

# Hybrid Composite Laminates from UPE/ESOA Blend Reinforced with Chitosan and Bamboo Fiber: A Study of Mechanical and Thermal Properties

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The development of an inter-cross-linked polymer network of thermoset-thermoset blends have been extensively studied due to their enhanced mechanical properties. Among various polymer blends, modifications of unsaturated polyester (UPE) resin with epoxidized soybean oil acrylate (ESOA) combinations are an attractive route to promote the performance of the thermoset matrix and to overcome the inferior properties of both the components. Biodegradable and effectively accessible chitosan biodegradable waste material can shape the new stage for cutting-edge innovation items. Blend of both recyclable fibrous reinforcement and eco-friendly filler with two miscible thermosetting polymers will provide enhanced properties. At this time, chitosan up to 15 wt% (based on matrix weight) was utilized as reinforcing filler. At last, an interesting result was built up by confirming that chitosan filled chemically tailored bamboo and UPE/ESOA (80:20) biocomposites offered enhanced properties by 10 wt% of filler concentration with the most enhancements in whole properties. They have extensive variety of applications in the sector of low cost housing, structural projects and structural laminates.

Keywords: Unsaturated polyester, Soybean oil acrylate, Mechanical properties, Dynamic mechanical analysis, Thermal stability.

## **INTRODUCTION**

Currently, blending of polymer has supported the concept to execute another objective for plotting limitless variety of modern polymeric composite materials of completely new yield beautified with financially sound, light weight, high quality and high performance based properties without giving up their natural properties. Ecological concerns identified with the utilization of man made non-biodegradable composites have impelled the improvement of composite materials in light of common or sustainable sources [1,2]. The principal hypothesis in this new procedure is to acknowledge the offer of these hybrid polymer based systems of two thermosetting resin based miscible blends that have productively demonstrated their ingredients for giving improved mechanical characteristics and predominant candidature for application in different fields. In current situation unique blend based hybrid biocomposites are termed as "smart materials". These are reinforced with natural fibers and bio based fillers that may be effectively called as biocomposites. These biocomposites are utilized as a replacement of basic materials like steel, wood and metals because of their

enhanced quality even in little specific weight. They have unique properties like less density, more flexibility, high strength with more noteworthy specific modulus.

Regardless of the way that glass fiber-reinforced composites have incredible properties, because of numerous ecological issues; like the disposal and reusing techniques have been strictly accepted [3]. This has brought about rising prospective for bio-fiber based hybrid composites to make future substitutions that give advantages like simple accessibility, minimum price, low thickness, adequate specific properties, upgraded energy recuperation, biodegradability and recyclability [4,5]. Ecological conventions and ethical concerns have set off the new scan for novel materials that are naturally benevolent. Recent trend is the use of natural fillers with natural fibers.

Biofillers are major interest as reinforcing materials because of their appealing points of potentials like ease of availability, natural cordiality and accessibility [6,7]. Natural fillers may be derived from animal origin or plant origin. Chitin is one of the animal origins based on waste materials. Fisheries activities produce this chitin from the outer part of fishes, crabs, prawns as biodegradable waste materials. Chitosan is the deacetylated

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product of chitin. This can be utilized as reinforcing filler for preparing strong hybrid polymer biocomposites. The impregnation of this biofillers in common fiber can strengthen the polymer composites and may make better change in the mechanical properties of the composites [8,9]. In this regard, the particular target of current investigation is to create a new class of hybrid polymer based biocomposites reinforced with different types of chemically treated (alkali and silane after alkali treated) bamboo fibers and chitosan filler with various weight ratios and study their physical, mechanical and water absorption properties.

### **EXPERIMENTAL**

Unsaturated polyester resin matrix (isophthalic polyester, from Vasavi Bala Resins, VBR-4301, viscosity 0.3 Pa s) was used along with styrene. It was a pale yellowish clear liquid with excellent chemical resistance, low shrinkage, excellent wetting and bonding to various fibers. The epoxidized soybean oil acrylate (ESOA) was purchased from Sigma-Aldrich, which had the following characteristics: oxygen-oxirane content: 0.012; iodine value: 8 g/100 g; acid value: 1.15 mg (KOH)/mg; refractive index: 1.4873; and viscosity: 25.336 mPa s. Benzoyl peroxide (BPO with peroxide content: 50 wt%) initiator, *N*,*N*-dimethylaniline (DMA) accelerator, HEA, dicumyl peroxide (DCP) were also purchased from Sigma-Aldrich. Jute fibers in the form of Hessian cloths were collected from Southern Jute Industries, India (207gsm). All chemicals and solvents were used without any modifications.

**Preparation of UPE/ESOA polymer blends:** Thermosetting polymer ESOA was added in the unsaturated polyester (UPE) resin and stirred properly till clear solutions were obtained. The 3% MEKP (w/w) catalyst was mixed with continuous stirring for 4 h to confirm the complete dissolution of catalyst. Now 0.5% cobalt naphthanate (w/w) was added to the solution. Curing was occurred at 120 °C in a convention oven for 2 h.

Alkali treatment (mercerization) of bamboo fiber: At first bamboo fibers were soaked into 1 wt% NaOH solution for 1 h by a reported method [2]. Then the alkali treated fibers were washed several times with distilled water until neutral. Finally, the mats were dried at 80 °C for 12 h in vacuum oven. This whole procedure is well known as alkali treatment or mercerization.

Silane modification after mercerization of bamboo fiber: Silane coupling agent was added dropwise into ethanol/ water solution (silane:ethanol/water volume ratio 95:5).The pH must be maintained at 9.0 by using NaOH solution. The mixture was stirred for 30 min to confirm the hydrolysis process. Now the mercerized bamboo mat was added to it .The resulting suspension was dried at 70 °C for 1 h. After completion of the reaction, the mat was separated and dried at 80 °C for 24 h.

**Fabrication of chitosan reinforced UPE/ESOA/bamboo fiber hybrid composite:** Different matrix formulations using UPE/ESOA (80:20) blend, raw chitosan (5, 10, 15 wt%) and curing agent (3% MEKP (w/w) catalyst and 0.5% cobalt naphthanate (w/w) accelerator) on the basis of 3-layer bamboo mat were prepared. Initially, gel coat with 2 wt% DCP was homogeneously brushed in both the side of the mould. After 1 h, when curing of gel coat was finished, the layer of fiber was pre-impregnated with polymer matrix by hand layup technique. Care was taken to uniformly assign the fibers in the mould to produce a uniform sample. Then the mold was subjected to hot-press for 1 h at 110 °C with pressure of 5 tons.

**FTIR analysis:** FTIR spectra were collected using Thermo-Nicolate Model 400 instrument equipped with a controlled temperature cell (Model HT-32 heated demountable cell used with an Omega 9000-A temperature controller).

**SEM analysis:** SEM was utilized to qualitatively examine the microstructure of pure BisGMA and its blends. The samples were gold coated and examined using a Philips 420T scanning transmission electron microscope with a secondary electron detector, operating at 60 KV in the SEM mode.

**Tensile test:** The specimen size used for all the mechanical testing was  $12 \text{ mm} \times 10 \text{ mm} \times 3 \text{ mm}$ . The tensile test was conducted according to ASTM D790-03 standard. Tensile testing was carried out using Instron universal testing machine model 3369. Five specimens of each formulation were tested and average values were reported. Young's modulus and elongation at break tests were carried out according to ASTM D790-03 standard using the Kalpak universal testing machine. Five specimens of each formulation were tested and average values were reported.

**Dynamic mechanical analysis (DMA):** For this analysis, test specimens (56 mm × 13 mm × 3 mm) were cut from the center section of an ASTM Type I tensile bar. The dynamic mechanical properties like storage modulus and damping coefficient (tan  $\delta$ ) were evaluated using a DMA tester (Model Q800).

**Thermogravimetric analysis (TGA):** It was conducted on a Perkin-Elmer Series 7 thermal analyzer with an air purge in dry  $N_2$  atmosphere at a heating rate of 10 °C/min. The weight loss of the tested specimens was taken as a measurement for determining the function of temperature.

**Ageing studies:** The ageing of the blend was evaluated by keeping the samples immersed in water medium. Testing specimens (25 mm × 25 mm) were kept in distilled water at 25 °C for 30 days. The samples were taken out, dried at room temperature and their weights were taken.

#### **RESULTS AND DISCUSSION**

**Nomenclature and specification of hybrid biocomposites:** The nomenclature and abbreviation of chitosan reinforced UPE/ESOA/modified bamboo fiber hybrid biocomposites with varying content of filler loading are shown in Table-1.

Synthesis of chitosan reinforced UPE/ESOA/bamboo based hybrid biocomposites: The possible reaction mechanism for compatibility of chitosan reinforcing filler in the UPE/ESOA/ bamboo (both alkali treated and silane after alkali modified) hybrid composite are given in Figs. 1 and 2, respectively.

**FTIR analysis:** FTIR analysis of chitosan reinforced UPE/ ESOA/alkali modified bamboo and silane after alkali modified bamboo hybrid biocomposites have been shown in Figs. 3 and 4, respectively. Both figures showed common major FTIR band of hydroxyl group at 3475 cm<sup>-1</sup> and carboxyl group at 1750-1650 cm<sup>-1</sup> due to the chemical groups present in the UPE/ESOA blend. The peak observed at 3305 cm<sup>-1</sup> indicated the presence of NH *str*. band of amide. This unique band frequency confirms the successful reaction of secondary amide due to the interaction



 $UEB_ACS_{10} = UPE/ESOA/alkali treated bamboo with 5 wt% chitosan loaded biocomposite$  $<math>UEB_ACS_{10} = UPE/ESOA/alkali treated bamboo with 10 wt% chitosan loaded biocomposite$  $<math>UEB_{AS}CS_{5} = UPE/ESOA/alkali treated bamboo with 15 wt% chitosan loaded biocomposite$  $<math>UEB_{AS}CS_{5} = UPE/ESOA/alkali and silane treated bamboo with 5 wt% chitosan biocomposite$  $<math>UEB_{AS}CS_{10} = UPE/ESOA/alkali and silane treated bamboo with 10 wt% chitosan biocomposite$  $<math>UEB_{AS}CS_{15} = UPE/ESOA/alkali and silane treated bamboo with 10 wt% chitosan biocomposite$  $<math>UEB_{AS}CS_{15} = UPE/ESOA/alkali and silane treated bamboo with 15 wt% chitosan biocomposite$  $<math>UEB_{AS}CS_{15} = UPE/ESOA/alkali and silane treated bamboo with 15 wt% chitosan biocomposite$  $<math>UEB_{AS}CS_{15} = UPE/ESOA/alkali and silane treated bamboo with 15 wt% chitosan biocomposite$  $<math>UEB_{AS}CS_{15} = UPE/ESOA/alkali and silane treated bamboo with 15 wt% chitosan biocomposite$  $<math>UEB_{AS}CS_{15} = UPE/ESOA/alkali and silane treated bamboo with 15 wt% chitosan biocomposite$  $<math>UEB_{AS}CS_{15} = UPE/ESOA/alkali and silane treated bamboo with 15 wt% chitosan biocomposite$  $<math>UEB_{AS}CS_{15} = UPE/ESOA/alkali and silane treated bamboo with 15 wt% chitosan biocomposite$  $<math>UEB_{AS}CS_{15} = UPE/ESOA/alkali and silane treated bamboo with 15 wt% chitosan biocomposite$  $<math>UEB_{AS}CS_{15} = UPE/ESOA/alkali and silane treated bamboo with 15 wt% chitosan biocomposite$  $<math>UEB_{AS}CS_{15} = UPE/ESOA/alkali and silane treated bamboo with 15 wt% chitosan biocomposite$  $<math>UEB_{AS}CS_{15} = UPE/ESOA/alkali and silane treated bamboo with 15 wt% chitosan biocomposite$  $<math>UEB_{AS}CS_{15} = UPE/ESOA/alkali and silane treated bamboo with 15 wt% chitosan biocomposite$  $<math>UEB_{AS}CS_{15} = UPE/ESOA/alkali and silane treated bamboo with 15 wt% chitosan biocomposite$  $<math>UEB_{AS}CS_{15} = UPE/ESOA/alkali and silane treated bamboo with 15 wt% chitosan biocomposite$  $<math>UEB_{AS}CS_{15} = UPE/ESOA/alkali and silane treated bamboo with 15 wt% chitosan biocomposite$ 



Fig. 1. Possible chemical interaction of UPE/ESOA blends with chitosan and alkali treated bamboo fiber

among the NH<sub>2</sub> groups of chitosan with -OH group of blend. Again, a stake shaped peak present at 1655 cm<sup>-1</sup> correspond to the C=O group of -NHCO- group. For NH bending, a peak is observed at 1580 cm<sup>-1</sup>. A peak is also observed at 1160 cm<sup>-1</sup> assigned as the C-O-C ester group formed due to the reaction of chitosan with the alkali modified bamboo fiber. All these peaks are observed with the peaks of UPE/ESOA blend and confirmed the possibility of the reaction. In Fig. 4 some peaks are observed at 1035 and 1140 cm<sup>-1</sup>, which are associated with Si-O-Si and Si-O-C stretching vibrations, respectively. This indicated the effective reaction between the chitosan group and the silane after alkali modified bamboo fiber biocomposite.

## Properties of hybrid biocomposites

**Tensile and flexural strength:** The assessments of mechanical characteristics have been discussed here in connection with the alterable proportion of chitosan biofillers in the alkali

and silane after alkali treated bamboo reinforced UPE/ESOA hybrid biocomposite. Table-2 represented the overall improvement in the evaluations of tensile and flexural strength with the addition of chitosan into the prepared biocomposites. Chitosan effectively reacted with the UPE/ESOA blend as well as with differently modified fibers. So, chitosan operated as the support that can withstand optimum load by empowering effective interfacial pressure exchange and acted as the medium to enhance the strength of the biocomposite. Initially, at 5 wt% of chitosan content the biocomposites showed better tensile and flexural properties than the hybrid composite without chitosan reinforcement. But, the rising pattern is observed up to 10 wt% of chitosan biofillers loading for both the modified fiber reinforced biocomposites and after which the properties degrade. At the maximum filler concentration of (15 wt%), chitosan cannot scatter satisfactorily in the network on account of their high interfacial energy and agglomeration tendency



Fig. 2. Possible chemical interaction of UPE/ESOA blends with chitosan and silane after alkali treated bamboo fiber



Fig. 3. FTIR of chitosan reinforced UPE/ESOA/alkali treated bamboo biocomposite

to produce large cluster like structure. It is only due to the nonuniform scattering of the filler particles in the matrix network that causes a lessening in the estimations of elasticity and flex-



Fig. 4. FTIR of chitosan reinforced UPE/ESOA/alkali and silane treated bamboo biocomposite

ural quality. The enhanced property of the biocomposites up to a certain level might be attributed to particular interactions like hydrogen bonding and dipole-dipole associations among the molecules of the constituent polymers [10].

TABLE-2 TENSILE AND FLEXURAL PROPERTIES OF THE BIOCOMPOSITES						
Materials -	Tensile properties			Flexural properties		
	Stress (MP)	Strain (%)	Modulus (GP <sub>a</sub> )	Stress (MP <sub>a</sub> )	Strain (%)	Modulus (GP <sub>a</sub> )
UEB <sub>A</sub> CS <sub>5</sub>	$82 \pm 2$	$2.0 \pm 0.1$	$3.92 \pm 0.1$	91 ± 3	$2.06 \pm 0.3$	$4.45 \pm 0.3$
UEB <sub>A</sub> CS <sub>10</sub>	$108 \pm 4$	$1.5 \pm 0.2$	$6.91 \pm 0.3$	$112 \pm 2$	$1.92 \pm 0.2$	$5.75 \pm 0.1$
UEB <sub>A</sub> CS <sub>15</sub>	$78 \pm 4$	$1.7 \pm 0.3$	$4.32 \pm 0.2$	85 ± 4	$1.63 \pm 0.3$	$5.32 \pm 0.1$
UEB <sub>AS</sub> CS <sub>5</sub>	$102 \pm 3$	$1.1 \pm 0.2$	$5.90 \pm 0.1$	$114 \pm 2$	$1.44 \pm 0.2$	$7.83 \pm 0.2$
UEB <sub>AS</sub> CS <sub>10</sub>	$120 \pm 2$	$1.9 \pm 0.2$	$7.21 \pm 0.2$	$128 \pm 2$	$1.59 \pm 0.2$	$8.12 \pm 0.1$
UEB <sub>AS</sub> CS <sub>15</sub>	85 ± 3	$1.49 \pm 0.3$	$5.85 \pm 0.3$	$106 \pm 3$	$1.54 \pm 0.2$	$6.86 \pm 0.3$

Among all of the biocomposites, UEBASCS10 gave better tensile and flexural properties may be due to better coordination between the silane after alkali modified fiber, filler and the UPE/ESOA blend. It is due to improved roughness of the fibers by the presence of polysiloxane groups. As a result of which a good reaction occurred between the silane treated fiber, chitosan filler and UPE/ESOA blend.

Impact strength and fracture strain: The influence of chitosan biofillers on the impact strength and fracture strain of UPE/ESOA blended matrix based bamboo fiber reinforced hybrid composites is given in Table-3. The outcomes proposed an improvement in the properties with the addition of this chitosan reinforcing filler into the hybrid biocomposite. But the biocomposites achieved the maximum result up to 10 wt% of filler. The fundamental factors for this improvement may be due to the regular dispersion of filler particles on the surface of modified bamboo fibers and UPE/ESOA blend. At 5 wt% of biofillers content, the quantity is very less to disperse uniformly on the surface. But at this concentration the biocomposites showed better fracture and impact properties than the corresponding composite without chitosan reinforcement. At 10 wt% of the fillers concentration, the fiber surface has been covered by properly distributed fillers. The reduction in the properties at 15 wt% might be attributed to the nucleation of filler.

TABLE-3 FRACTURE STRENGTH AND IMPACT STRENGTH OF THE BIOCOMPOSITES				
Composites	Fracture strain (%)	Impact strength (J/m)		
UEB <sub>A</sub> CS <sub>5</sub>	$5.07 \pm 0.3$	$90.3 \pm 3$		
UEB <sub>A</sub> CS <sub>10</sub>	$6.72 \pm 0.2$	$98.3 \pm 2$		
UEB <sub>A</sub> CS <sub>15</sub>	$4.92 \pm 0.4$	$81.6 \pm 2$		
UEB <sub>AS</sub> CS <sub>5</sub>	$6.12 \pm 0.2$	$117.8 \pm 4$		
UEB <sub>AS</sub> CS <sub>10</sub>	$7.23 \pm 0.3$	$147.8 \pm 6$		
UEB <sub>AS</sub> CS <sub>15</sub>	$4.17 \pm 0.2$	$102.6 \pm 4$		

So, the brittle and crystalline nature of such class of hybrid biocomposites encourages the reduction of free movement of molecules present in the polymeric backbone. This trend may cause micro-cracks while impact occurs, forming easy crack proliferation. Moreover, the larger agglomeration tendency of chitosan can make the mechanical properties of the hybrid biocomposites crumble [11].

Dynamic mechanical analysis: Dynamic mechanical spectral properties as the plots of storage modulus and loss modulus (tan  $\delta$ ) by taking temperature as a function are represented in Fig. 5a and 5b, respectively. An enhanced pattern of storage modulus of the biocomposites was noticed with the introduction of varying content of chitosan filler and differently modified bamboo fibers. Around 7% improvement in the storage modulus was observed in case of UEBACS10 biocomposite at glassy state region as compared to the 5 wt% of chitosan filler reinforced biocomposites (UEBACS5). It indicated a good interaction of chitosan with the UPE/ESOA blend and the alkali modified fiber surface, which can tolerate higher stress applied at the interfacial point because of the increase in rigidity, uniformity in dispersion and decrease in the mobility of polymer chain. It is found that the storage modulus declines with gradual enhance in the temperature for all the composites because of the enhanced kinetic energy and decreased in crosslink density of the molecules in the polymeric chain. The biocomposite with 15 wt% of chitosan content (UEBACS15) showed reduced storage modulus as well as lower T<sub>g</sub> than the 10 wt% chitosan filled biocomposite (UEBACS10) because of the particle agglomeration that resulted in the less energy absorption by polymer molecules to travel freely. Such type of effects also happened with the chitosan filled silane after alkali treated bamboo fiber reinforced UPE/ESOA hybrid composites. But the highest Tg of 155 °C is observed for UEBASCS10 composite due to balanced confinement effect and curing reaction. Due to the highest mechanical properties of UEBASCS10 biocomposite, it showed the maximum storage modulus and glass transition temperature. This composite showed about 30% increased storage modulus than the corresponding UEBACS10 biocomposite and around 5% enhanced value than the UEBASCS5 biocomposite. These actions indicated the hydrophobic character of Si-O-Si linkage and successful elimination of celluloses that improved the association between the silane after alkali modified bamboo fiber, chitosan filler and UPE/ESOA blend with no interfacial voids. Again, the balanced distribution and proper orientation



Fig. 5. DMA analysis of the fabricated biocomposites with chitosan reinforce

of the chitosan filler restricted the chain segmental mobility due to successful formation of new cross-linking bonding between the different components of the biocomposites with no free space availability.

Tan  $\delta$  is independent of the hardness of composite and used to study the viscoelastic response of the materials. The variation of tan  $\delta$  with different concentration of chitosan biofillers are depicted in Fig. 5b. The peak height and width in tan  $\delta$  give details about relaxation behavioor of composites. With the introduction of chitosan filler the  $T_g$  increased slowly. Both the composites showed more  $T_g$  value at 10 wt% of chitosan filler than their corresponding 5 wt% based biocomposites. Again, the T<sub>g</sub> value increased additionally in case of the silane modified bamboo reinforced composite given in Table-4. The peak intensity of tan  $\delta$  is reduced as the same order of storage modulus of the composite. Lowest peak and highest Tg of UEBASCS10 biocomposite was observed due to highest bending resistance, better adhesion and segmental immobilization of the matrix and fiber. The practical increase in the storage modulus value with a positive shifting of tan  $\delta$  peaks towards the larger temperature region indicates an increased bending resistance of fabricated samples.

TABLE-4 DYNAMIC MECHANICAL ANALYSIS (DMA) DATA OF THE BIOCOMPOSITES WITH CHITOSAN REINFORCEMENT				
Composites	Storage modulus (E' = MPa)	$T_{g}$ (°C)	Maximum Tan δ	
UEB <sub>A</sub> CS <sub>5</sub>	4795	120	1.20	
UEB <sub>A</sub> CS <sub>10</sub>	5052	126	0.97	
UEB <sub>A</sub> CS <sub>15</sub>	4912	114	1.03	
UEB <sub>AS</sub> CS <sub>5</sub>	6776	132	1.12	
UEB <sub>AS</sub> CS <sub>10</sub>	7012	155	0.55	
UEB <sub>AS</sub> CS <sub>15</sub>	6030	148	0.59	

**Thermal analysis:** Fig. 6 showed the thermograms of the chitosan reinforced biocomposites and the relevant data are summarized in Table-5. Reinforcement of chitosan biofillers and modified fibers has significant consequence on this property as coordination of them with the polymeric matrix have very important role to determine the thermal degradation of a comp-

osite. The thermogram shows only one stage decomposition because the T<sub>g</sub> curves have only one large plateau. The initial step weight loss is because of the moisture loss and the loss of low molecular weight compound and the second stage degradation occurred in the temperature ranging from 500 to 650 °C for the entire hybrid biocomposites. It may be due to the whole degeneration of chitosan fillers, fibers and polymeric matrix. This thermal behaviour of hybrid biocomposites can successfully determined from the values of onset temperature, ending temperature and the residual weight % denoted as the char. Introduction of both biodegradable fillers and modified bamboo fibers helped to improve the overall thermal stability of the UPE/ESOA blend. Weight loss at this particular temperature reduces for reinforcement of 15 wt% chitosan than that of 5 wt% of chitosan. Because for both type of biocomposites, aggregation of filler have been occurred at 15 wt% chitosan concentration. Again, 5 wt% chitosan concentration was very less to affect the thermal properties of the biocomposite. So, UEBASCS10 sample has showed highest degradation value of 675 °C due to the introduction of uniformly distributed chitosan biofillers that reacted effectively with both the silane treated bamboo fibers and the UPE/ESOA blend based matrix. As a result of which, a covering layer of hydrogen and covalent bond was formed on the surface and indicated effective interaction among the three phases (filler, fiber and polymer matrix). Existence of this uniformly distributed layer of chitosan filler helped the biocomposites to decompose at a higher temperature by enhancing the overall thermal stability as compared to the hybrid composites without filler.

TABLE-5 THERMOGRAVIMETRIC ANALYSIS OF THE FABRICATED BIOCOMPOSITES WITH CHITOSAN REINFORCEMENT					
Composites	Onset (°C)	T <sub>50%</sub> (°C)	Endset (°C)	Char yield (%)	
UEB <sub>A</sub> CS <sub>5</sub>	475	550	675	52.35	
UEB <sub>A</sub> CS <sub>10</sub>	502	605	702	67.33	
UEB <sub>A</sub> CS <sub>15</sub>	410	515	662	48.87	
UEB <sub>AS</sub> CS <sub>5</sub>	508	652	732	72.28	
UEB <sub>AS</sub> CS <sub>10</sub>	522	675	755	89.21	
UEB <sub>AS</sub> CS <sub>15</sub>	498	634	705	65.15	



Fig. 6. (a) TGA and (b) DTG of chitosan reinforced biocomposites

Again the char content of UEBASCS10 hybrid biocomposite was turned to 89% and confirmed the flame retardancy of the system and represented an excellent correlation between the thermal stability and char yield. It may be due to the significant effect of better interaction between the chitosan filler and modified bamboo fiber with the matrix, which prevented the segmental motion of chain.

Ageing properties: Generally, both the chitosan filler and bamboo fiber are prone to moisture, as they are biodegradable in nature. So, the biocomposites specimens were undergone water absorption study to determine their usefulness in day to day purposes. A deviation in the mass of biocomposites after going through the water medium has been shown in Table-6. Chitosan reinforced alkali treated bamboo based biocomposites displayed a little weight gain. However, it was noticed that the prepared biocomposites indicated minimum weight change than the corresponding raw bamboo based UPE/ESOA composites. It is because raw bamboo is extremely hydrophilic due to the presence of groups like celluloses, hemicelluloses, lignin, etc. In addition, for alkali treated bamboo based biocomposites the change in weight increased with the enhancement in the chitosan content. This might be because of the hydrophilic nature of chitosan filler. Also, when ageing characteristic was considered, the alkali treatment may not give better bonding with the filler and blend. But in case of UEBASCS biocomposites at 10 wt% of chitosan content the value came to minimum. It may be the result of effective interaction among the polymer resin, filler and fiber reinforcement. The presence of polysiloxane groups made the surface of the silane after alkali treated bamboo fiber more hydrophobic, rough and crystalline. So, it can successfully bind the chitosan filler and UPE/ESOA blend on its surface. Improved coordination cannot allow the water molecules to enter into the surface. Again, with enhanced chitosan content up to 15 wt% (UEBASCS15), the water takeup increased. This is based on the fact that with increase in filler concentration, voids are created on the biocomposite surface due to the agglomeration of filler. Generally, water packed voids create a possibility of interfacial de-holding at the surface. This generates micro-cracks on the interface of the biocomposites. When water enters within the biocomposites materials, chitosan begins to swell and the polymer matrix undergoes reorientation by bringing about weak mechanical properties.

TABLE-6 AGEING STUDIES OF CHITOSAN REINFORCED BIOCOMPOSITES				
Hybrid biocomposites	Water absorption (%)			
UEB <sub>A</sub> CS <sub>5</sub>	0.62			
$UEB_ACS_{10}$	0.37			
UEB <sub>A</sub> CS <sub>15</sub>	0.71			
UEB <sub>AS</sub> CS <sub>5</sub>	0.35			
UEB <sub>AS</sub> CS <sub>10</sub>	0.23			
UEB <sub>AS</sub> CS <sub>15</sub>	0.58			

**Chemical resistance studies:** Interfacial properties of a composite are one of the imperative properties as it is associated with the surface qualities. The capacity of biocomposites to withstand chemical environment, for example, acidic, basic and solvent were examined and the outcomes are presented in

Table-7, which clearly demonstrated that all the fabricated composites indicate least weight reduction. The biocomposites showed a minimum solvent take-up or enhanced chemical opposition. The introduction of biochitosan as reinforcing filler improved the interfacial bonding among filler, fiber and blend bringing about lesser chance of void formation. This enhanced adhesion further increases with filler loading which creates an unmovable polymeric environment around the filler. These parameters offer higher protection to the biocomposites framework from the entrance of solvent molecules into their network. Controlled equilibrium method has been utilized as an effective technique by numerous scientists to examine the characteristics of filler, fiber and polymer matrix in the biocomposites systems [12,13]. The solvent up taken by biocomposites systems decreased with enhanced filler concentration and reached at lower value at 10 wt% of chitosan loading. But the presence of voids in UEBASCS15 sample speeds up the solvent flow towards the matrix system by making the composite inappropriate for any structural field applications. Therefore, interfacial connection brings about lower dissolvable take-up by composites frameworks. Along these lines, the solvent take-up by composites frameworks diminished with enhanced biofillers concentration and achieves least value at 15 wt% chitosan content.

TABLE-7 CHEMICAL RESISTANCE STUDIES OF CHITOSAN REINFORCED BIOCOMPOSITES					
Hybrid biocomposites	HNO <sub>3</sub>	NaOH	$H_2O$	$\text{CCl}_4$	
UEB <sub>A</sub> CS <sub>5</sub>	1.560	0.834	0.621	0.176	
UEB <sub>A</sub> CS <sub>10</sub>	0.823	0.562	0.368	0.132	
UEB <sub>A</sub> CS <sub>15</sub>	1.445	0.923	0.726	0.189	
UEB <sub>AS</sub> CS <sub>5</sub>	0.735	0.325	0.349	0.127	
UEB <sub>AS</sub> CS <sub>10</sub>	0.324	0.124	0.227	0.018	
UEB <sub>AS</sub> CS <sub>15</sub>	0.958	0.204	0.578	0.138	

#### Conclusion

This work described the proper utilization of chitosan waste biofillers by introducing it in UPE/ESOA blend based matrix and surface modified bamboo fibers. Actually biocompatible filler materials have achieved a good deal concentration due to their ability to gain properties higher than the original polymer. The fillers have the potency to achieve better distribution with improved interfacial adhesion to the matrix and modified fibers to enhance the overall required properties. The chitosan biofillers positively improve the properties that represented minimum formation of microcracks with improved wetting properties particularly when they are used in hybrid form. The studies discovered that the biocomposites have a great deal of application in various engineering and structural fields. However, a variety of other aspects such as effect of various chemicals on the biocomposite, thermal stability and ageing properties have proved its candidature for a promising future material.

## **CONFLICT OF INTEREST**

The authors declare that there is no conflict of interests regarding the publication of this article.

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