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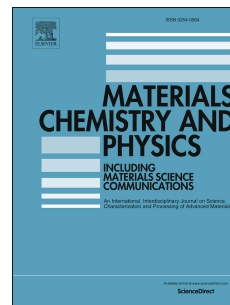
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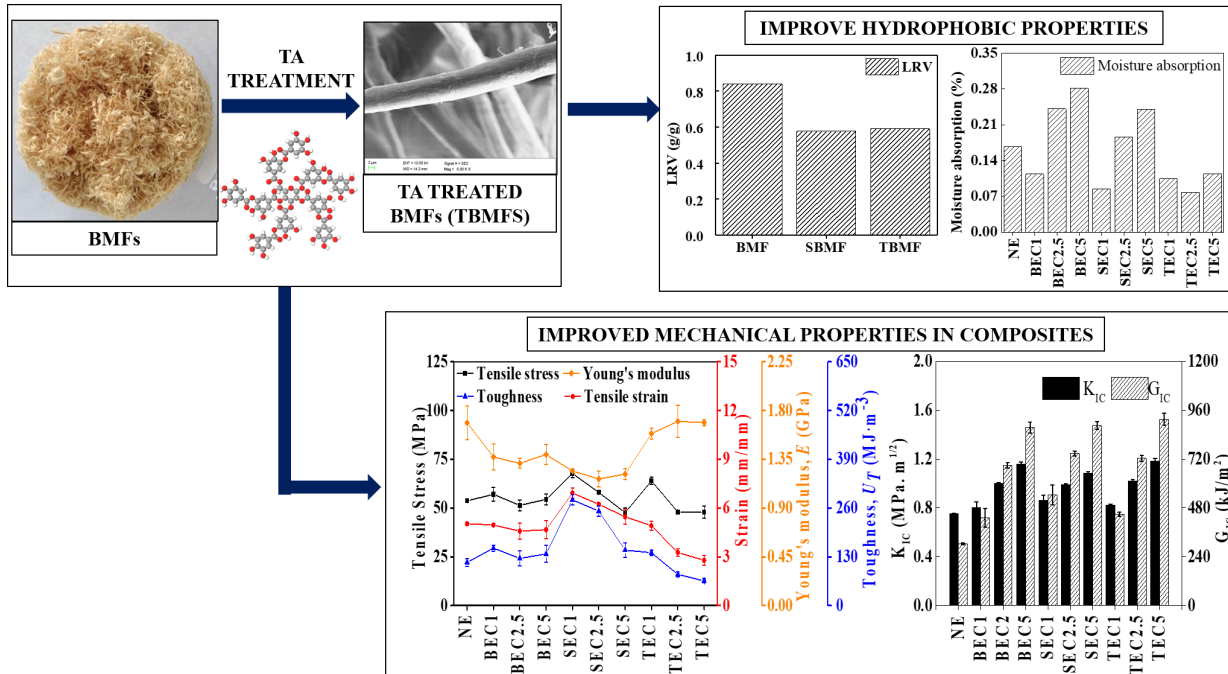
Tannic Acid Functionalization of Bamboo Micron Fibes: Its Capability to Toughen Epoxy Based Biocomposites

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Abstract

Despite various properties and functionalities of natural fillers, their use as a toughening agent in biocomposites is hindered because of their hydrophilicity. Synthetic and costly functionalization agents such as silanes are generally used to reduce the hydrophilicity of natural fillers. Herein the performance characteristics of epoxy biocomposites are evaluated by replacing silane functionalized bamboo micron fibers (BMFs). An efficient and eco-friendly method to functionalize BMFs using tannic acid (TA) is proposed in this work to prepare toughened biocomposites. The TA akin to the silanes reduces the liquid retention value of the BMFs by ~30%. However, silane functionalized BMFs is found to offer limited resistance to mechanical constraint in the biocomposites. The TA treatment helped regain the capability of BMFs to offer stiffness modulation at the interfaces within the epoxy network. Even though the polysiloxane oligomers on BMFs significantly improves the tensile strength of the biocomposites by ~26 % but the TA coated BMF showed their considerable capacity

to increase the tensile strength by ~19 %. Noteworthy improvement in the fracture toughness and fracture energy by ~60 %, and ~212 % respectively is demonstrated by the biocomposites prepared using TA treated BMFs. Our work shows that TA can be a safe, natural, and eco-friendly alternative functionalization agent for natural fillers and to exhibit the untapped nature of TBMFs in toughening the epoxy biocomposites.

Keywords: Bamboo micron fibers; surface functionalization; biocomposite; mechanical properties

1. Introduction

Given the demand by the modern industrial world to implement lignocellulosic fillers in composite materials through a sustainable approach, rehabilitation is tried for the manufacturing of biocomposites [1]. However, to date, most of the lignocellulosic based resources are underutilized due to the advantageous applicability of the inorganic/carbon-based fillers in composites [2,3]. Production processes of these inorganic/carbon-based fillers are not only technologically complicated but also consumes a tremendous amount of energy [4]. On the other hand, economical processing, renewable nature, ease in the processability, sustainability, and biodegradability of lignocellulosic based fillers makes them a potential bearing candidate for prime filler material. Out of many sources to produce lignocellulosic based fillers, the abundant natural bamboo resource is largely adopted in view of the analogous property on its counterpart wood [5].

Natural fillers tend to have decreased interfacial properties in a polar matrix such as epoxy due to its hydrophilic nature. The molecular units of natural fiber such as bamboo fiber contain up to three alcohol hydroxyls that bind with other cellulose and absorbs moisture making them hydrophilic [6,7]. To overcome this hydrophilicity in the natural fillers, surface

modification methods such as benzoylation and silanization have been effectively tried and the utilization of these surface-treated natural fillers in composites has shown to have improved mechanical performance as well as reduced hydrophilicity [8–10]. Nevertheless, most of these organic chemicals used for the surface functionalization of the natural fillers are not environmentally friendly and is costly for the mass production of functionalized natural fibers [11]. Green and eco-friendly methods of surface functionalization of natural fillers can overcome the difficulties of using traditional functionalization agents for mass production.

Natural occurring polyphenolic compounds can effectively modulate the surface chemistry various substrates and thus might be a potential surface modifying agent for natural fillers. Tannic acid (TA) is one of the naturally-derived polyphenolic compounds and possesses versatile bonding abilities [12]. It consists of a pentagalloyl glucose core with an average of five more secondary or tertiary ester-linked gallic acid moieties that can cross-link with another surface by hydrogen bonding. In the work reported by Kozlovskaya et al., TA-based gels have been used to produce membrane through layer-by-layer assembly[13]. The high cross-linking of the TA can easily lead to form a hydrogel. Improvement in the mechanical properties by treating gelatin with TA have been reported, which resulted in an improvement of the mechanical properties [14]. Fan et al. have studied the effectiveness of the hydrogen bonding by studying the hydrogel formation with a series of commercially available water-soluble polymers [12]. Bedran-Russo et al. reported that after treating dentine matrix by using TA, have resulted in improving the stiffness as well as bonding strength for the adhesive system [15]. The strong hydrogen bonding can also result in permanent cross-link as reported by Ya-Nan et al., which resulted in high tensile strengths (up to 2.88 MPa) and high elongations (up to 1100%) [16]. Another cross-linking ability of TA can be explained

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by the report of Mohammad N. et al., who mention tensile stress and modulus improvement by incorporating it with kafirin films [17].

In this study, the surface chemistry of the bamboo short micron fibers was modulated by TA treatment and is incorporated in the epoxy network to prepare high-performance biocomposites. We theorize that the use of TA can enhance the interfacial properties of bamboo short micron fibers by introducing stiffness modulation enabled surface groups that endorse improved adherence with the epoxy matrix in the composites. This work demonstrates in detail the capability of natural and eco-friendly TA as an efficient alternative functionalization agent for bamboo micron fibers to reduce hydrophilicity and better interact with the epoxy matrix to produced toughened biocomposites.

2. Materials and Method

2.1. Materials

BMFs were extracted by using bamboo (Bambusa Balcooa) obtained from a local source, Assam, India. Chemical used for silanization, (3-Aminopropyl) triethoxysilane (APTES) was sourced from Spectrochem Pvt. Ltd., India. Tannic acid was purchased from Merck Specialities Pvt. Ltd., India. Araldite® LY556, which is an anhydride-cured, low-viscosity standard matrix system is used as a matrix. Anhydride hardener, Aradur®906 and imidazole Accelerator DY070, was purchased from Huntsman Advanced Materials, India Pvt. Ltd.

2.2. Synthesis of functionalized BMFs and epoxy composites

Extraction of bamboo fiber was carried out using a mechano-chemical process, as described in our previous work [18]. The silanization of the BMFs was performed in the presence of APTES, where the fibers were soaked for 24 hours in ethanol and distilled water (in a ratio of 4:1) having 10 wt. % of APTES. The ratio of the fiber weight to the silane solution was kept

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at 1:40. The silanized BMFs (SBMFs) was filtered and washed with acetone repeatedly to remove the unreacted APTES and dried overnight in an oven at 105°C. For the synthesis of TA treated BMFs (TBMFs), firstly tannic acid (TA) solution at a 5 mM concentration is prepared by dissolving 0.851g of TA with 100 ml double distilled water in a beaker and stirred by at 200 rpm. After that tris buffer solution was added at a concentration of 10mM. The pH of the resultant solution was adjusted to 8.5 by using HCl and NaOH. BMFs were then soaked in the solution for 30 mins then rinsed and dried in an oven at 60°C for 6 hours and at 105°C overnight.

The different composite samples, i.e., BMF epoxy composites (BEC), SBMF epoxy composites (SEC) and TBMFs epoxy composites (TEC) were prepared with varied filler content that is 1 wt.%, 2.5 wt.% and 5 wt.% of that of the epoxy system. For preparing samples, epoxy resin LY556 and hardener HY906 (100:95) and accelerator DY070 (taken at 1.5 wt.%) are mixed together for 10 minutes to obtain a homogenous mixture. Fibers are added and mixed it with a mechanical stirrer at 3000 rpm for 1 hour. The sample was placed in a vacuum chamber to remove the dissolved air caused by the high-speed agitation. It was then poured in a metal mold designed as per ASTM standard and later cured with curing cycles of 2 hours at 120°C followed by 8 hours at 160°C. The sample composition of the different epoxy composite is listed in Table S1 in the supporting information.

2.3. Testing and characterization

Bare and functionalized BMFs were mounted with KBr FTIR spectrum was performed in FTIR-Spectrum 1 (PerkinElmer, Inc., USA). The spectrum recorded was from 400 cm^{-1} to 4000 cm^{-1}. The liquid retention value (*LRV)* test was carried out similar to ISO 23714:2014, which is for the determination of water retention value (*WRV*) in the pulp. Ultraviolet to visible absorption spectra were recorded in Agilent Cary 60 UV-Vis Spectrophotometer

(Agilent, INDIA) in the range 200-800 nm. The dynamic mechanical analysis was carried out in Perkin Elmer DMA 800 (PerkinElmer, USA) from room temperature to 250°C working in single cantilever bending mode. The samples were cast into thin rectangular strips with dimensions of about $9 \times 8 \times 2$ mm^3. Measurements were performed in isochronal conditions at 1 Hz, and the temperature varied between 35 to 250°C at a rate of 5°C/min. The tensile testings of epoxy composite samples were carried out in the Instron 5969 Dual Column Tabletop Testing System (Instron, USA) at a loading speed of 1 mm/min. Testing was performed according to ASTM standard D638 Type IV. Single edge notched beam (SENB) test of epoxy composites was done using three-point flexural test procedure according to ASTM Standard D5045 to find out the plane strain fracture toughness K_{IC} and strain energy release rate, $G_{IC.}$ Moisture absorption study was performed according to ASTM D570. The calculation for the % increase in weight was carried out by using the relation given in equation 1.

$$\% \ Increase \ in \ weight = \frac{Wet \ weight - Conditioned \ weight}{Conditioned \ weight} \times 100 \qquad 1$$

The thermal degradation study was evaluated on Netzsch Jupiter 449 simultaneous TGA-DTA system (Netzsch, Germany). The samples were subjected to a temperature up to 600°C from room temperature to study their thermal degradation behavior. Nitrogen gas of purity 99.99% was used for purging at 60 ml/min during the test.

The determination of the total crystallinity index (*TCI*), lateral order index (*LOI*) and hydrogen bond intensity (*HBI*) is done according to the details provided in the discussion S1, of the supporting information.

3. Results and discussions

3.1. Morphology and surface chemistry of bare and surface functionalized BMFs

The treated and surface modified BMFs were investigated under FESEM, as shown in Fig. 1. On the surface of the extracted BMFs, lose holocellulose components in the form of scalloped structures are visible as shown in Fig. 1a. The SBMFs (Fig. 1b) on the other hand, shows cleaner surfaces, which may be due to the dissolution of the holocellulose component during treatment. Interestingly, surface for TBMFs is found smoother in comparison to others. The TBMFs are having significantly reduced scalloped components on their surfaces as can be seen in Fig. 1c. The evidence of either broken cell wall or other components is found entirely missing. This is probably due to the camouflaging effect due to the catechol group from the TA aqueous solution on the hemicellulose and other compounds on the fiber surface.

The surface chemistry of the bare and functionalized BMFs was assessed from the FTIR analysis. FTIR analysis shows distinct broad peak centered at ~3338 cm^{-1} for TBMFs, representing stretching vibration of the hydroxyl group (O-H) from assimilating moisture due to the intramolecular hydrogen bonding in the cellulose, as can be seen in Fig. 2. There is a noteworthy reduction in peak intensity at ~3338 cm^{-1} indicating ionic bonding of the catechol group with the hydroxyl group due to the TA coating. Furthermore, a secondary peak is observed at ~3290 cm^{-1} corresponding to the phenolic OH stretch, which indicates the presence of the galloyl moieties of TA on the TBMFs[19]. The peak centered at ~2900 cm^{-1} is attributed to the C-H and CH_2 stretching vibration from cellulose, lignin, and hemicellulose, which is found decreased for TBMFs indicating dissolution of hemicellulose and other compounds[20]. For SBMFs bands at ~1639 cm^{-1} and ~1236 cm^{-1} corresponding to N-H bending and stretching confirms successful silanization of BMFs [21]. In the case of TBMFs, the peak exhibited at ~2078 cm^{-1} is corresponding to $v(CO)_{ads}$ and peak at 1992 cm^{-1} represents C=C=C stretching vibration [22]. The peaks at ~837 cm^{-1}, ~1267 cm^{-1} and ~1374 cm^{-1} corresponding to =CH out of the plane vibration, and in-plane CH bending in BMFs due

to the presence of lignin and skeletal, and aromatics vibrations from lignin structure and from hemicellulose, are found minimized for TBMFs[23]. The disappearance of these peaks for TBMFs confers again the camouflaging of the lignin and other hollocellulose components due to the surface coating by TA molecules onto BMFs. The presence of the peak at ~707 cm^{-1} is indicative of the ring deformation modes from benzene derivatives of TA as well as indicative of the substitution of the hydroxyl group that can be perceived by the presence of the aromatic C-H angular deformation [24].

LRV test was conducted to study the moisture absorption of the surface modified BMFs, i.e. SBMFs and TBMFs. LRV test reveals that the moisture uptake of the BMFs is of 0.84 g/g. However, a reduced LRV of 0.58 g/g is observed for SBMFs demonstrating a reduction by ~31% from that of the BMFs. Interestingly, a similar LRV reduction by ~30 % (0.59 g/g) is found for TBMFs also. The reduction in LRV for SBMFs is due to the presence of the polysiloxane oligomers on the fiber surface, which restricts the penetration of the moisture. However, the coating of the TA moieties on the TBMFs also provides restriction for moisture absorption into the fibers.

To discover further about the TA coating on the BMFs, UV-vis spectra of TA aqueous solution at pH 8, before and after treating the BMFs was obtained and the result is shown in Fig. 3a. For TA aqueous solution before treating the BMFs, three peaks are observed at 328, 295 and 246 nm respectively. After treating the BMFs with TA aqueous solution, the peak at 246 nm is shifted to 248 nm, while the peak at 328 nm shifted to 323 nm. The peak at 295 nm for TA aqueous solution attributed to the non-bonding orbitals (n–π* transitions) of their surface-states and functional groups that govern the emission, which was found decreased [25]. This signifies that TA aqueous solution in contact with the BMFs becomes stable by bonding with the BMFs. At 350 nm, a broad shoulder appears after treating BMFs with the TA aqueous solution. To check whether TA is bonded to the BMFs, both BMFs and TBMFs

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were treated with a FeCl$_3$ aqueous solution and the outcome is presented in Fig. 3b after drying. A visible color change of BMFs to bluish brown can be seen for TBMFs. For BMFs, their hydroxyl groups and the Fe^{III} ions participate in d$_2$sp$_3$ hybridization and undergo a complexation to form a BMF-Fe^{III} complex, therefore makes the color brown[26]. After treating BMFs with TA aqueous solution, a stable compound of ferric-tannate by the reaction of the Fe^{III} ions with the TA moieties of TBMFs responsibly changes the color to bluish brown[27,28].

For further investigation on the effective surface functionalization, thermophysical behavior of the BMFs, SBMFs, and TBMFs was studied and the results are shown in Fig. 4 and also listed in Table S3 of the supporting information. A two-step degradation occurs for all the fiber. The preliminary degradation occurs around 110°C, due to the moisture which is being absorbed from the surrounding environment and can be termed as moisture degradation temperature of natural fibers. It can be observed that there is a weight loss of ~9 % in BMFs and ~6 % in SBMFs respectively, in the initial degradation temperature (T_{IDT}) region, which was reduced to ~3 % in the case of TBMFs. This indicates a reduction in atmospheric moisture adsorption after coating of BMFs with TA. The delay in thermal degradation for both SBMFs and TBMFs suggest the presence of silane oligomers or TA moieties on the surfaces of BMFs. Apart from above, a low char yield for TBMFs depicts enhanced stability of BMFs after TA coating.

3.2. Thermomechanical and mechanical performance of BMF epoxy composites

For analyzing the storage modulus (E') and tan delta (T_g) of the BMF epoxy composites, DMA analysis was performed. E' represents the stiffness, which contributes to the viscoelastic part of the BMF epoxy system and can be directly related to the interfacial strength between the fiber and the matrix. Fig. 5a shows the variation of E' with temperature

for neat epoxy and BMF epoxy composites (BEC) and the obtained E' is also tabulated in Table S4. The storage modulus of the BEC having a filler content of 1 wt.% and 2.5 wt.%, i.e., BEC1 and BEC2.5, is found higher than the neat epoxy (NE) by ~12 % (~875.45 MPa) and ~7 % (~847.91 MPa). This increase in the E' suggests that the BMFs offers mechanical constraints to the epoxy network along with recoverable viscoelastic deformation leading to an increased stress transfer at the fiber-matrix interface [29]. Although natural fibers have an aversion to polar polymer matrixes that generally deteriorates the composite properties, in our case, E' enhancement exposes the compatibility of BMFs with the non-polar epoxy resin system [30]. In addition, the enhanced modulus for BEC is contributed by the resistance offered by BMFs to mechanical loading wherein a large amount of energy has to be spent in order to destroy its structure. However, with BEC5, there is a decrease in E' by ~12 % (~684.25 MPa). This might have caused by the defective fibers in the epoxy matrix. The chance of creating defective fiber surface is inevitable as a high concentration of NaOH was used during the extraction process of BMFs. A higher concentration of BMFs in BEC might have enforced the dominating effect of fiber surface defect to suppress the stress transfer at the fiber-matrix interface. The E' value is found decreased for SBMF epoxy composite (SEC) samples, which indicates poor structural mobility than that of the NE (Fig. 5b). In SECs, the effect of silane oligomers such as improving the surface adhesion, lubrication, plasticizing, wetting of the fiber to enhance their deformation that facilitates lowering the plastic behavior of the viscoelastic matrix polymer, might have occurred separately or in combination [31]. However, it is difficult to identify which mechanism has a dominating role in our case. For SBMFs condensation process in the presence of APTES gives out soluble products that after fiber drying either generates solid macromolecular polysiloxane layers or entangled polysiloxane networks on their surfaces[10]. The hindrance offered due to the fast condensation reaction of APTES might have led to the formation of large silane monomers

and have been restricted by the highly entangled BMFs to form uniform solid

macromolecular polysiloxane layers or entangled polysiloxane networks on their surfaces.

For the TEC1 sample (Fig. 5c), the E' value increases by ~4% (~808.90 MPa) over NE

(779.73 MPa). However, the storage modulus decreases for TECs having high content of

TBMFs. This can be correlated with the reduction in the intermolecular forces at high filler

content that might have led to more mobility in the components and hence resulted in

decreased E'. Furthermore, the inclusion of hydrogen bonds and the compact polymer

network by the catechol moieties that induces cross-linkages on the surface might have

resulted in the weaker interfaces leading to a decreased value of E'. As the filler content

increases, the effect of self-tangling and non-uniform dispersion of the TBMFs due to the

accumulation of the ionically bonded TA moieties at the surfaces of TBMFs creates low

interfacial strength at the juncture of fibers and the matrix. Also, the possibility of the

plasticizing property of TA can result in the thermomechanical property decrease[14].

The T_g of a polymer indicates the point of transformation from a glassy and a rigid state to a

flexible and rubbery state. The plot of $tan\ \delta$ value, which represents the T_g, versus

temperature for different composite samples is given in Fig. 5d-f and also tabulated in Table

S4. T_g is also linked to the thermo-mechanical stability and thus dictates its service

temperature range. For NE, the obtained T_g is 169°C, which increases to 172°C for BEC1

and then decreases to 164°C for BEC5. Interestingly two peaks are noticed for SEC samples

which are β- relaxation of the T_g and α transition. The inclusion of α transition in the tan

delta peak suggest that there is some relaxation process, which has occurred within the SECs.

This generally occurs due to the cellulosic structure held by the non-uniform solid

macromolecular polysiloxane layers within the epoxy matrix acting as a plasticizer [32].

However, for both BEC and SEC, the intensity of T_g is found decreases and is suggestive

towards the reduction of the damping property of the composites by polymeric molecules

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movement restriction. For TECs, the least T_g is 151°C (TEC1), and the highest T_g occurs at 169°C for TEC2.5 which finally decreases to 163°C for TEC5. The tan delta peak intensity of the TECs is found slightly higher than that of the NE mainly due to the surface coverage by the TA moieties.

3.3. Mechanical performance of BMF epoxy composites

The effect of bare and surface functionalized BMFs on the tensile stress (σ), Young's modulus (E), strain (ε) and toughness (U_T) of the resulting epoxy composites are depicted in Fig. 6a and also tabulated in Table S5 in supporting information. In comparison to the neat epoxy sample (NE), BEC1 showed increased σ by ~6% (57.04±3.41 MPa). For epoxy composite SEC1, the presence of polysiloxane oligomers on the SBMFs is responsible for the improvement in σ for SEC1 forming a covalent bond with the epoxy matrix thereby significantly improving in σ by ~ 26% (67.69±2.14 MPa) with respect to NE. In the case of TECs, the increase in σ is as ~19% (63.93±1.94 MPa) for TEC1 owing to the better interface predicted between the fillers and the matrix due to the presence of the hydroxyl groups of the TA moieties. Higher filler content for all the variants diminishes the tensile strength of the composites. The introduction of TA enhances not only the bond strengths but also the inter- and intro-molecular interaction due to its aromatic nature and high polarity, which led to higher cohesive energy[33]. With the increase in filler content, filler entanglement might have decreased the σ. The decrease in E value is observed for BECs samples as fiber content increases. Similar behavior is found for all the SEC variants too. For SECs this decrease in E value predicts the non-uniform interaction of the polysiloxane oligomers between the fibers and the matrix. However, TEC2.5 demonstrates a significant increase in E than BECs and SECs for all of its variants. This behavior suggests that the TA moieties on BMFs binds the

fiber to the matrix at the interface by ionic bonding and modulates the stiffness at the

interfaces, leading to strengthening the composites by mechanical locking.

Single edge notched beam test was carried out to determine the toughness of the composite

materials in term of the critical-stress-intensity factor (K_{IC}) at fracture initiation and fracture

energy (G_{IC}). The different K_{IC} and G_{IC} values of different composite samples are shown in

Fig. 6b shows and are also tabulated in Table S5 in supporting information. The K_{IC} and G_{IC}

of the NE are 0.74 ± 0.01 MPa.m$^{1/2}$ and 296.30 ± 6.09 kJ/m^2, respectively. For all the variants

of BMF composites, the maximum K_{IC} and G_{IC} are obtained at higher filler content. BEC5

has an enhancement over NE with ~54% (1.16 ± 0.02 MPa.m$^{1/2}$) and ~189% (874.87 ± 27.53

kJ/m^2) in K_{IC} and $G_{IC,}$ respectively. This increase for BECs is probably due to the fibrous

nature of the sample which restricts fracture initiation and increases fracture energy. On the

other hand, the increase for SEC5 was ~44% for K_{IC} (1.09 ± 0.01 MPa.m$^{1/2}$) and ~199% for

G_{IC} (883.86 ± 19.16 kJ/m^2). TEC5 accounts for an enhancement of ~60% (1.18 ± 0.02

MPa.m$^{1/2}$) in K_{IC} and ~212% for G_{IC} (915.40 ± 28.80 kJ/m^2) with respect to NE. The presence

of the TA moieties on the surface of the TBMFs might have resulted in uniform interfacial

strength, thus leading to substantial enhancement of K_{IC} and G_{IC}. These results exhibited the

untapped nature of TBMFs in toughening the epoxy network. For a clear understanding of the

enhancement of mechanical and fracture performance of epoxy composites having

functionalized BMFs, fracture surface was analyzed under FESEM and result is shown in

Fig. 7. NE shows smooth and featureless fracture surface under FESEM. For BEC5, FESEM

fractography reveals the presence of agglomerated fiber bundles as shown in Fig. 7b. This

agglomeration of the fibers creates stress concentration zones, minimizing the restriction to

failure. For SEC5, the fibers are well dispersed and mostly pulled out entirely from the matrix

(shown by the black arrow). Furthermore, micron-sized deflected holes (DH) with crack tails

(CT) can be visualized at multiple positions (encircled by white circles), suggesting matrix

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tearing during the fiber pull out (Fig. 7c). Altogether, a highly rough fracture surface for SECs demonstrates the capability of SBMFs to create more zones of failure restriction within the epoxy network. FESEM fracture surface investigation of TEC5 reveals mostly partial fiber pullout with fiber breakage (indicated by black arrows in Fig. 7d). Moreover, a noticeable amount of epoxy matrix is found on the pulled-out fiber surfaces of TBMFs, suggesting better adhesion between the fiber and the matrix. Features like DH with crack tails are found comparatively less than that of SECs. The textured fiber surface caused by the interaction between the matrix and the fiber that results in absorbing more energy during crack propagation for TEC5.

3.4. Moisture uptake BMF epoxy composites

Moisture creates a disorder in polymeric composites by decreasing the bond strength of the fibers by creating a bond with the OH ions present on the BMFs. The amount of filler content may influence the moisture uptake in composites [34]. The % increase in moisture intake for different BMF epoxy composite sample is given in Table S6 in supporting information. An increase of ~27 %, 90 %, and 116.67 % in moisture uptake is observed for BEC1, BEC2.5, and BEC5 respectively. SEC samples showed similar behavior, but the intake is found reduced in comparison to BECs. On the other hand, there is a noteworthy decrement in moisture intake for all the TEC samples even with the increase in filler content. A decrease ~7.2 %, ~18 % and ~48.2 % in moisture uptake is observed for TEC1, TEC2.5, and TEC5 respectively. This proves that the moisture restricted to penetrate and absorbed into the epoxy composites having TBMFs.

4. Conclusion

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BMFs were treated with natural polyphenolic compound (TA) and compared with that of silane treated BMFs when used as fillers in the epoxy composites. TBMF surface under FESEM is found well covered with TA moieties evidenced by the reduced scalloped components. The spectroscopic analysis demonstrates reduced lignin and skeletal aromatics vibrations from lignin structure and from hemicellulose for TBMFs. TGA analysis of TBMFs demonstrates a significant reduction in preliminary degradation arising from moisture absorption from the surrounding. There is ~30% reduction in LRV value for TBMF, which again confers the reduction in moisture uptake by the TBMFs. The E' value is found decreased for SEC samples, which indicates poor structural mobility than that of the NE. The treatment of BMFs by TA shows a noteworthy influence to improve the stiffness of epoxy composites. On the other hand, the increase in K_{IC} and G_{IC} is found significant for TEC5 (~60% and ~212%) with respect to NE. Substantial enhancement of K_{IC} and G_{IC} for TEC is expected from the uniform interfacial strength of the TBMFs, which was confirmed from FESEM fractographic investigation. TA can be efficiently utilized as a surface treatment for natural fibers to conjugate the functional moieties applicable to enhance interfacial stiffness in epoxy composites. The work clearly identifies the potential of the use of TA as a surface modifying agent for improving the compatibility of the bamboo fibers as well as improving the mechanical properties in the composite applications.

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Figure captions

Figure 1. FESEM pictographs of (a) BMFs, (b) fiber surface for SBMFs, and (c)

camouflaged fiber surface for TBMFs.

Figure 2. FTIR Spectroscopy curves of BMFs, SBMFs, and TBMFs.

Figure 3. (a) UV spectra of TA solution before and after BMF treatment (b) Color change of

TBMFs to bluish brown after $FeCl_3$ treatment.

Figure 4. Thermophysical degradation behavior of the BMFs, SBMFs, and TBMFs

Figure 5. (a) Showing increased E' for epoxy composites having BMFs (1 and 2.5 wt%). (b)

Storage modulus vs. Temperature of BEC samples (b) No change in E' value for an epoxy

composite having 1 wt% of SBMFs higher % of SBMFs reduces the E'. (c) A marginal

increase in E' value for TEC samples having 1wt% of filler. (d) Tan delta vs. temperature of

BEC samples. (e) β- relaxation of the T_g and α transition can be seen in SEC samples (f) Tan

delta peaks of the TECs is found slightly higher than that of the NE.

Figure 6. (a) Tensile property variation composites due to bare and modified BMFs. (b)

Plane strain fracture toughness and fracture energy enhancement due to the modified BMFs.

Figure 7. (a) Smooth FESEM fracture surface of NE. (b) Agglomerated fiber bundles and

pulled out holes are visible for BEC5. (c) Well-dispersed pulled out fibers, DH with CT can

be seen at multiple positions for SEC5. (d) Partial fiber pull-out with fiber breakage is noticed

for TEC5.

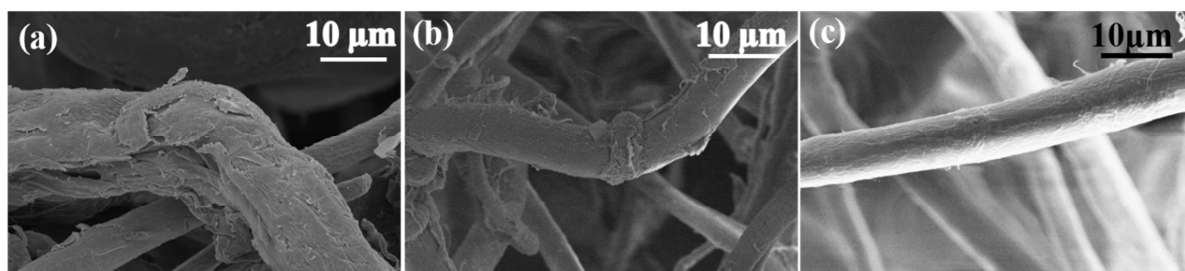Supporting Information
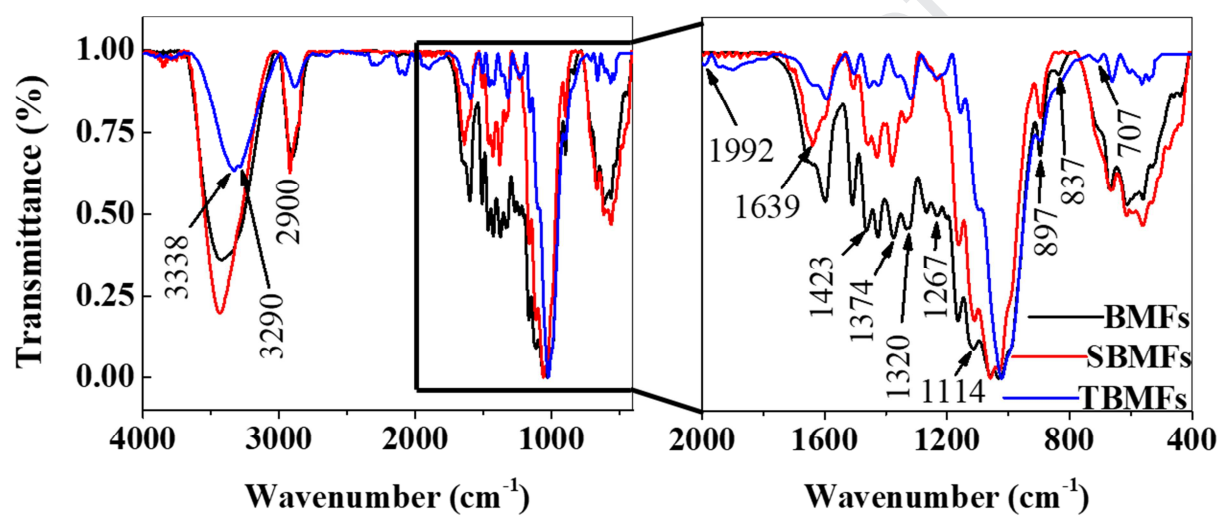
Tables S1–S6.

Discussion S1

Figure 1.

Figure 2.

Figure 3.
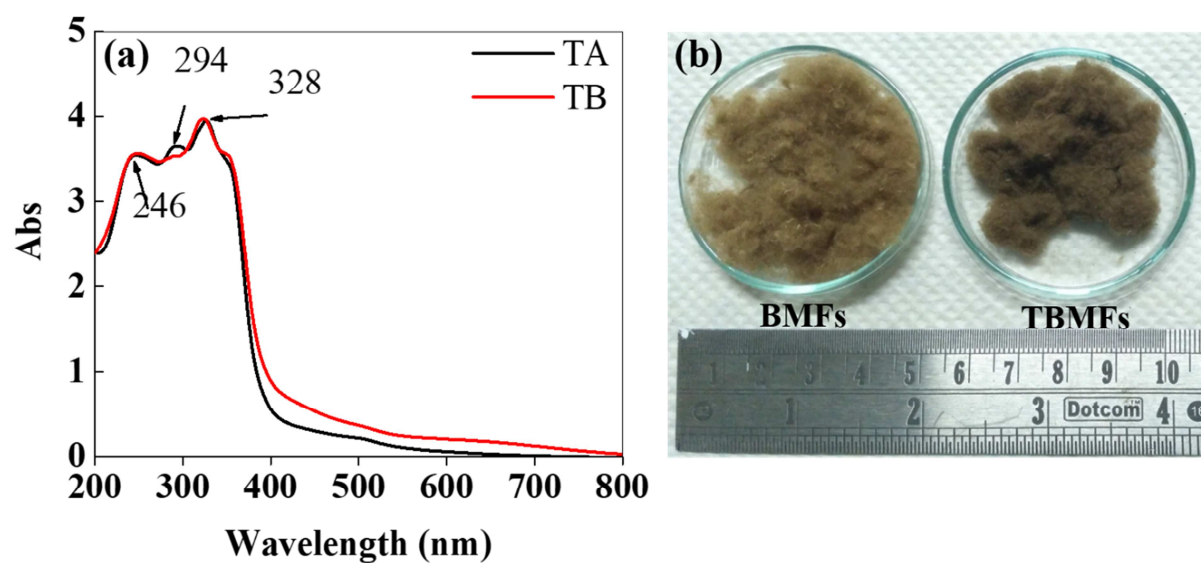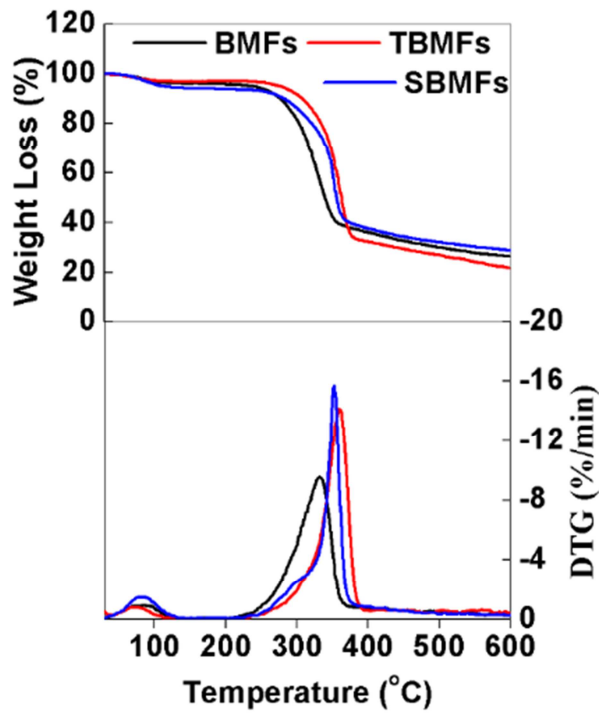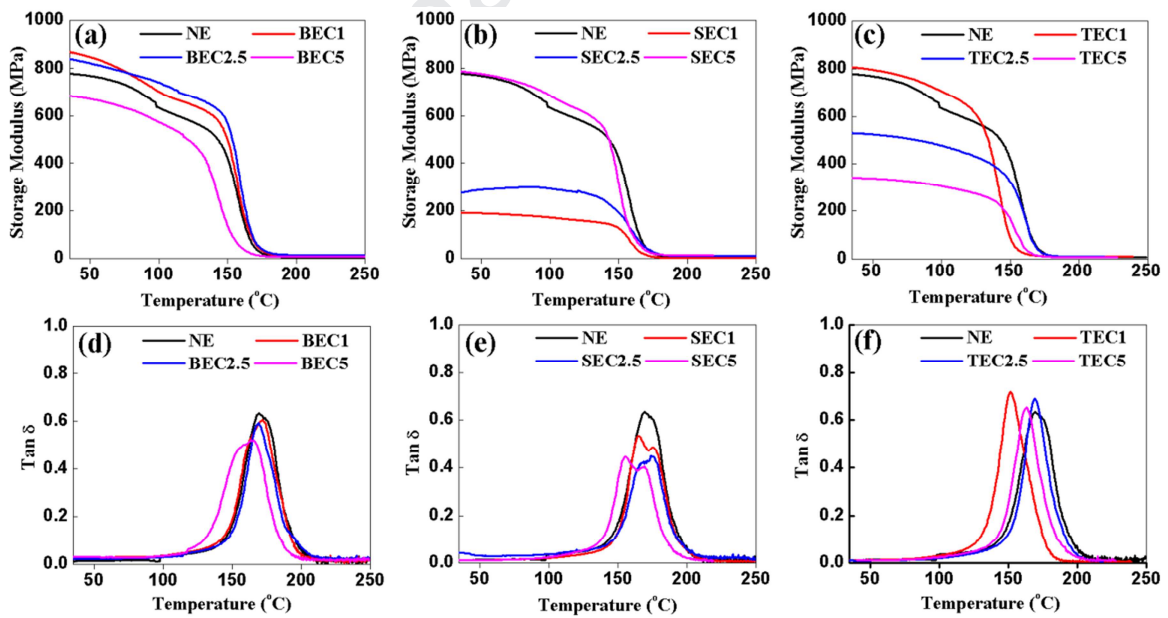
Figure 4.

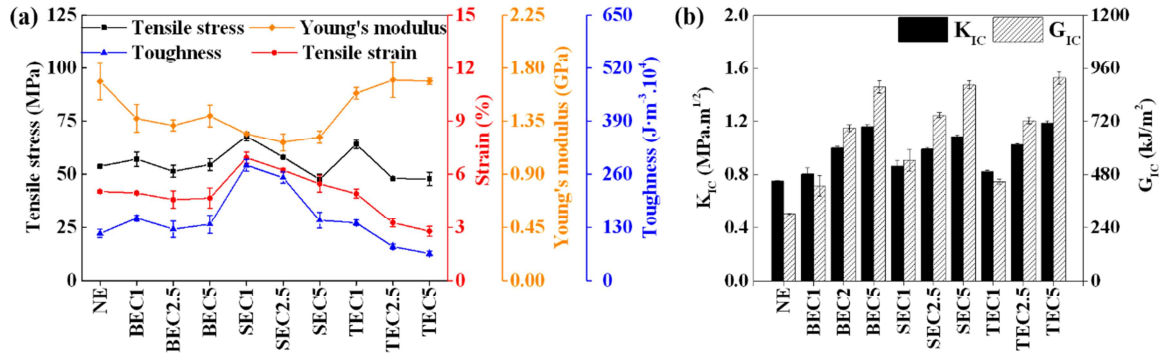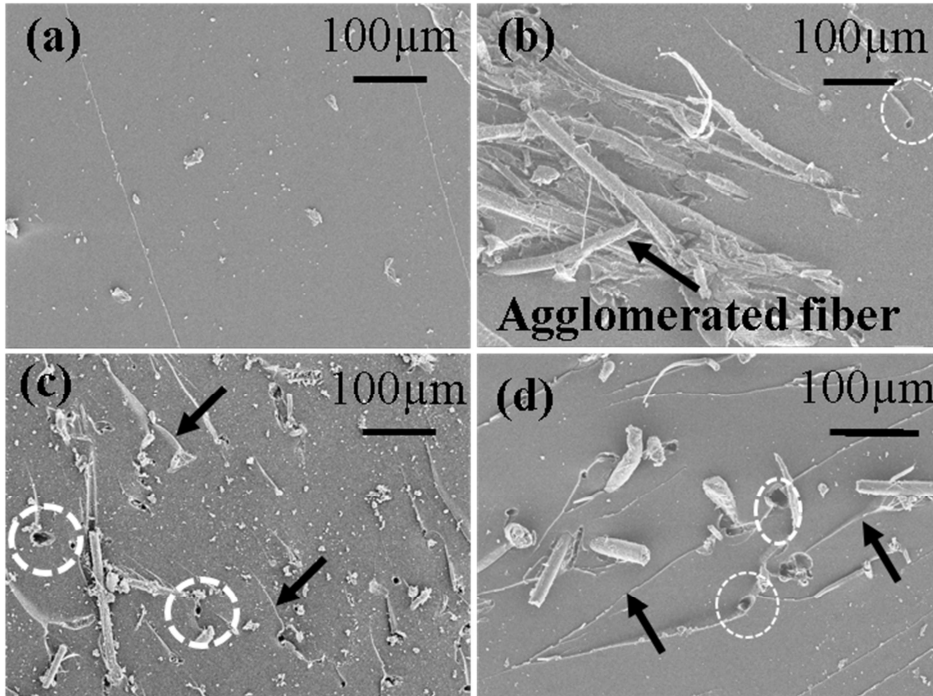**Figure 5.**

Figure 6.

Figure 7.

- Green process of functionalizing bamboo micron fibers (BMFs) by Tannic acid (TA).

- TBMFs based composites demonstrate a significant increase in Young's modulus (*E*) than the other composite samples.

- Improved fracture toughness by ~60 % and fracture energy by ~212 % in comparison to the neat epoxy.

- Reduction in moisture retention for TBMF as well as for the composites.