

Study on the effect of woven sisal fiber mat on mechanical and viscoelastic properties of petroleum based epoxy and bioresin modified toughened epoxy network

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ABSTRACT: Sisal fiber reinforced biocomposites are developed using both unmodified petrol based epoxy and bioresin modified epoxy as base matrix. Two bioresins, epoxidized soybean oil and epoxy methyl soyate (EMS) are used to modify the epoxy matrix for effective toughening and subsequently two layers of sisal fiber mat are incorporated to improve the mechanical and thermomechanical properties. Higher strength and modulus of the EMS modified epoxy composites reveals good interfacial bonding of matrix with the fibers. Fracture toughness parameters K_{IC} and G_{IC} are determined and found to be enhanced significantly. Notched impact strength is found to be higher for unmodified epoxy composite, whereas elongation at break is found to be much higher for modified epoxy blend. Dynamic mechanical analysis shows an improvement in the storage modulus for bioresin toughened composites on the account stiffness imparted by fibers. Loss modulus is found to be higher for EMS modified epoxy composite because of strong fiber–matrix interfacial bonding. Loss tangent curves show a strong influence of bioresin on damping behavior of epoxy composite. Strong fiber–matrix interface is found in modified epoxy composite by scanning electron microscopic analysis. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42699.

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INTRODUCTION

Polymer composite materials have traditionally been made with petroleum based thermoplastic or thermosetting resins as matrices. But environmental concerns and rapid drop in fossil based resources has motivated us to develop polymer matrices and fillers from renewable resources.¹

Further, high performance biocomposite is obtained by tri-corner approach such as matrix modification, effective treatment of natural fibers and optimization of processing conditions as reported by Mohanty *et al.*² Out of these approaches, matrix formulation plays a vital role in achieving superior biocomposite which is generally carried out by blending the polymer matrix with bioresin derived from renewable sources.³

Plant oils are the best candidate for synthesizing polymer precursor or prepolymers as they have unsaturated triglycerides, which can be chemically converted to different functional groups.⁴ In recent years, soybean oil based bioresins have drawn significant attention in research areas of biobased polymers because of having high amount of unsaturation (51% linolic

content) and abundantly available. Epoxidized oils and esterified epoxidized oils have been synthesized in recent years.^{5,6} Several authors have reported on the epoxidized soybean oil (ESO) based epoxy blends for its toughening nature.^{7–11} Similarly esterified soybean oil based epoxy blends with improved properties has been reported by Wang *et al.*,¹² Zhu *et al.*,¹³ and Cheng *et al.*,¹⁴ Haq *et al.*,¹⁵ and Sahoo *et al.*¹⁶ in recent years. From the previous literature, it is evident that the addition of bioresin toughened the matrix, but simultaneously reduced the mechanical and thermophysical properties of parent polymer to a great extent.

Fiber-reinforced polymer composites are tremendously used in the automotive, aerospace, and wind energy industries because of their high specific strength and modulus. Light weight, and reduction in carbon dioxide emissions are required to meet legislative demands in the automotive sectors.¹⁷ In this regard, composites reinforced with natural fibers have been getting more attention as glass, carbon, and aramid fibers are expensive and they have a negative impact on the environment.¹⁸ In addition to this, natural fibers give numerous benefits over synthetic fibers including good acoustic property, low density,

nonabrasive, and biodegradable. However, use of natural fibre reinforced composites has been constrained because of poor wettability, its high moisture affinity, low thermal stability, and poor adhesion with the matrix.

Several authors have developed composites using chemically modified vegetable oil based thermoset as matrix to get better wettability and adhesion of fibers as well as improvement in mechanical performance.^{19–32} Woven-fabric composites are receiving growing attention in structural applications better packing of fibers, high volume fraction of fiber content and superior mechanical performance.³³ In recent years, woven fabrics of natural fibers have been used to develop toughened epoxy composites with higher tensile and flexural properties.^{33–37} Among all the fibers, sisal fiber is widely used (Agave sisalana) as fillers for thermosets because of its abundant availability, less density, economical processing, low cost, higher specific strength, better impregnation, and good interfacial interaction with thermoset resins.³⁸ Sisal fiber contains higher cellulosic content (66–78%) and higher microfibrillar angle (10°–22°) as compared to other natural fibers like banana, jute, kenaf, palm, abaca, and flax fibers, which are generally used to make biocomposite.¹⁷ More cellulosic interaction with resin matrix results in better tensile strength and modulus and its larger microfibrillar angle yields high impact toughness.¹⁷ Further, sisal fibers have lesser cells with large cellulose aspect ratio and big lumen size which yields higher strength. These unique properties have made it viable to be used as fillers in widely used thermoset composites for civil and industrial applications.³⁸

In our previous work,¹⁶ we reported the synthesis of two bioresins ESO and EMS from soybean oil by epoxidation and transesterification process. Two bioresins were found to have lower viscosity and contain epoxide ring thus could act as reactive diluents which can undergo random copolymerization with epoxy. EMS has lower viscosity and higher reactivity than ESO because of conversion of triglyceride to monoglyceride esters after transesterification. In this context, toughened bio-based epoxy blends were developed by addition of two bioresins at variable weight percentage and it was observed that 20 wt % bioresin content. In the current study, we have tried to maintain stiffness–toughness balance by developing sisal fiber mat reinforced composites. Both unmodified epoxy resin and bioresin modified epoxy have been used as matrix to compare the effect of sisal fiber on the mechanical and dynamic mechanical properties. Morphological study of composites was carried out using SEM analysis to investigate fiber–matrix interface.

EXPERIMENTAL

Materials

Sisal fiber (SF) mat (surface density 405 g/m²) was procured from WDO, Dehradun, India. The physical properties of sisal fibers are depicted in Table I. Diglycidyl ether of bisphenol A based (DGEBA) epoxy resin of grade EPOXIL-25 with an epoxy equivalent weight 190–195 g/mol and Ambient temperature curing agent triethylene tetramine (TETA) of grade MH-91 were obtained from the M/s Marshal Polymers, Kolkata, India. Epoxidized soybean oil and epoxy methyl soyate were synthesized.

Table I. Physical Properties of Sisal Fibers

Property	Value
Density	1.45 g cm ⁻³
Diameter	200 μm
Tensile strength	400–600 MPa
Young's Modulus	9.4–22 GPa
Elongation at break	2.5–2.7%

Soybean oil (180 g) was epoxidized in the presence of peracetic acid generated *in situ* by 2 : 1 molar ratio of hydrogen peroxide (30 wt %) to ethylene unsaturation and 1 : 1 molar ratio of acetic acid to ethylene unsaturation in presence of 25 wt % Amberlite catalyst IR120 stirred at 500 rpm with heating at 60°C for 6 h. Then 50 g of synthesized epoxidized soybean oil was transesterified to form epoxy methyl soyate by 15 ml of methanol catalyzed by 1 wt % sodium methoxide with heating at 50°C and stirred at 500 rpm for 2 h. as reported in Ref. (16). All unsaturations are expected to convert into epoxy groups and oxirane content is not much affected by transesterification.

Methods

Preparation of Epoxy Biocomposites. The synthesized epoxidized soybean oil and epoxy methyl soyate bioresin was blended with epoxy resin at variable weight ratio to overcome the brittleness of epoxy matrix. The formulations containing 20 wt % bioresin were optimized based on impact strength and fracture toughness.¹⁶ The unidirectional sisal fiber mat was first dried at 100°C in vacuum oven to remove moisture. The DGEBA was mixed with bioresin at an optimized ratio of 80 : 20 by mechanical stirring at 2000 rpm and ultrasonicated for 30 min. Subsequently the mixture was kept in a vacuum oven to eliminate air bubbles and then cooled to room temperature. Two layers of unidirectional sisal fiber mat were incorporated as reinforcement in epoxy resin with maximum 16.7% volume content. The bioepoxy resin blend and TETA hardener mixture was poured into the mould layer by layer, keeping the fiber laminas oriented in unidirectional pattern. All types of biocomposites were fabricated using hand lay-up method followed by compression molding technique. Aluminium mold of dimension 180 × 180 × 3 (mm × mm × mm) was used for the fabrication of biocomposite. A uniform weight of 20 kg was placed over the laminate undisturbed for 24 h. Initial curing was done at room temperature for 24 h and postcuring was carried out at 80°C for 2 h and 120°C for 1 h, respectively. Samples were subjected to postcuring under the pressure of 150 psi. Test specimens of different dimensions were prepared according to ASTM standards. EPSE, EPESOSE, and EPEMSSF biocomposites are coded for unmodified epoxy, ESO modified epoxy and EMS modified epoxy biocomposite, respectively.

Characterization

FTIR and NMR Analysis. Fourier Transform Infrared (FT-IR) spectra were recorded with 4 cm⁻¹ resolution on an FT-IR spectrometer (Thermo Scientific, model Nicolet 6700, Waltham, MA). Data was acquired using FT-IR software (Thermo Scientific, OMNIC series suite, Waltham, MA) which has been

applied widely for lipids, because lipids have functional groups with absorption bands in the infrared region. ^1H nuclear magnetic resonance (NMR) spectra of ESO was obtained on a spectrometer (Varian, Inc., model 300; Palo Alto, CA) taking chloroform (CDCl_3) as a solvent.

Mechanical Property. Rectangular specimens of unmodified and bioresin modified epoxy composites of dimensions $175 \times 25 \times 3$ mm, were subjected to tensile testing as per ASTM-D-3039, using Universal Testing Machine (Instron 3382 M/s Lloyd Instruments, UK). A crosshead speed of 1 mm/min and a gauge length of 50 mm was used to carry out the test.

All types of biocomposite of dimensions $127 \times 12.7 \times 3$ mm, were subjected to flexural test, under three-point bending using the same Universal Testing Machine (UTM), according to ASTM-D 790.

Izod impact strength was measured for notched specimens having dimensions $63.5 \times 12.7 \times 3$ mm \times mm \times mm to study the toughening of epoxy by incorporation of bioresin. The specimens were notched having notch depth of 2.54 mm and notch angle 45° using a notch cutter (Tinuous olesan, UK). The tests were carried in an izod impact tester (Tinuous olesan, UK) as per ASTM-D-256.

The fracture toughness parameters, critical stress intensity factor (K_{IC}), and critical strain energy release rate (G_{IC}) of epoxy biocomposite were determined using eqs. (1) and (2) by single-edge-notched (SEN) test in a flexural three-point bending set up which was performed using the same universal testing machine according to the ASTM D 5045. The dimension of the single-edge notch specimen (SEN) was approximately $30 \text{ mm} \times 6 \text{ mm} \times 3 \text{ mm}$ with the initial notch length of approximately 2.54 mm. The specimen was then slid with a fresh razor blade to generate cracks. The span length was set at 24 mm which is about four times the width of the specimen and the load was applied with a crosshead speed of 1 mm/min.

Critical stress intensity factor:

$$K_{\text{IC}} = \frac{6YP}{BW^{1/2}}$$

$$\text{where } Y = 1.93 \left(\frac{a}{W}\right)^{1/2} - 3.07 \left(\frac{a}{W}\right)^{3/2} + 14.53 \left(\frac{a}{W}\right)^{5/2} - 25.11 \left(\frac{a}{W}\right)^{7/2} + 25.80 \left(\frac{a}{W}\right)^{9/2} \quad (1)$$

a is the precrack length, P is the maximum load, B is the specimen thickness, and W is the specimen width.

Thermomechanical Study. The dynamic mechanical analysis of all the biocomposite samples was carried out using a DMA analyzer (Q 800 M/s TA Instruments) at three point bending mode of the equipment and corresponding viscoelastic properties of the materials were measured as a function of temperature at a fixed frequency of 1 Hz and strain of 0.1%. The temperature was varied from 30 to 200°C , with a heating rate of $10^\circ\text{C}/\text{min}$.

Surface Morphology. The morphological analysis of fractured unmodified and modified epoxy composites was carried out using an SEM analysis (EVO MA 15, Carl Zeiss, SMT,

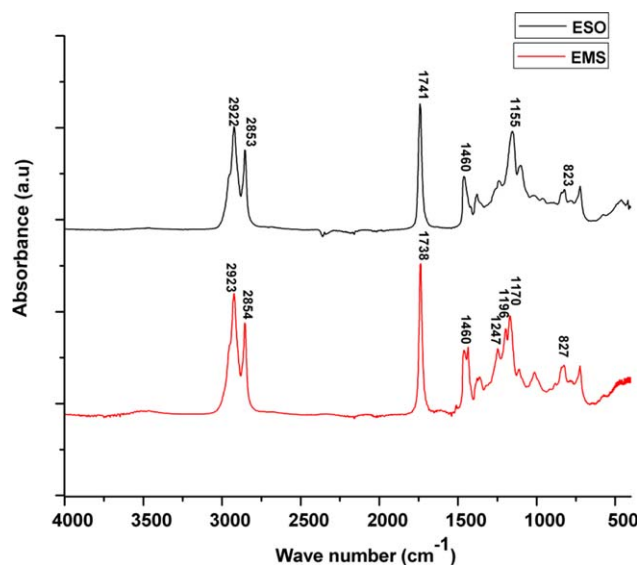


Figure 1. FTIR spectra of ESO and EMS bioresin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Germany) to investigate the interfacial adhesion between fibers and matrix. The samples were sputtered with platinum and were dried for half an hour at 70°C in a vacuum, prior to imaging.

RESULTS AND DISCUSSION

FTIR and NMR Analysis of Bioresin

FTIR spectra of ESO and EMS in absorbance mode is depicted in Figure 1. In case of ESO, the band at 1741 cm^{-1} signifies $\text{C}=\text{O}$ stretching of carboxylic group of fatty acids. The $\text{C}-\text{O}-\text{C}$ stretching from oxirane ring found at 823 cm^{-1} (encircled portion) confirms the epoxidization of ESO. Similar spectra was observed in epoxidized oils as reported earlier.^{5,8} On the other hand, a prominent band at 1738 cm^{-1} with high intensity is observed in EMS, which represents $\text{C}=\text{O}$ bond of aliphatic ester. In addition to that, three bands at 1247, 1196, and 1169 cm^{-1} signifies characteristic of fatty acid methyl esters. The similar findings in methyl ester from linseed oil based epoxidized methyl ester.⁶ The appearance of broader band at $3400\text{--}3500 \text{ cm}^{-1}$ shows the presence of hydroxyl group (OH stretch) which is prominent in EMS due to partial opening of epoxy group.

^1H NMR spectra of ESO and EMS depicted in Figure 2 confirms the successful epoxidation and transesterification of soybean oil. From the figure, the weak peaks at 5.1–5.3 ppm corresponds to $\text{CH}=\text{CH}$ unsaturation in ESO which remained unreacted during epoxidation while the peak is disappeared in EMS. The $-\text{CH}-$ protons of the epoxy ring are appeared at 2.9–3.12 ppm encircled in Figure 2 confirms the presence of oxirane content in both ESO and EMS.^{5,6} It shows oxirane content is preserved even after transesterification of ESO. A methyl ester peak at 3.65 ppm is observed and has no traces of glycerol moieties. Signals in the range of 4.12–4.27 ppm attributed to CH and CH_2 proton of glyceride moieties of ESO are absent in epoxy methyl soyate due to attachment of CH_3 group.

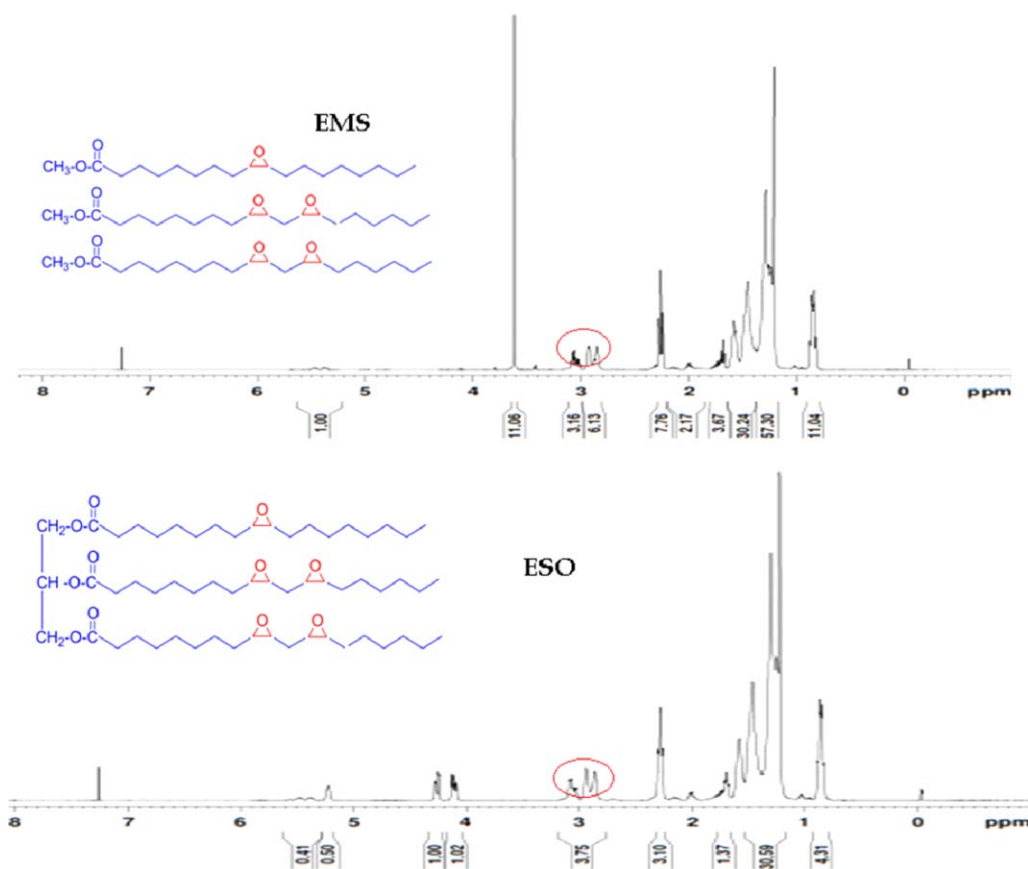


Figure 2. ^1H NMR spectra of ESO and EMS bioresin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Mechanical Property

The tensile strength of unmodified and modified epoxy biocomposite are depicted in Figure 3. It has been reported in literature that the incorporation of organic oil in to the matrix increases the interaction of fibers with the matrix at the interface resulting in higher tensile strength and modulus.³² The same trend is observed here that the tensile strength of EPESOSF and EPEMSSF composites are much higher than unmodified EPSF

composite. Figure 3 shows that the reduced tensile strength of epoxy by the addition of ESO and EMS bioresin reported in Ref. (16) is tremendously improved after incorporation of sisal fibers restoring the property of parent epoxy.

The tensile strength is measured to be 78.2 MPa for EPSF, 95.2 MPa for EPESOSF, and 116.2 MPa for EPEMSSF composite. The higher value of strength is because of the strong interfacial interaction of bioresin modified epoxy matrix with fibers which

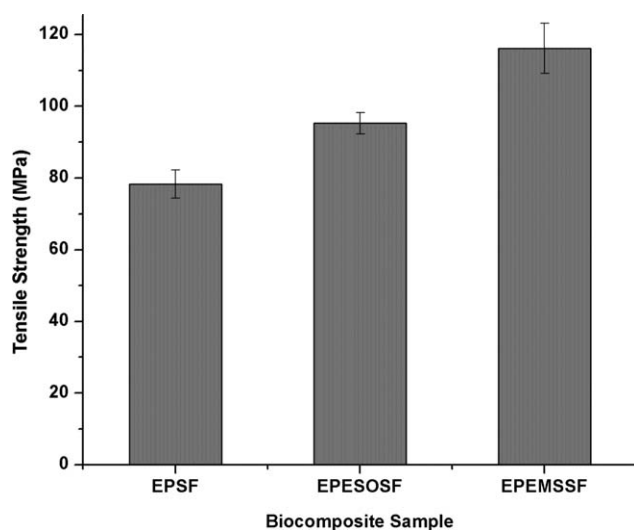


Figure 3. Tensile strength of unmodified and modified epoxy biocomposites.

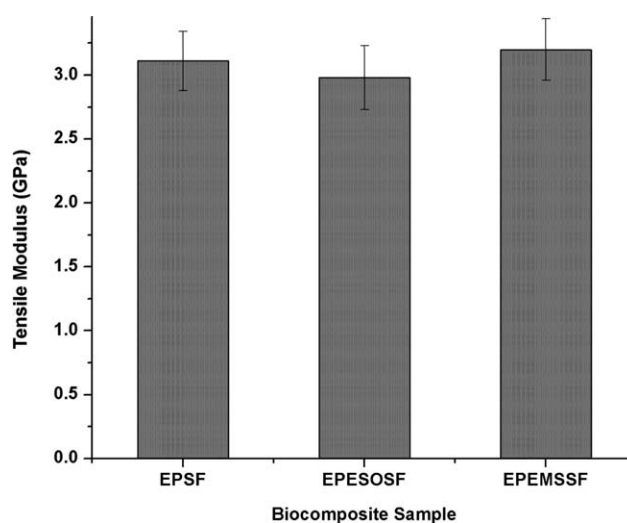
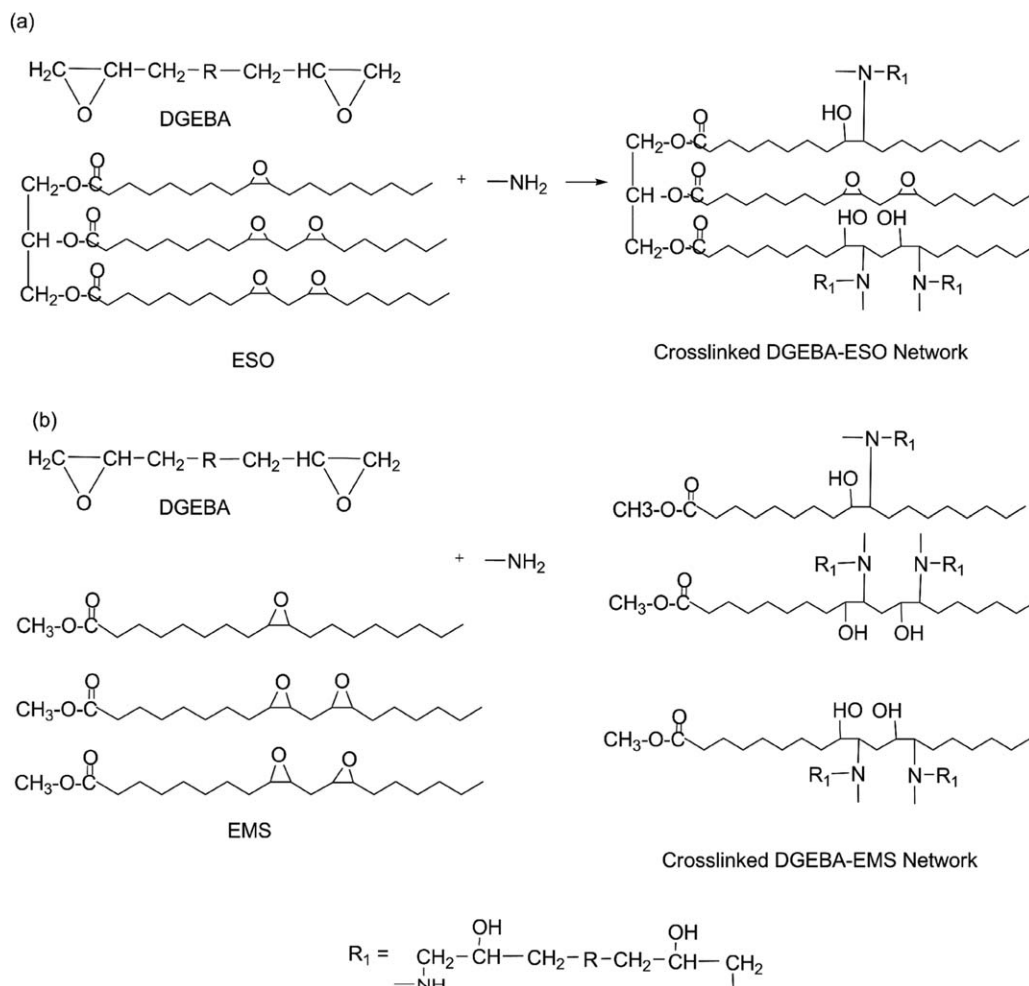


Figure 4. Tensile modulus of unmodified and modified epoxy biocomposites.

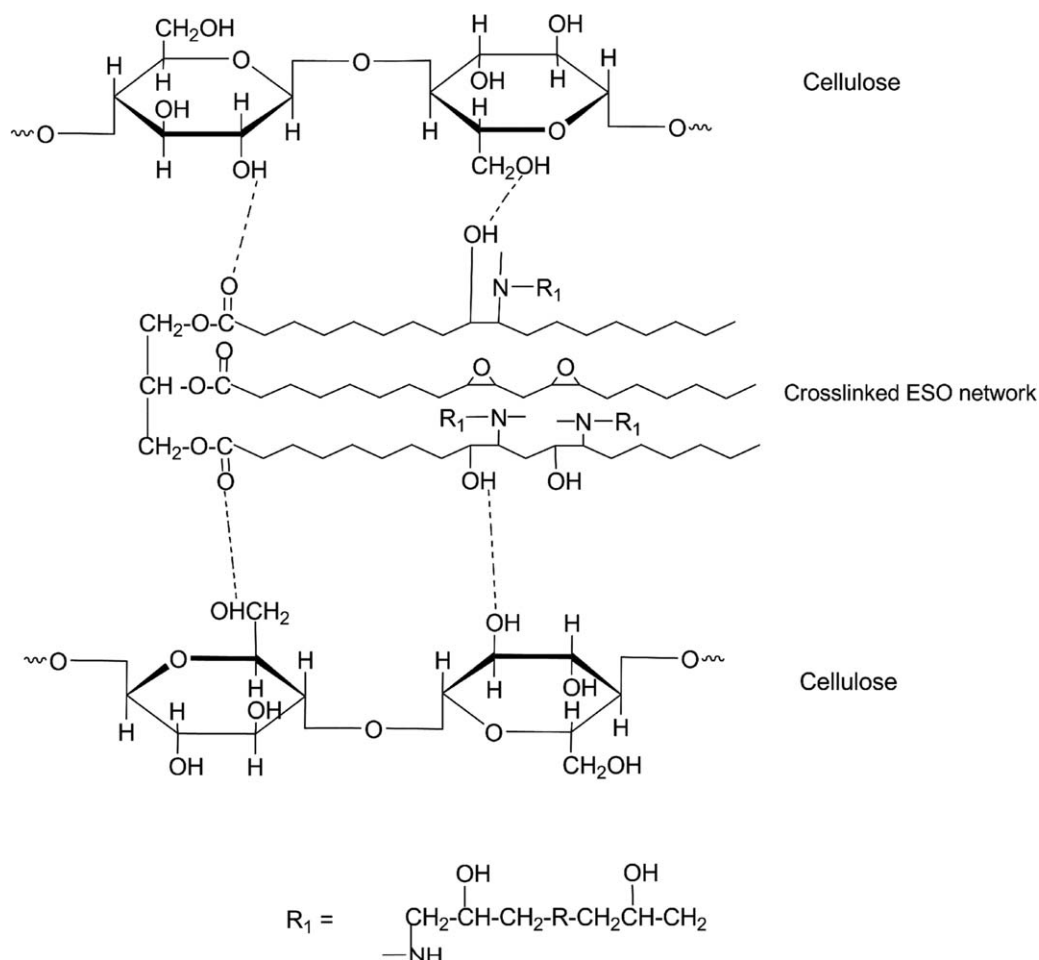


Scheme 1. Possible crosslinked network of (a) DGEBA/TETA modified with ESO and (b) DGEBA/TETA modified with EMS.

allows better stress transfer from the matrix to the fibers. Conversely, the tensile modulus of EPSF is lower than EPMSF and slightly higher than EPESOSF as shown in Figure 4. It is because of lower stiffness of flexible ESO based epoxy blend and highly stiffened EMS based epoxy network.¹³ Triglycerides of ESO increases the flexibility and reduces the modulus and strength in comparison to monoglycerides esters of EMS bioresin.

In composites, the bioresins form crosslinked network by copolymerization with DGEBA epoxy as shown in Scheme 1(a,b) as well as interacts with cellulosic part of the sisal fibers as shown in Schemes 2 and 3. Ring opening of all oxirane group is not possible as some epoxy groups of ESO could not react with amine curing agent because of steric effect and electronic effect. On the contrary, there is a possibility of ring opening of all epoxy groups in EMS based epoxy formulation on the account of separated monoglyceride ester chain with epoxy group which have a better contact with amine hydrogen. Hence, the strength and stiffness of EMS based network is higher than ESO and unmodified epoxy network. The cellulosic fibers themselves contain hydroxyl groups that may form hydrogen bonds with the hydroxyl and carboxyl groups of the bioresin and allow the resin to adhere to the fiber. Bioresin has abundant hydroxyl

groups through ring opening of epoxy linkage after crosslinking reaction with amine. The fatty acids have more carboxyl groups in which a hydrogen is bound to an electronegative oxygen, generating a dipole making the hydrogen partially positively charged. The electronegative oxygen of the resin also can form a hydrogen bond with hydrogen atoms in the fiber that have positive dipoles induced by electronegative atoms, such as oxygens to which the hydrogen is attached (Schemes 2 and 3). Thus, the bioresin act as binders in composite which can enhance the hydrogen bonding between the resins and fibers. Similar explanation regarding bonding of cellulose with binder has been reported in Ref. 39. Hydrogen bonding is a strong bond which helps in raising the mechanical properties which is prominent in bioresin modified epoxy and quite less in unmodified epoxy. Relatively less number of hydroxyl groups formed during crosslinking and carboxylic groups of ESO as shown in Scheme 2 form intermolecular hydrogen bonding with cellulose. The same type of reaction is also expected in case of EMS formulation with higher reactivity as shown in Scheme 3 because of short chains, reduced viscosity and better miscibility with epoxy resin. All epoxy group of EMS is expected to participate in crosslinking process and more hydroxyl groups are formed on account of reduced chain structure and better contact with amine curing



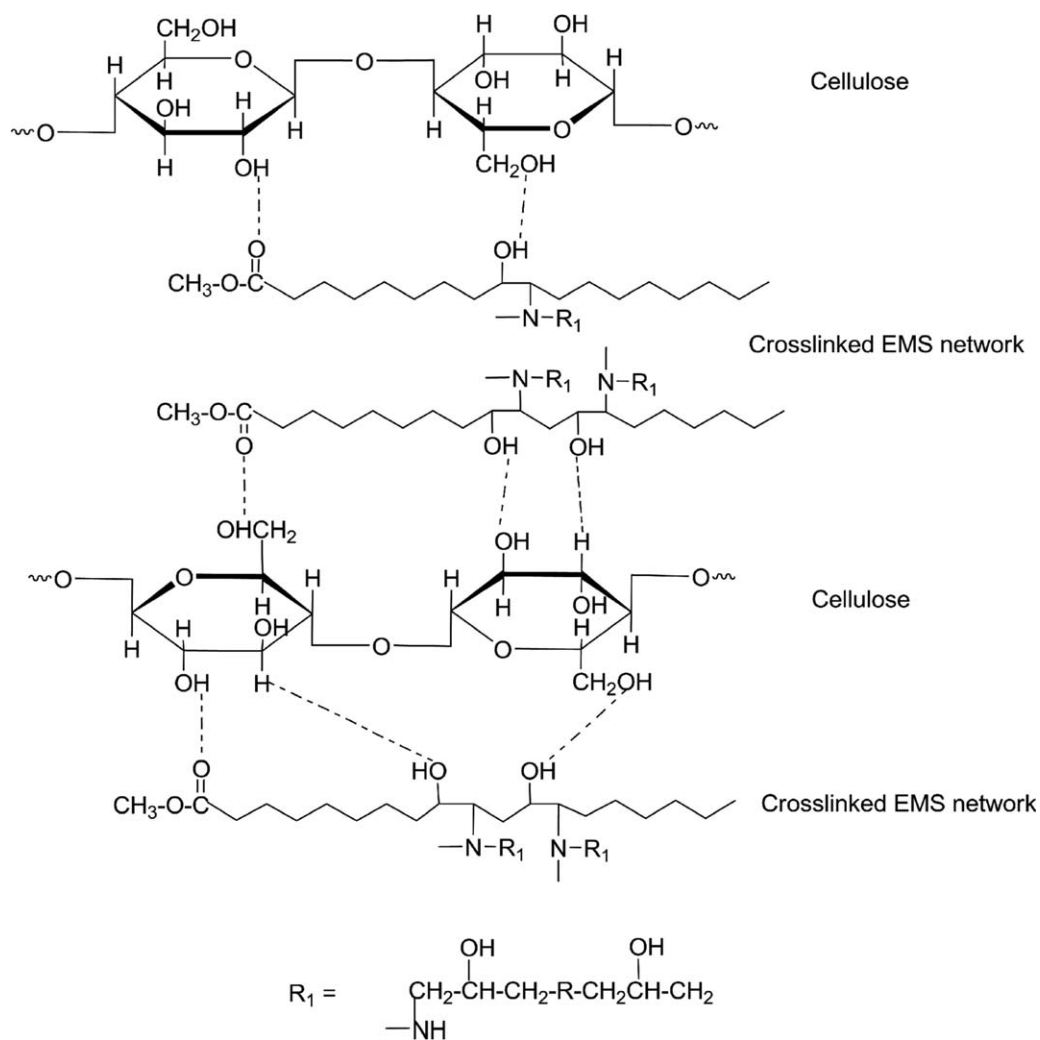
Scheme 2. Chemical interaction of cellulose and crosslinked DGEBA-ESO network.

agent. On the contrary, the middle epoxy groups of ESO are not able to interact with curing agent as well as with fibers on account of steric hindrance and electronic effect. Hence, less amount of hydroxyl groups are generated after reacting with amine. Further the impregnation of fibers in EMS based formulation is improved because of short chain structure hence stiffened the matrix effectively.

Further, oil based bioresins in fiber reinforced composite decreases the microhardness of surface of the composite, maintains the flexibility and rigidity, improves the compatibility between cellulosic fibers and resin.³² The low viscous oil based epoxy resin is completely absorbed by the sisal fibers and allows proper penetration of resin through the sisal fabric. Hence, the sisal fibers impart high rigidity through strong physical and chemical interaction with epoxy matrix and resulted in a stronger composite. Uniaxial orientation of sisal mat resulted in improved interlaminar adhesion between laminates which raised the mechanical properties.

Bertomeu *et al.* reported similar enhancement in tensile strength and tensile modulus for flax fiber laminated ecofriendly epoxy composite compared to its petroleum based counterpart.²⁴ Analogs improvement in tensile strength and modulus of oil based natural fiber reinforced composites has also been reported by

several authors.^{20,23,25,26,28,30} An increasing trend is observed in flexural strength of biocomposites after matrix modification as shown in Figure 5. Maximum flexural strength is found to be 122 MPa for EPMSF and minimum value of 106 MPa to be for EPSF composite. Similar reasons like intermolecular hydrogen bonding and crosslinking process as mentioned in tensile part can explain the difference in flexural properties of the unmodified and modified epoxy composite. Addition of oil resulted in a superior flexibility at the fiber/matrix interface and allows the fibers to elongate more freely before breakage.³² Here, incorporation of ESO and EMS as a reactive modifier enabled the matrix for better deformation and reduced the viscosity of the epoxy resin and helps the fibers for formation of strong intermolecular bonding with epoxy resin. It is also observed from Figure 6 that the flexural modulus of ESO and EMS modified epoxy composites is increased by 11.5 and 19.5%, respectively, with respect to EPSF composite on account of the higher fiber stiffness and strong fiber-matrix interface. Oxirane content, viscosity of the resin system and interaction of fiber with matrix play key role in deciding the strength and modulus of the composite.²⁴ The epoxide content of ESO and EMS are almost similar, but the reactivity of EMS is higher because of reduced viscosity and better wettability or adhesion. The reaction Schemes 2 and 3 explain the improved interaction



Scheme 3. Chemical interaction of cellulose and crosslinked DGEBA-EMS network.

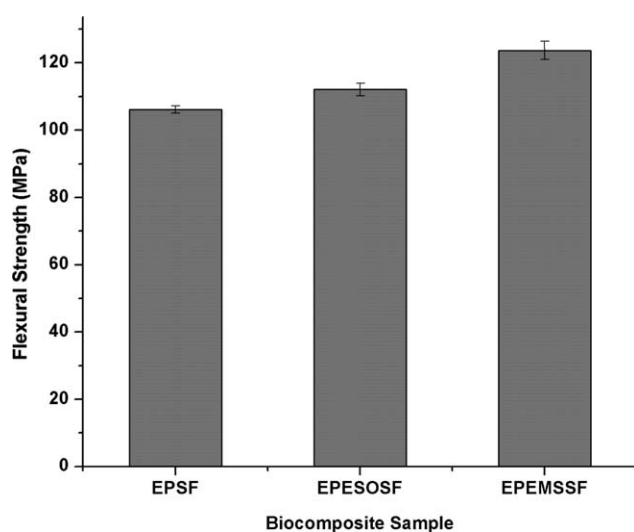


Figure 5. Flexural strength of unmodified and modified epoxy biocomposites.

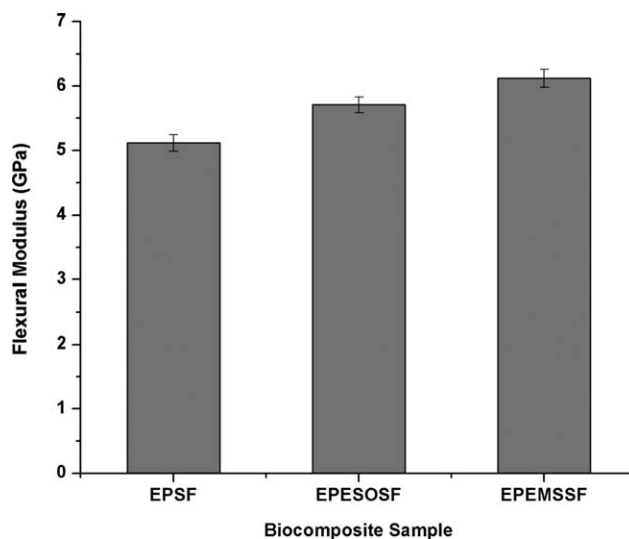


Figure 6. Flexural modulus of unmodified and modified epoxy biocomposites.

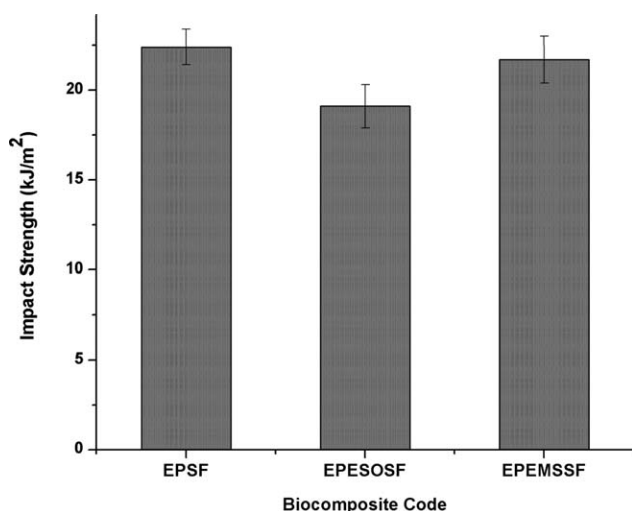


Figure 7. Impact strength of unmodified and modified epoxy biocomposites.

of EMS based epoxy resin with cellulosic fibers on account of having more hydroxyl group through ring opening of epoxy. Hence, the EMS modified epoxy composite exhibits higher mechanical properties on account of stiffened nature of ester.^{13,16}

Lower value of flexural strength and modulus in the unmodified epoxy composite (EPSF) can be accredited to the interfacial failure and delamination of fiber mat rather than the fiber breakage. Similar values in flexural properties of ecofriendly epoxy laminated composites compared to petrol based epoxy composite have been reported by Bertomeu *et al.*²² Equivalent flexural results have also been described for natural fiber reinforced soybean oil based composite by Akkenson *et al.*,²³ Adekunle *et al.*^{26,28} and Manthey *et al.*³⁰

The impact response of fiber composites is highly influenced by the interfacial bond strength, the matrix and the fiber properties. Figure 7 represents the notched Izod impact strength which measures the energy required to break the specimen which depends on the ductility of the composite. Stiffness is oppositely related to ductility hence higher strength and modulus indicates low deformation capacity or less ductility.²⁴ Energy absorption is directly related to deformation capacity of the material. However, in our case the biomodifier network (Scheme 1) increases the flexibility hence toughness on account of their aliphatic chain structure and ability to form random copolymers with DGEBA.¹⁶ Simultaneously, the fibers are well adhered to the bioresin blend through hydrogen bonding and stiffened the matrix appreciably maintaining stiffness–toughness balance. The impact strength is highest (about 22.4 kJ/m²) for unmodified petrol based epoxy composite while the values are slightly lower for bioresin modified composite. In case of EPESOSF and EPEMSSF composites, the impact strength is slightly decreased due to the sudden transfer of stress from the matrix to the fibre takes place during impact loading and it surpasses the fibre strength resulting in the fracture of fibres without any pull out.^{35,36} However, the impact strength of bioresin modified composite is comparable with that of unmodified epoxy

composite due to plasticization effect of ESO and EMS. EMS incorporates higher strain at break within epoxy matrix in comparison to ESO because of the effective shear yielding process by homogeneous distribution of smaller cavities.¹⁶ The impact energy obtained is in well accordance with literature values.^{26,28} The work of debonding and pullout needs more energy and thus the impact energy increased for sisal fiber laminated unmodified epoxy composites compared to modified epoxy composite. The fiber-pullout and weak interfacial adhesion with matrix yield better energy absorbance of the unmodified epoxy composite,^{24,36} whereas the flexibility imparted by bioresins in to the epoxy matrix owes to comparable value of.

Woven mat laminated composite plays key role in enhancing the fracture toughness compared to nonoven mat reinforced composite. The toughness of the fiber reinforced composites is generally accessed by the interfacial parameters and the modes of failure like fracture toughness, interlaminar shear strength, debonding, single fiber pullout, etc. The critical strain energy release rate (K_{IC}) of the laminated composites is given in Figure 8. The value of K_{IC} is found to be 4.3, 4.8, and 5.8 MPa m^{1/2} for EPESF, EPESOSF, and EPEMSSF, respectively. Higher K_{IC} value is observed in bioresin modified epoxy composite because of strong interfacial bonding between fibers and bioresin based matrix and deformation capacity through crack propagation mechanism. ESO and EMS crosslinked network and cellulose–bioresin interaction restricted the crack propagation in epoxy composite, hence improved fracture toughness properties of composite. The K_{IC} values are similar to woven flax fiber mat reinforced epoxy composite with fiber volume fraction $V_f = 0.3–0.4$.³⁶ Similarly, an increasing trend in K_{IC} value is reported for jute and hemp fiber laminated polyester composite compared to unreinforced matrix for a higher volume fraction of fibers.³⁷ However, here this is achieved at 0.17 V_f sisal fiber laminated unmodified and modified epoxy composite.

It can be concluded that the laminated composites have improved energy absorption property with higher strength and stiffness compared to its base matrix.

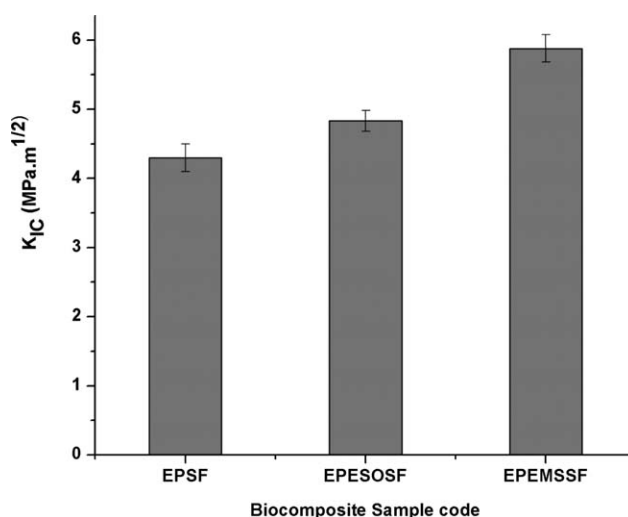


Figure 8. Fracture toughness of unmodified and modified epoxy biocomposites.

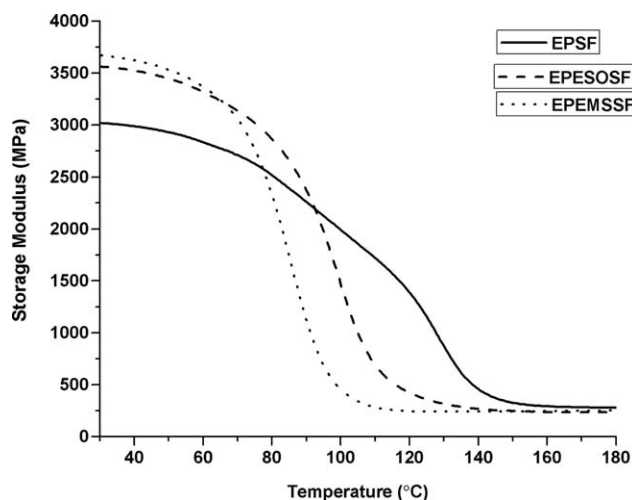


Figure 9. Storage modulus of unmodified and modified epoxy biocomposites.

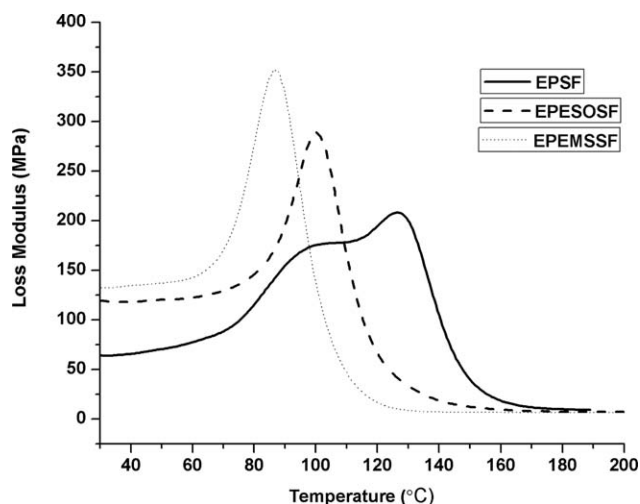


Figure 10. Loss modulus of unmodified and modified epoxy biocomposites.

Thermomechanical Properties (DMA)

The storage modulus, loss modulus and $\tan \delta$ graph as a function of temperature are shown in Figures 9–11, respectively, and the corresponding parameters are provided in Table II.

Storage Modulus. As shown in Figure 9 and Table II, the storage modulus (E') value at room temperature measured to be 3017, 3542, and 3651 MPa for EPSE, EPESOSEF, and EPEMSSF, respectively. The improved storage modulus of composite compared to its base matrix [reported in Ref. (16)] is because of the addition of sisal fibers within the matrix. The higher modulus of EPESOSF and EPEMSSF is because of immobilized macromolecular chains resulting from strong fiber–matrix interaction at the interface as described in morphology section. The addition of epoxidized oils improves the chemical interactions amid the linoleic content of bioresin with epoxy resin and cellulosic fibers thus make the composite stronger. Higher storage modulus of EMS based composite is owing to more amount of cellulosic interaction and strong adhesion of monoglyceride ester chain as described in mechanical section. This indicates that the sisal fibers impart stiffness to the toughened epoxy blend by putting constraints on the mobility and deformability of the matrix.²⁶ Lower storage modulus of EPEF composite is on account of poor fiber–matrix interaction which is in accordance with the mechanical properties. In bioresin modified composite, the reinforcement of fibers allowed a greater degree of stress transfer at the fiber–matrix interface. However, in the rubbery region, storage modulus of EPSF composite is higher than its counterpart because of higher crosslink density. Similar

improvement has been reported in AESO oil based composite by Donnel *et al.*²¹ and ecofriendly epoxy composite by Boquillon *et al.*,²² and ESO based composite by Åkesson *et al.*,²³ and Adekunle *et al.*,^{26,28} and epoxidized hemp oil based epoxy composite.³⁰

Loss Modulus. The loss modulus of all the epoxy composite system is shown in Figure 10 and Table II. The α relaxation is related to chain segment mobility in the crystalline phases which is probably due to reorientation of defect areas in the crystals. Loss modulus corresponding to α relaxation temperature increased accordingly, with the viscous dissipation being more for epoxy/EMS/SF biocomposite than its counterparts, which is attributed to constraints on segmental immobilization of the matrix chains at the fibres surface. The maximum loss modulus of EPESF, EPESOSEF, and EPEMSSF are found to be 208, 288, and 351 MPa, respectively. Greater loss modulus indicates the superior interfacial interaction in fiber–matrix interface, which reduces the polymer chain mobility. The results are in accordance with the tensile and flexural results of the biocomposites. The higher loss modulus at relaxation temperature is probably due to strong interfacial bonding of sisal fibers with matrix, which reduced the flexibility of the material.²⁶ More broadening of the curve with soldier head in the unmodified epoxy composite is due to inhibition of the relaxation process within the composites with the addition of fibres.

Loss Tangent ($\tan \delta$). Figure 11 shows the loss factor or $\tan \delta$ curve as a function of temperature for epoxy biocomposites.

Table II. Dynamic Mechanical Parameters of Unmodified and Modified Epoxy Biocomposite

Sample	Storage modulus (MPa) at room temperature	Maximum loss modulus (MPa)	Tan δ Value	Glass transition temperature (°C)
Epoxy/SF	3017	208	0.255	135
Epoxy/20 wt % ESO/SF	3542	288	0.251	106
Epoxy/20 wt % EMS/SF	3651	351	0.336	96

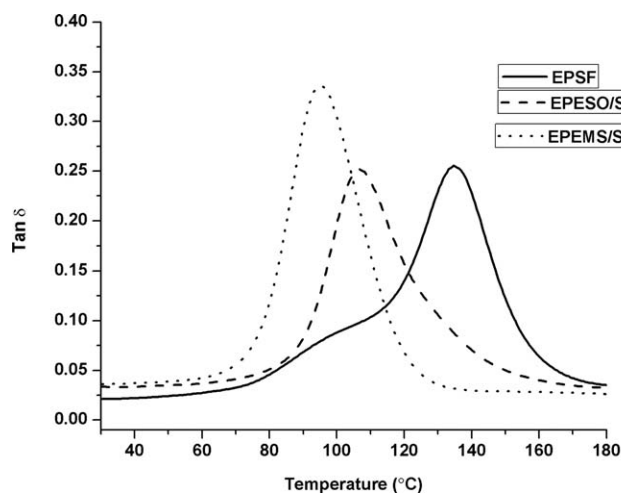


Figure 11. Loss tangent curve of unmodified and modified epoxy composites.

The intensity and area under the curve of the $\tan \delta$ peak reveals the damping behavior of the samples. Systems with broader peaks are generally consists of heterogeneous structures which yield a broader temperature range, to initiate significant viscous

chain motions for the various components. From the Figure 11, it is observed that the area under the $\tan \delta$ curve of EPESOSF and EPEMSSF is higher than EPSF composite which confirms the presence of more elastomeric components in modified epoxy composite. As shown in the Figure 11, the damping peak is a boarder and of less intense in the case of EPSF composite compared to modified epoxy composite. The highest damping factor of 0.33 (Table II) and larger area under the $\tan \delta$ in EPEMSSF composite is observed which can be attributed to plasticized EMS modified epoxy matrix and strong fiber–matrix interface. The EPESOSF composite The flexible network shown in Schemes 2 and 3 are responsible for enhancing the dampening property. The monoglyceride epoxidized esters (EMS) plasticizes the matrix more effectively in comparison to epoxidized triglycerides (ESO). It concludes that the EMS modified epoxy composite have better damping properties than ESO modified composites under vibrating conditions. Energy dissipation occurs in both modified matrix and fiber interface. The glass transition temperature of the unmodified epoxy composite is higher than that of modified counter parts on account of higher crosslink density, higher modulus value in rubbery region. This can also be explained because of lower T_g of epoxy/20% EMS blend and epoxy/20% ESO blend compared to that of

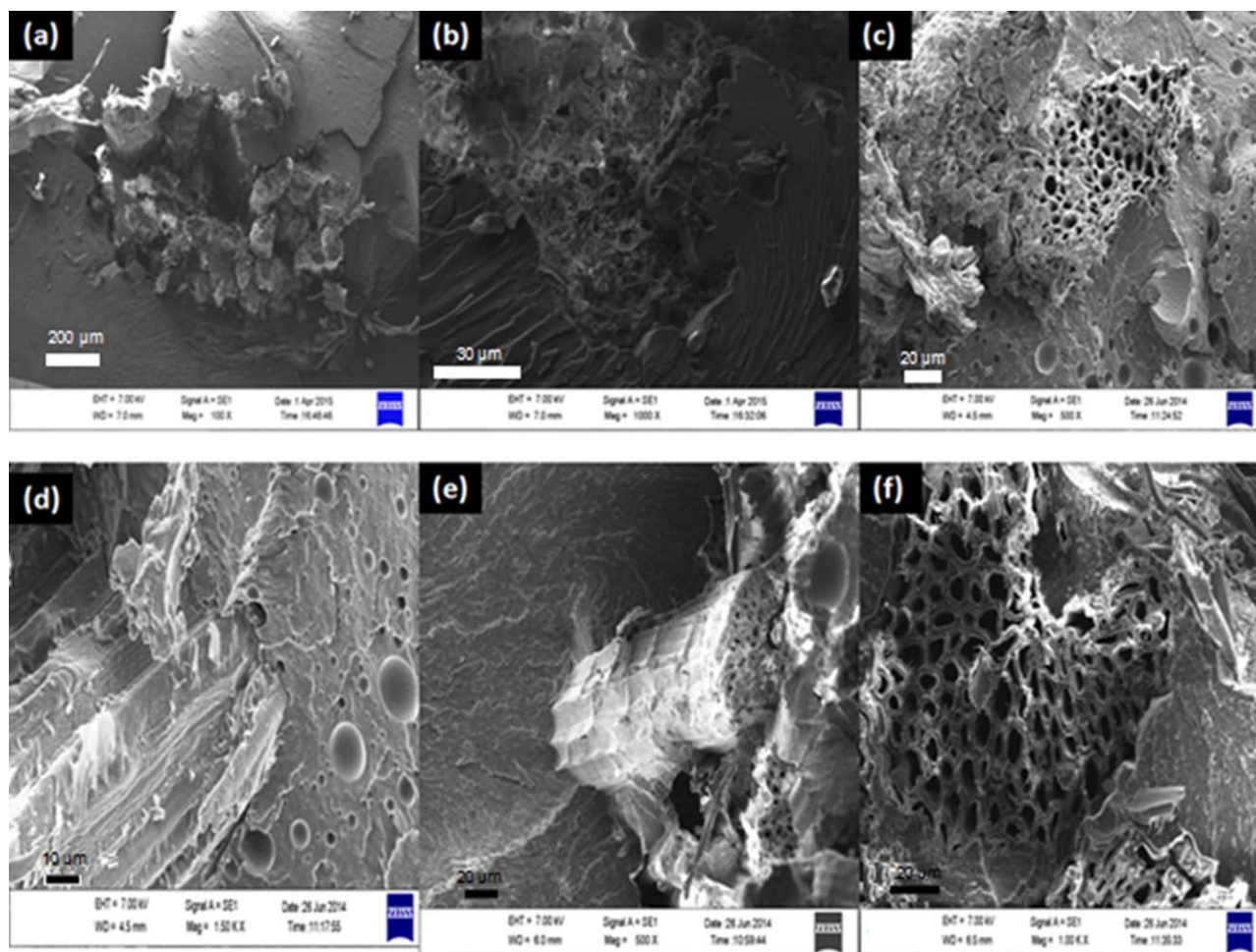


Figure 12. SEM micrographs of (a) and (b) EPSF, (c) and (d) EPESOSF (e) and (f) EPEMSSF composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

unmodified or virgin epoxy on account of its lower crosslink density and plasticization effect of ester groups. The glass transition temperature of EPEMSSF biocomposite is less than EPE-SOSF composite because of the reduced T_g of EMS based blend as compared to ESO modified epoxy blend.¹⁶ Further, the determined T_g may be inaccurate in because of broadening of curve due to presence of heterogeneous components and cavities.

Similar improvement in storage modulus and a decrease in $\tan \delta$ values have been reported in the literature.^{23,26,30}

Morphological Study

SEM study of the impact fractured surface was carried out to investigate the fiber–matrix interaction for all the composites and shown in Figure 12. As shown in Figure 12(a,b), fracture surface of unmodified epoxy composite shows poor fiber–matrix adhesion with a gap between fiber and matrix. Weak fiber–matrix interaction leads to lower strength and modulus with early failure.²² On the contrary, strong fiber–matrix adhesion with no interfacial gap in case of bioresin modified epoxy composite is observed. This allowed easy stress transfer from matrix to fiber resulted in higher strength and stiffness which is in accordance with the mechanical properties.³⁴ No interfacial gap in modified epoxy composites is due to better impregnation of fibers with low viscous resin mixture. Thus, the strength and stiffness is more strengthened in EMS based composite as explained in tensile and flexural properties.

Further unmodified epoxy composite shows surface with debonding and fiber pull out resulted in higher impact strength. Similar findings have been reported in other thermoset composite literature.²⁴ Nonuniform voids and cavities formed in ESO modified epoxy composite lower the impact strength compared to EMS modified epoxy composite [Figure 12(c,d)]. While EMS form uniformly spread small domains or cavities within the epoxy matrix phase [Figure 12(e,f)] which increased the impact strength through the shear yielding process.¹⁶ Uniform dispersion and homogenous size of domains toughened the matrix effectively by proper stress transfer between epoxy and cavities which was difficult to maintain in ESO modified epoxy composite because of un reacted oils forming macrocavities and hand layup process technique.³⁶ In case of EPEMSSF composite [Figure 12(e,f)], it shows good interfacial adhesion between fiber and matrix which was already confirmed in mechanical study. Unmodified epoxy composite laminate absorbs the majority of loads through fiber pullout mechanism and interfacial gap whereas modified epoxy composites absorb the energy through the shear yielding process within the matrix.

CONCLUSIONS

In the current study, unidirectional sisal fibers were incorporated within the unmodified petrol based epoxy and soy based bioresin modified epoxy to develop biocomposites. The tensile and flexural properties of bioresin modified epoxy composite are higher than unmodified epoxy composite because of cellulosic fiber–matrix interaction. Impact strength of EPSF epoxy composite was found to be greater in comparison to its counterparts on account of more energy absorption by fiber pullout and weak fiber–matrix adhesion. On the contrary, the fracture

toughness was measured to be highest for EPEMSSF composite because of strong fiber–matrix adhesion and ductility in the epoxy/EMS matrix.

The storage modulus of EPEMSSF and EPEMSSF biocomposites have increased values compared to EPSF composite at room temperature, which indicates that fibers carry a greater extent of stress and allow only a small part of it to strain the interface in glassy region. Higher damping factor and larger area under the loss tangent curve of EPEMSSF composite confirms the damping behavior under vibrating conditions. SEM micrographs reveal the strong interfacial adhesion between the fibers and modified epoxy matrix resulting in improved mechanical performance.

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