

## Mechanical Properties of Surface-Treated Banana Fiber/Polylactic Acid Biocomposites: A Comparative Study of Theoretical and Experimental Values

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**ABSTRACT:** Current study evaluates the effect of fiber surface treatments on the mechanical properties of banana fiber (BF) reinforced polylactic acid (PLA) biocomposites. Experimental results indicate increase in tensile modulus and strength upon surface treatments of BF with various silanes (APS and Si69) and NaOH. Approximately, an increase of 136% in tensile strength and 49% in impact strength was obtained in case of biocomposites with Si69-treated BF compared with the untreated BF biocomposites. Also, experimentally determined mechanical modulus of untreated and surface-treated BF biocomposite has been compared with the mechanical modulus calculated using various micromechanical models. Models such as Hirsch's, modified Bawyer and Bader's, and Brodnyan model showed good agreement with the experimentally determined results. Similarly, other models like Halpin-Tsai, Nielson modified Halpin-Tsai, and Cox's model also have been tried for the comparative study with the experimental data. Surface modification of BF showed increased interfacial adhesion between the fiber and the matrix which was evident from lowered difference between the experimentally and theoretically derived mechanical modulus. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** PLA; banana fiber; Si69; Brodnyan model

Received 27 May 2011; accepted 22 April 2012; published online

DOI: [10.1002/app.37978](https://doi.org/10.1002/app.37978)

### INTRODUCTION

Fiber reinforced composites widely substitute conventional materials for numerous structural applications like automotive, aerospace, constructions, etc.<sup>1–5</sup> Aiming good mechanical properties and reduced cost of final products, fibers like glass, aramid, carbon, etc. extensively use as reinforcement within various polymeric matrices for last few decades.<sup>6,7</sup> Currently, growing environmental awareness and new rules and regulations forces to divert the research interests for searching, alternative ecofriendly solutions for polymers based utilities. In this view, developing ecofriendly materials based upon renewable resource based matrices and fillers grabs much attention recently. Natural fibers from sisal, banana stem and leaf, pine apple leaf fiber (PALF), jute, flax, coconut, etc. already established as good reinforcing materials for polymer matrices.<sup>8–14</sup> Their renewable origin, together with ecofriendly characteristics, relatively high strength and modulus, light weight, and low price are the potential advantages of the natural fiber reinforced polymer composites.<sup>15–18</sup>

However, these composites can easily undergo various damage phenomenons such as matrix cracking, interfacial debonding,

fiber pull outs, and fracture. Prediction of such kind of damage possibilities is very much important to propose these materials for various end use applications. In this view, adequate knowledge about the factors which cause such kind of damage phenomenon is prerequisite for designing them for specific applications. Predominant damage mechanism may vary according to fiber volume fraction and aspect ratio, orientation and distribution in the composite, strength of the interface and each constituent and loading mode. Hence to estimate the overall response of the composites, all the above-mentioned micromechanical phenomenons have to keep in consideration. However, due to the complexity of the microstructure, the damage mechanisms in the fiber reinforced polymer composites are least understandable from the experimental point of view. For this purpose, micromechanical analysis using various mathematical models can use as to simulate the damage response in randomly oriented fiber reinforced composites.<sup>19</sup>

Einstein's equation for predicting the mechanical properties is one of the most utilized micromechanical model in this area of study. Further, many workers modified Einstein's equation

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according to the modern demands and present conditions. Nielsen and Landel proposed a micromechanical analysis to predict the elastic modulus and the strength of a random fiber reinforced composites, based up on Halpin-Tsai analysis.<sup>20</sup> Similarly, Meraghni and Benzeggagh identified damage mechanism in randomly oriented discontinuous fiber reinforced composite through a micromechanical analysis based on a modified version of the Mori-Tanaka model.<sup>21</sup>

In the present investigation, a comparative study in between experimentally determined mechanical properties of banana fiber (BF) reinforced polylactic acid (PLA) biocomposites with suitable micromechanical models have been conducted. In the area of synthetic polymer/natural fiber composites, such kinds of studies were reported by various scientists. Prediction and comparative studies of tensile modulus and tensile strength of PP/sisal fiber composite have been reported by Kalaprasad et al.<sup>22</sup> The author predicted that the micromechanical models like Hirsch's model and modified Bowyer and Bader's model are suitable to predict the tensile modulus of such composites with high level of accuracy. Amirhossain reported effective application of modified Halpin-Tsai analysis to predict the tensile modulus of PP/jute and PP/glass fiber composites.<sup>23</sup> Wirawan et al. also reported similar kind of application of modified Halpin-Tsai analysis to predict the tensile modulus of PVC/natural fiber composites.<sup>24</sup> In the present investigation micromechanical models like Hirsch's model, modified Bowyer and Bader's model, Cox's model, Halpin-Tsai, Nielson-modified Halpin-Tsai and Brodnyan models have been used to predict tensile modulus of BF-reinforced PLA biocomposites. The work also comprises the effect of surface treatments of BF on mechanical properties of the biocomposites. A detailed analysis of a comparative study of variation in the mechanical behaviour of PLA-BF interface after various surface treatments with the help of above-mentioned micromechanical models also has been encompassed in the present investigation. Surface-treated BFs such as mercerized BF (Na-BF), aminopropyltriethoxysilane (APS)-treated BF (APS-BF), and *bis*-(3-triethoxy silyl propyl)tetrasulfane (Si69-BF) have been utilized for the comparative study along with untreated BF (UBF).

## THEORY

In the current study, the biocomposite system that has been studied belongs to the category of rigid reinforcement i.e. particulate and fibrous; within a rigid polymer matrix. Based on this, the following theories have been successfully studied for PLA/BF biocomposite system.

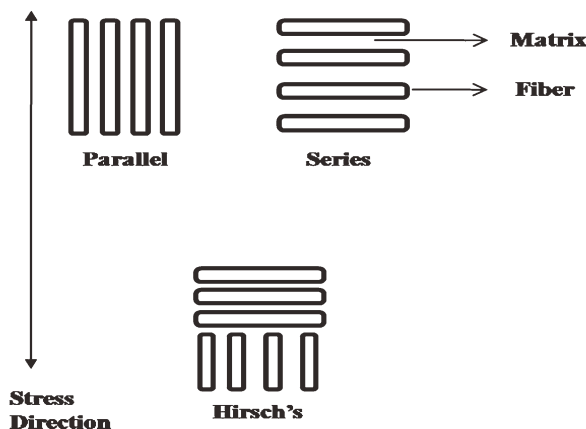
### Hirsch's Model

Hirsch's model is a modified form of parallel and serial model. According to the parallel model, elastic modulus and strength can be calculated using the following equation.

$$M_c = M_f V_f + M_m V_m \quad (1)$$

$$T_c = T_f V_f + T_m V_m \quad (2)$$

Where  $M_c$ ,  $M_m$ , and  $M_f$  are the Young's modulus of the composite, matrix and fiber and  $T_c$ ,  $T_f$ , and  $T_m$  are tensile strength of the composite, fiber, and matrix, respectively. Here in this



**Figure 1.** Schematic representation of stress distribution in Hirsch's, Parallel and series model.

model, an isostrain condition has been assumed for both matrix and fiber. But according to series model, a uniform distribution of stress has been assumed in the composite system and proposed equation for modulus and strength are as follows.

$$M_c = M_m M_f / (M_m V_f + M_f V_m) \quad (3)$$

$$T_c = T_m T_f / (T_m V_f + T_f V_m) \quad (4)$$

Both the above conditions have to be taken into consideration in case of a randomly oriented fiber reinforced composite. In such a case, Hirsch's model has been reported to predict the properties with better precision. Schematic representation of stress distribution in Hirsch's, Parallel and serial model have been given in Figure 1.

The tensile modulus and strength using Hirsch model can be calculated as follows,

$$M_c = x(M_m V_m + M_f V_f) + (1 - x) \cdot (M_f M_m / [M_m V_f + M_f V_m]) \quad (5)$$

$$T_c = x(T_m V_m + T_f V_f) + (1 - x) \cdot (T_f T_m / [T_m V_f + T_f V_m]) \quad (6)$$

The value "x" is a main determining factor in describing the actual behavior of short fiber composites. The factor actually determines the stress transfer between the fiber and the matrix. The value of "x" mainly depends on fiber orientation, fiber length and stress amplification effect of the fiber ends.

### Cox's Model

Cox proposed the following micromechanical models for calculating tensile modulus and strength. The theory has been derived on the basic assumption that an elastic nature in mechanical response in the composite system. Further, a perfect fiber-matrix interface has been assumed where no axial load is transmitted through the fiber ends.

$$M_c = M_f V_f [1 - (\tan \delta \beta 0.5 / \beta 0.5)] + M_m V_m \quad (7)$$

where  $\beta = [2\Pi G_m / (M_f A_f \ln(R/r))] 0.5$

$M_m$  and  $M_f$  are the Young's moduli of matrix and fiber, "r" is the radius of the fiber,  $G_m$  is the shear modulus of the matrix,

$R$  is the center to center distance of the fibers, and  $A_f$  is the area of the fibers.

The value of  $R$  can be calculated as given below:

$$R = [2\Pi r^2 / 30.5 V_f]^{0.5} \quad (7a)$$

for hexagonally packed fibers

$$R = r[\Pi / 4 V_f]^{0.5} \quad (7b)$$

for square packed fibers

$A_f$  the surface area of fiber has been calculated based up on one of the basic assumption that the BF fillers are cylindrical in shape.

According to Cox's model, tensile strength  $T_c$  is given by

$$T_c = T_f V_f [1 - (\tan \delta \beta 0.5 / \beta 0.5)] + T_m V_m \quad (8)$$

A graphical representation of the fiber matrix interface by Cox's is shown in Figure 2.

#### Modified Bowyer and Bader's Model (MBB)

This model proposed that the tensile strength of short fiber-reinforced thermoplastic composite is the sum of contributions from subcritical and super-critical fibers and also from the matrix.

Tensile strength is given by

$$T_c = T_f K_1 K_2 V_f + T_m V_m \quad (9)$$

Where,  $K_1$  is the fiber orientation factor which is depending upon the fiber orientation.  $K_2$  is known as fiber length factor and for fibers with  $l > l_c$

$$K_2 = l - (l_c / 2l) \quad (9a)$$

For fibers with  $l < l_c$

$$K_2 = l / 2l_c \quad (9b)$$

where  $l$  is the length of the fiber and  $l_c$  is the critical length of the fiber. The tensile modulus can be calculated using the following equation

$$M_c = M_f K_1 K_2 V_f + M_m V_m \quad (10)$$

#### The Halpin-Tsai Model (H-T)

It is one of the most widely used micromechanical model to predict the properties of fiber reinforced composites with polymer matrix. This model has been successfully used for polymer blends as well as composites. The model predicts the properties of composite in accordance with the individual properties of matrix and filler along with the factor "A" which particularly determines the fiber geometry, its distribution and loading conditions.

$$M_c = M_m [(1 - A\eta V_f) / (1 - \eta V_f)] \quad (11)$$

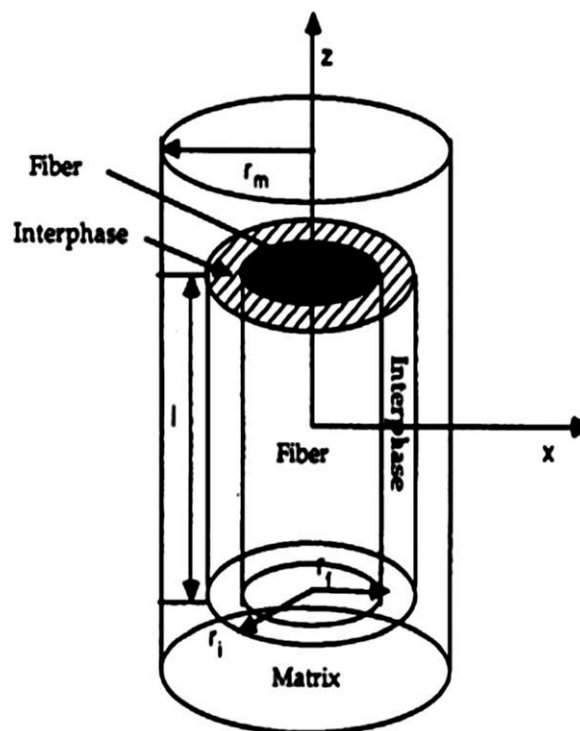


Figure 2. Graphical representation of the fiber matrix interface by Cox.

where  $\eta = [(M_f / M_m) - 1] / [(M_f / M_m) + A]$

$$T_c = T_m [(1 - A\eta V_f) / (1 - \eta V_f)] \quad (12)$$

where  $\eta = [(T_f / T_m) - 1] / [(T_f / T_m) + A]$

"A" can be determined from the Einstein coefficient  $k$  as per the study conducted by Amirhossain.<sup>23</sup>

$$A = k - 1$$

Einstein's coefficient "k" value can be determined from the  $l/d$  ratio of the filler.

$$k = l + (2l/d)$$

#### Nielson Modified Halpin-Tsai Model

Giving more importance to the nature of packing of filler in the matrix, Nielson modified H-T equation by including " $\psi$ " which depends upon the filler packing fraction. As per his modified equations, the properties can be predicted as below.

$$M_c = M_m [(1 + A\eta V_f) / (\eta \psi V_f)] \quad (13)$$

$$T_c = T_m [(1 + A\eta V_f) / (\eta \psi V_f)] \quad (14)$$

$$\Psi = 1 + (1 - \varphi_{\max}) V_f / \varphi_{\max}^2$$

$$A = K - 1$$

$$K = 1 + (2l/d)$$

Here the  $\varphi_{\max}$  is the maximum packing fraction and its values were predicted by Nielson according to the orientation of the filler in the matrix. For square arrangement of filler, it will be

0.785, 0.907 for hexagonally oriented arrangement and in case of random packing of filler, composite value of  $\varphi_{\max}$  will be 0.82.

### Brodnyan Model

Mooney equation (1951) for the prediction of elastic modulus of composites has been derived from the Einstein equation.

$$M_c = M_m \exp[k V_f / (1 - V_f / \varphi_m)] \quad (15)$$

The Mooney equation modified by Brodnyan by incorporating the aspect ratio of the particulate. According to Brodnyan model, the  $\alpha$  value have to be greater than 1 and less than 15 for nonspherical particulate. According to him,

$$M_c = M_m \exp[(2.5 V_f + 0.407(\alpha - 1)1.508 V_f) / (1 - V_f / \varphi_m)] \quad (16)$$

$$T_c = T_m \exp[(2.5 V_f + 0.407(\alpha - 1)108 V_f) / (1 - V_f / \varphi_m)] \quad (17)$$

## MATERIALS AND METHODS

### Materials

Poly(lactic acid (V-PLA) (Grade 4042D) with a density of 1.24 g/mL, melt flow index (MFI) between 1 and 2 g/10 min(190°C, 2.19 kg),  $M_w = 110,000$  g/mol and  $M_w/M_n = 2.1$ , L-lactide and D-lactide ratio 92 : 8, was purchased from M/s Nature-works. Banana fiber (BF, *Musa sepentium*) obtained from M/s Tripura Mushroom Growers welfare Society, Tripura, with a density of 1.35 g/mL was used as reinforcement; 3-aminopropyltriethoxysilane (APS) was supplied by M/s Aroma Chemical Agencies Pvt., India, and bis-(3-triethoxy silyl propyl) tetrasulfane (Si69) obtained from M/s Sigma Aldrich Co., Germany, has been used as surface modifying agents for banana fiber. All other chemicals and reagents of AR grade were collected from M/s Merck Specialties Pvt., Mumbai, India.

### Methods

**Surface Treatment.** Banana fibers, in the form of bundles were cut into length of 13 to 15 cm, and scoured in mild detergent solution at 60°C for about 2 hr to remove dust and other impurities. Finally the fibers were washed in distilled water and dried in air for 2 days.

**Mercerization.** Mercerization of the BF was carried out by immersing the fibers in 1(N) NaOH solution for 1 hr at room temperature. The fibers were then washed with distilled water containing few drops of acetic acid, followed by washing under continuous stream of water until complete removal of NaOH. Subsequently, the mercerized fibers were dried at room temperature for 24 hr and then in a vacuum oven at 80°C for 12 hr, for further studies.

**Silane treatment.** Respective silane coupling agent (5 wt %) [3-amino propyltriethoxysilane (APS) or bis-(3-triethoxysilylpropyl)-tetrasulfane (Si69)] with respect to the weight of fibers has been taken in a mixture of water-ethanol (40 : 60 w/w) system. The pH of the solution was adjusted to 4 with acetic acid and stirred continuously during 1 hr. Then the detergent treated banana fiber was soaked in the above prepared solution for 3 hr and washed with distilled water and dried in air for 2 days followed by vacuum drying for about 12 hr at 80°C.

All the treated fibers were chopped using an electronic fiber cutting machine to short fiber of length 2 to 3 mm, for composite fabrication and characterization. Cutting of the treated BFs has been done only after the surface treatments and proper drying to avoid the agglomeration of short fibers.

**Preparation of Biocomposite.** Before compounding, treated or untreated banana fibers and PLA were predried at 80°C in a vacuum oven at 700 mm of Hg for 12 hr. Subsequently, the fibers and PLA matrix were melt blended in a batch mixer (Haake Rheomex OS, Germany) at various weight % (10%, 20%, 30%, 40%), respectively. The above weight percentages are mentioned in the discussion in terms of volume fractions also. Volume fractions of matrix and BF have been calculated from the respective densities of the components as mentioned in the material section. Based on this the volume fractions of BF were calculated as 0.09, 0.18, 0.28, and 0.38, respectively for 10%, 20%, 30%, and 40% by weight of fiber loading. The mixing was carried out at 180°C with a rotor speed of 40 rpm for 10 min. The melt mixed biocomposite obtained, were cooled to room temperature, granulated, and conditioned at 80°C for 2 hr before specimen preparation. Finally compression molded sheets of  $3 \pm 0.1$  mm thickness were prepared using a 80T compression press (M/s Neoplast, Mumbai) at 190°C, 80 kg/cm<sup>2</sup> pressure over a total cycle time of 15 min. Specimens were prepared from these sheets as per various ASTM standards using a count cut copy milling machine (M/s Ceast, Italy).

**FTIR Spectroscopy.** FTIR spectra of untreated and various surface treated BF have been taken to confirm surface modification of banana using an FTIR spectroscope NICOLET 6700, within a scanning range of 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> and a scanning resolution of 60 cycles.

**Mechanical Testing.** The tensile measurements of untreated and treated banana fibers and various biocomposites were carried out in Universal Testing Machine (Instron 3386, UK). For fiber testing tension grips of gauge length 30 mm and cross head speed of 1 mm/min as per ASTM D 3822-07, were employed. In case of biocomposites, dumbbell-shaped specimens of dimension 165 × 12.7 × 3 mm as per ASTM D 638 have been used. The gauge length was fixed at 50 mm with a cross head of 5 mm/min for conducting the test.

Specimens of dimension 63.5 × 12.7 × 3 mm have been taken for measurement of impact test in an impact tester (M/s Ceast, Italy) as per ASTM D 256. The specimens were notched at angle of 45° and depth of 2.54 mm using notch cutter (M/s Ceast, Italy) before test. For all the compositions a minimum of five specimens were used for tensile and impact analysis and the data reported are from the average of five.

**Dynamic Mechanical Analyzer (DMA).** A dynamic mechanical analyzer (Q800, M/s TA Instruments) was employed for measuring viscoelastic properties of PLA and the biocomposites. Samples of dimension 63.5 × 12.7 × 3 mm were used for testing under a temperature range of 40 to 140°C and a fixed frequency of 1 Hz.

**Scanning Electron Microscopy (SEM).** The SEM of tensile fractured composite specimens were carried out using Zeiss EVO MA, UK Instrument. The samples were coated with gold using a

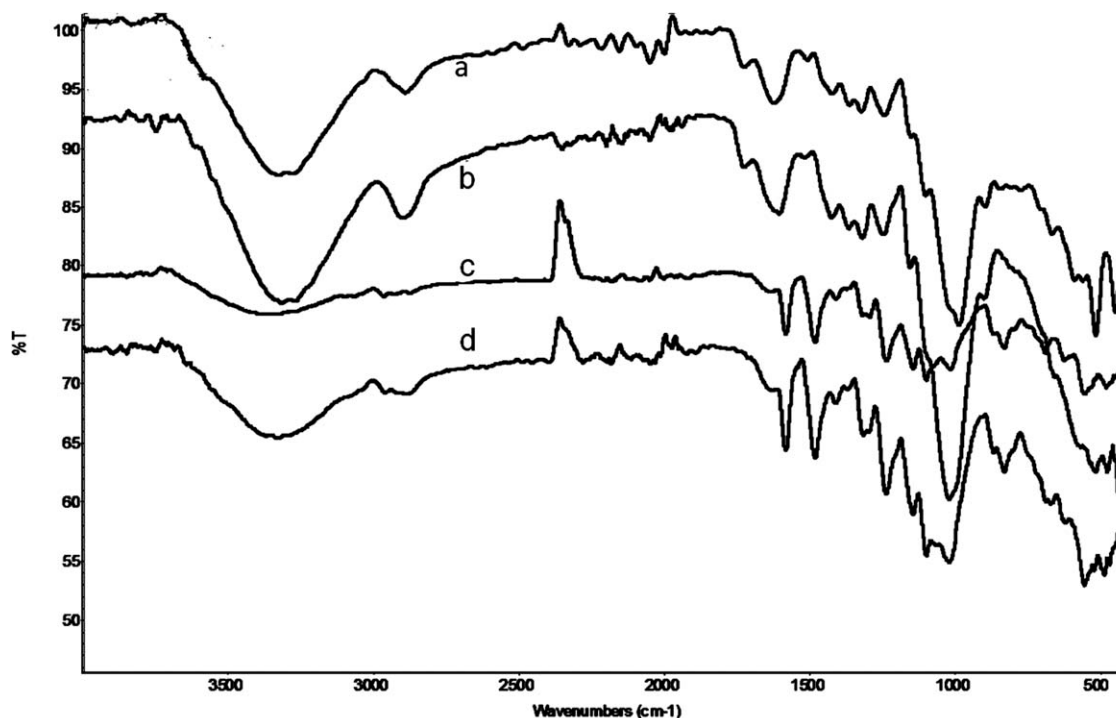


Figure 3. FTIR spectra of treated and untreated banana fibers.

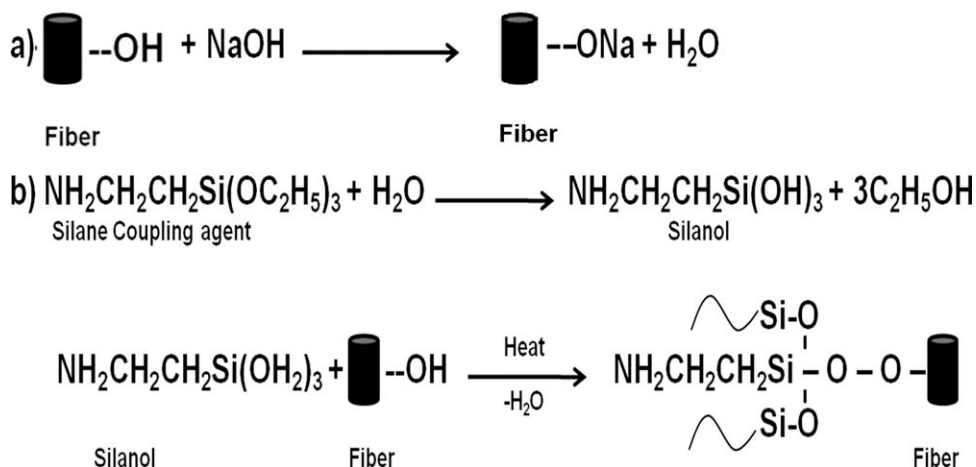
vacuum sputter coater before test to improve the surface conductivity.

## RESULTS AND DISCUSSION

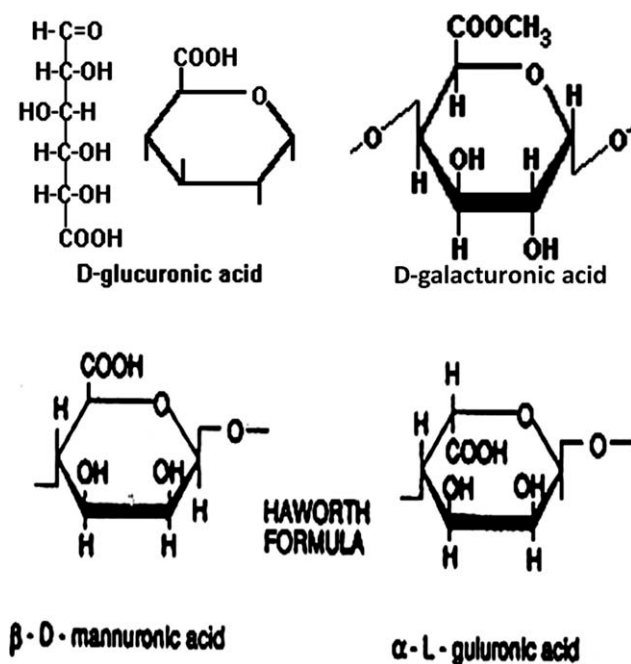
### Confirmation of Surface Treatments of Banana Fiber Using FTIR Spectroscopy

Figure 3 shows FTIR spectrum of the functionalized BF surface as a result of chemical treatments in comparison with untreated BF. The expected way of surface modifications using NaOH and various silanes are given in Scheme 1. In the Scheme 1, (a) represents the expected changes on the surface of BF by NaOH treatment and (b) represents that for silane treatments in general.

As the main components of natural fibers are cellulose, hemicelluloses, and lignin, the observed FTIR spectra of untreated and all the treated BF featured mainly of these components. Peak in the region of  $1030$  to  $1150\text{ cm}^{-1}$  is primarily due to C-O-C and C-O stretching of primary and secondary hydroxyl group in the cellulose, lignin, and their glycoside linkages. Similarly, the peaks near to  $1654\text{ cm}^{-1}$ , corresponds to  $\text{C}=\text{O}$  stretching due to the carbonyl groups that belongs to the hemicellulose chain. Apart from the polymers from sugar based monomers like glucose, xylose, mannose, and arabinose, hemicelluloses contain polymers from acidic origin also. Mannuronic acid, glucuronic acid, guluronic acid and galacturonic acid are the examples for the monomers of acidic origin polymers in the hemicelluloses,



Scheme 1. Expected chemical changes as a result of surface treatments of banana fiber.



**Scheme 2.** Polymers from acidic monomer origins in hemicellulose.

Scheme 2. Carbonyl groups from mannuronic, glucuronic, guluronic, and galacturonic acid based polymers may be responsible for the  $\text{-C=O}$  stretching in the FTIR spectra of natural fibers.<sup>25</sup> In addition, peak around  $3400\text{ cm}^{-1}$  due to the stretching vibrations of hydroxyl groups from the above-mentioned sugar and acidic based polymers also observable in all the four FTIR spectra of surface treated and untreated BF. Peak around  $1600\text{ cm}^{-1}$  and broadening of the O-H peak toward higher frequency region reveals the free water molecules due to the moisture absorption by BF. Also characteristic peak near  $2900\text{ cm}^{-1}$  indicates the  $\text{-C-H}$  stretching from the backbone of the carbohydrate polymers.

Figure 3(c) shows the FTIR spectra of mercerized BF (Na-BF). As observed from the spectra, the mercerized fiber shows the lowering of peak intensity in the region around  $1650$  to  $1770\text{ cm}^{-1}$ . This is due to the partial dissolution of hemicellulose group bearing the major carbonyl functionalities during mercerization process. The result confirms the successful mercerization of BF.

In general silane coupling agents introduce organosiloxo group to the surface of BF. The expected change in FTIR spectra in case of silane treated fibers are the introduction of peaks corresponding to symmetric  $\text{-(Si-O)}$  and  $\text{-(C-Si)}$  stretching frequencies and asymmetric  $\text{-O-Si-O-}$  and  $\text{-Si-O-C-}$  stretching in a region around  $700$  to  $1150\text{ cm}^{-1}$ .<sup>26</sup> However, this region corresponds to the finger print region of IR spectra, so it is relatively difficult to identify the peaks in the region. By analyzing the APS-BF spectra, Figure 3(a), peaks around  $793\text{ cm}^{-1}$  and  $845\text{ cm}^{-1}$  are attributed to the Si-C symmetric stretching. A small peak is obtained at  $704\text{ cm}^{-1}$  which is probably due to  $\text{-Si-O-Si-}$  symmetric stretching and whereas the peak at  $1102\text{ cm}^{-1}$  corresponds to its asymmetric stretching. The band around  $1158\text{ cm}^{-1}$  may be due to  $\text{-Si-O-C-}$  asymmetric stretch-

ing  $\text{-Si-O-Si-}$  bond. In this view,  $\text{-Si-O-Si-}$  linkage indicates the deposition of polysiloxanes on the fiber surface whereas  $\text{-Si-O-C-}$  confirms condensation reaction between the silane coupling agent and the fiber.

Similarly, in case of Si69-BF, Figure 3(d), IR spectra also exhibited symmetric stretching frequencies of Si-C and Si-O-Si around  $784\text{ cm}^{-1}$  and  $713\text{ cm}^{-1}$ , respectively. Also, the asymmetric stretching of Si-O-Si and  $\text{-Si-O-C-}$  identified at around  $1105\text{ cm}^{-1}$  and  $1161\text{ cm}^{-1}$  in the FTIR spectra. However, the intensities of the peaks of APS treated fibers were comparatively higher than that of Si69.

### Mechanical Properties

**Tensile Properties of Single-Strand Banana Fiber.** The tensile properties of single strand of BF (untreated and treated) were evaluated and the results are tabulated in Table I. The tensile strength of untreated BF (UBF) was found to be  $1572\text{ MPa}$  with a modulus of  $67\text{ GPa}$ . Test results reveal that surface treatments of BF with NaOH results in decrease in the tensile strength by 19% as compared with UBF. Similarly, the tensile modulus also showed marginally lesser values (3%) for the NaOH treated fibers (Na-BF). Treatment of cellulose fibers with alkali brings about the process of swelling and the surface hemicelluloses are removed from the interfibrillar region. As a result, the fiber becomes less dense and less rigid which contributes to decrease in the strength.

Conversely, both the silane treatments tend to enhance the tensile properties of untreated BF. Approximately an increase of 15% and 35% in tensile strength and 4% and 13%, in tensile modulus was obtained upon treatment with 3-aminopropyltriethoxysilane (APS) and bis-(3-triethoxysilylpropyl) tetrasulfane (Si69), respectively. Thus, silane can act as a coupling agent between different cellulose strands through covalent and hydrogen bonding that might have resulted in an increase in the tensile properties of BF. Elongation at break also increased marginally for all the treated banana fibers than the untreated counterpart. Lower elongation of untreated BF is probably due to three-dimensional network linkages of carbohydrate strands of cellulose and lignin. Surface treatments might have resulted in restructuring of the surface lignin and removal of disordered polymeric strands. This would have probably contributed in improving the ductility in the treated BF. Mishra et al. reported a similar phenomenon in case of chemically modified pineapple leaf fibers (PALF), where in there was an appreciable decrease in the tensile properties of the fibers.<sup>27</sup> The authors reported this decrease due to the substantial delignification and degradation of cellulosic chain during chemical treatment.

**Table I.** Mechanical Properties of Surface-Treated Single Banana Fiber

Fiber sample	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (Eb%)
UBF	$1572 \pm 29.33$	$67 \pm 1.2$	$1.45 \pm 0.8$
Na-BF	$1272 \pm 32.14$	$65 \pm 3.7$	$2.04 \pm 53$
APS-BF	$1812 \pm 21.23$	$70 \pm 2.1$	$2.29 \pm 1.1$
Si69-BF	$2125 \pm 26.33$	$76 \pm 1.9$	$2.89 \pm 1.0$

**Table II.** Mechanical Properties of PLA/BF Composites at Different Fiber Loading

Materials	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Impact strength(J/m)
V-PLA	38.00 ± 6.5	3546 ± 36.66	2.91 ± 0.32	24.70 ± 2.3
PLA/BF (0.09 volume fraction of BF)	10.55 ± 4.2	3963 ± 44.58	1.45 ± 26	14.66 ± 3.6
PLA/BF (0.18 volume fraction of BF)	13.00 ± 3.3	4210 ± 56.12	1.14 ± 61	15.18 ± 5.9
<b>PLA/BF (0.28 volume fraction of BF)</b>	<b>14.61 ± 14</b>	<b>4631 ± 38.26</b>	<b>1.08 ± 28</b>	<b>19.10 ± 4.2</b>
PLA/BF (0.38 volume fraction of BF)	7.76 ± 4.5	4705 ± 33.91	0.90 ± 0.51	13.52 ± 4.6

**Effect of Fiber Loading on Mechanical Properties of Biocomposites.** The variation of the tensile modulus of V-PLA as a function of fiber loading is represented in Table II. It is evident that the tensile modulus of the composites shows a consistent increase with the increase in fiber loading from 0.09 to 0.38 volume fractions. V-PLA shows a tensile modulus of 3.5 GPa which increased to 39.6 GPa at 0.09 volume fraction of BF loading, thereby showing an increase of 11.76% as compared with V-PLA. A similar increase in the tensile modulus was obtained with 0.18, 0.28, and 0.38 volume fraction of fiber loading to the tune of 21.81%, 34%, and 36.14% respectively.

On the contrary, the tensile strength of V-PLA (Table I) exhibited a considerable decrease with the incorporation of untreated banana fibers. This decrease in strength may be due to the poor stress transfer from the matrix to the fiber as a result of weak interfacial adhesion. The composite at 0.09 volume fraction of fiber loading showed a tensile strength of 10.55 MPa which is 72% lesser value than that of V-PLA. Further, there is an increase in the tensile strength with the increase in fiber concentration to 0.18 and 0.28 volume fractions as compared with the biocomposite at 0.09 volume fraction of BF loading. An increase of approximately 23% and 38% in tensile strength was obtained at fiber loading of 0.18 and 0.28 volume fractions respectively, when compared with the biocomposites with 0.09 volume fraction of BF. Even though the values are still 65.78 and 62.73% lower than that of tensile strength of V-PLA. Further, beyond 0.28 volume fraction of fiber loading, there is a significant decrease in tensile strength. Incorporation of 0.38 volume fraction of BF loading tends to reduce the tensile strength by nearly 26% as compared with biocomposites at 0.09 volume fraction of fiber loading. It is 80.36% lower than that of tensile strength of V-PLA. This behavior is probably because of the fiber agglomeration at higher fiber loading, which results poor stress transfer across the matrix fiber interface. As a result decrease in tensile strength at higher fiber loading in the PLA matrix. The elongation at break also decreased from 2.9% of V-PLA to 1.08% at fiber loading of 0.38 volume fraction, as observed in all filled systems. The impact strength also exhibited a decrease

from 24.7 J/m to 19.10 J/m with fiber loading of 0.38 volume fraction, thus confirming incompatibility of the BF within the PLA matrix. Considering the tensile and impact properties of the untreated BF reinforced PLA biocomposites, composition with 0.28 volume fraction of fiber loading was optimized and used for the preparation of surface treated BF biocomposites.

**Effect of Surface Treatments on Mechanical Properties of Biocomposites.** The mechanical properties of randomly oriented fiber reinforced composite strongly depends upon the factors like fiber orientation, stress concentration at the fiber ends, and transfer of stress from matrix to fiber, critical fiber length etc. Surface treatment of BF increases interaction between the fibers and the polymer matrix, contributing an enhanced stress transfer from the matrix to fiber. The effect of surface treatment on the mechanical properties of the biocomposites is depicted in Table III.

From the results, it is evident that mercerization of BF results, improvement in interfacial bonding between BF and V-PLA. This behavior is probably because mercerization of BF results in distraction of fiber mesh by removing the cementing material and splitting the fibers into finer elements. This further contributes to interpenetration of the fibers at the interface, thereby increasing the strength in the biocomposites. A marginal increase in tensile strength, tensile modulus, and impact strength was observed in PLA/Na-BF biocomposites as compared with the untreated samples. Similar investigations have also been reported Mohanty et al., showed that higher strength in biocomposites is obtained with NaOH treatment of natural fibers as compared with untreated fibers.<sup>28</sup> The author reported the fact that NaOH treatment results in removal of surface imperfection of the fibers which helps in efficient mechanical interlocking with the matrix. However, 19.43% improvement in tensile strength of biocomposite was observed when BF was treated with 3-aminopropyltriethoxysilane (APS) as compared with the untreated biocomposite. Duparz and Meer suggested that APS has the ability to interact with polylactide chain which plays a vital role in making it compatible with BF.<sup>29</sup> During the

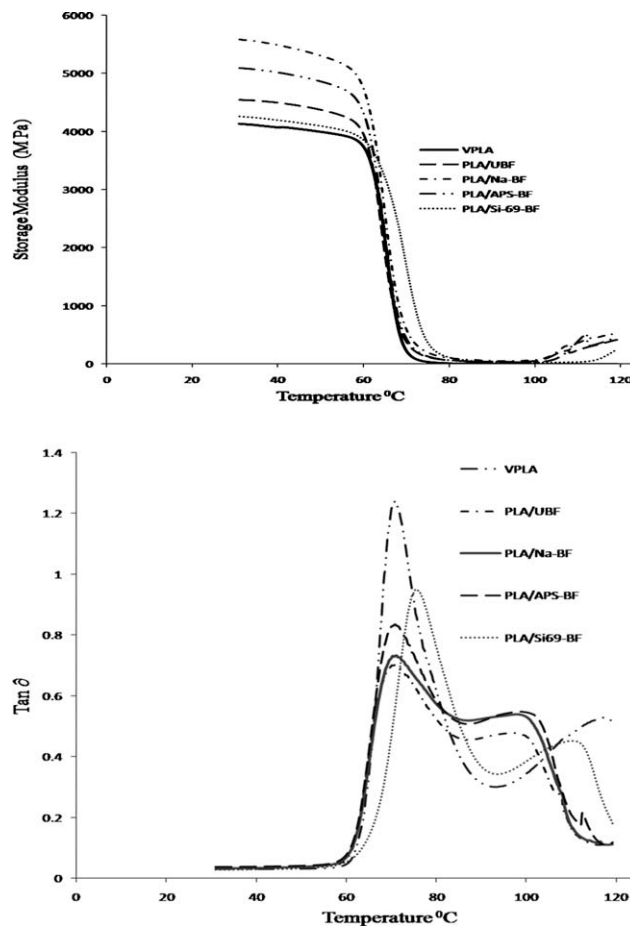
**Table III.** Mechanical Properties of PLA/BF Biocomposites as a Function of Chemical Treatments

Materials	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (Eb%)	Impact strength (J/m)
PLA/UBF	14.61 ± 1.6	4631 ± 36	1.08 ± 0.02	19.10 ± 1.02
PLA/Na-BF	16.01 ± 1.9	4636 ± 55	0.67 ± 0.03	19.69 ± 2.01
PLA/APS-BF	17.45 ± 0.63	4703 ± 22	0.85 ± 0.05	24.99 ± 2.1
PLA/Si69-BF	34.44 ± 0.95	4815 ± 29	2.31 ± 0.02	29.95 ± 1.9

chemical treatment, APS hydrolyzes to silanol, which can bond effectively with carboxylic groups of banana fiber through ester linkage. Amino groups from APS can form hydrogen bonds with  $-C=O$  sites on the PLA backbone. This ends up with an increase in the compatibility of the BF with PLA matrix thereby increases in the strength. Zhang and Wang also reported similar fact that functional groups like  $-NH_2$  or  $-OH$  of APS may interact with carbonyl groups of PLA.<sup>30</sup> In addition, polar Si-O bonds can also tend to enhance the interaction between fiber and matrix. Even though, the tensile modulus value of PLA/APS-BF did not result in appreciable increase as compared with the UBF biocomposites modulus value, but the impact strength showed a noticeable increase from 19.10 J/m to 24.99 J/m, respectively. The value in fact is comparable with the impact strength of V-PLAs 24.7 J/m.

In fact the most significant improvement in tensile properties has been observed in case of Si69-treated BF biocomposites. The tensile strength has been increased by 136% with the incorporation of *bis*-(3-triethoxysilylpropyl)tetrasulfane (Si69) treated BF in to the PLA matrix in comparison with the UBF composite. The value (34.44 M Pa) is also comparable with the V-PLA tensile strength of 38 M Pa. The ethoxy group of the Si69 reacts with the carbonyl group of the cellulosic fiber in ethanol media which further interacts with PLA through hydrogen and covalent bonds. The sulphur atom present in Si69 can also impart polarity in the system to enhance the interaction with the PLA matrix. Thus, it forms a bridge in between fiber and matrix, enhances the interfacial interaction between them. Sreekala et al. suggested similar results that silane-treated cellulose fiber composites showed an increased strength as compared with the untreated fiber composite.<sup>31</sup> Increased nucleation as a result of Si69, yielded smaller and better crystals that results in a trans-crystalline interphase region, which improves the bonding between the fiber and the matrix.

In case of tensile modulus also PLA/Si69-BF has been shown an optimum value in the present investigation. This further confirms the increased interaction between fiber and matrix with the presence of silane coupling agent, Si69. According to Agarwal and Broutman chemical treatments have a significant effect on the fiber stiffness as observed in case of tensile strength results.<sup>32</sup> One of the most important outcomes of the present investigation is increased impact strength achieved by the PLA/Si69-BF. According to Maya and Thomas, randomly oriented short natural fibers can act like nucleating agents within various polymer matrices and also the nucleating capacity is directly proportional to the extent of interfacial interaction in between the matrix and filler.<sup>33</sup> Modified interface in between the PLA matrix and BF after Si69 treatment may tend to enhance the nucleating capacity of the fiber and may result in increased crystallinity in the PLA matrix. Increased crystalline domain in the matrix polymer automatically affects positively on the impact properties of the biocomposite. Anyway this part of changes in crystallinity needs further characterization and reserved it for another communication. PLA/Si69-BF showed impact strength of 29.95 J/m which is 21.25% better value than that of V-PLA and the value is 56.80% better than that of UBF biocomposite.



**Figure 4.** (a) Storage modulus of various surface-treated BF reinforced biocomposites. (b)  $\tan \delta$  of various surface-treated BF reinforced biocomposites.

**Dynamical Mechanical Analysis of Biocomposites as a Function of Fiber Surface Treatments.** The variation in storage modulus as a function of temperature of V-PLA and its biocomposites are given in the Figure 4(a). It is evident from the Figure 4(a) that the storage modulus of biocomposites is higher than the PLA matrix. This indicates the reinforcing capacity imparted by the fibers that results in effective stress transfer from the fiber to the matrix.<sup>34</sup> As observed from Figure 4(a), mercerized banana fiber composite has higher storage modulus than that of the untreated fiber composite. This suggests higher interfacial adhesion between the PLA matrix and mercerized BF as compared with the untreated biocomposites. As reported by various workers, mercerization helps in the removal of lignin and surface impurities from the BF, thereby contact surface area of BF with the polymer matrix increases. Also the process helps in fibrillation of fibers that contributes improved dispersion within V-PLA. These factors may be the reasons for increased storage modulus ( $E'$ ) of PLA/Na-BF biocomposites as compared with the untreated sample. Further, it was observed that all the surface treated biocomposites showed higher  $E'$  as compared with the virgin matrix as well as PLA/BF biocomposites. As shown in Figure 4(a) in all the cases, storage modulus decreased with the increase in temperature, and there was a significant fall



in the regions between 55°C and 70°C which is probably the  $T_g$  region of matrix. Surface-treated fiber reinforced composites indicated a broader plateau on the storage modulus curve than that of virgin PLA. PLA/Si69-BF biocomposites displayed important variations in primary relaxation temperature, which can be linked to both, interactions resulting in decrease in chain mobility and the reinforcing effect imparted by the fibers. The results are consistent with the static mechanical behaviour, wherein the properties vary according to the fiber loading. All surface-treated BF biocomposites showed a very higher modulus at elevated temperatures which is predominantly attributed to the change in molecular structure of the polymer due to interaction with the organofunctional groups.

The organofunctional groups of silane forms interpenetrating polymer networks that are believed to cause the change in the polymer structure. These changes increased the storage modulus in the biocomposites. It is observed that the storage modulus increased with the incorporation of BF, which implies an increase in thermal stability of the neat PLA matrix with the addition of treated BFs. Silane treated biocomposites represented higher  $E'$  as well as the thermal stability, confirming efficient interfacial adhesion between the fiber and the matrix.

Damping ( $\tan \delta$ ) is an important parameter related to the study of dynamic behavior of fiber reinforced composites structure. Change in temperature is related to the damping significantly. In case of surface treated BF reinforced PLA biocomposites  $\tan \delta$  peak also shifted considerably [Figure 4(b)]. Untreated BF reinforced biocomposites and V-PLA has lowest peak height as shown in Figure 4(b). This indicates contribution of the fiber to the damping is extremely low as compared with that of PLA matrix. This suggests that the combined attenuation of banana fiber reinforced biocomposites would be mainly caused by the molecular motion of PLA and the interaction at the fiber/matrix interface. The maximum shift in the peak of the  $\tan \delta$  curve was observed from 66°C of VPLA matrix to 76°C in case of Si69 treated BF reinforced biocomposite. This further indicates about the improved fiber/matrix interaction. Also, the cross-linking density of the interfacial network is reduced due to the presence of unreactive organic groups from the organosilane when fiber is treated with silane coupling agent. This contributes to an increase in magnitude of damping as compared with PLA/UBF or PLA/ Na-BF composites.

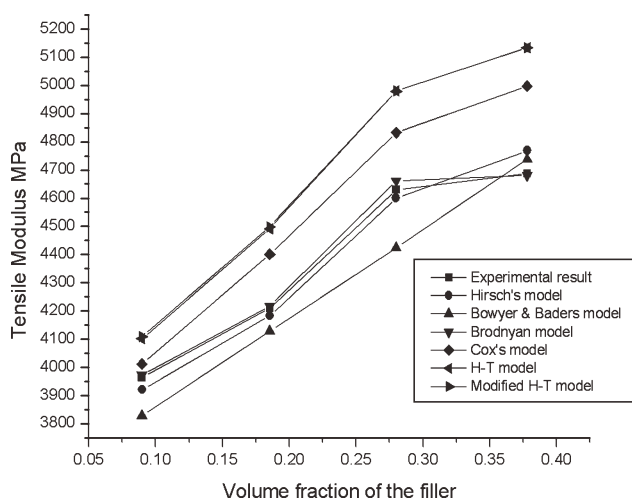
Damping curves exhibited two peaks within the experimental temperature region, one at the temperature between 70 and 80°C and the other around 100 to 110°C. As discussed during the storage modulus section former peak corresponds to the glass transition of the PLA matrix. The peak around 100 to 110°C may be associated with cold crystallization of the PLA macromolecules. As a result of crystallization process molecules get rearranged to a particular crystalline pattern which imparts some rigidity to the biocomposites at that temperature region, so that the biocomposites can show enhanced storage modulus, thereby correspondingly enhanced  $\tan \delta$ .

**Comparative Study of Tensile Modulus of Biocomposites with the Various Theoretical Values.** Theoretical tensile modulus of the composites was calculated as per previously discussed

micromechanical models and the same is represented as a comparative study in Figure 5. In Figure 5 mechanical modulus of the biocomposites has been plotted against volume fraction (which has been used for the theoretical calculation of the mechanical modulus) of the filler for each of the biocomposites. Considering the Hirsch's micromechanical model it is evident that the theoretically determined values are in good agreement with the experimental results. In case of biocomposites at 0.09 volume fractions, 0.18 volume fractions and 0.28 volume fractions of fiber loading, the variation in the theoretical and experimental tensile modulus are reported only 1%, 0.6%, and 0.65%, respectively. As reported by other authors Hirsch's method is the combination of the basic theories, series and parallel models which deals with both the kind of filler alignments, as illustrated in Figure 1. According to the micromechanical model, " $x$ " is a predominant factor in determining the behavior of short randomly oriented fiber reinforced composites. It is observed that the variation of " $x$ " from 0.1 to 0.5, results in significant changes in the properties of the biocomposites. In the present investigation the value of " $x$ " has been taken to be 0.4 corresponding to random orientation, which shows good correlation with the experimental data. Similar observations have also been reported by Kalaprasad et al., 0.38 volume fraction fiber loading the theoretical value deviate significantly from the experimental results which is probably due to fiber agglomeration at higher fiber loading that results in micro crack formation at the interface and hence poor composite properties.

Similarly, the tensile modulus of the biocomposites as per modified Bowyer and Baders (M-BB) model is also represented in Figure 5. It is observed that the theoretical values are inferior to experimental values up to a fiber content of 0.28 volume fraction. The difference between the theoretical and experimental values are 2.5%, 1.9%, and 2% respectively for 0.08 volume fraction, 0.18 volume fraction, and 0.28 volume fraction fiber content in the biocomposites. Further increase of BF as like in Hirsch's model, M-BB model also shows significant deviation between the theoretical tensile modulus and experimentally determined values to the tune of 4.5% for 0.38 volume fraction of fiber loading. This behavior confirms that Hirsch's micromechanical model fits well at lower loading of short fiber ie: 0.09 to 0.28 volume fraction. However, at higher loading, the model shows deviation from the experimental datas. On other hand in case of M-BB model the predicted values are not in good agreement with the experimental values within the complete fiber loading range.

Predicted values using M-BB model primarily depend on the factors  $K_1$  and  $K_2$ , the factors signify fiber orientation and fiber length, respectively. The value of  $K_1$  for short randomly oriented biocomposites has been assumed as 1 on the basis of previous literatures. The fiber length factor  $K_2$  can be calculated using the eq. (9b), by assuming that the fiber length taken here is less than the critical length, (i.e.,  $l < l_c$ ). Even though, introduction of these factors, which depends on the orientation and the length factor not become as much effective here for the prediction of the properties. As the length of the fiber kept at constant range, variation in fiber orientation may be the reason for mismatching the theoretical modulus by M-BB model with experimental modulus values. As mentioned earlier, the mechanical



**Figure 5.** Tensile modulus predicted by various micromechanical models.

properties of randomly oriented fiber reinforced composite strongly depends on the factors like fiber orientation, stress concentration at the fiber ends, critical fiber lengths, etc.

Similarly, the experimental tensile modulus of the biocomposites has been compared with the theoretical values using Cox's model depicted in Figure 5. It is observed that the predicted values of tensile modulus using Cox's model did not show much resemblance with the experimental value as compared with the previous two models discussed above. The calculated results displayed in Figure 5 reveal that at less fiber content of 0.08 vol %, the experimental values are in good agreement with the theoretical data. However, beyond 0.08 vol %, the theoretical values for all the compositions using this model are comparatively higher than that of the experimental values.

This behavior reveals the primary applicability of the Cox's model in a composite with perfect fiber-matrix interface wherein there is no axial transmitte through the fiber ends. Also the model assumes elastic nature for both the fiber and the matrix which makes it more theoretical friendly than practical applicability. In the current study, less fiber matrix interaction and nonelastic nature of filler might be the reasons for significant deviation in experimental data and theoretical values. Also, introduction of factors like  $\tan \delta$ ,  $G_m$ , and  $R$ , the maximum damping factor, shear modulus of matrix and center to center distance of the fibers, respectively does not have any considerable effect in the prediction of properties of BF-reinforced PLA biocomposites. The calculation of  $R$  value has been done using eq. (7a) and (7b), respectively. The equation corresponding to square packed fiber orientation inside the biocomposite has given better values of modulus as compared with those assuming hexagonal packing. Calculation of average center to center distance between the fibers is also critical in the property calculation. Lesser agreement between the calculated and real distance value between the fibers may also be a reason for the deviation of predicted values from the experimental values.

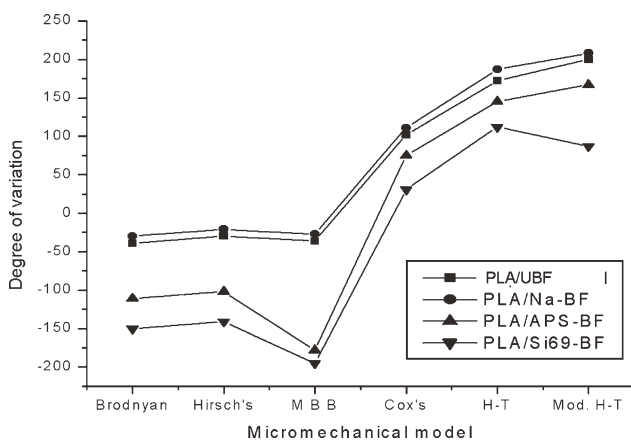
The Einstein's equation based micromechanical models like Halpin-Tsai (H-T) and Nielson modified H-T model, have also been used in this study. Both the equations give almost similar

values as depicted in the Figure 5. As observed from the Figure 5, it is evident that in the case of H-T and Nielson modified H-T model the calculated values are far higher than that of experimental values for both the equations. The factor "A" in H-T equation has been the vital factor for the calculation of mechanical properties of the random oriented fiber composite. In the present study "A" has been calculated using Einstein's coefficient "K" as per the study of Nielson.<sup>35</sup> The factor "K" strongly depends upon fiber geometry, fiber distribution, and fiber loading conditions. In the current comparative study fiber geometry and fiber distribution may be the determining factors for lower experimental values than that of the theoretical values. Surface imperfections on the untreated banana fiber do not provide a perfect cylindrical shape to the filler. The equation for "K" has been derived based on the assumption that perfect cylindrical shape for the fiber filler materials. It has been noted that after the surface modifications of banana fiber the experimental values show lesser deviation from the theoretical values which indicates the importance of fiber geometry. The delignification process during the chemical treatments smoothen the fiber surface to better cylindrical shape, provides better interaction with the matrix. Similarly, fiber distribution may also effects significantly in the current study where some improper distribution of fillers has been observed due to lower interaction between fiber and matrix for PLA/UBF biocomposites. Modification of H-T equation by Nielson has been done by introducing the constant maximum packing fraction ( $\chi_{max}$ ) of the reinforcement. According to Nielson, the value of  $\chi_{max}$  varies with the fiber arrangement in the biocomposite. More uniform fiber distribution results more better results. Here the less uniformity in the dispersion of fiber in the matrix due to poor interfacial adhesion may be the reason for a large deviation in experimental values than the values predicted by Nielson modified H-T equation. For a random packing arrangement the value assumed to be 0.82 has been used here in this study, and so the introduction of  $\chi_{max}$  of fiber has negligible effect on the prediction of tensile modulus of the biocomposite.

Brodnyan model has given the best results in comparison with all other models discussed in the present investigation. This equation is also a modified form of Einstein's equation. Brodnyan modified the equation by introducing fiber aspect ratio ( $\alpha$ ) along with maximum packing fraction as in the equation 16 and 17. The mechanical properties of the composites significantly depend on the fiber aspect ratio. Here, the introduction of such a factor to the Einstein's equation shows better results, shows least deviation from the experimentally determined values. As per the equation  $\alpha$  value for nonspherical particles has to be always  $1 < \alpha < 15$  for better prediction tensile properties. Here in the current study the fiber aspect ratio has been kept as around 4, which is in between the above-mentioned range.

#### Comparative Study of Tensile Modulus of Surface Treated Banana Fiber Composites with Theoretical Models

A comparative account of experimental tensile modulus of surface treated BF reinforced PLA biocomposites with the theoretical mathematical models is represented in Figure 6. The deviation from the theoretical value predicted by each micromechanical model has been represented in  $y$ -axis as degree of

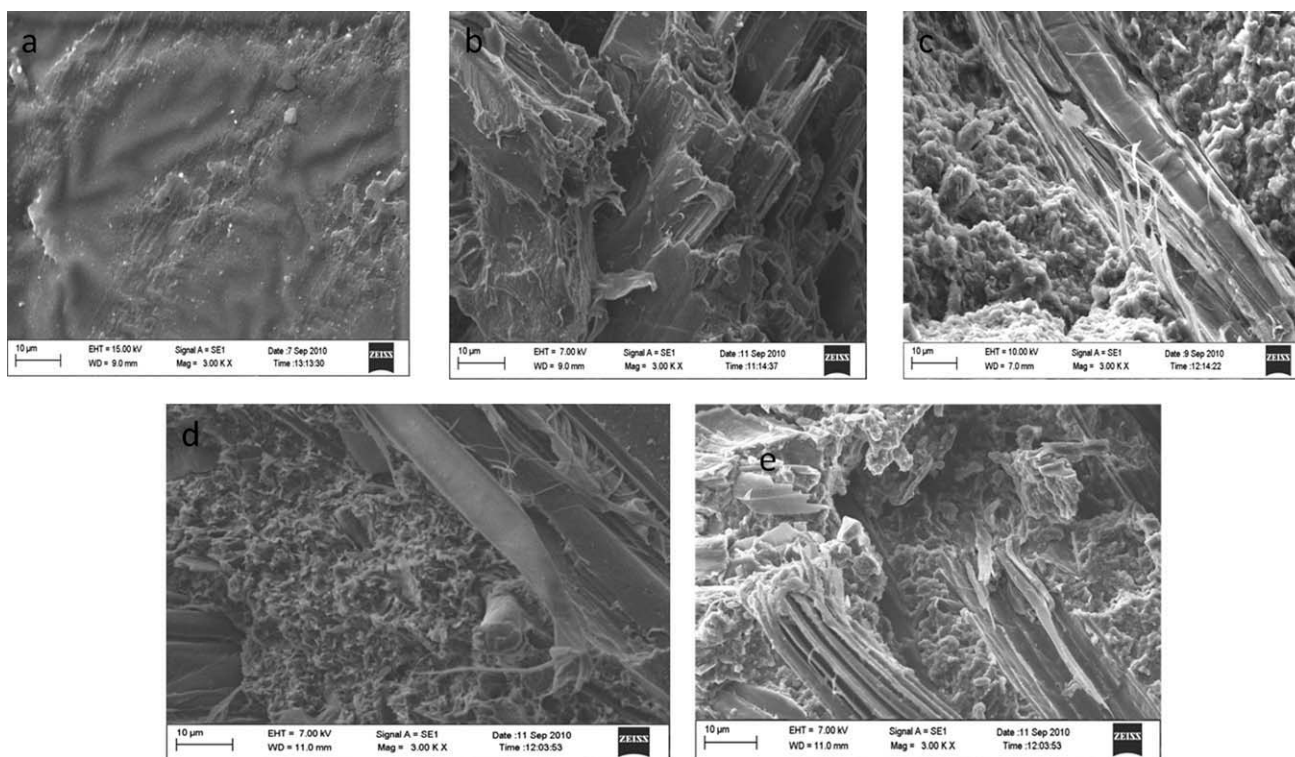


**Figure 6.** Degree of variation of tensile modulus as a result of surface treatments.

difference. The negative values indicate the lower experimental values than that of the predicted values and the positive values indicate higher values from each of the individual micromechanical models. As present in the previous discussions, the mechanical properties of the biocomposites increased considerably by the surface treatments of BF. Many of the mathematical models discussed in the earlier sections exhibit higher values of tensile modulus than PLA/UBF biocomposites. However, surface treatments of BF reduce the difference between the experimental values and the theoretical results as evident from Figure 6. As the mechanical modulus of biocomposites increased as a function of BF surface treatments, the difference between theoret-

cally calculated and experimental values decreased considerably after the incorporation of surface-treated BF into the biocomposites. This has been observed significantly in case of Cox's, H-T, and Nielson modified H-T model. All these models are derived based on the ideal conditions like perfect interface between the filler and matrix, elastic nature of the components as mentioned earlier. In case of surface-treated biocomposite there is a considerable improvement in the interface of the system through fiber surface treatments which tends to reduce the difference between the experimental and theoretical values predicted by various models. This further confirms the effective bond formation at the interface due to silane treatment. Further PLA/Si69-BF biocomposite exhibited good agreement with the theoretical models, thus corroborating the fact that the ethoxy group of the Si69 reacts with the carbonyl group of the cellulosic fiber in ethanol media which further interacts with PLA through hydrogen and covalent bonds. The sulphur atom present in Si69 can also impart polarity in the system to enhance the interaction with the PLA matrix. Thus it forms a bridge between fiber and matrix, enhancing the interfacial interaction between them. Sreekala et.al suggested similar results that silane-treated cellulose fiber composites showed an increased strength as compared with the untreated fiber composite.<sup>36</sup> In this case, the differences from the theoretical values are only 2%, 3%, and 3%, respectively for Cox's, H-T, and Nielson modified H-T model.

For PLA/UBF biocomposites, in comparison with Hirsch's, modified Bawyer–Baders model, and Brodnyan models the experimentally determined values were higher than that of theoretical values. Successful surface modifications of BF results better mechanical properties for biocomposites. This increase in



**Figure 7.** SEM micrographs of the impact fracture surface (a) V-PLA (b) PLA/UBF, (c) PLA/Na-BF, (d) PLA/APS-BF, (e) PLA/Si69-BF.

the tensile modulus values for surface-treated BF composites end up with further deviation from the theoretical values predicted by above three mechanical models than that of the PLA/UBF biocomposites.

### Morphology of Biocomposites

SEM micrographs of the impact fractural surface of PLA/UBF biocomposites are shown in Figure 7. Figure 7(a) shows the fractural surface of V-PLA and Figure 7(b) represents that of PLA/UBF biocomposites. In case of PLA/UBF biocomposites the SEM micrographs shows the fiber aggregates due to the improper distribution of BF in the PLA matrix. Fiber breakage with fiber pull outs from the matrix during fracture process suggests poor interfacial interaction between PLA and BF. SEM micrograph of PLA/Na-BF has been given in Figure 7(c). It is evident from the Figure 7 that comparably smooth fiber surface as a result of delignification from the surface of BF. As a result, fibrils are well trapped within the matrix leads to good adhesion between PLA and BF. Further, both the silane treated biocomposites give a smooth topography due to better interaction between the matrix and fiber, which could have contributed to significant increase in mechanical properties as explained in earlier sections. Figure 7(d,e) represents the morphology of PLA/APS-BF and PLA/Si69-BF, respectively. This has been noted earlier that from the mechanical properties of the PLA/Si-69 which shows the highest value of impact property even better than V-PLA.

### CONCLUSION

The tensile modulus of PLA/BF biocomposites have been successfully determined by both experimentally and theoretically. Micromechanical models like Hirsch's, modified Bawyer-Baders model, and Brodnyan model have been shown good agreement with the experimentally determined modulus of PLA/UBF biocomposites. Other models like Cox's, H-T, and modified H-T model have been given larger values for tensile modulus than that of experimentally determined values. However, increased fiber interphase interaction with PLA matrix by surface treatment of BF using various silanes reduces the difference between these theoretical values from experimental values. Among the treated biocomposites PLA/Si69-BF showed best interfacial interaction in between the matrix PLA and BF. Also it shows the least difference in between the theoretical values and experimental values of tensile modulus.

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