

Enhancing the Static and Dynamic Mechanical Behaviours of Vinyl Ester Matrix using Surface Modified Luffa Fibers



S. Ramakrishnan, T.P. Sathishkumar

Abstract: This study focuses on enhancing the static and dynamic mechanical behaviours of vinyl ester matrix using surface modified Luffa fibers. The density of Luffa fiber, which belongs to Cucurbitaceae family, is 1.2 g/cc. The Luffa (Ridge gourd) vegetable was dried in sun-light and the required fiber layers were then obtained by using manual extraction process. The fiber layers were then treated with alkali (5% of NaOH) solution at ambient temperature (28° C) for 24 h. From the SEM images, it can be inferred that the chemical treatment did not degrade the fiber surface and retained its reinforcing nature. The Luffa fiber reinforced vinyl ester composites were developed by hand layup technique by varying the number of fiber layers (1, 2 and 3). The morphological and mechanical behaviours of the developed composites were analyzed as per ASTM standards and compared with pure resin. The static and dynamic mechanical properties of vinyl ester composites exhibited significant improvement with fiber surface treatment and increase in number of fiber layers. Among the different composites tested, the composite specimen with three layers of alkali treated fiber exhibited the highest tensile strength (18.88 MPa) compared to untreated fibers (16.83 MPa). The improvement in properties of Luffa fiber reinforced composites can be attributed to the removal of lignin and waxy substances from the fiber by chemical treatment, which was confirmed by SEM. The obtained results indicate that composites reinforced with three layers of surface modified Luffa fibers showed overall improvement in static and dynamic mechanical behaviours.

Keywords: Natural fiber, mechanical behaviours, polymer matrix, surface modification.

I. INTRODUCTION

Natural fibers or lignocellulosic fibers are fast emerging as cost-effective, light-weight and environmentally superior alternatives to synthetic or man-made fibers and the specific properties of the natural fiber based composites are in some cases better than those of synthetic fiber composites. This suggests that natural fiber composites offer promising potential to replace synthetic fibers in many industrial and light-weight applications [1]. The light weight lignocellulosic fiber composites help to increase fuel efficacy and decrease

emissions in the automobile component applications. When compared to natural fibers, the synthetic fibers possess twice the weight of natural fibers, abrasive in nature cause damage to human beings and require more energy for extraction [2]. Natural fibers have been reinforced with thermosets due to their excellent property enhancement and partial recyclability [3]. The development of bio-composites from natural fibers and biodegradable polymers played a major role in the composite science, due to complete degradation and non-emission of any toxic components [4]. Usually natural fibers are composed of cellulose, hemicellulose, pectin, lignin and wax. Cellulose is a crystalline structure that can be clustered into microfibrils with adequate stability. Usually, cellulose fibers have over than 500,000 cellulose molecules. The increased tensile strength of a natural fiber is attributed to the presence of H-bonds in cellulose molecules.

Even though natural fiber based composites are commonly used, they have few disadvantages such as poor fiber-matrix compatibility and high moisture uptake. Thus, chemical treatments are widely used to modify the fiber surface properties [5, 6]. Velumani et al. had studied the mechanical behaviours of sisal fiber reinforced polymer composite with different lengths of fibre (10, 30 and 50 mm) and various fibre loading (15, 30 and 45%). The factorial design and genetic algorithm techniques were used for optimizing the response variables [8]. The vinyl ester composites are widely used in marine applications [9, 10]. Dipa ray et al. had attempted to evaluate the thermo-mechanical behaviours of pure vinyl ester resin and jute/vinyl ester composites at different fibre loading (23 - 35%) and using fibers treated with 5% NaOH (4 and 8 h), in the temperature range between 30 °C and 210 °C [11]. Even though, extensive work has been done related to natural fiber based thermoset polymer composites, the studies relevant to Luffa fiber constitute lesser degree. The main objective of this article is to prepare vinyl ester composites with untreated and alkali treated Luffa fiber. The mechanical (static and dynamic) behaviours of the prepared composites has been analyzed using tensile test and Dynamic Mechanical Analysis respectively. The behaviour of the double-layered ligno-cellulosic Luffa (ridge gourd) fiber belonging to Cucurbitaceae family were studied and chemical, spectral, and thermal analysis of this fiber were carried out before and after alkali treatment. The thermal degradation of the fiber was reported at 260 °C, which is the initial degradation temperature of this fiber [7].

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II. MATERIALS AND METHODS

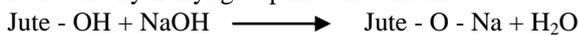
A. Materials

Vinyl ester resin (POLYFLEX GR 200-60, Pale brownish Liquid, Brookfield viscosity @ 25 °C = 325 cps, Density @ 25 °C = 1.052 gm/cm³,

Volatile content = 41.8%) was provided by M/s Covai Seenu Company, Coimbatore (South India). Luffa fibers, which are in abundance throughout Tamil Nadu, a southern state of India, are extracted via simple manual extraction procedure. The ripe Luffa (Ridge gourd) vegetables are commonly allowed to dry in the sun for few days. When its skin has hardened and turned brown, it is gently crushed to remove the outer layer. The tubular fiber is cut open carefully to get rectangular fiber mat. Alkali solution (NaOH) for fiber surface treatment, resin curing system with cobalt (accelerator) and Methyl Ethyl Ketone Peroxide (MEKP as catalyst) were bought from Sigma-Aldrich Co. Ltd., India.

B. Surface modification of fiber

Coarse fiber surface permits better penetration of resin into the micro-pores and hence improves the reinforcing efficiency of the fiber with the polymer matrix. Walls of Luffa fiber are covered with waxy layer of substances like hemicellulose, lignin, and other impurities. Alkaline treatment (mercerization) is one of the regularly used chemical treatment method for natural fibers when used as reinforcement for thermoplastics and thermosets. The significant change imparted by mercerization involves disruption of hydrogen bonding in the network structure, thus increasing surface roughness. This treatment eliminates a definite quantity of lignin, wax and oils on the outer surface of the fiber cell wall. Furthermore, it depolymerizes cellulose and uncovers the crystallites of small length. Accumulation of aqueous alkali (NaOH) solution to any natural fiber converts the hydroxyl group into the alkoxide.



Alkaline treatment induces the following two effects on the fiber: (i) It improves mechanical interlocking by increasing surface roughness, (ii) It augments the quantity of exposed cellulose on the fiber surface and thus rises the number of possible sites of reaction.

Alkaline Treatment: The Luffa fiber layers are immersed in 5 wt./vol.% of NaOH solution for one day at room temperature of 28 °C. Further, the fibers are rinsed several times with distilled water with few drops of acetic acid for eliminating alkali fragments sticking on to the fiber surface. A final pH value of 7 is maintained. Further, the fibers are sun dried for 2 days.

C. Composites preparation

The simple hand lay-up method is used to fabricate composites specimen with various fiber layers (1, 2 and 3). Preceding the preparation of composites, both resin and fiber are dried at 80 °C and 50 °C under vacuum for 2 h to remove the moisture content. Steel dies are designed to prepare the composite specimen. Initially the releasing agent is applied over both the sections (male and female) of the die for easy removal of the specimen after the solidification process. The surfaces are then allowed to dry and the fiber layer(s) are spread over the die. Then, a layer of matrix is spread over it. The process is repeated with the required number of layers.

The steel rollers are used to maintain the uniform orientation of fiber mat in the composite plates. Afterwards, the molds are closed and placed under the hydraulic press to obtain a single mat.

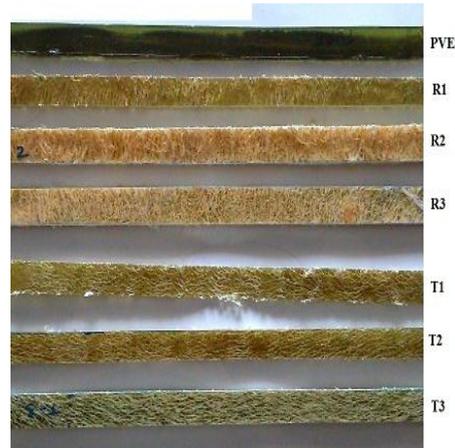


Figure 1. Prepared composite specimen plates

Curing reaction is carried out by adding 1 vol.% of cobalt and MEKP in vinyl ester resin and the specimen is permitted to cure for one day at room temperature. Dimension of the prepared specimen are 300 × 300 × 3 mm³. The prepared samples are shown in Fig. 1.

D. Experimental Procedure

FTIR spectral analysis

FTIR spectral analysis is done to determine the nature of chemical bond that exists in the Luffa fiber before and after surface treatment. The extracted fiber samples are cryogenically cooled and powdered. In mortar pestle, powder sample was closely pulverized with solid KBr and a thin pellet was prepared. The NEXUS- 870 FTIR instrument is used in the region 500–4000 cm⁻¹ to record the FTIR spectra of the untreated and alkali-treated samples.

Mechanical properties

The tensile properties of composites were determined by the Universal Testing Machine (INSTRON model). This test was conducted as per ASTM D638 standards specification. The length, width and thickness of the specimens are 160 mm, 12.5 mm and 3 mm, respectively. The crosshead speed was sustained at 50 mm/min. The test was conducted at room temperature condition. In each instance, 5 specimen were tested and the average of the values were tabulated.

Dynamic mechanical analysis (DMA)

The E' and tan δ values are found out for pure and Luffa fiber reinforced vinyl ester as a function of temperature (40 °C – 160 °C). DMA 2980 (TA instrument) equipped with dual-cantilever bending fixture was utilized for carrying out the analysis. Testing was conducted at frequency of 1 Hz, strain amplitude of 10 μm and heating rate of 5 °C/min. The specimen dimensions are 35 mm × 10 mm × 4 mm.

III. RESULTS AND DISCUSSION

FTIR spectra

The FTIR spectra of the Luffa fiber sample before and after NaOH treatment are presented in Fig. 2.

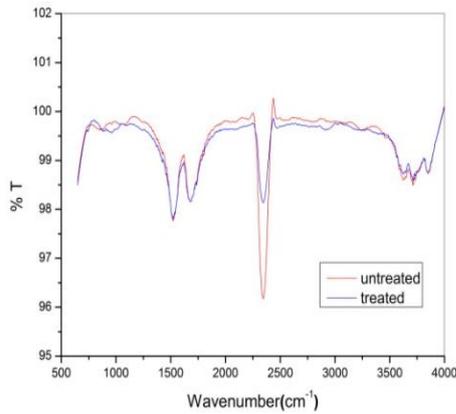


Figure 2. FTIR spectra of Luffa fiber

The figure shows the distinct bands present at around 3640, 2290, 1730, 1460 cm^{-1} spectra. When comparing the bands of untreated and NaOH treated fiber, an extra band is found at around 1210 cm^{-1} for untreated fiber, due to the presence of hemicellulose. But this band intensity decreases on treated fiber, which confirms the removal of hemicellulose.

The presence of α -cellulose is confirmed by similar band around 3640 cm^{-1} , while remaining bands shows lignin in the fiber. The intensity of the bands of lignin has decreased on alkali treatment than untreated and this trend indicates the lowering of lignin content due to alkali treatment. When comparing the bands of untreated and NaOH treated fiber, an extra band is found at around 1210 cm^{-1} for untreated fiber, due to presence of hemicellulose. But this band intensity decreases on treated fiber, which confirms the removal of hemicellulose. The presence of α -cellulose is confirmed by similar band around 3640 cm^{-1} , while remaining bands shows lignin in the fiber. The band intensity of lignin has decreased due to NaOH treatment and this trend indicates the lowering of lignin content owing to alkali treatment.

Tensile Properties

The tensile property (strength) values of untreated and NaOH treated Luffa fiber reinforced vinyl ester composites with various numbers of layers (1, 2 and 3) are determined.

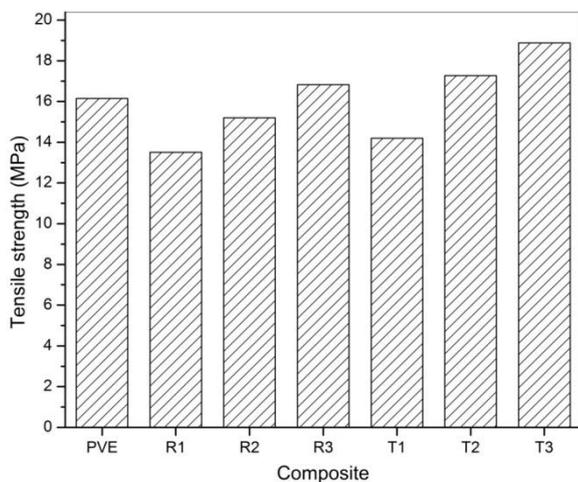


Figure 3. The tensile strength of untreated and NaOH treated Luffa fiber/vinyl ester composites

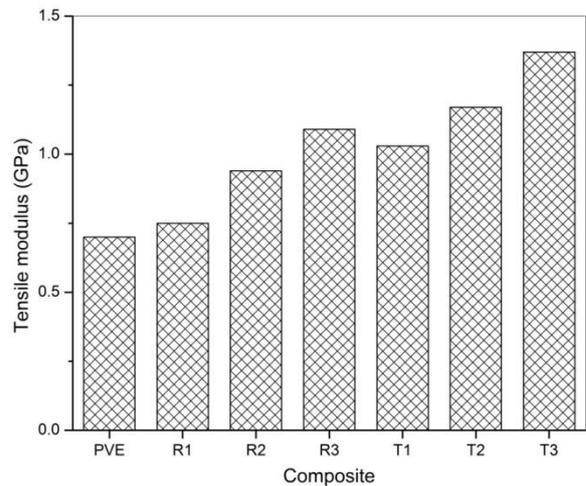


Figure 4. The tensile moduli of untreated and NaOH treated Luffa fiber/vinyl ester composites

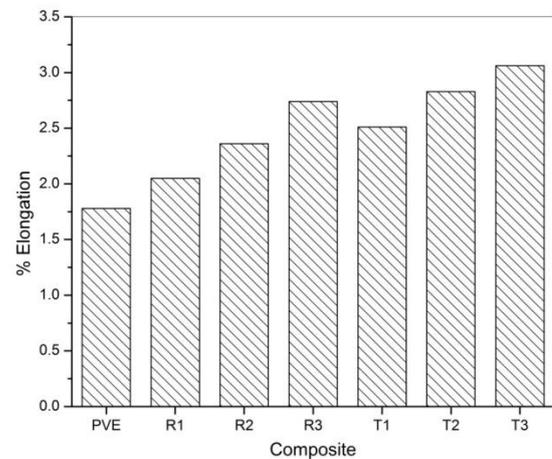


Figure 5. The percentage elongation of untreated and NaOH treated Luffa fiber/vinyl ester composites

These results are represented as bar diagrams in Figure 3. The sample codes are given as PVE for pure vinyl ester resin, raw (untreated) fiber composites with 1, 2, 3 number of layers are denoted by R1, R2, R3 and alkali treated composites with 1, 2, 3 number of layers are denoted by T1, T2, T3 respectively. The Fig. 3 shows that the tensile strength of Luffa/vinyl ester composites has augmented when subjected to alkali treatment. The tensile strength of the Luffa/vinyl ester composite samples with 2 and 3 layers has increased marginally by 15.2 and 16.83 MPa over the untreated composite with single layer of fiber. In case of alkali treated ridge gourd fiber composite samples, it is noticed that the tensile strength has improved from 16.83 to 18.88 MPa (12.18% increment). So, alkali treatment has enriched the tensile strength of composites even considering the number of fiber layers [5]. Because the fragile hemi-cellulose layer on the fiber got detached by alkali treatment, the surface gets clean and surface roughness is increased which helps for better fiber – matrix adhesion between [12]. The tensile moduli of Luffa fiber reinforced vinyl ester composites are presented in Fig. 4. The trend of tensile moduli values under varying number of layers is found to be similar to tensile strength.

Here also, the NaOH treatment improves the tensile modulus of the prepared composites and the results of specimen T3 are more efficient than 1 and 2 fiber layers. The tensile modulus improved from 1.09 to 1.37 GPa (25% increment) for the composite with 3 layers. Fig. 5 shows the percent elongation of Luffa/vinyl ester composites with various numbers of layers. From the figure, the elongation at break is found to be 2.74% and 3.06% for composites with 3 layers of untreated and treated fiber respectively. This indicates that the alkali treatment increases the percent elongation of fiber than untreated one [6]. Also, it is established that the composite samples are rigid, but not ductile.

SEM results

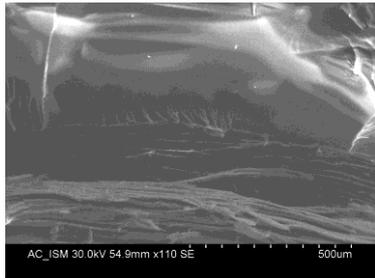


Figure 6. SEM of untreated Luffa fiber composite

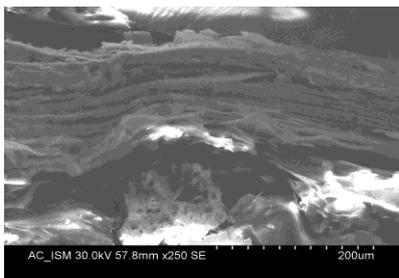


Figure 7. SEM of treated Luffa fiber composite

The surface morphology of Luffa fiber reinforced composites at the tensile fractured surface was studied by SEM, shown in Fig. 6 and 7. Figure 6 exhibits the cellular structure of the untreated fiber, indicating the porous structure of untreated fiber composite due to the presence of lignin and pectin. The adhesion bonding between matrix and fibers is reduced by these impurities. The irregular shape of Luffa fiber together with poor adhesion (due to hydrophilic nature) to the vinyl ester matrix (hydrophobic nature) is main factors for the deterioration of tensile strength.

DMA results

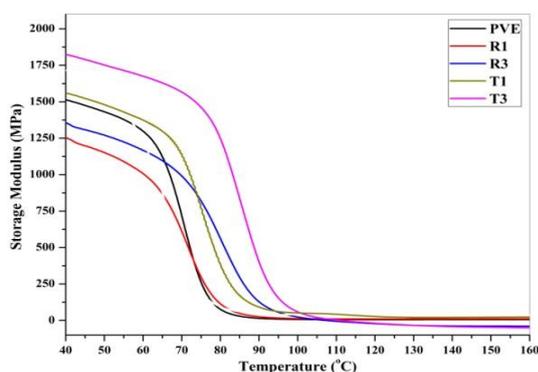


Figure 8. E' of untreated and alkali treated Luffa fiber/vinyl ester composites

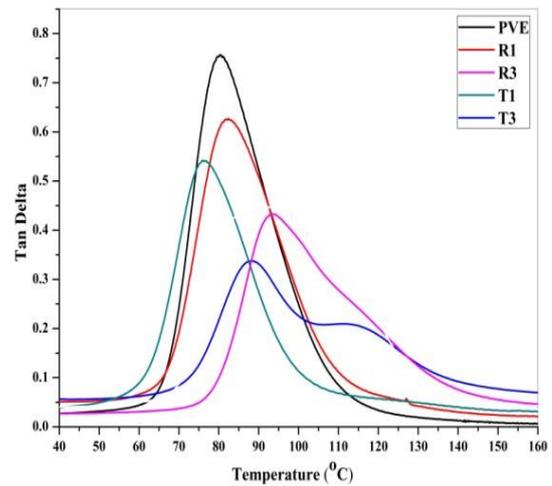


Figure 9. Tan δ of untreated and NaOH treated Luffa fiber/vinyl ester composites

The E' and tan δ of pure vinyl ester, untreated and NaOH treated Luffa fiber reinforced vinyl ester composites with various fiber layers are indicated in Fig. 8 & 9. The storage modulus (E') is a function of the load bearing capacity of a material measured as per ASTM-D 790. The E' and tan δ values of vinyl ester containing different fiber layers of Luffa fiber, indicated in Fig. 8 & 9 respectively, exhibit an interesting trend. The storage moduli values of the specimen have been determined as the function of temperature. On examination, it is evident that the storage modulus of pure vinyl ester is marginally higher than that of raw Luffa fiber reinforced vinyl ester composites (1, 2 and 3 layers). The hydrophilic nature of raw or untreated fiber is found to influence the storage modulus value. However, the storage moduli values of alkali treated Luffa fiber reinforced vinyl ester composites exhibit slight increase. This increase is attributed towards the surface treatment of fiber. Due to surface treatment, the reinforcing nature of Luffa fiber has improved significantly. The stiffness of the matrix also increases. On the other hand, the tan δ peak tends to decrease with incorporation of fiber in vinyl ester. The peak also exhibits a slight shift from the mean value of pure vinyl ester. With increase in number of fiber layers, the tan δ value decreases as a result of better reinforcement.

The lowest tan δ value is observed in the vinyl ester composite specimen with 3 layers of alkali treated Luffa fiber. The heat buildup is significantly reduced as evident from the reduced peak intensity of tan δ . The damping characteristics of the vinyl ester composites show remarkable improvement with fiber incorporation.

IV. CONCLUSION

The composite samples were successfully prepared with various layers (single, double & triple) of Luffa fiber using hand layup technique. The static and dynamic properties of the prepared vinyl ester composites before and after alkali treatment are studied. The following conclusions have been arrived at from the present work. The ultimate tensile strength and elastic modulus of the vinyl ester composites improve gradually with incorporation of fiber layers.

The maximum value of tensile strength (18.88 MPa) is achieved for the specimen with three layers of alkali treated Luffa fiber. Similarly, the highest value of tensile modulus (1.37 GPa) is observed for the specimen (T3) with three layers of surface modified Luffa fibers. The same trend is noticed for percent elongation of the various composite specimen. By NaOH treatment the tensile properties of composites are observed to exhibit significant improvement. The tensile properties were maximum for 3 layer fiber composite sample compared to the 1 and 2 layer composite samples, under both untreated and alkali treated conditions. The DMA values also establish the reinforcing ability of surface modified Luffa fiber through the increase in E' and shift in tan δ peaks. The mechanical properties are summarized in Table 1.

Table 1. Mechanical properties of epoxy resin and composites.

Composite Sample	Tensile strength (MPa)	Tensile modulus (GPa)	% Elongation
PVE	13.72	0.7	1.78
R1	13.81	0.75	2.05
R2	15.2	0.94	2.36
R3	16.83	1.09	2.74
T1	14.2	1.03	2.51
T2	17.27	1.17	2.83
T3	18.88	1.37	3.06

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