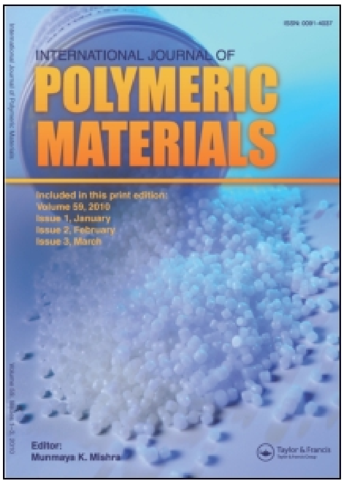

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Mechanical and Morphological Behavior of Bismaleimide-Modified Soy-Based Epoxy Matrices

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This study is concerned with the preparation and mechanical characterization of bio-based polymers from renewable resources. Epoxidized soybean oil at various concentrations is cured with an amine curing agent. The prepared matrices have been chemically modified with three types of bismaleimides, namely N, N′-bismaleimido-4, 4′-diphenyl methane (BMI-1), 1,3-bis(maleimido)benzene(BMI-2) and 3,3′-bis(maleimido phenyl)phenyl phosphineoxide (BMI-3). The crosslinked matrices thus developed were characterized for their mechanical properties such as tensile strength, tensile modulus, flexural strength, flexural modulus, and impact strength. The incorporation of bismaleimides in the soy-based matrices significantly enhances the mechanical properties. The morphological behavior of matrices is also studied using a scanning electron microscope. The results indicate that the bismaleimide-modified soy-based epoxy resin at appropriate concentration holds great potential as a replacement for petroleum-based materials in engineering applications.

Keywords: bismaleimides, mechanical properties, morphology, soy-based epoxy

INTRODUCTION

Use of renewable resources in the areas of energy and materials has been a major scientific and technological issue for the past few decades. Renewable resource-based biopolymers including cellulose plastics (plastics made from wood), polylactic acid (corn-derived plastic), polyhydroxy alkonate (bacterial polyester), thermoplastic starch and vegetable oils (linseed oil, castor oil and soybean oil) are of significant importance from both industrial and economic viewpoints [1–9].

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Vegetable oils made of triglycerides possess double bonds, which are used as reactive sites in coating. They can also be functionalized by epoxidization [10]. These triglycerides possess aliphatic chains, and consequently the triglyceride-based materials are incapable of the necessary rigidity and strength required for high performance applications [11]. Several attempts have been made to improve the thermal and mechanical properties of vegetable oil-based polymers by reinforcing natural fibers [5,12] and metal oxide [13]. A new class of green organic-inorganic hybrid materials was also produced by incorporating clay [6,14,15] and silica network [16,17] in vegetable oil-based polymer.

Although they are biodegradable and cost competitive, the green composites, exhibit some inferior thermomechanical behavior unsuitable for high performance applications. Hence, development of hybrid composites involving both naturally occurring resins and synthetically available chemical intermediates is required to make hybrid composites suitable for high performance applications.

In this context, the present work aims to develop hybrid composites based on bismaleimide-modified soy-based epoxy resins with improved thermomechanical properties suitable for high performance applications.

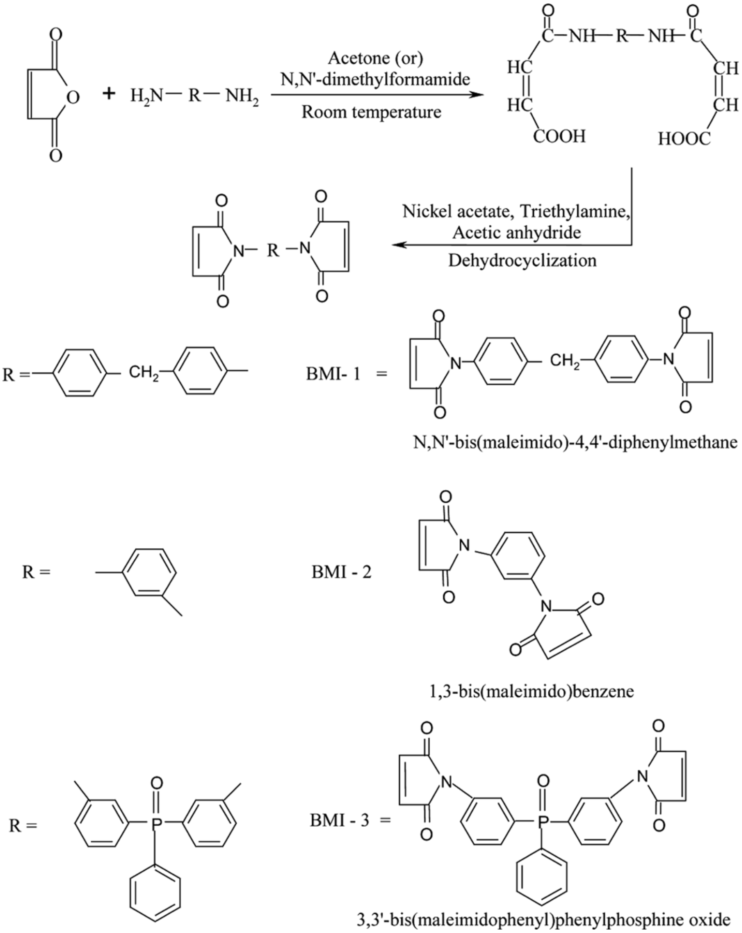
EXPERIMENTAL

Materials

Commercial grade epoxidized soybean oil with epoxy equivalent weight 260–270 (as determined by ASTM-D-1652) was purchased from Pondy Oxide India Limited. LY556 [diglycidyl ether of bisphenol A (DGEBA)], the base epoxy resin used in this study with epoxy equivalent of about 180–190, and 4, 4′-diamino diphenyl methane (DDM) were obtained from Ciba-Geigy Ltd., India. Maleic anhydride and triphenyl phosphineoxide were obtained from Alfa-aesar. Tin(II)chloride was obtained from SRL India Ltd.

Synthesis of Bismaleimides

Three different types of bismaleimides, namely N, N′-bismaleimido-4, 4′-diphenyl methane (BMI-1), 1,3-bis(maleimido)benzene (BMI-2) and 3,3′-bis(maleimido phenyl)phenyl phosphineoxide (BMI-3), were synthesized as per the reported procedure [18–20], and recrystallized from toluene. The reaction sequences are presented in Scheme I.



SCHEME I Synthesis of various bismaleimides.

Preparation of Soy-Based Epoxy Matrices

Soy-based epoxy matrices were prepared by mixing soy epoxy resin with base DGEBA resin at various concentrations such as 10%/90%, 20%/80%, and 30%/70% at 60°C with vigorous stirring. The homogeneous mixture thus obtained was mixed with stoichiometric amount of DDM at 90°C. The mixture was degassed to remove the trapped air bubbles and poured into a preheated mold. The castings were cured at 120°C for 3 h, then at 180°C for 2 h and finally removed from the mold and characterized.

Preparation of Bismaleimide-Modified Soy-Based Epoxy Matrices

Soy epoxy was mixed with DGEBA at 30%/70% concentration to obtain a homogeneous mixture. The calculated amount of bismaleimide was then dissolved at 125°C under vigorous stirring. After the complete dissolution of bismaleimide, a stoichiometric amount of DDM was added and the stirring continued at 90°C until a homogeneous system was obtained. The product was degassed to remove the trapped air bubbles and poured into a preheated mold. The castings were cured at 120°C for 3 h and then at 180°C for 2 h, and finally removed from the mold and characterized.

Measurement and Techniques

FTIR spectra were recorded on a Perkin – Elmer 781 infrared spectrometer with KBr pellets for solid samples. The viscous liquid samples were directly applied by dubbing on a KBr pellet.

The tensile (stress–strain) properties were determined using dogbone-shaped specimens according to ASTM-D-3039, using Instron testing machine model 6025 UK at a crosshead speed of 2 mm per min. The flexural strength was measured as per ASTM-D-790, using Instron testing machine model 6025 UK at a crosshead speed of 2 mm per min. As many as five test pieces were used to generate the data points for all the mechanical tests.

The Izod impact strength was measured for neat epoxy and BMI-modified soy-based epoxy matrices at 25°C. Izod impact specimens with the same dimension as prescribed in the ASTM-D-256 standard were tested with a 453 g pendulum. The dimensions of the notched Izod impact specimens were 63.5 mm (length) X 12.0 mm (width) X 3 mm (thickness). All specimens were cast in silicone molds having the same dimensions. The specimens were held as a vertical cantilever beam and impacted on the notched face by a single swing of the pendulum.

The fracture surfaces of different soy epoxy matrices and BMI-modified soy-based epoxy matrices were observed with scanning electron microscopy (SEM). A JEOL JSM 6360 SEM with field emission filament was used to collect SEM images of all the samples. A gold coating, a few nanometers thick, was made on the fracture surfaces to aid feature resolution.

RESULTS AND DISCUSSION

Spectral Analysis

The formation of an epoxy network structure was evaluated by IR spectroscopy. The characteristic IR absorption peak for the epoxide ring of soy-based epoxy resin appears at 825 cm^{-1} and 914 cm^{-1}. The disappearance of peaks at 914 cm^{-1} and decrease in the intensity of peaks at 825 cm^{-1} was used to confirm the reaction between epoxy resins and amine. The peak at 3102 cm^{-1} is due to H−C= vibration and is widely accepted as a reference to follow the conversion of BMI double bond. The disappearance of the peak at 3102 cm^{-1} was used to ascertain the homopolymerization of BMI in the presence of epoxy resin mixture and the formation of network structure.

Tensile Properties

Soy-Based Epoxy Matrix System

The values of tensile strength of neat DGEBA, soy-based epoxy systems, and various bismaleimide-modified 30 wt% soy-based epoxy resins cured with DDM are presented in Table 1. The incorporation of soy epoxy up to 30 wt% in the DGEBA system enhanced the values of tensile strength and tensile modulus. Beyond this concentration the tensile strength values decreases. For example, the tensile strength value of DGEBA system increased to 11.6, 17, 23 and 10.3% by the incorporation of 10, 20, 30 and 40 wt% of the soy-based resin, respectively. The improvement in the tensile strength may be explained due to the increased crosslinked network between aliphatic and aromatic epoxy resin and also due to the flexible nature of aliphatic soy epoxy resin. The decrease in tensile strength beyond 30 wt% of soy epoxy-based resin is due to the incomplete curing. It is observed that when the soy epoxy resin is dominant in the mixture, i.e., above 40 wt% of soy epoxy resin in the DGEBA matrix, it leads to loss of mechanical properties due to the incomplete curing of the aliphatic epoxy resin. A similar trend is observed for the tensile modulus values of the soy-based epoxy systems.

Bismaleimide-Modified Soy-Based Epoxy Matrix Systems

The introduction of varying amounts of bismaleimides in the 30 wt% soy-based epoxy system enhanced the values of tensile strength marginally (Table 1). The incorporation of 5, 10, 15 and

TABLE 1 Mechanical Properties of Neat DGEBA, Soy-Based Epoxy, Bismaleimide (BMI-1, BMI-2, BMI-3) Modified Soy-Based Epoxy Systems

Sample code	Tensile strength (Mpa)	Tensile modulus (Mpa)	Flexural strength (Mpa)	Flexural modulus (Mpa)	Impact strength (J/m)
$D_{100}SE_0\ B_0$	62.8 ± 5	6671.3 ± 35	108.0 ± 7	1804.1 ± 40	98.2 ± 6
$D_{100}SE_{10}\ B_0$	70.1 ± 5	7224.9 ± 33	104.5 ± 3	1749.8 ± 31	170.7 ± 5
$D_{100}SE_{20}\ B_0$	73.5 ± 4	7413.6 ± 34	102.7 ± 3	1599.8 ± 26	175.8 ± 4
$D_{100}SE_{30}\ B_0$	77.8 ± 3	7560.2 ± 29	97.4 ± 6	1433.2 ± 31	180.7 ± 8
$D_{100}SE_{40}\ B_0$	69.3 ± 4	7422.6 ± 34	83.7 ± 6	906.6 ± 27	145.7 ± 6
$D_{100}SE_{30}B_{1-5}$	79.9 ± 3	7590.7 ± 30	115.6 ± 6	1522.0 ± 28	176.2 ± 5
$D_{100}SE_{30}B_{1-10}$	80.2 ± 5	7886.4 ± 36	117.7 ± 6	1584.6 ± 29	149 ± 3
$D_{100}SE_{30}B_{1-15}$	83.2 ± 4	8262.5 ± 31	123.0 ± 6	1644.2 ± 29	129 ± 4
$D_{100}SE_{30}B_{1-20}$	86.9 ± 5	8916.3 ± 29	125.1 ± 5	1686.6 ± 31	110 ± 4
$D_{100}SE_{30}B_{2-5}$	82.5 ± 5	7622.9 ± 31	119.2 ± 2	1582.6 ± 35	165.7 ± 5
$D_{100}SE_{30}B_{2-10}$	86.3 ± 4	82157 ± 30	120.4 ± 4	1629.3 ± 39	149.7 ± 6
$D_{100}SE_{30}B_{2-15}$	86.6 ± 3	8758.5 ± 31	126.3 ± 4	1697.5 ± 39	118.7 ± 6
$D_{100}SE_{30}B_{2-20}$	89.8 ± 6	8986.5 ± 34	127.9 ± 3	1819.9 ± 36	86.5 ± 5
$D_{100}SE_{30}B_{3-5}$	80.9 ± 3	7610.6 ± 34	111.1 ± 4	1438.7 ± 32	168.1 ± 4
$D_{100}SE_{30}B_{3-10}$	82.4 ± 5	7916.3 ± 32	113.3 ± 3	1482.1 ± 32	132.9 ± 6
$D_{100}SE_{30}B_{3-15}$	83.4 ± 6	8753.6 ± 39	115.1 ± 3	1598.3 ± 29	116.6 ± 2
$D_{100}SE_{30}B_{3-20}$	88.6 ± 5	8956.4 ± 30	117.31 ± 4	1623.5 ± 32	106.6 ± 2

D – DGEBA epoxy; SE – soy based epoxy; B – bismaleimide; B1-N,N′-bismaleimido-4,4′-diphenyl methane(BMI-1); B2 – 1,3-bis(maleimido) benzene (BMI-2); B3 – 3,3′-bis-(maleimido phenyl) phenyl phosphine oxide (BMI-3).

Understanding the composition of systems from sample code e.g., $D_{100}SE_{30}B_{1-5}$, means DGEBA (100 wt%), soy epoxy (30 wt%), BMI-1 (5 wt%).

20 wt% of BMI-1 in the 30 wt% soy-based system enhanced the tensile strength by 0.4, 4.3, 9.2 and 17.9%, respectively. For the same weight percentage of BMI-2 modified 30 wt% soy-based system, the tensile value increased by 6, 10.9, 11.3 and 15.4% and for BMI-3 modified system by 3.9, 5.9, 6.9 and 11.6%, respectively, when compared to the unmodified 30 wt% soy-epoxy system. This may be explained due to the increase in crosslinking density due to the homopolymerization of BMI, which results in crosslinked networks [21–23]. Among the different bismaleimide-modified systems, BMI-2 exhibits higher tensile strength when compared to BMI-1 and BMI-3; this may be explained due to the higher number of reactive molecules when compared with the same weight percentages of BMI-1 and BMI-3, and also due to its lower molecular weight which favors the formation of a highly crosslinked network. Tensile modulus values exhibited similar trends as in the case of tensile strength.

Flexural Properties

Soy-Based Epoxy Matrix System

The values of flexural strength and flexural modulus for neat DGEBA, soy-based epoxy matrices at different concentrations and different bismaleimide-modified soy-based epoxy systems are presented in Table 1. The introduction of 10, 20, 30 and 40 wt% of soy epoxy decreases the value of flexural strength and modulus due to the rubbery nature imparted by the aliphatic chains of soy epoxies.

Bismaleimide-Modified Soy-Based Epoxy Matrix Systems

The incorporation of various bismaleimides into a 30 wt% soy-based epoxy system increased the flexural strength and flexural modulus (Table 1). The enhancement in the values is due to the homopolymerization of BMI and the rigidity imparted by the heteroaromatic ring along with the crosslinked network structure.

Among the bismaleimide-modified soy-based epoxy system, the BMI-2 modified system exhibits higher values of flexural strength and modulus than those of BMI-1 and BMI-3 modified systems. For example, flexural strength of 5, 10, 15 and 20 wt% of BMI-2 modified 30 wt% soy-based epoxy system increased 22.3, 23.6, 29.6 and 31.3%, respectively, when compared to unmodified 30 wt% soy-based epoxy system. The flexural strength values for the same weight percentage of BMI-1 modified system are 18.6, 20.8, 26.2, and 28.4%, respectively, and for BMI-3 modified systems are 14, 16.3, 18 and 20.4%, respectively. A similar trend is observed for the flexural modulus values of the bismaleimide-modified systems.

Izod Impact Strength

Soy-Based Epoxy Matrix System

The value of the Izod impact strength of neat DGEBA, soy-based epoxy matrices with varying concentrations and different bismaleimide-modified 30 wt% soy-based epoxy systems are given in Table 1. The percentage increase in the values of Izod impact strength for the 10, 20, 30 and 40 wt% soy-based epoxy matrices are 74, 79.1, 84.2 and 48%, respectively. The incorporation of soy epoxy in the DGEBA improved the impact strength up to a certain weight percentage, then decreased when compared to neat DGEBA. The improvement in impact behavior may be explained due to the long flexible and resilient network structure exhibited by the soy epoxy systems.

Bismaleimide-Modified Soy-Based Epoxy Matrix Systems

The incorporation of different bismaleimides in the 30 wt% soy-based epoxy systems decreased the impact strength based on the percentage of bismaleimides incorporated. The restricted chain mobility due to the formation of heteroaromatic bismaleimide rings is the cause of decreased impact strength. Among the various bismaleimides, the maximum reduction in impact values is exhibited by BMI-2 modified systems due to the attainment of higher cross-linking density.

Scanning Electron Microscope (SEM) Investigation

The morphology of the various bio-based epoxy matrices was investigated by SEM. The SEM photographs of unmodified pure DGEBA system (Figure 1) show a smooth, glassy and homogeneous microstructure without any plastic deformation. Similarly, the neat soy epoxy in Figure 2 also shows homogeneous single-phase microstructure. The micrographs of 30 wt% soy-based epoxies are shown in Figure 3. The circular areas in the figure clearly indicate the presence of second phase, i.e., rubbery phase, which imparts heterogeneous morphology to the structure. From the micrograph it is evident that the rubbery phase particles are uniformly distributed in the matrix. This indicates the familiar characteristics of phase separation. It is this rubbery matrix which imparts the impact strength to the matrix.

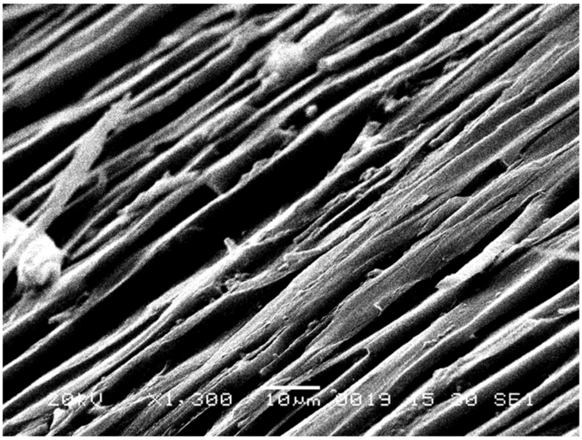


FIGURE 1 SEM micrograph of neat DGEBA epoxy at scale bar 10 μm.

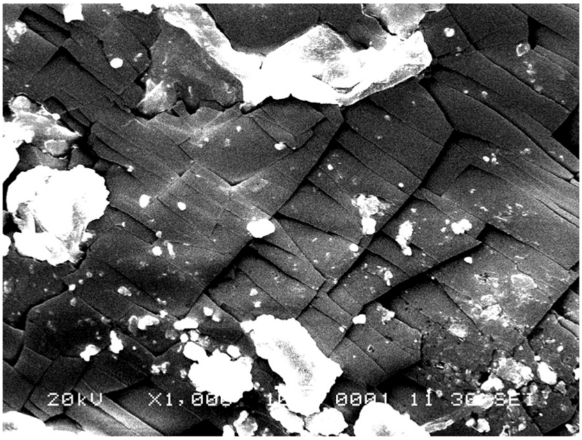


FIGURE 2 SEM micrograph of neat soy epoxy unmodified at scale bar 10 µm.

The micrographs of different bismaleimide-modified 30 wt% soy-based epoxy system clearly shows that heterogeneity is maintained; also a smooth fracture surface is observed with increasing BMI content. This may be due to brittle behavior imparted by the BMI skeleton. Figures 4, 5 and 6 show the morphology of 5 wt% and 20 wt% BMI-1 modified 30 wt% soy-based epoxy matrix systems. The micrograph, show that with the increase in the BMI content, the uniformity increases with the reduction in the rubbery phase. Figures 7 and 8

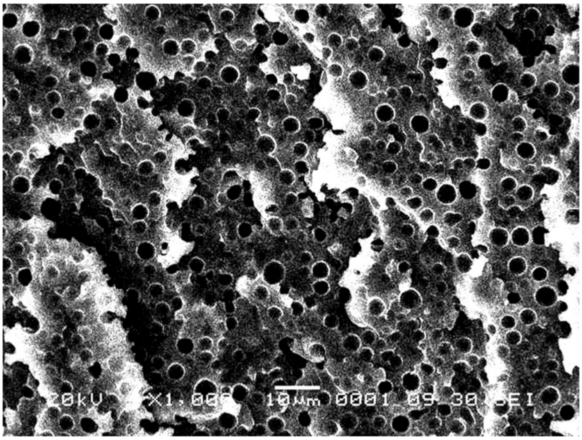


FIGURE 3 SEM micrograph of 30 wt% soy-based epoxy at scale bar 10 µm.

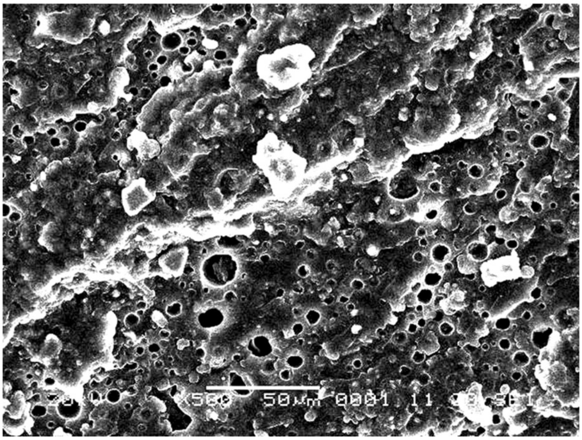


FIGURE 4 SEM micrograph of BMI-1(5%) modified 30 wt% soy-based epoxy at scale bar 50 μm.

show the surface morphology of a BMI-2 modified system. From the figures it is clearly evident that the increase in concentration of BMI-2 greatly reduces the rubbery phase and imparts a uniform surface to the matrix. Reduction in the value of impact strength for the bismaleimide-modified system is mainly due to the rigidity of the matrix. Figures 9, 10 and 11 show the surface morphology of bulky

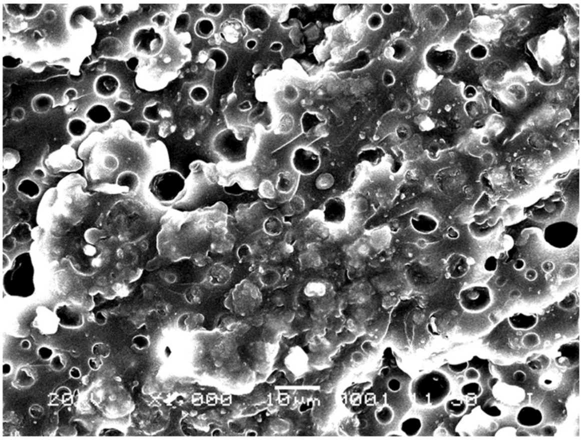


FIGURE 5 SEM micrograph of BMI-1(5%) modified 30 wt% soy-based epoxy at scale bar 10 μm.

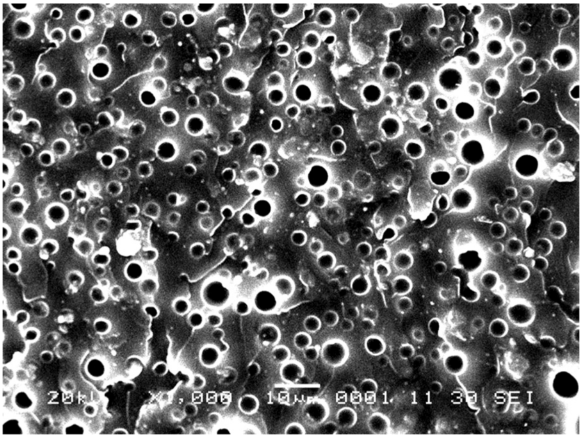


FIGURE 6 SEM micrograph of BMI-1(20%) modified 30 wt% soy-based epoxy at scale bar 10 µm.

triphenyl phosphineoxide group containing BMI-3 modified soy-based epoxy system.

It is also observed that the pure DGEBA epoxy and neat soy epoxy are transparent, whereas the soy-based epoxide matrices and bismaleimide-modified soy epoxy matrices are opaque. The loss of transparency in matrices was the result of phase separation.

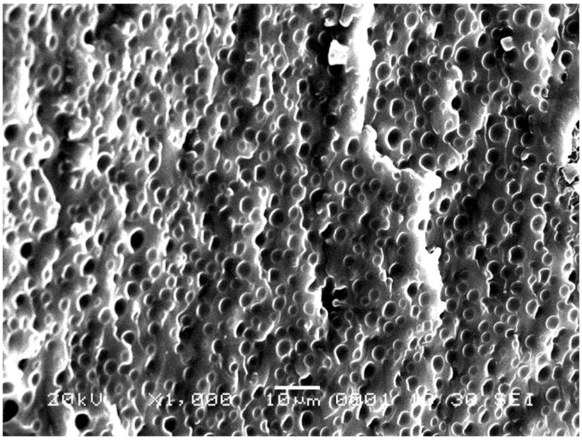


FIGURE 7 SEM micrograph of BMI-2(5%) modified 30 wt% soy-based epoxy at scale bar 10 µm.

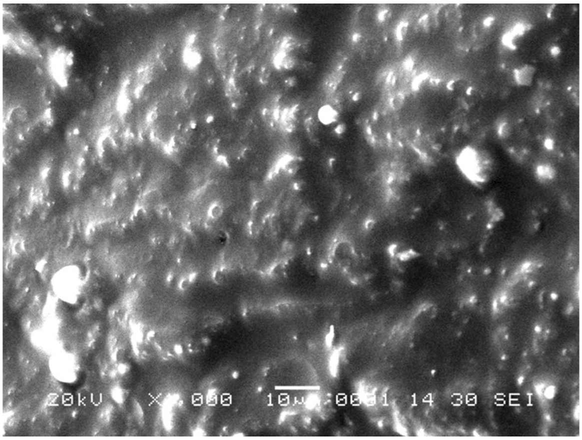


FIGURE 8 SEM micrograph of BMI-2(20%) modified 30 wt% soy-based epoxy at scale bar 10 µm.

CONCLUSIONS

Triglyceride oils are an abundant natural resource that has yet to be fully exploited as a source for polymers and composites. Moreover polymers derived from these resources possess poor mechanical properties. In this article the mechanical and morphological properties of soy-based epoxy matrices are improved by incorporating three

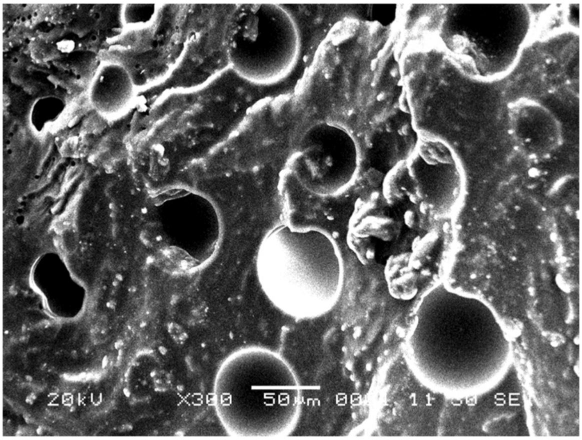


FIGURE 9 SEM micrograph of BMI-3(5%) modified 30 wt% soy-based epoxy at scale bar 50 µm.

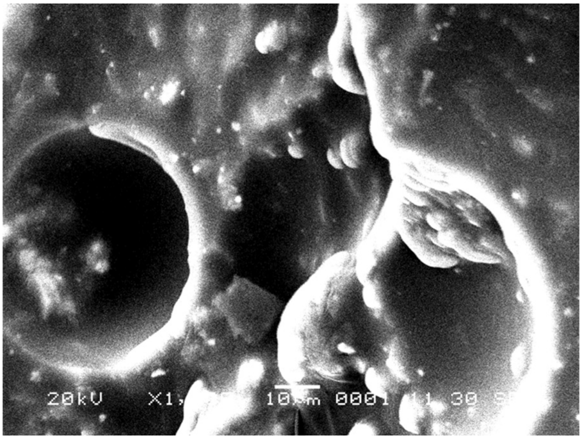


FIGURE 10 SEM micrograph of BMI-3(5%) modified 30 wt% soy-based epoxy at scale bar 10 μm.

different bismaleimides. The mechanical studies indicate that the incorporation of soy epoxy in the base epoxy resin increases the tensile strength and impact strength and decreases the flexural strength. Further, the incorporation of bismaleimides enhanced the stress-strain properties with marginal reduction in the impact strength. SEM observations show that the incorporation of soy epoxy in the base

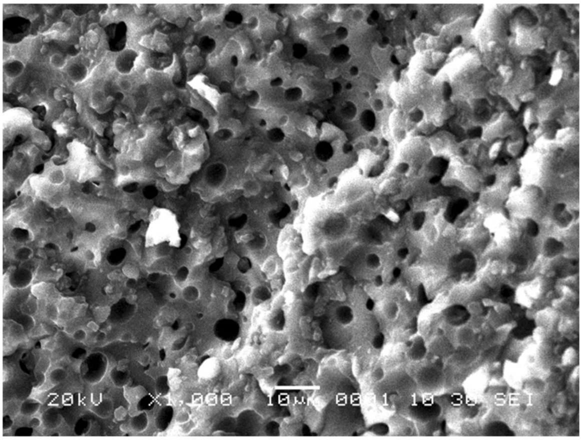


FIGURE 11 SEM micrograph of BMI-3(20%) modified 30 wt% soy-based epoxy at scale bar 10 μm.

epoxy resin imparts a rubbery nature to the matrix and heterogeneous morphology to the structure. These matrix systems act as a potential substitute to petrobased systems and may be used to fabricate advanced composites for automobile and other engineering applications.

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