

Synthesis and Characterization of Bio-based Epoxy Blends from Renewable Resource Based Epoxidized Soybean Oil as Reactive Diluent*

Sushanta K Sahoo, Smita Mohanty** and Sanjay K Nayak

Laboratory for Advanced Research in Polymeric Materials (LARPM), Central Institute of Plastics Engineering & Technology (CIPET), B/25, CNI complex, Patia, Bhubaneswar 751024, Odisha, India

Abstract A novel bioresin, epoxidized soybean oil was synthesized by *in situ* method and was characterized employing FTIR and NMR. The bioresin was blended with epoxy (DGEBA) at different ratios as reactive diluents for improved processability and toughened nature. The composition with 20 wt% bioresin exhibited improved impact strength to the tune of 60% as compared to virgin epoxy. Fracture toughness parameters critical stress intensity factor (K_{IC}) and critical strain energy release rate (G_{IC}) were evaluated using single edge notch bending test and demonstrated superior enhancement in toughness. Dynamic mechanical, thermal, thermo mechanical and fracture morphological analyses have been studied for bio-based epoxy blends. Curing kinetics has been evaluated through DSC analysis to investigate the effect of bioresin on cross-linking reaction of neat epoxy with triethylenetetramine as curing agent.

Keywords: Bio-based epoxy; Soybean oil; Fracture toughness; Curing kinetics; TMA.

INTRODUCTION

Rapid depletion of fossil resources and environmental concerns have considerably propagated in to utilization of the renewable feed stocks towards sustainable development of polymeric materials in last decades. Most imperatively, the process to convert polymers from renewable materials meets the principles of green chemistry such as design for degradation, pollution prevention, energy efficiency and use of renewable feed stocks^[1].

Usually petro-chemical based thermoset resins such as epoxy, polyester and vinyl ester are used to develop composites for structural application because of their valuable properties^[2]. Comparing all the thermoset resins, epoxy resin has been widely used in various high performance applications due to its high stiffness, good chemical resistance, better dimensional stability, low curing shrinkage and low expansion coefficient. However, it has several impediments such as brittleness characteristics, non-biodegradability, high cost, energy consumption and health hazards^[3].

Accordingly, synthesis of novel bio-resins from renewable feed stocks like vegetable oils has been a subject of research since many years^[4]. In order to transform to resin precursors from plant oils, it's triglyceride chain must be chemically modified at the unsaturated double bonds or carboxyl functionalities by the process of epoxidation, acrylation, hydroxylation, transesterification, maleination^[5, 6]. *etc.* Among all plant based oils, soybean oil is the most attractive alternative to petroleum resource because of its unique composition (51% linoleic acid, 25% oleic acid, 10% palmitic acid, 7% linolenic acid and 5% stearic acid) and takes a great importance as a raw material to produce the bio-based pre-polymers and even polymers^[7]. However, even

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** Corresponding author: Smita Mohanty, E-mail: papers.journal@gmail.com

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extremely functionalized soybean oil based bioresins individually cannot provide sufficient mechanical and thermal properties for structural application due to their long aliphatic chain structure and low crosslink density^[8–11]. Consequently, derivatized soybean oil based bioresins can be used for partial replacement of petroleum based counterparts to adequately fulfill the requirements of reactive diluents which not only enhance the processibility by reducing viscosity of the epoxy resin system also toughen the epoxy matrix.

The major shortcoming of epoxy is its poor toughness which limits its wider exploitation in structural application. Toughening can be accomplished by different methods like reducing the crosslink density or adding plasticizers or incorporating a second phase in form of particles^[12]. In the last decades so many modifiers have been reported as toughening agents to overcome the inherent brittleness of epoxy network^[13, 14]. However, these modifiers result in the increase in viscosity corresponding to decrease in resin flow and processing difficulty and most importantly they are not bio-based. Looking at these above issues, epoxidized soybean oil (ESO) based bioresin can be a most suitable alternative to modify the virgin epoxy as reactive diluents. It can well mix with the virgin epoxy, reduce the viscosity of resin and enhance the reactivity of the resin system as well as toughen the matrix due to its flexible aliphatic chain. In addition to this, it has environmental advantages to be used as reactive modifier or diluents. Epoxy reactive diluents has very important effect on performance of the material because of the presence of the epoxy group and will not affect some valuable properties of the virgin epoxy system^[15]. It can take part in crosslinking reaction hence allowing the diluents to become chemical bound in to the crosslinked network. Most favorable crosslinking process depends on understanding the curing kinetics, the curing mechanism and accurate modeling of the curing process. Since ESO is to be used as reactive diluents, curing kinetics modeling helps in determination of the mechanism, or the appropriate kinetic equation for the analyzed bio-based system, and activation energy of the reaction.

Numerous works on development and characterization of biobased epoxy blends derived from epoxidized soybean oil (ESO) were reported in recent years^[17–28]. In the present investigation, epoxidized soybean oil was synthesized by *in situ* epoxidation process and used as diluent for DGEBA based epoxy with amine curing agent. ESO based bio-based epoxy blends were synthesized and characterized in detail employing characterization like fracture toughness, dynamic mechanical analysis, thermomechanical analysis along with mechanical, thermal and morphological properties. A non-isothermal curing kinetics model was proposed to explore the effect of ESO bioresin on crosslinking reaction of epoxy.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A-based (DGEBA) epoxy resin of grade EPOXIL-25 with an epoxy equivalent weight 196 g/mol and ambient temperature curing agent triethylene tetramine (TETA) of grade MH-91 were obtained from the M/s Marshal Polymers, Kolkata, India.

Soybean oil (iodine value ≈ 130 , density = 0.92 g/mL and average molecular weight ≈ 1000) of commercial grade was purchased from local sources and epoxidized to be used as reactive diluents. Glacial acetic acid, hydrogen peroxide, toluene, anhydrous sodium sulfate and sodium carbonate of AR grade were procured from M/s Merck India. All other chemicals were of analytical grade and used as received.

Methods

Epoxidation of soybean oil

The epoxidation process was followed as reported earlier^[26]. 200 mL of soybean oil, 50.4 mL glacial acetic acid, 50 mL of toluene were mixed at 50 °C for 30 min in a 500 mL three-neck round bottom flask equipped with a thermometer, a dropping funnel, a cold-water condenser and oil bath. The mixture was subjected to magnetic stirring at 400 r/min. Subsequently, 158.8 g of H₂O₂ (30 wt%) was added drop by drop, while maintaining the temperature of the reaction system at 55–60 °C for 8 h. The reaction mixture was then washed twice with Na₂CO₃ aqueous solution (5 wt%) and the product was separated by decantation. The product was washed again with distilled water, and dried on anhydrous sodium sulfate. Toluene was removed by distillation under vacuum

and epoxidized soybean oil was dried at high vacuum and at 70 °C overnight. The possible scheme of epoxidation of soybean oil is shown in Fig. 1 wherein it is assumed that all the unsaturated bonds have been converted to oxirane ring.

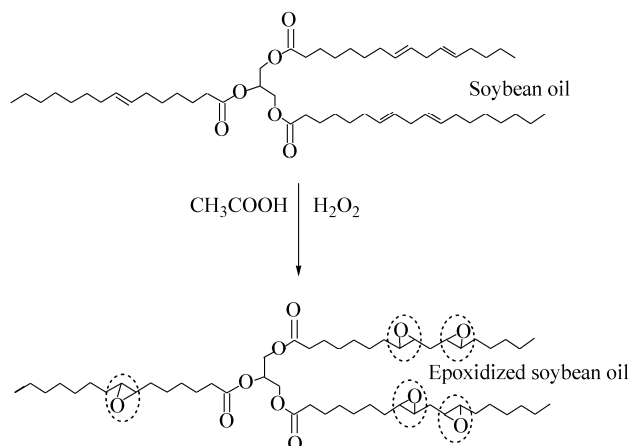


Fig. 1 Scheme for epoxidation of soybean oil

Synthesis of toughened bio-based epoxy blend network

Bio-based epoxy blends were prepared by blending ESO bioresin with petroleum based epoxy resin (DGEBA) at different ratios 0:100, 10:90, 20:80 and 30:70. The blend was mixed at variable ratios of ESO:DGEBA by mechanical stirring and ultrasonicated for 30 min and subsequently kept in vacuum oven to eliminate air bubbles and then cooled to room temperature. Subsequently, the curing agent TETA was added to the bio-based blends in a ratio of 100:12.3 which was then poured into an aluminium mold. Initial curing was done at room temperature for 24 h and post curing was carried out at 100 °C for 2 h and 120 °C for 2 h respectively. The blends were fabricated using hand layup method followed by compression molding technique. Test specimens of variable dimensions were prepared according to ASTM standards.

Characterization

Iodine value and oxirane oxygen content

Iodine value is the mass of iodine in grams that is consumed by 100 g of substance. It indicates the unsaturation of the oil or fatty acids which is in the form of double bonds that react with iodine compounds. Soybean oil has high amount of iodine value because it contains high amount of linoleic acid (54%) which has double bonds in its fatty acid chain. Iodine value is determined by American Oil Chemists Society (AOCS) ASTM D 1959-97 before and after epoxidation of soybean oil.

Oxirane oxygen content shows the presence of epoxy groups in the oil after epoxidation. The oxirane content (OC) of the ESO was determined by HBr-CH₃COOH titration procedure (American Oil Chemists Society cd-9-57 (1998)).

Functional group analysis of resin by FTIR and NMR

Fourier transformation infrared (FTIR) spectra were recorded with 4 cm⁻¹ resolution on an FTIR spectrometer (Nicolet 6700, Thermo Scientific, Waltham, MA, USA). Data was acquired using FTIR software (OMNIC series suite, Thermo Scientific, Waltham, MA, USA) which has been applied widely elsewhere for lipids, because lipids have functional groups with absorption bands in the infrared region. Crosslinked resin systems were also analyzed by FTIR spectra.

¹H nuclear magnetic resonance (NMR) spectra of ESO was obtained on a spectrometer (Varian, Inc., 300; Palo Alto, CA, USA) using deuterated chloroform (CDCl₃) as a solvent.

Mechanical Properties

In order to investigate the effect of bioresin on the properties of DGEBA based epoxy, rectangular specimens of virgin epoxy and bio based epoxy blend networks of dimensions 165 mm × 25 mm × 3 mm were subjected to tensile testing as per ASTM-D-3039, using Universal Testing Machine, (Instron 3382, UK). A crosshead speed of 1 mm/min and a gauge length of 50 mm were used for carrying out the test.

All bio-based epoxy specimens, along with virgin epoxy of dimensions 127 mm × 12.7 mm × 3 mm, were taken for flexural test, under three-point bending using the same Universal Testing Machine (UTM), in accordance with ASTM-D 790.

Izod impact strength was determined for the notched and un-notched specimens having dimensions 63.5 mm × 12.7 mm × 3 mm to study the toughening of epoxy by incorporation of bioresin. Notch depth of 2.54 mm and notch angle 45° were made using a notch cutter (Tinuous olesan, UK). The tests were carried out with an Izod impact tester (Tinuous olesan, UK) as per ASTM-D-256.

Single edge notch bending (SENB) fracture toughness

The fracture toughness parameters, critical stress intensity factor (K_{IC}) and critical strain energy release rate (G_{IC}) of epoxy and its blends were evaluated following Eqs. (1) and (2) by single-edge-notched (SEN) test in a flexural three-point bending set up which was performed on an universal test machine (Instron Model 3382 mechanical tester, UK) according to the ASTM D 5045^[16]. The dimension of the single-edge notch specimen (SEN) was approximately 30 mm × 6 mm × 3 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 cross head speed of 1 mm/min.

$$\text{Critical stress intensity factor } K_{IC} = 6YP/BW^{1/2} \quad (1)$$

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

a is the pre-crack length, P is the maximum load, B is the specimen thickness and W is the specimen width.

The critical strain energy release rate, G_{IC} was calculated using the equation

$$G_{IC} = K_{IC}^2/E \quad (2)$$

where E is Young's modulus.

Thermal Properties

Thermogravimetric analysis

Thermal degradation behavior of virgin epoxy as well as the bio epoxy blends were carried out using thermogravimetric analysis, (TGA) (Q 50 TA Instruments, USA). Samples of 8–10 mg weight were scanned from 40 to 750 °C at a heating rate of 10 K/min in nitrogen atmosphere. Corresponding initial and final degradation temperatures were noted.

Differential scanning calorimetry

Glass transition temperature of all samples was determined by differential scanning calorimetry DSC (Q20, M/s TA Instrument, USA) in a temperature range of 25–200 °C at a heating rate 10 K/min. The curing behavior of ESO, pure epoxy and bio-based epoxy blends were analyzed employing DSC from room temperature to 400 °C at heating rate of 10 K/min under N₂ atmosphere. Curing agent TETA was mixed with resin at a stoichiometric epoxide/amine ratio at room temperature and stirred properly to form homogeneous mixture. Curing kinetics of epoxy and optimized epoxy blend was studied at heating rates of 10, 15 and 20 K/min employing Kissinger and Ozawa equations as follows.

$$\ln(\beta/T_p^2) = \ln A - E_a/RT_p \quad (\text{Kissinger equation}) \quad (3)$$

$$\lg \beta = C - 0.457 E_a/RT_p \quad (\text{Ozawa equation}) \quad (4)$$

where β = heating rate, A = pre-exponential co-efficient, C = constant, E_a = activation energy, T_p = peak temperature.

Kissinger and Ozawa methods were applied in this study, instead of other non-isothermal methods, because they do not require prior knowledge of the reaction mechanism to quantify kinetic parameters^[15].

Dynamic mechanical analysis

The dynamic mechanical analysis of the samples were carried out using a DMA analyzer (Q 800 M/s TA Instruments, USA) at three point bending mode of the equipment and corresponding viscoelastic properties of the materials were determined as a function of temperature at a fixed frequency of 1 Hz. The temperature range used in the present investigation was varied from 30 °C to 200 °C, with a heating rate of 10 K/min.

Thermo mechanical analysis

Co-efficient of thermal expansion (CTE) of the sample was determined by using a thermo mechanical analyzer (TMA) (Perkin Elmer Diamond TMA, USA) to analyze the dimensional stability. Samples of dimension 5 mm $\times$ 5 mm $\times$ 3 mm are tested within a temperature range from ambient to 250 °C in argon environment at a heating rate 10 K/min.

Morphological Properties

Scanning electron microscopy (SEM) analysis

The morphological analysis of impact fractured blends was carried out using SEM analysis (EVO MA 15, Carl Zeiss, SMT, Germany). The samples were sputtered with gold and palladium mixture and were dried for half an hour at 70 °C in vacuum, prior to imaging.

RESULTS AND DISCUSSION

Functional Group Analysis of Bioresin

The oxirane oxygen content of ESO was determined to be 6.3% and iodine value was found to be 7 after epoxidation. Conversion of all unsaturation to epoxides is difficult to achieve because of steric factors, electronic effects and some side reaction like hydrolysis, reaction with residual H_2O_2 and CH_3COOOH which may open the epoxy ring^[11].

Epoxidation of soybean oil was confirmed by both FTIR and NMR spectra. From FTIR spectra of ESO (Fig. 2), C—H stretch was observed at 2920 and 2850 cm^{-1} and C=O stretch was assigned at 1740 cm^{-1} . The transmittance signals C—O—C stretching from oxirane vibration appeared at 1250 cm^{-1} and 823–843 cm^{-1} as reported by authors earlier^[9, 11, 26]. The most representative signal of small intensity at 823 cm^{-1} revealed the oxirane group of ESO.

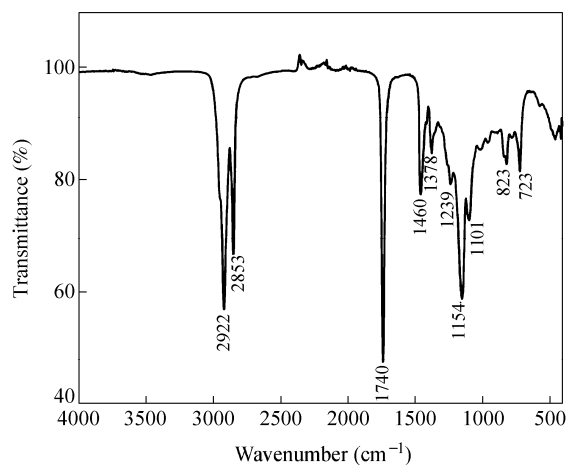


Fig. 2 FTIR spectrum of epoxidized soybean oil (ESO)

NMR spectra of ESO is depicted in Fig. 3. As observed from the figure, a methylene proton of the $-\text{CH}_2-\text{CH}-\text{CH}_2-$ backbone was observed at $\delta = 5.1-5.3$ which is primarily attributed to $\text{CH}=\text{CH}$ unsaturation and the signals in the range of $\delta = 4.12-4.27$ are attributed to CH and CH_2 protons of glyceride moieties. The presence of $-\text{CH}-$ protons of the epoxy ring was observed at $\delta = 2.9-3.12$ which again confirmed the chemical structure of ESO^[11, 26]. The signals at $\delta = 1.2-1.3$ represent saturated methylene whereas those at $\delta = 1.4-1.5$ are attributed to $\beta\text{-CH}_2$. Four CH_2 protons adjacent to two epoxy group at $\delta = 1.65-1.8$, six protons of $\alpha\text{-CH}_2$ to $> \text{C}=\text{O}$ at $\delta = 2.2-2.4$ and six protons of $\beta\text{-CH}_2$ to $> \text{C}=\text{O}$ at $\delta = 1.55-1.7$ were observed. The chemical shifts located between $\delta = 0.8-0.9$ and 2.3 could be assigned to CH_2-CH_3 and $\text{O}-\text{CH}_2$ protons respectively.

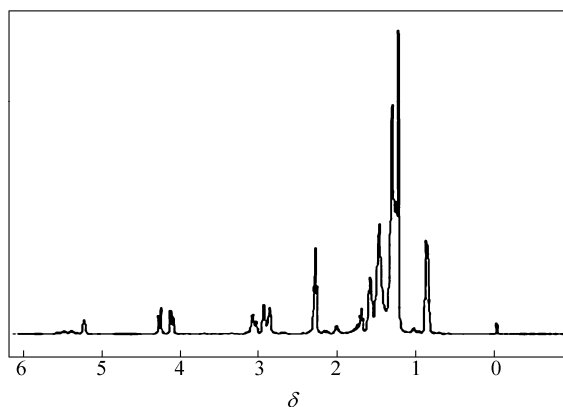


Fig. 3 ^1H -NMR spectrum of epoxidized soybean oil (ESO)

FTIR Analysis of Crosslinked Blends

FTIR spectra of crosslinked ESO/TETA, crosslinked DGEBA/TETA epoxy resin and of crosslinked DGEBA/20 wt% ESO/TETA are presented in Fig. 4 to explain the curing behavior.

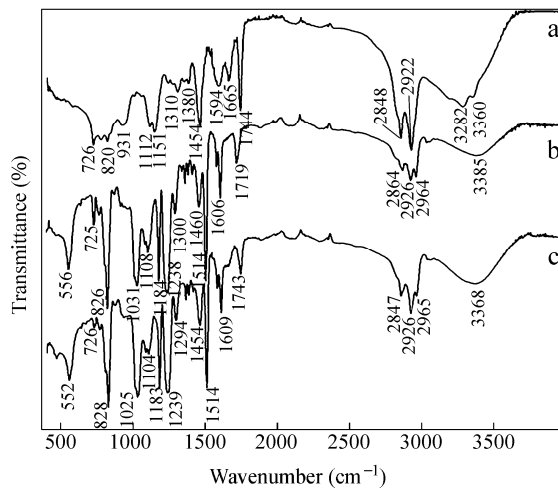


Fig. 4 FTIR spectra of (a) ESO/TETA (b) Epoxy/TETA and (c) Epoxy/20% ESO/TETA

During the curing reaction, first step is the reaction between the primary amine hydrogen with the epoxy group, followed by a reaction between the secondary amine hydrogen with another epoxy as shown in the reaction scheme (Fig. 5).

Small characteristic O—H band was observed at 3360 cm^{-1} confirming the reaction of epoxy with amine to form hydroxyl groups while secondary N—H band at 3282 cm^{-1} is attributed to amine group as shown in Fig. 4(a). It can be observed that the stretching vibration band specific to the C—O of epoxide ring (915 cm^{-1}) almost disappeared in the case of crosslinked DGEBA/TETA sample and the hydroxyl groups generated during the cure also react with the epoxy ring catalyzed by tertiary amine, forming ether (C—O—C stretch) bonds detected near 1030 cm^{-1} (Figs. 4b, 4c). The bands formed at 1594 and 1665 cm^{-1} in crosslinked ESO/TETA (Fig. 4a) are primarily attributed to asymmetric C—O and C=O bonds respectively which were absent in ESO (Fig. 2). The absence of band at 823 cm^{-1} in crosslinked DGEBA/ESO/TETA and crosslinked ESO/TETA revealed that, ESO reacts with TETA. Further, intensity of bands at 1744 cm^{-1} and 2927 cm^{-1} got decreased which confirms the reaction of ESO with amine. No significant change was observed between crosslinked epoxy/ESO/TETA and virgin epoxy/TETA which indicates the overlapping of crosslinked ESO peaks with crosslinked epoxy ones. Only increment in intensity of carbonyl ester band and hydroxyl band was observed.

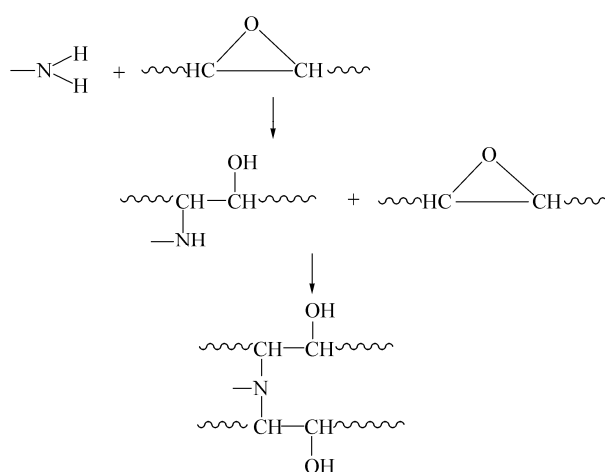


Fig. 5 Reaction scheme for reaction of epoxy group with amine

Mechanical Properties

The tensile and flexural properties of virgin epoxy and bio-based epoxy blends at variable concentrations (10, 20 and 30 phr) of bio-resin (ESO) are summarized in Table 1.

Table 1. Tensile and flexural properties of virgin epoxy and bio-based epoxy blends

Sample (Epoxy:ESO)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)	Flexural strain (%)
100:0	55.13 ± 4	2107.13 ± 51	3.1 ± 0.2	110.1 ± 5	3891.81 ± 120	3.2 ± 0.4
90:10	43.25 ± 2	1753.42 ± 27	3.4 ± 0.1	114.4 ± 7	2984.39 ± 127	3.8 ± 0
80:20	30.27 ± 1	1353.78 ± 56	3.6 ± 0	81.91 ± 4	2361.00 ± 74	4.4 ± 0
70:30	15.47 ± 3	689.67 ± 38	3.9 ± 0.2	41.86 ± 2	1437.21 ± 107	5.0 ± 0.6

It is evident that the tensile strength and tensile modulus decrease gradually with the increase in ESO content. This behavior is probably due to its ductile aliphatic long chain structure and low crosslink density of ESO. However, the elongation at break increases with increasing ESO content which indicates the plasticizing effect of the bio-resin, that is also confirmed from the reduced T_g depicted in the later section.

Further, as observed from the test results depicted in Table 1, the decrease in the tensile strength and tensile modulus was modest till 20 phr content of ESO, which subsequently exhibited a drastic reduction beyond 20 phr. Similar findings were also observed in flexural strength and flexural modulus with exception in flexural strength at 90:10 composition as previously reported^[23] due to improvement in flexibility caused by micro phase

separation.

Nearly 50% decrease in tensile strength and tensile modulus was obtained in case of epoxy/30%ESO blend as compared with blend prepared at 20 wt% ESO. However, blend at 30 wt% ESO exhibited significant increase in percentage of elongation and flexural strain to the tune of 25% and 56% respectively as compared with virgin epoxy matrix. This fact can be correlated with the earlier findings^[18].

Most prominently, toughening of epoxy occurs through the incorporation of ESO as reactive diluents in parent epoxy resin which overcomes the inherent brittleness. Plasticization occurs as ESO has good compatibility with epoxy initially and phase separation is induced in the epoxy matrix during curing. Phase separation is a boundary condition for toughness improvement in modifier containing thermosetting resin. Since ESO has intermediate miscibility, before curing it remains miscible with the epoxy and undergoes a reaction-induced phase separation with the advancement of curing reaction, leading to the formation of a two-phase microstructure as previously reported^[12]. Unreacted soybean oil induces cavitation in epoxy matrix through which toughening of network takes place by shear yielding process. The impact strength of virgin epoxy and bio-based epoxy blend is depicted in Table 2. It is found that impact strength of the modified epoxy is gradually increased with increase in bioresin content upto 20 phr due to the phase separated network. The blend prepared at 20 phr of ESO exhibited optimum impact strength which was nearly 60% increase for notched and 500% increase for un-notched specimen as compared with virgin epoxy. Similar result was previously reported^[20]. However, at 30 phr of bioresin, phase inversion occurs which reduces the impact strength. In case of higher content of bioresin, the excess modifier either exudes out from the matrix or macro-phase separation takes place^[14]. The phase separation mechanism is explained briefly in morphology study.

SENB Fracture Toughness

The fracture toughness parameters, critical stress intensity factor (K_{IC}) and critical strain energy release rate (G_{IC}) of epoxy and its blends up to 30% ESO composition were evaluated and summarized in Table 2.

Table 2. Impact strength and fracture toughness of modified epoxy blends

Sample (Epoxy:ESO)	Impact strength (J/m)		Critical stress intensity factor (K_{IC}) (MPa·m ^{1/2})	Critical strain energy release rate (G_{IC}) (kJ/m ²)
	Un-notched	Notched		
100:0	32.33 ± 6	17.6 ± 2	1.36	0.87
90:10	75.59 ± 4	22.7 ± 1	2.02	2.32
80:20	190.45 ± 12	28.3 ± 2	2.07	3.16
70:30	53.65 ± 1	23.8 ± 0.5	1.92	5.34

It was found that K_{IC} of virgin epoxy is 1.36 MPa·m^{1/2} due to its inherent brittleness which was overcome by incorporation of ESO by increasing the flexibility property. The fracture toughness was gradually increased with increase in ESO content and optimum value of 2.07 MPa·m^{1/2} was achieved at 20 phr of ESO. Similar results were reported earlier by Park *et al.*^[21] and Tan *et al.*^[3]. The decrease in K_{IC} value at higher content of ESO can be explained due to phase inversion or macro-phase separation in bio epoxy blends.

G_{IC} value provides a measure of the critical energy required to extend a crack over a unit area which was found to be increased with increase in ESO content^[16]. For virgin epoxy, G_{IC} value was found to be 0.87 kJ/m² which got increased up to six times at 30% ESO composition. It may be explained due to inverse proportionality of G_{IC} with Young's modulus (E) which got reduced drastically by addition of ESO at higher content. This study has revealed that the incorporation of ESO bioresin effectively toughens the epoxy matrix by increasing the K_{IC} and G_{IC} values.

Thermal Properties

Thermogravimetric analysis (TGA)

The thermal behavior of neat epoxy network is similar to that for all bio-based cross linked systems as shown in Fig. 6.

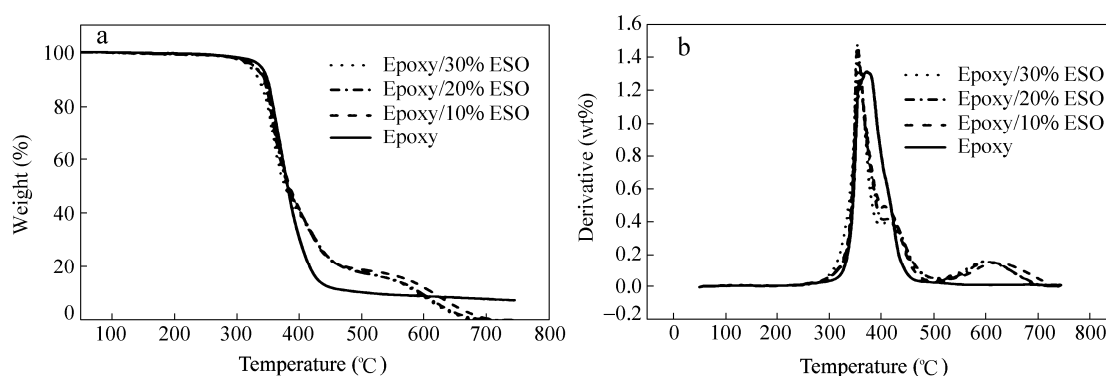


Fig. 6 (a) TGA and (b) DTG graphs of virgin epoxy and bio-based epoxy blends

The thermal parameters like T_{onset} , the temperature at which the degradation starts, T_p , the temperature at which degradation rate is maximum, T_{endset} , the temperature at ending process, T_{10} and T_{50} , the temperatures corresponding to 10 wt% and 50 wt% weight losses are determined by TGA and DTG thermograms and are presented in Table 3.

Table 3. TGA and DTG parameters of ESO modified epoxy blends

Sample	T_{onset} (°C)	T_{10} (°C)	T_{50} (°C)	T_{p1} (°C)	T_{p2} (°C)	$T_{\text{end set}}$ (°C)
Epoxy	315	348	381	372		450
Epoxy /10 wt% ESO	308	343	384	357	623	728
Epoxy /20 wt% ESO	304	344	382	353	610	725
Epoxy /30 wt% ESO	301	335	377	356	605	720

From the data it is revealed that T_{onset} , T_{10} and T_{50} of modified epoxys have marginally less values as compared with the virgin epoxy which showed that upto 20% ESO content the degradation temperature of matrix polymer has no appreciable effect. On the contrary all the bio-epoxy blend systems show two stage degradation behavior while the virgin shows single stage degradation.

It is clearly noted in Fig. 6 that ESO modified epoxy experiences two-stage thermal decomposition when being heated up to 750 °C. First stage of decomposition, from 300 °C to 450 °C is believed to be due to the pyrolysis of the cross-linked epoxy resin network and dehydration of hydroxyl groups. This behavior is possibly attributed to the structural similarity of the blend system in previous report^[26]. The second loss stage from 550 °C to 700 °C was considered to be the complete decomposition of un-reacted long chain fragments of ESO. ESO residuals decompose completely as the heating temperature is further increased up to 750°C. Similar decomposition behavior of ESO has been reported earlier^[7, 21], wherein two different thermal decomposition stages have been present in TGA graph. From DTG graph Fig. 6, it is revealed that the rate of decomposition for biobased epoxy blend system is marginally higher and it occurs at lower temperature with reference to virgin epoxy network.

Differential Scanning Calorimetry (DSC) Analysis

The glass transition temperature (T_g) of virgin epoxy and bio-based epoxy blends have been determined employing DSC thermograms and the results are tabulated in Table 4. It is evident that incorporation of ESO within the epoxy matrix decreased the T_g of the polymer matrix.

Table 4. Glass transition temperature of cured epoxy and modified epoxy blends

Sample	Glass transition temperature T_g (°C)
Epoxy	87.8
Epoxy/10 wt%ESO	76.8
Epoxy/20 wt%ESO	75.2
Epoxy/30 wt%ESO	64.4

Considerable depression in T_g was found to be in case of compositions having higher content of ESO which can be explained due to inverse phase separation or excess plasticization effect^[19, 21, 26]. Hence, it is evident that incorporation of bio resin enhances the flexibility and mobility of the molecular chains in the epoxy blend network^[29]. The reduced T_g and plasticizing effect can also be corroborated from the mechanical findings wherein there was a decrease in modulus with an increase in elongation and flexural strain in the blends.

Non-isothermal Curing Study

Since ESO is having epoxy functionality, it also takes part in cross-linking reaction. The degree of epoxidation and type of curing agent also plays an important role in the curing of ESO because of the internal epoxy groups and low reactivity. As TETA is widely used as a curing agent for epoxy, non-isothermal curing kinetics of optimized bio-based epoxy with this crosslinking agent has been studied.

The dynamic DSC thermograms of ESO, epoxy and biobased epoxy blends at a heating rate of 10 K/min are depicted in Fig. 7.

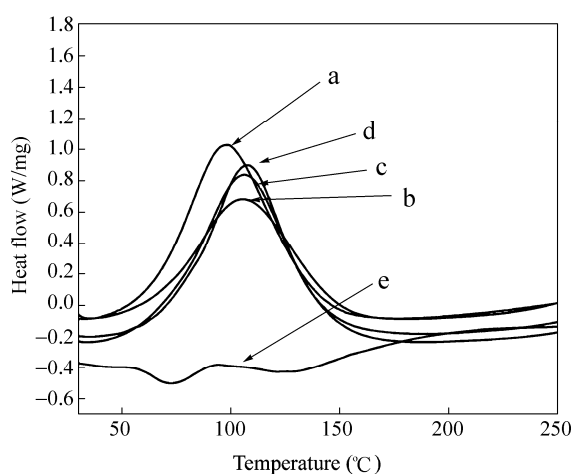


Fig. 7 DSC thermograms of bio-epoxy blends at heating rate 10 K/min: (a) Epoxy, (b) Epoxy/10% ESO, (c) Epoxy/20% ESO, (d) Epoxy/30% ESO and (e) ESO

It is observed that ESO resin blends cured with TETA exhibited high maximum peak temperatures as compared with virgin epoxy, and the increment in concentration of ESO to the DGEBA-TETA mixture changed the shape of the exothermic peaks. This effect was also accompanied by change in the total heat of reaction as presented in Table 5.

Table 5. DSC parameters of epoxy and modified epoxy blends of different compositions

Epoxy:ESO	Enthalpy of reaction (J/g)	Peak temperature T_p (°C)
100:0	317	98
90:10	245	105
80:20	319	107
70:30	292	108
0:100	34	90

Less value of enthalpy of reaction of ESO may be attributed to the hindered oxirane functionalities present in the middle of the fatty acids in the ESO molecule that might have reacted slowly with amine curing agents in polymerization reactions^[19, 21].

Since the blend prepared at epoxy:ESO ratio of 80:20 exhibited optimum enthalpy of reaction and toughness, this composition along with the virgin matrix has been taken for further kinetic analysis. The DSC curing curves of virgin epoxy and Epoxy/20 wt% ESO blend at variable heating rates are represented in Fig. 8.

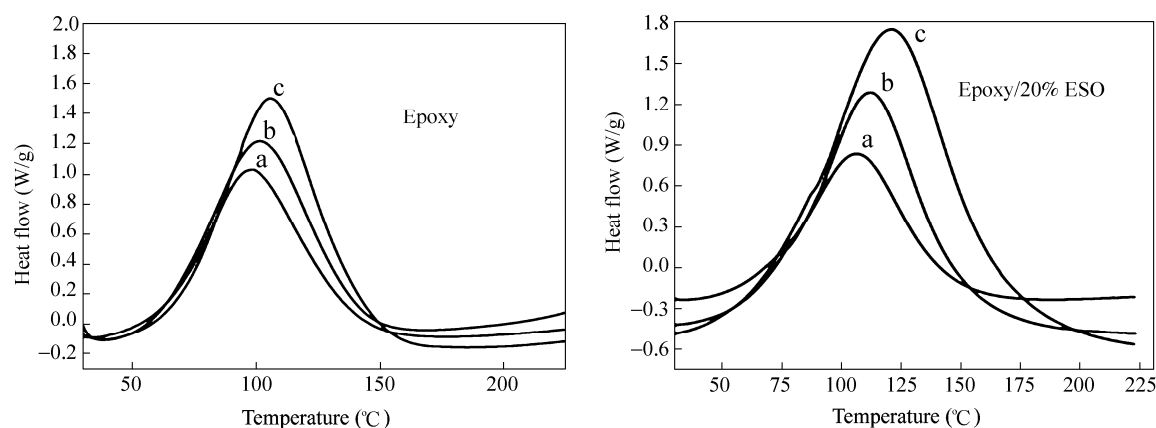


Fig. 8 DSC curing curves of Epoxy and Epoxy/20% ESO at variable heating rates: (a) 10 K/min (b) 15 K/min and (c) 20 K/min

It is observed that the peak temperature shifted to higher values with the increase in heating rate for a particular composition. Kinetic analysis was performed using two kinetic models, the Kissinger and Ozawa models as shown in Fig. 9 and Fig. 10 respectively.

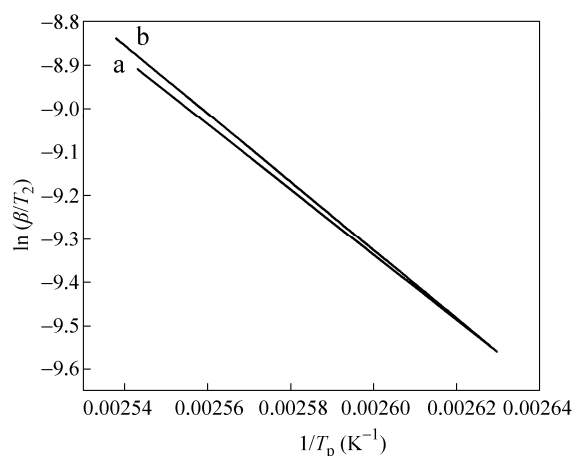


Fig. 9 Kissinger plot of (a) Epoxy and (b) Epoxy/20% ESO cured with TETA

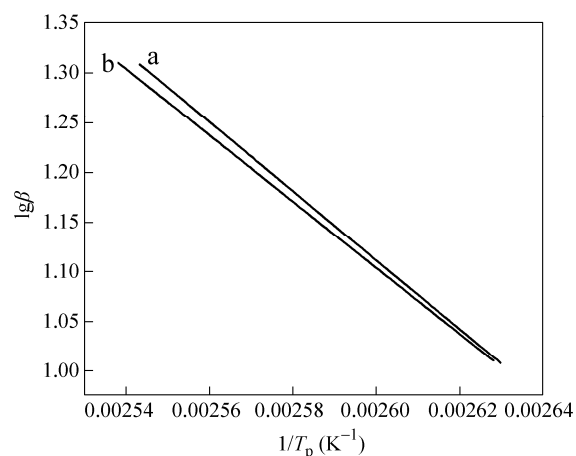


Fig. 10 Ozawa plot of (a) Epoxy and (b) Epoxy/20% ESO cured with TETA

Applying both the equations, activation energy (E_a) and the pre-exponential factor ($\ln A$) were determined and summarized in Table 6.

Table 6. Kinetic parameters from DSC scans

Sample	Activation energy E_a (kJ/mol)		Pre-exponential factor $\ln A$ (min^{-1})
	E_a Kissinger	E_a Ozawa	
Epoxy	91.4	92.9	19.38
Epoxy/20% ESO	57.4	60.8	8.60

It was found that E_a has the higher value for neat epoxy sample, with reference to the values of ESO modified epoxy. This fact can be attributed to the low viscosity of the modified epoxy resin, which permits a better contact between the epoxy ring and active protons of the TETA cross-linking agent enhancing the reactivity as reported by Mustata *et al*^[26].

Dynamic Mechanical Analysis (DMA)

As observed from the Fig.11, virgin epoxy exhibited higher storage modulus (E') over the entire investigated range of temperature as compared with the biobased epoxy blends. The room temperature storage moduli of the matrix polymer decreased from 2890 MPa to 2532, 2212 and 1241MPa in case of 10% ESO, 20% ESO and 30% ESO respectively which is due to the less reactivity and long flexible aliphatic chain structure of ESO. The high storage modulus of the epoxy resin is attributed to the presence of bulky bisphenol groups in the polymeric networks and a higher degree of crosslinking which remained almost constant at lower temperatures, but showed a sharp drop followed by a rubbery plateau as the temperature increased. Whereas in case of epoxy-blend systems, fall in storage modulus was not abrupt rather there was a slow decrease in broader manner with the increment in ESO content due to presence of different regions with different conversions or degree of entanglement.

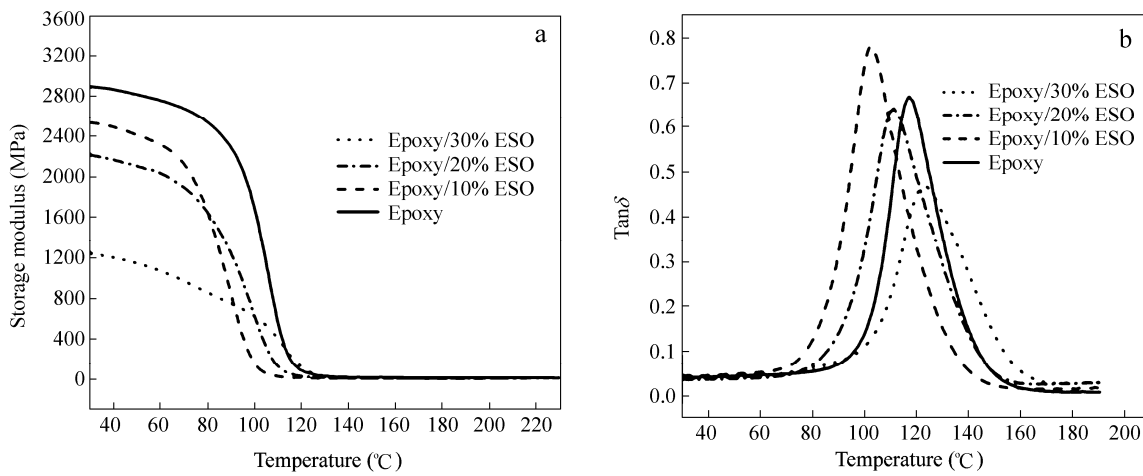


Fig. 11 Variation of (a) storage modulus and (b) $\tan\delta$ of virgin epoxy and its biobased blends

Crosslink density of all the networks were determined by the following kinetic theory of rubber elasticity equation $E' = 3\nu_e RT$

where E' is the storage modulus at $T = (T_g + 30)$ absolute temperature, R = gas constant and ν_e = crosslink density. T_g was taken from the maximum peak value of the $\tan\delta$ curve.

It is found that the crosslink density of cured bio-based epoxy blends got decreased by increment of ESO content as shown in Table 7 which leads to the decrease in storage modulus as compared with virgin epoxy. Similar results were reported earlier by many authors^[21, 22].

Table 7. Crosslink density of epoxy and bio-epoxy blends

Sample	Storage modulus (MPa) at $(T_g + 30)$ °C	Crosslink-density $\nu_e (\times 10^3 \text{ mol/m}^3)$
Epoxy	23.72	2.32
Epoxy/20 wt%ESO	19.81	1.98
Epoxy/30 wt%ESO	12.65	1.22

The $\tan\delta$ curve gives the measure of damping behavior of polymers which is very useful for structural application. The width of the $\tan\delta$ peak indicates homogeneity of a system. Systems with broad peaks are generally consisting of a blend of different polymer chain lengths or structures which yields a broader temperature range, to initiate significant viscous chain motions for the various components. On the other hand, systems with narrow peaks generally have more narrow distribution of chain types and molecular weights. Loss tangent curve having high intensity or broad peak means a good damping material for vibration^[22].

From the damping curve, it is observed that at 10 wt% ESO composition, the loss tangent peak shifted to lower temperature and intensity of the peak increased from 0.66 to 0.78 which reveals greater motion associated with the transition hence a good damping material. On further increasing ESO content, the tangent peak intensity decreased but curve becomes broader which confirmed the presence of more elastomeric components which can absorb more amount energy^[30]. Area under the loss factor curve signifies the amount of energy that can be absorbed. In our investigation, the large area under the $\tan\delta$ curve for blends having higher phr content of ESO indicates that these can absorb and dissipate energy well^[22]. As the $\tan\delta$ peak height decreases and shifts to higher temperatures, one may expect that the mobility of chain segments become more restricted and there is an increase in crosslink density. However, in the present study, lowering and broadening of $\tan\delta$ peak occur with the increase in bioresin content (above 10 wt% phr) in the blends which may be due to the heterogeneity of the cross-linked network structure and a broad distribution of chain segment mobility^[7, 27, 30, 31]. The gradual decrease in the intensity of $\tan\delta$ for the system indicates significant plasticizing effect of un-reacted ESO. That is, the excess bioresin gets dissolved to some extent in the epoxy resin and exerts some dilution effect or formulates macro phase separation^[31, 14].

Analysis of the damping curves may also be explained by both the lowering of the damping peaks and the shifting of the peak point to the effective stress transfers between the cavitation produced by ESO and epoxy matrix. ESO introduces irregularities within the network due to the inherent characteristics of the aliphatic fatty acids, their length, backbone and distribution^[31]. It may be concluded that different regions with different conversions or degree of entanglement are present in bio-based blend network which can explain the broader peak corresponding to a broader glass transition region. The glass transition also known as the α -relaxation occurs in the range in which the polymer chain segments acquire considerable mobility. Glass transition temperature determined from $\tan\delta$ curve of DMA specifies that T_g is decreased considerably at 10 wt% bioresin due to lower crosslink density and high flexibility. But, the broader loss factor peak at higher phr of bioresin (> 10 wt%) gives larger peak factor leads to incorrect determination of T_g ^[30]. Hence, T_g was measured by DSC to explain the rigidity of the material. The maxima of peak position of the loss tangent curves were located around 90–125 °C which exhibited a considerable outward shift with the increase in ESO concentration from 10–30 wt%. Excess plasticization at higher phr of ESO confirmed that wide glass transition is an interval of temperatures associated to the different cross-linked regions suggesting more complex nature.

Thermo-mechanical Analysis

Since modified epoxy with 20% ESO imparts good toughness without affecting much mechanical and thermal properties, the dimensional changes in the bio-epoxy networks as a function of temperature was studied by TMA in argon atmosphere. It is found that coefficient of thermal expansion (CTE) value is less in glassy state than in rubbery state for all types of polymer systems (Fig. 12). It was observed that in the glassy state (below T_g), the network has a higher density and thus reduced molecular mobility which decreases the material's volumetric response to temperature changes hence less value of CTE. The larger values of CTE in rubbery region (above T_g) are due to the increase in molecular mobility of the polymer network due to more free volume in the rubbery region. Most importantly, the CTE of the bio-based epoxy blend at the glassy and rubbery regions is marginally increased as compared to that of virgin epoxy. This might be due to the increased mobility of the chain segments due to the cavitations created by the addition of bio resin ESO which results in plasticizing effect of the system and lower crosslink densities of the epoxy/ESO system. The degrees of freedom available for mobility of the segments of the macromolecules in the three dimensional network structure are enhanced by the addition of ESO, resulting in higher value of CTE^[24, 29].

Fracture Morphology and phase Separation Behavior

Since the mechanical properties of the toughened materials are closely related to the morphology, the study on morphology control and phase separation mechanism has been focused. Morphology of phase separated network of bio-epoxy blend during curing can be explained by employing Flory-Huggins theory by considering the thermodynamics of phase separation. By combining the Flory-Huggins equation and the Hildebrand equation,

the free energy of mixing can be expressed as

$$(\Delta G_m)/V = \phi_1 \phi_2 (\delta_1 - \delta_2)^2 + RT(\phi_1/V_1 \ln \phi_1 + \phi_2/V_2 \ln \phi_2) \quad (5)$$

where ϕ_1 , ϕ_2 are the volume fractions and δ_1 , δ_2 are the solubility parameters and V_1 and V_2 are the molar volume of epoxy and bioresin respectively. Since both ϕ_1 , ϕ_2 are fractions the second term is always negative. For a fixed epoxy/ESO composition, ΔG_m at constant temperature depends on δ_1 i.e. the chemical nature of bio-resin and V_2 which is dependent on molecular weight of the bio-resin. Closeness of δ_1 , δ_2 values and low molecular weight favor the mixing process. If these two parameters are controlled in such a way that ΔG_m is negative then the bio-resin will be compatible with epoxy before the curing. Hence, initially ESO is compatible with epoxy resin before curing with the formation of homogeneous solution. But once the curing reaction proceeds, V_1 and V_2 increases due to increase in molecular weight of ESO and epoxy and at a certain stage ΔG_m will become positive. The phase separation starts at the cloud point conversion and final morphology is arrested at gelation due to tremendous increase in viscosity, though some changes in phase composition after gelation is also reported. At that point ESO starts undergoing phase separation called cloud point.

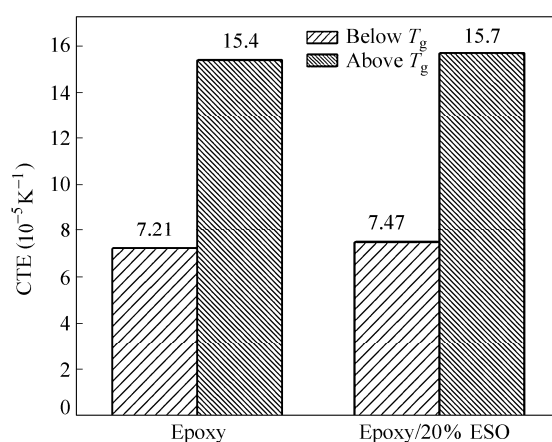


Fig. 12 TMA analysis of epoxy and epoxy/20 wt% ESO blend

The nature of morphology produced depends mainly on the location of the modifier composition in the blend with respect to the critical composition. The critical concentration for regular binary solutions of components of equal size is always $\phi_1 = \phi_2 = 0.5$. However a prominent asymmetry, a shift towards very low value of V_2 is estimated by Flory-Huggins theory^[32]. In our investigation, this critical volume fraction V_c takes the value of 0.10–0.20. Complete effective phase separation takes place up to 20 phr of ESO and shows two distinct phases which leads to useful toughening. On the other hand, in case of blends with higher ESO contents phase inversion occurs and simply imparts plasticizing effect. In the range of high modifier concentration, an inverse morphology is predicted, so that the dispersed phase becomes continuous and the continuous one becomes dispersed^[35].

From SEM micrographs depicted in Fig. 13, it was observed that the virgin epoxy network shows smooth glassy fractured surface with cracks due to its brittleness nature which results in poor impact strength. However, the resin modified with ESO form spherical domains of the oil (cavitation) dispersed uniformly within the epoxy phase which allows the shear yielding process throughout the matrix thereby contributing in enhancing the toughness of the system. The particle size distribution of cavities plays a vital role in toughening epoxy network^[33, 35]. Uniformity in size and distribution of the domains are responsible for toughening the matrix as reported by various authors^[12, 14]. Cavitations with less diameters (1–2 μm) are uniformly distributed throughout the matrix which effectively toughen modified epoxy resin with 20 phr ESO through proper stress transfer between epoxy and cavities. On the contrary, cavitations having large size (30–40 μm) and non-uniformly

dispersed fail to improve the toughening of the system as found in the compositions having 30% ESO bioresin. The increase in domain size and heterogeneous particle size distribution with the incorporation of high content of ESO is attributed to the coalescence of cavities^[34]. The morphological evidence can be corroborated well with the impact findings.

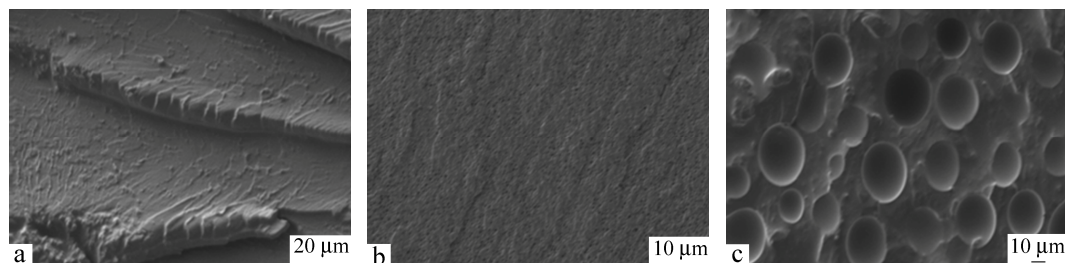


Fig. 13 SEM images of (a) Epoxy, (b) Epoxy/20% ESO and (c) Epoxy/30% ESO

CONCLUSIONS

Epoxidized soybean oil was synthesized by *in situ* epoxidation process which was used as reactive diluents for epoxy and its effect on parent epoxy resin has been investigated. Mechanical study confirmed that, maximum 20 phr of ESO can enhance the toughness of epoxy network without appreciable reduction of property which may be restored by reinforcement. Most importantly, elongation at break and flexural strain got increased with concentration of bioresin which indicates the flexibility property of the system. SENB fracture toughness study has demonstrated that the incorporation of 20 wt% ESO bioresin effectively toughens the epoxy matrix by increasing the K_{IC} and G_{IC} values.

TGA analysis showed no appreciable change in thermal stability of the virgin epoxy upon addition of ESO. DMA study reported that the ability to absorb energy increases on incorporation of bioresin within epoxy, as $\tan\delta$ curve became broader with increase in ESO content. Coefficient of thermal expansion of biobased epoxy/ESO blends was marginally higher than unmodified epoxy, which reveals similar dimensional stability for both the systems.

Non-isothermal curing kinetics was performed to look into the effect of ESO bioresin on crosslinking reaction of epoxy with TETA curing agent. Kissinger and Ozawa models predicted that the activation energy and pre-exponential factor of ESO modified epoxy were decreased appreciably which may be due to better contact between low viscosity resin and cross-linking agent. It is concluded that the incorporation of bio-resin enhances the curing process of epoxy resin and also renders good processability characteristics. Thus, biobased epoxy from synthesized vegetable oil at optimal concentration of epoxy and epoxidized oil can be effectively developed and tailor made for targeted end-use applications.

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