

Mechanical and Morphological Properties of Vinyl Ester /Guar Gum Treated Sisal Fibre Composites

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Abstract

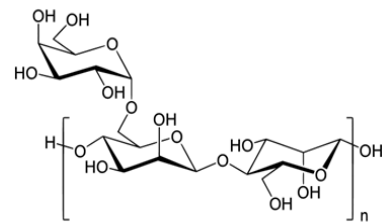
Tensile strength, toughness, flexural modulus and flexural strength of vinyl ester based composites are determined as a function of wt. % of sisal fibre (15, 25, 30 and 40) pre-treated with guar gum solution of different concentration. Thermal and viscoelastic properties of the composites are studied with dynamic mechanical analyzer in terms of storage modulus, glass transition temperature and $\tan\delta$ values. Surface treated sisal fibre filled composites show improved mechanical properties compared to untreated fibre filled composites. Glass transition temperature and storage modulus of the 0.2% guar gum treated fibre filled composites are highest compared to that of the others. Effect of water absorption on composite tensile properties is checked. Guar gum coating on the fibres has reduced water absorption by the composite. Composites with 0.1% and 0.3% guar gum treated fibre show a sharp brittle fracture whereas 0.2% guar gum treated fibre filled composites has shown shearing of the fibres at the tensile fractured surface.

Key Word:-bio-composite, dynamic mechanical analysis, fracture surface, natural resin, water absorption.

I. Introduction

Natural vegetable fibres are progressively replacing the man-made fibres use in composites where high strength and stiffness are not of priority. Plant fibres are non-hazardous, less abrasive and possess low density giving light composites. These are attractive in terms of sustainability and bio-degradability. The main constituent of these natural fibres are fibrils of cellulose molecules forming spirals along the fibre axis and smaller the spiral angle higher is the mechanical strength of it [1]. Lignin or lignin/hemicellulose acts as cementing material in between the hard distinct cells of these fibres. Lignin content of different natural fibres influences their properties. A waxy layer on the outer surface of these fibres controls adhesion characteristics of them. Due to the presence of large number of hydroxyl groups these natural fibres are originally hydrophilic though extensive hydrogen bonding makes them stiff also. Water absorption by unmodified fibres has become a major drawback of their use which leads to delamination, internal strain and porosity due to poor

adhesion between polymer matrix and fibre in the composites [2]. Sisal fibres contain higher cellulose (78%) and lignin content (8%) than that of other natural fibres e.g. jute, flax, hemp or ramie though the spiral angle is greater. Guar gum, obtained from the ground endosperm of guar bean, is basically a polysaccharide composed of the galactose and mannose (Fig.1). The backbone is a linear chain of β 1, 4-linked mannose residues to which galactose residues are 1, 6-linked at every second mannose, forming short side-branches [3]. These molecules, containing large number of free hydroxyl groups, are capable of interacting with cellulosic fibres and soluble in water at room temperature.



Scheme1. Chemical structure of guar gum resin

In the present study, sisal fibres are treated with guar gum solution. Composites are prepared with unidirectional fibres and vinyl ester resin by hand –lay-up technique. Vinyl ester resin, being cheaper than epoxy resin and showing better mechanical strength than polyester, has attracted composite manufacturers recently.

II. EXPERIMENTAL

Materials

Ravex Plasticizer Pvt. Ltd. New Delhi supplied vinyl ester resin (RPL 401 grade). The physical properties and mechanical properties of resins are given in table 1. Methyl ethyl ketone peroxide (MEKP), an organic peroxide has been used here as free radical initiator. Cobalt naphthenate and N, N'-Dimethyl aniline (DMA) have been used as promoter and accelerator respectively. Sisal fibre, used in the present study, is kindly donated by Chotanagpur Rope Works Pvt. Ltd.,

Ranchi. These fibres are imported from Kenya, Africa. The fibres have cellulose, lignin and hemicellulose by 64.08, 12 and 11% respectively [3]. Guar gum is obtained from ground endosperm of the seeds of guar plant. The resin used here is kindly donated by Indian Institute of Natural Resins and Gums, Namkum, Ranchi, which is originally imported from Vasundhara Gums and Chemicals Jodhpur, Rajasthan.

Table.1.Physical Properties of Vinyl Ester Resin (Supplied By supplier)

Physical Properties	Vinyl ester resin
Appearance	clean brownish liquid
Viscosity	450 cps @ 25 °C
Volatile content	45%
Acid value	8 mg KOH/gm.
Specific gravity	1.05
Gel point	20 min @ 25 °C

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METHODS

Fibre surface modification by Guar-Gum treatment

Guar-gum solution has been prepared by adding the dry guar-gum powder slowly into water with constant mechanical stirring to avoid lump formation. Solution of three different concentrations 0.1, 0.2, and 0.3 wt. % is prepared at room temperature. Sisal fibres are soaked in 0.1, 0.2, and 0.3% guar-gum solutions at 30°C while maintaining a liquor ratio of 15: 1. Fibres are immersed in the guar-gum solution for 30 min. They are allowed to dry at room temperature for 48 h, followed by oven drying at 100°C for 6 h.

Composite fabrication by hand lay up

Vinyl ester resin mixed with MEKP, Cobalt naphthenate, and DMA (2% each) is applied on fibres tied on a metal frame and laid on glass mould as shown

in the figure 1, by simple hand lay technique. Each layer of pre-weighed fibre is first tied and then impregnated with matrix materials so that care is taken to maintain practically achievable tolerance on the fibre alignment. Room temperature curing is allowed till solidification and post curing by oven heating at 60°C for 8 hrs. The composites containing 15, 25, 30 and 40 % by weight of sisal fibre are prepared using fibre length of 500 mm. The composites are denoted by symbols like 0.0GGSF, 0.1GG15SF, 0.2GG25SF, and 0.3GG30SF etc. In this notation the first number denotes concentration of guar gum solution used for treatment of fibre and second one denotes fibre weight % used in composites.

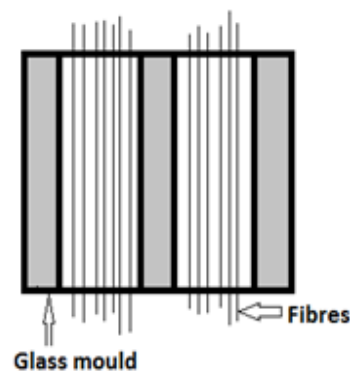


Fig. 1.Alignment of fibres on glass mould

Characterization

Characterization of matrix resin

Dynamic mechanical analysis

DMA measurements are carried out on DMA TQ 600, TA Instruments, USA. The test specimens of size 3 mm thickness x 13 mm width x 35 mm length are tested in a nitrogen atmosphere under a fixed frequency 1.0 Hz (oscillation amplitude 0.03 mm) and single cantilever mode at a heating rate of 5 °C/min. The samples are tested in the range from 25 °C to 175 °C. The strain amplitude is maintained at 0.01%.

Crosslink density

For thermosetting resin one frequently employed method is to calculate M_c (molecular weight between two crosslink points) by using the value of storage modulus in the rubbery plateau region. According to the theory of rubber elasticity at equilibrium [4] elastic modulus (E') is related to crosslink density (ρ) as below:

$$\rho = E'/3RT \dots \dots \dots (1)$$

Where crosslink density is expressed in moles of elastically effective network chains per cubic centimetre of sample, R is the gas constant and T is the absolute temperature at which the experimental modulus is determined.

The samples are tested at various stages of cure (Table 2). To directly investigate the effect of post curing on Tg of a material one-half of each material set has undergone a total of two DMTA scans: following a room-temperature cure for several weeks (noted as sample 'a', after being post-cured (sample 'c')).

Table.2. Curing History of the Tested Sample.

Sample	Resin
a	Room temperature cure
b	Cured on DMA immediately after the first run
c	Post cure: 99°C/2h

Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is used to characterize the synthesized resins in order to find out the exact changes in chemical structure of the resin due to crosslinking reactions. The FTIR analysis is carried out by Shimadzu Corporation, Japan (model-FTIR Prestige-21). The spectra are taken at a resolution of 4 cm⁻¹ and 20 scans are carried for each specimen. The scanning range is 4000 to 400 cm⁻¹ in ATR mode. Cured samples under three conditions have been checked. The samples used are crushed in fine powder to form KBr pellets.

Characterization of Reinforcement

Fourier Transform Infrared Spectroscopy

The FTIR study is carried out by the same instrument and under same conditions as done for matrix resin. The scanning range is 4000 to 400 cm⁻¹ in transmittance mode. FTIR spectra in the form of KBr pellets of unmodified, and Gaur gum treated sisal fibre are recorded.

Dynamic Contact Angle

Dynamic Contact Angle Tensiometer (DCAT-21), Data Physics, Germany has been employed for analyzing dynamic contact angle (DCA) by using Wilhelm plate

technique. The fibre bundles are dipped into the test liquid, water, up to a depth of 5 mm with a speed of 50 μm/s². Young's equation is used to determine the value of surface energy [6].

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta \dots \dots \dots (2)$$

Density

Density (ρ) of the fibres is determined at room temperature following Archimedes principle by the density measurement kit of Mettler Toledo, Japan. The following relation is used to find out the absolute value of the density:

$$P = A / (A - B) \times \rho_0 \dots \dots \dots (3)$$

Where ρ is density of sample in g/cc, A is weight of sample in air, B is weight of sample in liquid and ρ₀ is density of the liquid (toluene in this case) used to immerse the fibre.

Morphology

Scanning electron microscopy (SEM) has been conducted using JSM 6390 LV, JEOL, Japan with accelerating voltage of 20 KV and secondary electron image is taken at working distance of 20mm. The test samples are coated with gold to avoid electrical charging during examination. The test samples are scanned at magnification of 1000X.

Characterization of composites

Mechanical properties

Flexural properties of composites are measured by three point bending mode (ASTM D 790) using a universal testing INSTRON 3677 machine, USA in accordance with ASTM standard D-790. A minimum of five composite samples are tested. The entire tests are carried out at room temperature and under 50% relative humidity. For the test specimens with nominal dimensions of 60 x 13 x 3.5 mm, a span of 20 mm and a crosshead speed of 2mm/min are used. The applied load is perpendicular to the fibre direction. Flexural strength is determined by the following standard equation:

$$\text{Flexural strength} = 3PL / (2bd^2) \dots \dots \dots (4)$$

Where S = flexural strength, p = maximum load at the moment of break, b = width of the specimen, L = length of the span and d = thickness of specimen. The maximum strain (r) in the outer fibres is given by

$$r = 6Dd / L^2 \dots \dots \dots (5a)$$

Where, D is the deflection. The flexural modulus is calculated from slop of initial portion of the flexural stress strain curve.

Inter laminar shear strength (ILSS) of the composites is determined by using the following equation:

$$ILSS = 3P/4bd \dots \dots \dots (5b)$$

The tensile properties of the composites are measured on the same universal testing machine according to ASTM standard D-638. Rectangular specimen with dimensions 60 x 13 x 3.5 mm are tested with span length 20 mm and a crosshead speed of 2 mm/min are used for unidirectional oriented fibre composites. Properties like ultimate tensile strength, Young's modulus and elongation at break are determined at 27°C and 50% RH. Three test specimens are studied for each set. Properties are reported as function of wt% of fibre treated with different concentration of guar gum solution.

Dynamic mechanical analysis

Rectangular specimens having size of 35.5 x 13.5 x 3.5 mm are used for the dynamic mechanical experiments. The storage moduli and damping ($\tan \delta$) are measured using a dynamic mechanical thermal analyzer TQ 600, TA Instruments, USA. The temperature range over which properties are measured range from 25 °C- 150 °C and a heating rate of 5 °C/ minutes is maintained. The test is carried out at frequency 1 Hz at a strain rate of 0.01%. Storage modulus, $\tan \delta_{\max}$ and $\tan \delta$ at full width half maximum (FWHM) are reported as function of fibre loading.

Water Absorption

Water absorption study has been performed following the ASTM D 570-98 standard. Three samples of each variation are submerged in distilled water at room temperature in different containers. At an interval of 48 hours samples from each container are weighed and again submerged. In this way weighing is continued till the equilibrium weight is gained. After the constant

weight of samples is achieved they are removed from water and dried at room temperature by soaking the surface water with filter paper. Tensile test is performed with these samples to see the effect of water absorption on the properties of composites at 25°C temperature and 50% relative humidity using same cross head speed and with same size of samples as done with dry samples.

Water absorption of the composites is determined by using the following equation:

$$W_{(t)} = m_{(t)} - m_{(0)} / m_{(0)} \times 100 \dots \dots \dots (6)$$

Where $W_{(t)}$ is water uptake, $m_{(0)}$ and $m_{(t)}$ are the mass of the specimen before and after water absorption, respectively.

Morphology

The tensile fractured surfaces of the specimens are examined directly by scanning electron microscope. Composites with 25 wt. % fibre which are 0.2% guar gum treated were tested only due to limited scope of testing. The test samples are scanned at a magnification of 1000X.

II. RESULTS AND DISCUSSIONS

Effect of crosslinking of matrix on viscoelastic properties

Glass transition temperature, T_g values have been determined from the storage modulus curves of corresponding test sample. Storage modulus of sample 'a' is found to be much lower than that of post cured sample 'c'. This implies that at room temperature the curing of resin is not complete.

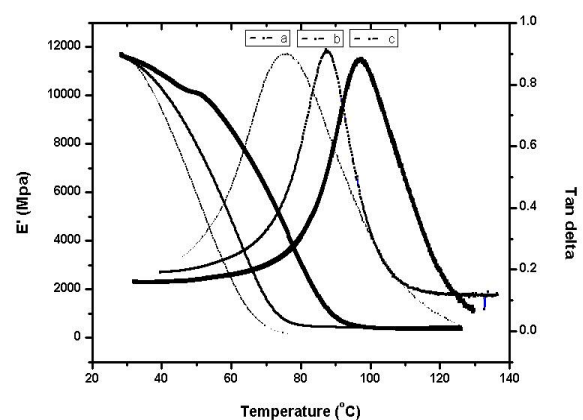
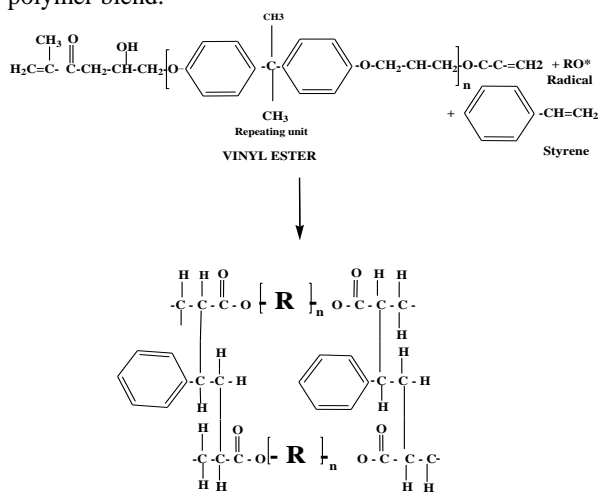


Fig.2. Typical DMA results of resin samples a-c. The E' curves and the maximum $\tan \delta$ peaks of the

b and c curing regimens show that further curing, either through post curing or first DMA run, increased Tg of the samples.

Crosslink density, typically measured as the average molecular weight between crosslinks (M_c), is an important factor governing the physical properties of cured thermoset resins. Vinyl ester oligomers have double bonds at each end that can be crosslinked. The crosslink density can be changed depending on the curing temperature, the molecular weight of vinyl ester oligomers and altering the state (and also possibly the rate) of conversion. Vinyl ester resin, when diluted with styrene monomer, forms crosslinked network under room temperature following the reaction mechanism as given in scheme 2. This reaction is essentially copolymerization of vinyl/divinyl monomers, in which vinyl ester resin gets crosslinked through the double bonds in them and styrene comonomers form the crosslinks between the vinyl ester chains [5]. For vinyl ester resin containing fixed amount of styrene diluent the number of crosslinks between resin chains may vary depending on the temperature of curing as has been found in the present case. At low temperature possibility of formation of polymeric crosslinks made up of styrene unit being less the reaction of vinyl ester resin takes place resulting only short crosslinks in between them (through C=C). Sample 'a' and 'c' show low storage modulus compared to sample 'b' in the rubbery plateau (starts at 120°C), probably due to plasticization effect caused by unreacted styrene and PS homopolymers in between vinyl ester molecules. On the other hand in case of post cured sample 'c' lower modulus and crosslink density than even sample 'a' possibly has been caused by preferable entrapment of PS homopolymer rather than crosslinks formation in between the vinyl ester molecules resembling a binary polymer blend.



Scheme.2. Crosslinking of vinyl ester resin diluted by styrene.

The PS homopolymers formed during room temperature curing may have shielded the remaining double bonds in the vinyl ester resin and later may have formed polymeric and mono/dimeric styrene crosslinks leading to compact and rigid network in the sample 'b' which is reflected in the crosslink density values of the later (table3). The PS homopolymers formed during room temperature curing may have shielded the remaining double bonds in the vinyl ester resin and later may have formed polymeric and mono/dimeric styrene crosslinks leading to compact and rigid network in the sample 'b' which is reflected in the crosslink density values of the later (table3).

Table.3. Crosslink densities of cured vinyl ester resins.

Sample	E' (Mpa)	Temp. corresponding to E'(K)	Crosslink Density (mole/cm ³)	FWHM (Tanδ)	tanδ _{max}
a	46.84	383	4.866 X 10 ⁻³	33.12	0.75635
b	86.84	403	8.639 X 10 ⁻³	26.81	0.7461
c	39.60	415	3.825 X 10 ⁻³	26.49	0.7468

However, presence of in situ formed rigid PS homopolymer has reduced damping of the sample 'b' and 'c' as is evidenced from tanδ_{max}. Broader the tanδ_{max} greater is the heterogeneity in the polymer system. Room temperature cured samples show maximum heterogeneity possibly because of existence of a mixture of PS homopolymers of different length and crosslinked vinyl ester [6]. In case of sample 'b' reduction in PS homopolymer phase at the expense of vinyl ester crosslinking has caused narrower and higher tanδ_{max} [7]. On the other hand heterogeneity in sample 'c' has been slightly compensated by the formation of more number of rigid PS homopolymer chains.

The temperatures corresponding to the maxima in the loss tangent curves are taken as the glass transition temperatures (T_g). Increase in segmental rigidity of the polymer always results in an increase in the T_g of the network. Room temperature cured samples show lower glass transition point than the immediate reset sample due to rigidity caused by higher crosslink density in the later. The post cured sample 'c' has exhibited highest Tg though the crosslink density is lowest. This may be explained in terms of the changes in composition of the system during curing [9]. Post cured sample consists of both rigid PS homo-polymeric crosslinks and entrapped PS homopolymers in between vinyl ester chains in contrast to sample 'b' where only polymeric and mono/dimeric styrene crosslinks are present. Higher

crosslink density gives restriction in molecular mobility at the same time it is responsible for the elasticity whereas inherent rigidity of homopolymers because of bulky side groups is always responsible for difficult segmental mobility. In sample 'c' probably effect of crosslinking has been outweighed by the segmental rigidity of PS homopolymers and hence higher Tg (table 4).

Table.4. Tg Values of Resin Samples from DMA.

Cure Schedule					
a		b		Pc	
(Tg- E')	(Tg- Tanδ)	(Tg- E')	(Tg- Tanδ)	(Tg- E')	(Tg- Tanδ)
70°C	75.24°C	90°C	100.40°C	98°C	104.80°C

FTIR Analysis of cured resin

Progress of curing reaction of vinyl ester resin is further studied by FTIR analysis of the sample after the DMA.

In fig.3. infrared transmittance at 943 cm^{-1} (C=C vinyl ester) and 910 cm^{-1} (styrene) are measured in respect of peak at 825 cm^{-1} (Polyhydroxyether) and the aromatic C-H deformation at 760 cm^{-1} .

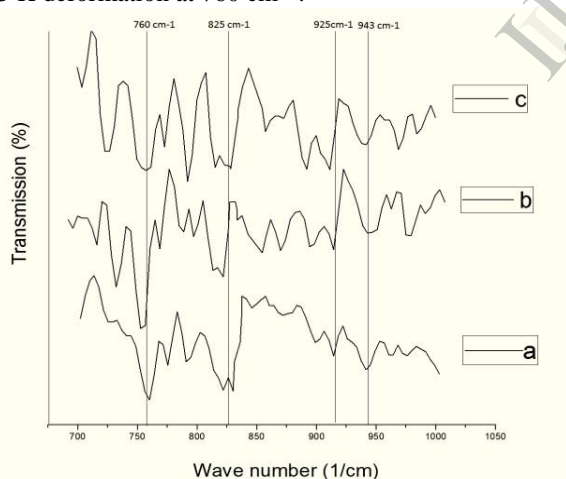


Fig.3. FTIR spectra of a vinyl ester resin during cure resin samples after DMA analysis a) room temperature cure b) immediate restart run of sample 'a' and c) post cure: 99 °C at 2 hrs.

In this study a gradually increasing transmittance at 943 cm^{-1} , compared to the intensity at 825 cm^{-1} indicates the decrease in vinyl group present (styrene) in the matrix resin due to crosslinking. Now, when the curing temperature increases area under the peak 943

cm^{-1} (C=C Vinyl ester) decreases along with the decrease in the area under 910 cm^{-1} (styrene). Thus the ratio of transmittance at 943 cm^{-1} and 825 cm^{-1} has given the extent of curing through double bonds conversion.

Table.5. Transmittance ratio of peaks for vinyl ester resin cured samples.

Sample	T ₉₄₃ /T ₈₂₅	T ₉₁₀ /T ₈₂₅
A	1.022	1.034
B	1.009	1.009
c	1.004	1.001

Characterization of sisal fibre

FTIR Analysis of fibre

IR spectra of raw untreated and gaur gum treated sisal fibre are shown in Fig.4. The characteristic features of the spectra of the fibre are due to its constituent's lignin, hemicelluloses and α -cellulose [9].

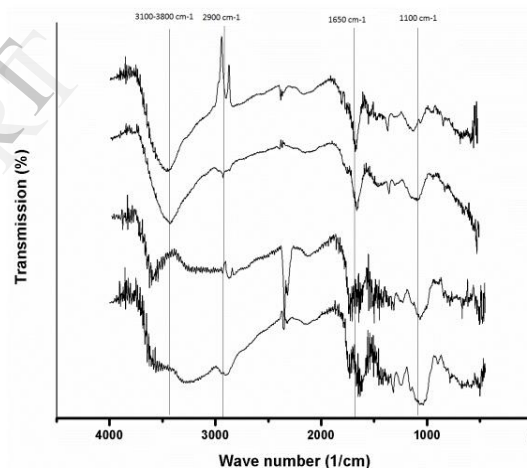


Fig.4. FTIR spectra of raw and Gaur gum treated sisal fibre (a) Raw sisal fibre (b) 0.1% GG (c) 0.2% GG (d) 0.3 % GG.

It is observed that maximum changes occurred by 0.2% Gaur gum (GG) treatment. The area under 3100–3800 cm^{-1} decreases in 0.1% GG fibres (b) compared to that of the untreated one (a) showing that lesser number of hydroxyl groups are engaged in H-bonding. Later on enhanced peak areas at the same position for 0.2% (c) and 0.3% GG fibres (d) have confirmed the fact that more gaur gum is coated on the fibre surface with increasing concentration of the gaur-gum solution. The sharp peak at 2900 cm^{-1} in raw sisal fibre became a little shoulder in 0.2% Gaur gum-treated fibres. Treatment of fibre with gaur gum has dissolved away probably the hemicelluloses and caused these changes in the peak positions [3]. The peak intensities at 1735 and 1715 cm^{-1} are considerably reduced in the 0.2%

treated fibres as some amount of C=O groups are on hemicelluloses. The little shoulder at 1650 cm^{-1} in raw sisal fibre due to absorbed water has become more prominent in the treated fibre indicating more hygroscopic nature of the fibres. The peaks in the region $1465\text{--}1530\text{ cm}^{-1}$ remained unchanged, indicating no change of the lignin component. A small sharp peak at $1000\text{--}1100\text{ cm}^{-1}$ due to β -glucosidic linkage in raw sisal fibre has undergone a shift to higher wave number in the 0.1%, 0.2% and 0.3% guar gum treated fibres. This may be due to the rotation of the glucose residue around the glucosidic bond, indicating change in the chemical nature of sisal upon treatment.

Dynamic contact angle

The measured contact angles of untreated sisal fibre and guar gum treated sisal fibre with different concentration of Guar gum solution are shown in table 6. A significant difference is found between treated and untreated sisal fibre. Untreated sisal fibre has high value of contact angle (139.45) compared to treated fibres because of greater polarity of the surface. Due to the presence of a highly hydrogen bonded -OH groups untreated sisal fibres tend to show low water spreadability. It is clear from the results that treated fibres have increased wettability compared to untreated fibres. Among the treated fibres 0.1GGSF show greater contact angle than 0.2GGSF and 0.3GGSF may be due to complete coating of the fibre surface with dilute solution. Again, due to the higher viscosity of the solution, in case of 0.3% GG treated fibres, a thicker and perhaps incomplete coating has caused drop in surface energy compared to that of 0.2% GG treated sample. This may be attributed to the partial penetration of liquid through the uncoated areas on the fibre surface (figure 6).

Table.6. Calculated values of contact angle and surface energy of untreated and Guar gum treated sisal fibre.

Samples	Mean contact angle (degree)	Surface energy (mN/m)
Untreated sisal fibre	139.45	26.45
0.1GGSF	94	27.45
0.2GGSF	90	29.19
0.3GGSF	90.62	29.12

Fig.5. has shown that after surface modification of fibre, its contact angle decrease. Such results can be related to the Theory of contact angle measurements [10]. This predicts that if contact angle is low, the

liquid spread and wet the substrate, while high value indicate poor wetting.

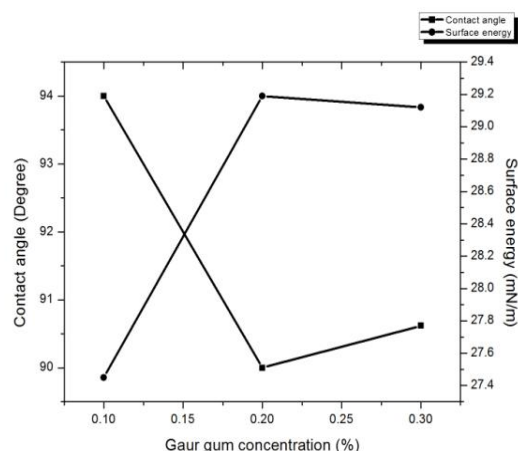


Fig.5. Change in contact angle and surface energy by surface modification of sisal fibre.

Density

Density (ρ) of the fibres is shown in table 7.

Table.7. Density of untreated and Guar gum treated fibre.

Sample	Density in Toluene (g/cc)
Untreated	3.14
0.1GGSF	1.22
0.2GGSF	0.751
0.3GGSF	1.246

Untreated fibre density is found greater than that of the treated fibres. Treated fibres show lower density may be because of loss in weight during treatment in the form of hemicellulose mostly. Also with increase in guar gum solution concentration there is variation in density. Fibres treated with 0.2% guar gum solution have shown lowest density and its density is not varying much with the nature of the medium in which density is determined. This may be attributed to uniform coating on the fibre surface (case B in figure 5) by the guar gum solution or in other words the viscosity of 0.2% solution is the optimum to treat the fibres [3]. Thus the whole fibre surface being covered by the GG solution it is unable to absorb the liquid during density measurement. Also polar hydroxyl groups on guar gum molecules are possibly interacting with the similar

groups on fibre and therefore less available for interaction with the density measuring liquid. Hence the density of 0.2% guar gum treated fibres is not very much affected by the medium polarity.

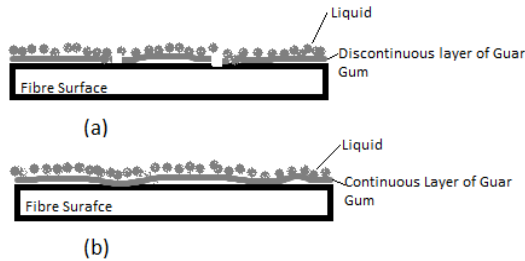


Fig.6. Physical interaction of coated fibre surface with the liquid.

Scanning electron microscopy

It has been observed from the scanning electron micrographs Fig.7 (a–d).of the untreated and treated fibres that their surface morphology differs. The raw fibre surface is very smooth in comparison to treated fibres. It is confirmed that in 0.3% Gaur gum treated fibre thicker but discontinuous coat on the fibre surface results. The resin is not seemed to be entrapped into the interlamellar structure of the sisal fibres when applied by very low (0.1%) solution concentration too. However the extent of resin coating on the fibres has increased with guar gum solution concentration. At low concentration insufficient wetting is evidenced whereas at 0.3% concentration excess resin coating has occurred. Fibres are found to be coated with guar gum resin covering maximum surface area at 0.2% solution concentration suggesting the viscosity of the solution being optimum.

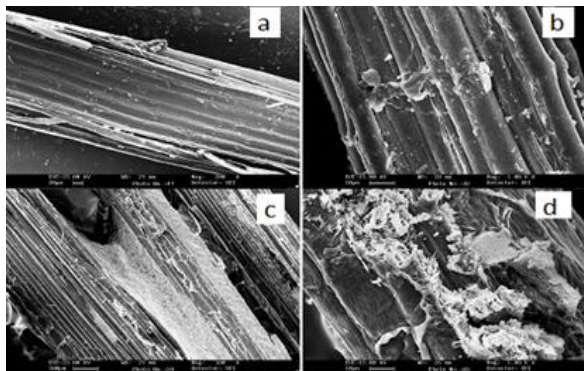


Fig.7. SEM of (a) Raw sisal fibre, (b) 0.1% gaur gum treated fibre (c) 0.2 % Gaur gum treated sisal fibre (d) 0.3% Gaur gum treated sisal fibre.

Characterization of composite

Flexural properties

The flexural properties of untreated and treated sisal fibre/vinyl ester resin composites are summarized in Table 8. The results from flexural tests are plotted in Figures 8 and 9. The flexural strength of all composites has increased with increase in fibre loading .This may be because the fibres act as load carrier and stress is transferred from the matrix along the fibres leading to stress distribution [12]. Generally, the best mechanical properties in a composite depend on fibre orientation, but the adhesion between the fibre and the matrix is also important. This is especially true for long fibre reinforced composites as in the present case.

Table.8. Flexural properties of untreated and treated sisal fibres/vinyl ester composites.

Sample	Fibre content (Wt. %)	Flexural strength (Mpa)	Flexural modulus (Gpa)
0.0GGSF	15	25.76	2.13
	25	28.62	2.22
	30	32.90	2.32
	40	31.22	2.30
0.1GGSF	15	40.45	2.16
	25	150.17	2.56
	30	181.65	2.96
	40	179.33	2.50
0.2GGSF	15	43.40	3.19
	25	179.82	3.67
	30	268.27	4.06
	40	265.25	4.01
0.3GGSF	15	72.05	3.13
	25	144.50	3.50
	30	225.82	3.98
	40	201.76	3.05

Effect of surface modification of fibre on flexural properties of fibre

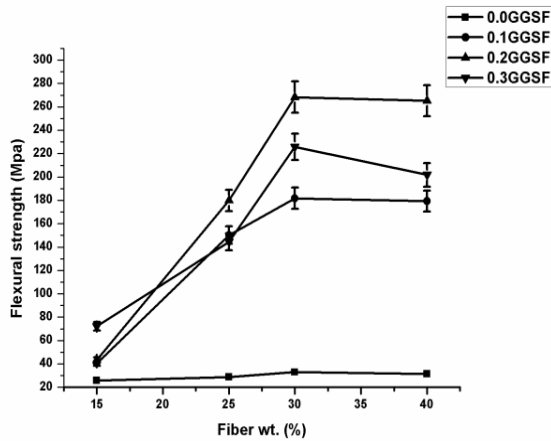


Fig.8. Flexural strength of Gaur gum treated (0.1%, 0.2% and 0.3%) and untreated sisal fibre/vinyl ester resin composites.

Fig.8. shows flexural strength of untreated and gaur gum treated sisal fibre/vinyl ester resin composite as a function of fibre concentration (wt.%). The increased Gaur gum concentration also has caused increase in the flexural strength gradually. The flexural strength of 30 % untreated fibre composite was 32.90 MPa, whereas for the 0.1, 0.2% and 0.3% of Gaur gum treated fibre composites with similar composition show 181.65MPa, 268.27MPa and 225.82Mpa respectively. The maximum strength is found for 0.2% gaur gum treated fibre composite. A uniform thin coating of guar-gum solution (figure 6) on the sisal fibre has enhanced the bonding between the fibre and the resin, which is reflected in their improved flexural properties. However, with a slight increase in the concentration of the guar-gum solution (0.3%), there is a decreasing trend in the flexural strength. In the 0.3% guar-gum treated composites, the thickly and discontinuously coated sisal fibres are bonded to the resin only at selected parts. Drop in flexural strength and modulus at higher fibre loading (40%) gives indication of poor fibre to resin bonding due to insufficient wetting of the fibres.

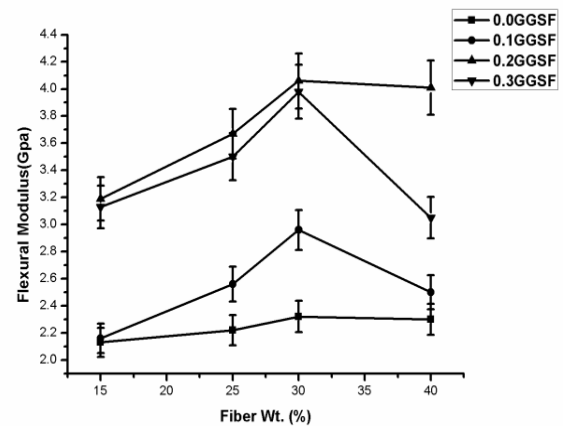


Figure.9. Flexural modulus of Gaur gum treated (0.1%, 0.2% and 0.3%) and untreated sisal fibre/vinyl ester resin composites.

The flexural modulus of the treated sisal fibre/vinyl ester composites are shown in Figure 8. The flexural modulus is seemed to be improved for all treated sisal fibre composites. The flexural modulus of 30 % untreated sisal fibre/vinyl ester composites is 2.32 GPa and that of 0.1, 0.2 and 0.3% treated fibre loaded (by 30 wt. %) composites are 2.96, 4.06, and 3.98 GPa, respectively. The reason for the improvement in modulus can be attributed to the change in the intrinsic structure and thereby the arrangement of the fibres [3].

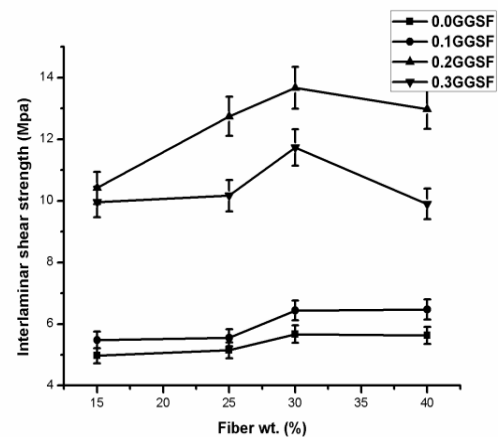


Fig .10. Interlaminar shear strength of Gaur gum treated (0.1%, 0.2% and 0.3%) and untreated sisal fibre/vinyl ester resin composites.

Fig.10. shows Interlaminar shear strength (ILSS) of untreated and gaur gum treated sisal fibre composite. The increase in the respective calculated ILSS values with increase in fibre loading is found for untreated and gaur gum treated sisal fibre/vinyl ester resin

composites. The increased Gaur gum concentration also has caused greater interlaminar shear strength. The ILSS of 30 % untreated fibre composite is 5.7 MPa, meanwhile for the 0.1, 0.2% and 0.3% of alkali concentration treatments 6.44, 13.67 MPa and 11.73 MPa respectively. The maximum strength is evidenced with 0.2% gaur gum treated fibre composite. The treatment with dilute solution of Gaur gum removes some lignin and hemicelluloses from the fibre surface, thus, the fibre surface area also increases. Such fibre surface increase results in a larger area of contact between the fibre and the matrix [13]. Then, the hydroxyl groups on the cellulose fibres can better interact with the vinyl ester resin through increased number of reaction sites. The increases in ILSS after Gaur gum treatment can be related to the better fibre–matrix interface due to less water absorption w.r.t untreated fibre composite. Due to the presence of a highly hydrogen bonded –OH group untreated sisal fibres tend to show low water spreadability. However this leads to dimensional variation of composites products and poor interfacial bonding between the fibre and matrix and hence inferior mechanical properties. The property of the interface controls the shear stress transfer between the matrix and the fibres. Generally, the best mechanical properties in a composite depend mainly on fibre orientation, but the adhesion between the fibre and the matrix is also important.

Tensile properties of composite

The ability of a material to resist breaking under tensile stress is one of the most important and widely measured properties of materials used in structural applications. The force per unit area (MPa) required to break a material under tension is the ultimate tensile strength or tensile strength at break. The tensile strength of the sisal fibre/vinyl ester composites are shown in Fig.11. Where it is found that increase in tensile properties is accompanied by increase in fibre loading. When the fibre surface is modified with Gaur gum solution the tensile properties of the composite show improvement may be due to physical interactions at the fibre/resin interface as the surface area of contact increases upon dissolution of hemicellulose during treatment. Tensile properties of the sisal fibre/vinyl ester composites are exhibited in table 9.

Table.9. Tensile properties of untreated and treated sisal fibres/vinyl ester resin composite.

Sample	Fibre content (Wt. %)	Tensile strength (MPa)	Young's Modulus (GPa)
0.0GGSF	15	27.94	1.02
	25	35.44	1.36
	30	44.90	1.79
	40	42.83	0.162
0.1GGSF	15	49.27	1.70
	25	62.49	1.79
	30	72.87	1.90
	40	52.34	0.176
0.2GGSF	15	77.39	1.39
	25	79.66	1.79
	30	83.11	1.92
	40	20.90	0.354
0.3GGSF	15	70.00	1.50
	25	73.02	1.59
	30	73.59	1.55
	40	32.072	0.244

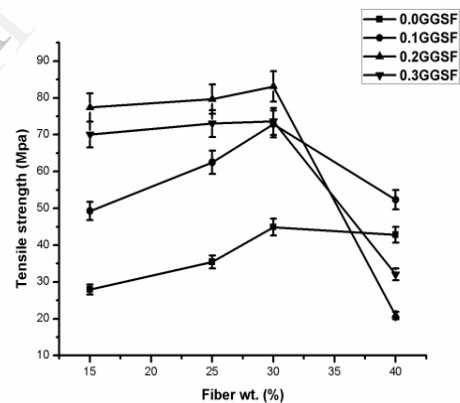


Fig.11. Tensile strength of Gaur gum treated (0.1%, 0.2% and 0.3%) and untreated sisal fibre/vinyl ester resin composites.

With increase in guar gum concentration from 0.1 to 0.2 % significant rise in tensile properties is observed may be due to the better surface area of contact between the resin and fibres having uniform thin coating on them. However concentrated solution (0.3%) of guar gum has not been proved to be good in this respect and falling trend in properties is observed. This may be because of higher viscosity of the solution and incomplete penetration and wetting of the whole fibre surface leading to delamination of the fibre from the matrix under tension. Therefore tensile modulus (figure 4.12) of 0.2 % Guar gum treated fibre composite is found to be highest whereas the modulus of 0.3% Guar gum treated fibre composite is lowest.

With increase in fibre loading tensile strength has increased upto 30% following rule of additivity and at higher fibre loading (40%) insufficient coating on fibre surface may have resulted delamination.

Fig.12. Tensile modulus of Gaur gum treated (0.1%, 0.2% and 0.3%) and untreated sisal fibre/vinyl ester resin composites.

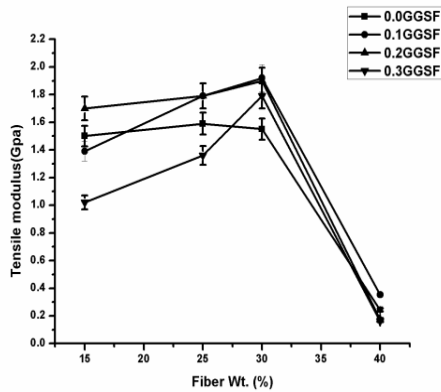


Fig.12. Tensile modulus of Gaur gum treated (0.1%, 0.2% and 0.3%) and untreated sisal fibre/vinyl ester resin composites.

Dynamic mechanical analysis

Dynamic modulus of composites is governed by (a) matrix type (b) fibre loading (c) fibre- matrix adhesion. Fig. 12 shows the variation of storage modulus and $\tan\delta$ of sisal fibre/vinyl ester resin composites with temperature.

Storage modulus

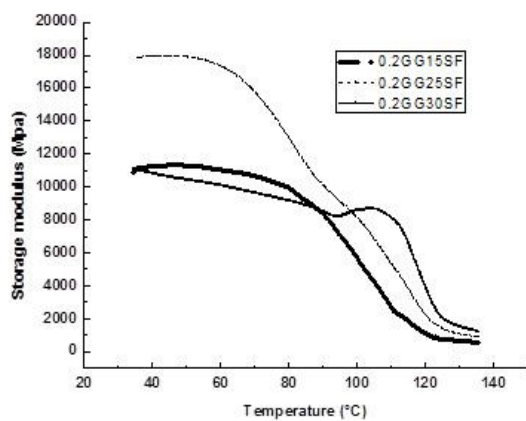


Fig.13.Storage modulus of 0.2% GGSF Sisal fibre/vinyl ester composites with variation in temperature.

Composites with 25 % fibre loading has shown highest E' at low temperature and two step falling trend with rise in temperature. The first step of storage modulus decrease may be due to the glass transition of

polystyrene homopolymer in the resin phase and the second corresponds to the glass transition of the vinyl ester. Such two-step decrease in E' is not observed with other samples but with 30 % GGSF fibre composite a distinct kink in the curve.

Storage modulus of guar gum treated sisal fibre loaded vinyl ester composites have shown gradually increasing trend (fig. 13) with increase in fibre loading within the range studied here (15-30wt%). 0.2% Guar gum treated fibres caused highest storage modulus for composites. Higher value of storage modulus indicates greater restriction in molecular mobility under load application. The incorporation of resin coated rigid fibres into the polymer matrix increases the stiffness of the material initially (0.1% guar gum) and this accounts for the higher E' values of composites. However the uniformity of resin coating on the fibre surface affects the interfacial interaction. E' decreases with 0.2% guar gum treated fibre composites may be due to better interfacial interaction and more gradual load transition from resin to fibre. Further decrease in modulus with 0.3% guar gum treated fibre filled composites may be attributed to the nonuniform coating on the fibre and therefore less effective interfacial interaction.

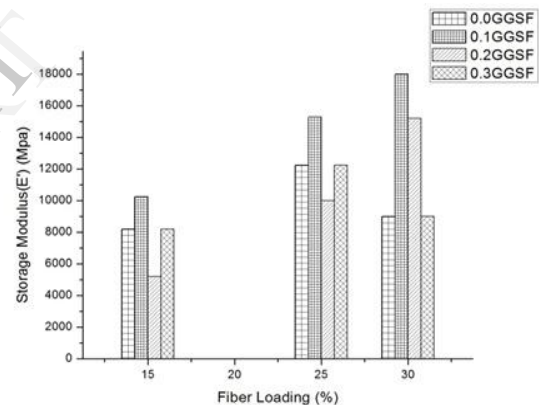


Fig.14. Variation of storage modulus in rubbery plateau of sisal fibre-VE composite I) UNSF II) 0.1GGSF III) 0.2GGSF IV) 0.3GGSF respectively as a function of fibre loading (1Hz frequency).

Damping behaviour of composite

The damping behaviour of composites in the glass transition region is governed by

- (1) Mechanical relaxation of the matrix and loaded fibre
- (2) The interface between fibre and matrix
- (3) Fibre loading.

At temperatures around T_g of the matrix, the molecular chains have higher flexibility and damping of the composite is due to that. Dong and Gouvin [14] showed that the damping performance of the composite materials is controlled by the nature of interfacial

region which may be two dimensional interphase or a three dimensional interface.

In the case of aligned fibre reinforced polymer composites, increase in damping with decrease in aspect ratio is also reported [16].

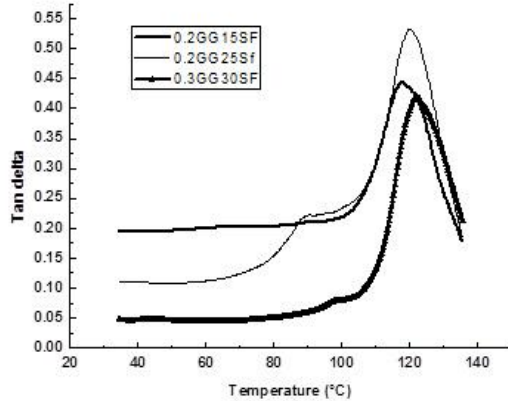


Fig.14. Variation in $\tan\delta$ for vinyl ester/sisal fibre composites (0.2%GGSF) with temperature.

It is also interesting to note that the amplitude of $\tan\delta$ peaks of the composites are lower than that of neat vinyl ester (table 10). Moreover, the peaks are narrower than that of neat vinyl ester. The peak width at half maxima and peak height under $\tan\delta$ curves of neat PS and sisal fibre-VE composites as a function of fibre loading and fibre modification are given. From these values, it is clear that the addition of fibre decreases height of the peak i.e. less damping and increases the width of the damping peak indicating the heterogeneity of the system.

Table.10. FWHM and $\tan\delta_{max}$ of sisal fibre/ vinyl ester composite.

Sample		FWHM	$\tan\delta_{max}$
Neat resin		34.63	0.769
UNSF	15wt%	16.024	0.392
	25wt%	27.208	0.323
	30wt%	19.494	0.313
0.1GGSF	15wt%	31.420	0.383
	25wt%	28.638	0.375
	30wt%	21.420	0.347
0.2GGSF	15wt%	16.336	0.343
	25wt%	23.040	0.335
	30wt%	21.413	0.323
0.3GGSF	15wt%	38.507	0.334
	25wt%	23.909	0.327
	30wt%	19.354	0.391

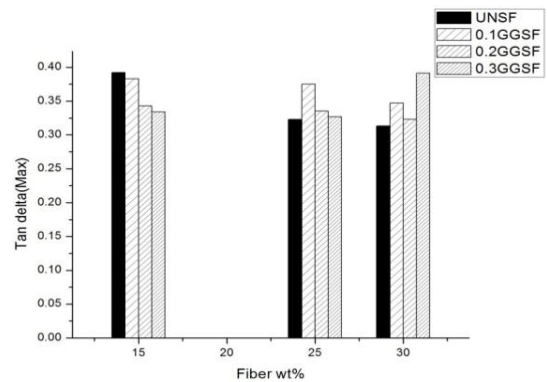


Fig.15. Variation of Tan delta (max) of sisal fibre-VE composite I) UNSF II) 0.1GGSF III) 0.2GGSF IV) 0.3GGSF respectively as a function of fibre loading at different temperatures at 1Hz frequency.

Water absorption

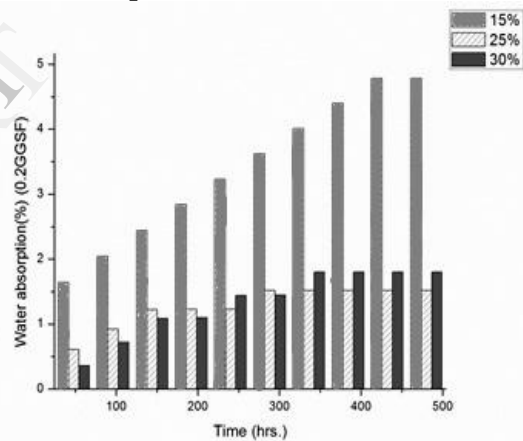


Fig.16. Water absorption by the vinyl ester /sisal fibre composites (0.2% guar gum treated) with variation in fibre loading.

The amount of water absorbed by the composites is calculated by the weight difference between the samples exposed to water and the dry initial samples. Fig.16 shows the % water absorption plotted against time for all the samples. Composites with 15 % fibre loading have shown maximum extent of water absorption and with increase in fibre loading the water absorption in decreased suggesting that composites with higher fibre loading may be capable of showing fairly good water resistance. This may be attributed to the fibre to resin bonding through some sort of interaction which has not allowed penetration of the water molecules at the interface. At the same time it

may be concluded that the increase in polarity of the fibre surface upon guar gum coating, as revealed in dynamic contact angle measurement, has improved its adhesion with the matrix resin through dipole-dipole interaction.

Table.11. Effect of water absorption on tensile properties of sisal fibre/vinyl ester composites.

Sample	Tensile strength (MPa)		Young's modulus(MPa)	
	Dry	Wet	Dry	Wet
UN15SF	27.94	25.23	1.02	1.0385
UN25SF	35.44	29.89	1.36	1.0409
UN30SF	44.90	40.99	1.79	1.0647
0.1GG15	49.27	41.44	1.70	1.0967
0.1GG25	62.49	61.06	1.79	1.3477
0.1GG30	72.87	40.28	1.90	1.6480
0.2GG15	77.39	43.96	1.39	1.3431
0.2GG25	79.66	61.92	1.79	1.6340
0.2GG30	83.11	84.25	1.92	1.7490
0.3GG15	70.00	38.05	1.50	1.4798
0.3GG25	73.02	51.60	1.59	1.6295
0.3GG30	73.59	64.05	1.55	1.7414

Moreover equilibrium water uptake of the composites with 0.2% guar gum treated fibre composites is found to reach earlier than that with 0.1 and 0.3% Guar gum treated fibre loaded composites which may be because of the more uniform coating on the fibre surface and stabilization of the interface between fibre and resin. Tensile strength and modulus of composites after and before water absorption are compared in table11. Tensile modulus of the composites has not changed much due to water absorption with 0.2% guar gum treated samples though the property has changed a lot with the other composites. This may be explained on the basis of better adhesion of fibre to resin thereby increase in restriction of molecular mobility.

Morphology

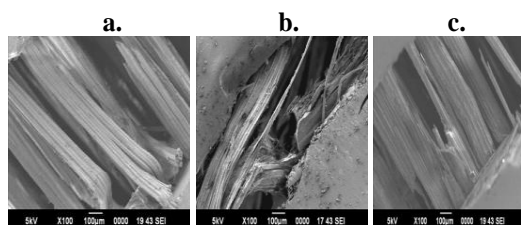


Fig.17. Scanning electron micrograph of tensile fractured 25% sisal fibre loaded composites with a) 0.1% GG b) 0.2% GG c) 0.3% GG treatment.

Fibre concentration in the composites being same the effect of guar gum solution concentration is readily

observed from the micrographs in fig.17 with increase in the guar concentration the coating layer thickness as well as uniformity of the layer varies. Therefore fibre to matrix adhesion has been found to vary accordingly. With more uniform coating of guar gum on fibre surface has definitely improved the bonding with matrix resulting in shear fracture during tensile testing as revealed in sample b in figure 17. On the other hand, 0.3% guar gum solution coated fibres have shown a brittle fracture, as if the fibres are stiffer, upon the tensile load application (sample c) may be due to the higher viscosity of the solution and less uniformity of the resin layer over the surface of the fibres. Thus for the fibres, treated with a higher concentration guar gum solution, the vinyl ester resin to fibre adhesion is inferior compared to the 0.2%GG treated fibre composites. Micrographs of 0.1% Guar gum treated fibre composites has shown heavy pull out of the fibres from composites at the tensile fracture surface due to incomplete coating and poor adhesion to matrix resin.

IV.CONCLUSION

Guar gum treatment of sisal fibres may be considered to be a viable technique of surface modification for manufacturing bio-composites for indoor use. Guar gum being a natural resin from plant source has many hydroxyl groups in its structure and is capable of binding with natural fibre like sisal. Thus it can make the fibre surface reactive and ready to combine with the liquid resin to be cured later. Vinyl ester being a cost effective thermosetting resin is considered to give mechanically stronger composites that unsaturated polyester based composites.

The decrease in hydrophilicity and increased compatibility of the treated fibre to combine with the polymer matrix are responsible for the improvement in the mechanical properties. This further evidenced from the SEM studies on tensile fractured samples and can be explained on the basis of better fibre-to-matrix adhesion through dipole-dipole interaction. With higher concentration of guar gum treated fibre composites brittle fracture is observed in contrast to the shear fracture at lower concentration (0.2%) of guar gum. The damping ($\tan\delta$) of the composites is lowered compared to neat resin due to stiffness of the fibres as the area under damping peak of the composites are lower and broader than that of neat VE. Based on these studies, it can be concluded that by suitable selection of the fibre treatment sisal fibre-vinyl ester composite with superior dimensional stability and mechanical properties can be developed. Increasing fibre content of bio-composite has increased its tensile (by 45.97%) and flexural strengths (by 87.70%), flexural modulus (by 42.85%) with respect to that of unmodified fibre composite and its water absorption capacity is

decreased. Maximum improvement in the composite properties was observed with 0.2 % gaur gum treated 30 wt. % Gaur gum treated sisal fibre composite. Due to the low density and high specific properties of treated sisal fibres, composites based on these fibres may have very good potential in the automotive and transportation industry.

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