in the diffusion rates and have been well documented¹⁴.

3.2 Mechanical properties

Fig. 7 to Fig. 10 show the effect of acetylation on the mechanical properties of the composites at various filler concentrations after water immersion. The tensile strength of pure unsaturated polyester showed a drastic reduction initially. After 21 days the tensile strength was seen to stabilise. The decrease was caused due to diffusion of water into the composite via micro-cracks and through the polymer matrix resulting in the decrease in tensile strength. The tensile strength of composites based on GG also showed an initial decrease after which it attained a steady state. The decrease in the tensile strength was attributed to de-bonding, a similar trend was observed at all concentrations. In the case of AGG based composites, the tensile strength was observed to initially decrease and as in the case of GG based composites attained a steady state. However, it was observed that the steady state was the greatest for AGG (0.21) based composites compared to that of GG and AGG (0.56) based composites. The superior performance of AGG (0.21) was attributed to the reduced de-bonding as compared to GG. On the other hand it was expected that AGG (0.56) with even greater DS would have the best performance, however, due to a greatly reduced particle integrity their composites showed reduced properties. It was also observed that at all filler concentrations, irrespective of the fillers used, the tensile strength of the filled composites were equivalent and in some cases greater than that of those of the pure unsaturated polyester, after 28 days immersion in water.

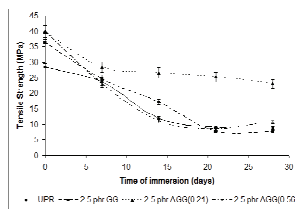


Fig. 7. Tensile strength of composites at 2.5phr concentration after immersion

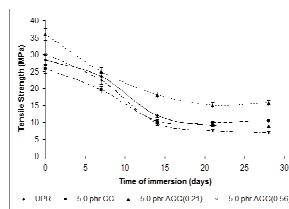


Fig. 8. Tensile strength of composites at 5.0phr concentration

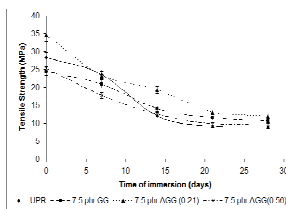


Fig. 9. Tensile strength of composites at 7.5phr concentration after immersion

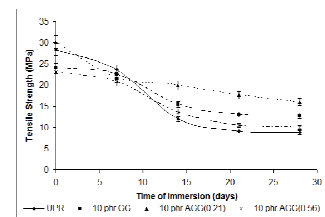


Fig. 10. Tensile strength of composites at 10phr concentration

Fig. 11 to Fig. 14 show the elongation at break of the composites after immersion in water. In the case of the unsaturated polyester casts the elongation at break of the composites decreased with time of immersion till 14 days, after which it remained steady. The trend observed in the case of elongation at break was similar to that observed for the tensile strength of the composites. The decrease in the elongation at break of the samples was similar to that cited for the tensile strength i.e. the penetration of water into the cast specimen, via micro-cracks and through the polymer itself. Composites based on GG showed an increase in elongation at break, which then remained steady as the time of immersion increased. The increase in the elongation at break was due to the plasticising action of water in the composites. GG is a hydrophilic polysaccharide soluble in water, with a high water binding capacity, due to which it absorbs water when the composites were immersed. This water, associated with the polysaccharide filler was not easily released on heating, which then behaved as a plasticiser, leading to the observed increase in elongation at break of the composites. When AGG was used, the elongation at break of the composites showed a decreasing trend. AGG (0.21) based composites had a marginally larger elongation at break than those based on AGG (0.56), again attributed to the increased integrity of the filler particle itself. The decrease in the elongation at break was observed till 14 days, after which it showed a reasonably steady value. As in the case of tensile strength of the composites, with the exception of GG based composites, the elongation at

break after 28 days was found to be comparable for AGG based composites and the pure UPR specimens.

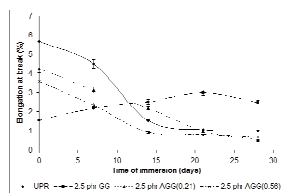


Fig. 11. Elongation at break of UPR composites at 2.5phr filler concentration

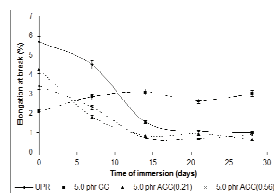


Fig. 12. Elongation at break of UPR composites at 5.0phr filler concentration

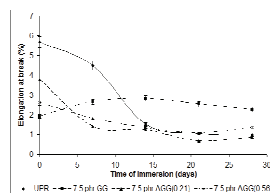


Fig. 13. Elongation at break of UPR composites at 7.5phr filler concentration

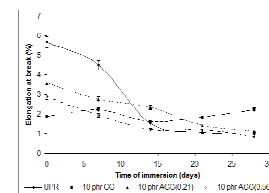


Fig. 14. Elongation at break of UPR composites at 10phr filler concentration

The variation in the flexural strength with time of immersion was depicted in Fig. 15 to Fig 18. From the plots it could be seen that the flexural strength of pure unsaturated polyester decreased on exposure to water, although after 21 days it seemed to reach a steady state. From the plots it was observed that the use of AGG (0.21) resulted in composites with the best resistance to water with respect to their flexural strength. This was attributed to the decrease in de-bonding occurring in this composite. Composites based on AGG (0.56) did not perform as well as that of AGG (0.21) and reflected the behaviour of the tensile strength and elongation behaviour. At 2.5phr GG based composites showed the lowest flexural strengths when compared to the other fillers, however above 7.5phr AGG (0.56) showed the lowest flexural strengths. In the case of the flexural strengths composites based on AGG (0.21) showed a consistent improvement over the pure UPR and so did GG based composites. Thus, immersion in water was seen to affect the pure UPR to a greater extent than those with the fillers.

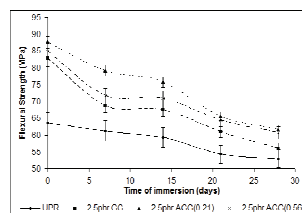


Fig. 15. Flexural strength of composites at 2.5phr filler concentration

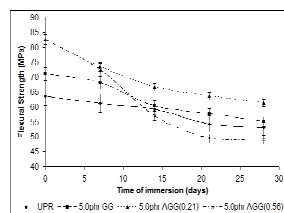


Fig. 16. Flexural strength of composites at 5.0phr filler concentration

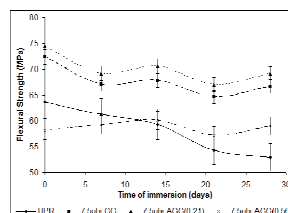


Fig. 17. Flexural strength of composites at 7.5phr filler concentration

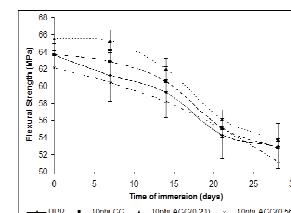


Fig. 18. Flexural strength of composites at 10phr filler concentration

From the data it we could see that the mechanical properties of the AGG (0.21) based composites surpassed the other filled compositions as well as that of the pure UPR. Thus the use of this modified GG as a particulate, reinforcing filler shows promise with respect to the mechanical properties, even in the event of the composites being exposed to moisture. The steady state observed in the mechanical properties on prolonged exposure to water suggested that the reduction in composite properties was solely due to de-bonding and not cellulose degradation as reported in other studies²⁴.

3. Conclusions

The incorporation of GG and AGG as particulate reinforcing fillers in unsaturated polyester resins resulted in composites that obeyed Fick's laws diffusion. The maximum moisture absorption was observed for composites with AGG as filler, and increased with the DS of the filler. The mechanical properties of the composites decreased on immersion in water, with AGG (0.21) showing the best mechanical properties, surpassing even that of the pure polyester. Thus using the modified GG as filler shows improved properties even under the influence of moisture and thus has the potential for use as eco-friendly filler.

4. Experimental

4.1 Materials

The unsaturated polyester resin, cobalt octanoate (accelerator) and methyl ethyl ketone peroxide (initiator) was obtained from M/s Mechamco Ltd. India. The unsaturated polyester resin was general purpose polyester based on propylene glycol, isophthalic acid and maleic anhydride with styrene as the reactive diluent. Guar gum (GG) was supplied by M/s Lucid Colloids Ltd., India and had a moisture content of 4-5%, intrinsic viscosity of 14.6 gm/dL and a particle size of 75-100 μ . Laboratory grade pyridine and acetic anhydride were purchased from SD.Fine Chemicals Ltd., Mumbai, India.

4.2 Acetylation of guar gum

GG (5.0 g, 0.03 mole) was acetylated using acetic anhydride (9.48 g, 0.093 mole) as the acetylating agent in the presence of pyridine (50 mL) as solvent and catalyst. The reaction was carried out at 90 °C and the reaction time varied in order to obtain derivatives with different degrees of substitution. The degree of esterification was estimated from the ester value of the GG derivatives. A weighed sample of GG, as the blank, and the derivative were dissolved in 25 mL of a 0.5 N aqueous alkali solution and the ester allowed to hydrolyse completely over a period of 18 hours. Unreacted alkali was then back titrated with hydrochloric acid, from which the degree of substitution (DS) of the GG derivative was found out as given in Eq. 3. The equation is a derivative of that used for calculating the theoretical ester value²³⁻²⁴.

$$D.S. = \frac{162 \times ()}{56100 - (43 \times (\text{ester value}))}, \quad (3)$$

where, 162 is the weight of the repeat unit i.e. each pyranose ring and 43 is the weight of the added acetyl unit. The FTIR of the acetylated guar gums was carried out on a Perkin–Elmer System 2000 FT-IR spectrophotometer using KBr pellets.

4.3 Preparation of Composites

The fillers were uniformly dispersed in the UPR along with the accelerator (0.5% w/w), followed by the addition of free radical initiator (2% w/w) and thorough agitation. The composition was then de-aerated to remove any entrapped air and poured in a metal mould maintained at 30 °C. The cure cycle was 30 °C/12 hours and 100 °C/2 hours.

The specimens were suspended in a glass tank filled with distilled water maintained at 30°C. The specimens were completely surrounded by water and were kept such that they were not in contact with the sides of the tank or neighbouring specimens. The specimens were accurately weighed, with accuracy of 1mg, at 24 hour time intervals. After immersion in water the specimens were removed from the tank, surface water wiped off using a tissue paper and immediately weighed. The percentage increase in weight was used to study the water absorption behaviour of the composites.

The composites were machine cut into the respective shaping for testing and the edges were uniformly ground to remove imperfections which could lead to errors in the test results.

4.4 Testing of Composites

The composites were tested for their tensile and flexural properties. The tensile strength, percentage elongation (Specimen Type IV^B) and flexural strength (specimen dimensions 60x25x3mm) 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 measurement and 8 mm per minute for the three point bending test. Tests were carried out on three samples and the averages have been reported as the test results.

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