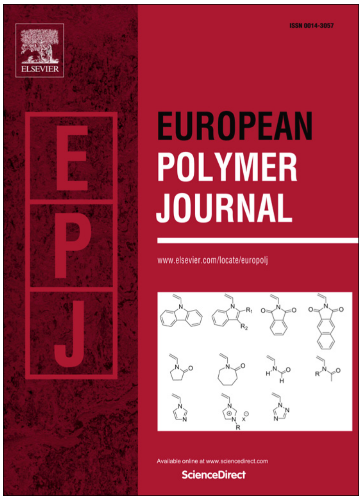

Advanced biocomposite from highly functional Methacrylated Epoxidized Sucrose Soyate (MAESS) resin derived from vegetable oil and fiberglass fabric for composite applications

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Advanced biocomposite from highly functional Methacrylated Epoxidized Sucrose Soyate (MAESS) resin derived from vegetable oil and fiberglass fabric for composite applications

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ABSTRACT

For the two last decades, the depletion of petrochemical resources and the increased global environmental awareness have led to a growing interest in polymers derived from renewable resources. Among the possible technical approaches, using plant-based polymers seems to be the most promising solutions. However, most of the bio-based polymers yield low glass transition temperature (T_g) and low mechanical properties such as modulus and hardness. In this paper, the development of a new generation of highly functional polyester-like polymers for using in composite applications was investigated. These materials were synthesized by mixing methacrylated epoxidized sucrose soyate (MAESS) with styrene as a reactive diluent and using a mixture of Luperox P and Trigonox 239A as a high temperature and room temperature initiators, respectively. E-glass fibers were also used as reinforcements. The prepared bio-based composites were characterized by tensile, flexural, and impact strength testing. Scanning electron microscopy and interlaminar shear strength

(ILSS) were examined to study the fiber–matrix interface behavior. To highlight the performance of bio-based MAESS resin in composites, the results of E-glass/MAESS composite were compared against E-glass/VE as a control. The tensile strength and modules of MAESS and VE resins reinforced with E-glass fibers are 532 MPa, 36.79 GPa and 536 MPa, 36.40 GPa, respectively. The impact strength of the composites with MAESS resin reinforced with E-glass fibers was 237 kJ/m^2, whereas that of the vinyl ester resin reinforced with same E-glass fiber was 191 kJ/m^2. The composites using MAESS were hard and ductile with high modulus and exhibit excellent interface and mechanical properties due to high functionality, rigid and compact chemical structures of MAESS oligomers in the thermoset resin. These bio-based composites have potential uses in variety of composite applications both at low and high temperatures.

KEYWORDS: E-glass fiber, Bio-based Composite, Compression Molding, Mechanical Properties

1. INTRODUCTION

Thermosetting polymers such as unsaturated polyester, epoxy resin, vinyl ester (VE) and phenol-formaldehyde resins have been widely used in the modern composites industry because of their low density, good mechanical properties, low cost, dimensional stability, and high corrosion resistance. Traditionally, most of these resins have been synthesized using petroleum-based chemicals as the raw materials. The replacement of the petroleum-based polymers with their bio-based counterparts is a recent innovation in the field of "green composites" [1-6]. Some economic advantages of using bio-based polymers include global accessibility and relatively low cost. Additionally, plant oils are one of the most important bio-renewable chemical feedstocks for the polymer industry because of their high annual production, high availability, low toxicity, and relatively low cost. These oils are predominantly made up of triglyceride molecules [7-10].

The biggest obstacle in the application of plant oils for the generation of polymers is the flexibility of the fatty acid chain, which leads to low glass transition temperature (T_g) and low mechanical properties such as modulus and hardness. In order to obtain a rigid polymer from plant oils for structural and engineering applications, introducing reactive sites such as epoxy, acrylate or methacrylate functions are necessary. This process is achieved by reactions using the double bonds on the fatty acid chains [11]. Besides, the modification of double bonds can add some functionality like maleates, hydroxyl or epoxy [12-14]. After oils are modified, in order to produce cross-linked thermosetting materials, various techniques of polymerization may be implemented such as free radical polymerization, polycondensation and ring-opening polymerization reactions. Epoxide ring-opening reactions cause the synthesis of composite resins such as hydroxy ester (ester alcohol), diol, amino alcohol, and alkoxy alcohol (ether alcohol), as well as the synthesis of novel monomers [15]. These polymers were found to be useful in composite applications.

The development of bio-based resins for structural applications is still a challenge for the polymer and composite industries. However, in order to obtain a rigid thermoset with high modulus, strength, durability, and resistance towards thermal stress and chemical attacks, Procter & Gamble (P&G) Chemicals produced a novel resin substituting sucrose with fatty acids to obtain sucrose esters of soybean oil. Sucrose esters of soybean oil provides molecules with a high number of double bonds due to the presence of eight fatty acid chains per molecule versus three for the soybean oil [15]. Pan et al. reported the synthesis of high functionality polyols which were prepared by ring-opening epoxidized sucrose soyate (ESS) with acids or alcohols in detail [15-17]. Previous studies reported a detailed description of the synthesis of methacrylated epoxidized sucrose soyate (MAESS) [18]. Compared to their counterparts based on triglyceride oils, thermosets based on substituted sucrose esters of fatty acids show much higher T_g and mechanical properties, which can be attributed to the rigidity of the sucrose core coupled with the large number of reactive functional groups [15, 19-24].

The objective of this study was to manufacture composites based on the novel MAESS resin from renewable origins as matrix materials with glass fibers as reinforcements. The mechanical and thermal properties for the new MAESS-based thermosets and its composites reinforced with unidirectional E-glass fibers up to 50% in fiber volume fraction was studied. In order to highlight the prominent thermal and mechanical properties of the current MAESS-based thermoset, properties of the ensuing composite were compared against those of petroleum-based composites.

2. Experimental and Methods

2.1. Materials and Composite Preparation

Two types of resins, bio-based and petroleum based and one type of fiber reinforcement were used in this study: Epoxidized Sucrose Soyate (ESS) resin was synthesized from fully esterified sucrose soyate as reported previously [17]. ESS was subsequently reacted with methacrylic acid to produce the MAESS as shown in Figure 1. The high functionality MAESS was prepared in the previous study [18]. The MAESS resin was too viscous to be used for thermoset formulations. Therefore, styrene was introduced as a reactive diluent to reduce the viscosity, as well as a co-monomer to increase the rigidity of the resulting thermoset. On the other hand, it reduces the renewable content of the material. 30 wt% Styrene was used which is the optimum formulation reported by Yan et al. [18]. The resin was cured using a mixture of Luperox P as a high temperature initiator, Trigonox 239A as a room temperature initiator, and cobalt naphthenate (CoNap) as a promoter. Styrene, Luperox P (t-butyl peroxybenzoate) and cobalt naphthenate (6% cobalt content) were purchased from Sigma-Aldrich. Cumyl peroxide, commercially available as Trigonox 239A, containing 45% cumene hydroperoxide, was generously provided by AkzoNobel. The mixing ratio of Luperox P, Trigonox 239A and CoNap were 2, 3, and 1 wt%, respectively.

The second resin is a vinyl ester (VE) system Hydropel® R037-YDF-40, provided by AOC resins. The hardener was a 2-butanone peroxide (Luperox® DDM-9) solution, which was obtained from Sigma-Aldrich Co. The unidirectional E-Glass fabric (237 g/m^2, 0.96 wide, 0.2 mm thick) with commercial proprietary sizing, was supplied by Fiber Glast Development Corp. This fabric had an 80 × 18 plain weave style, which was developed with 95% of the fibers in the principal direction and only 5% in the off-axis direction. E-glass fiber were used as received without any further treatments. The composites were prepared by hand lay-up technique for the preparation of the two types of composites reinforced with E-glass fibers. The samples were designed as E-glass/MAESS and E-glass/VE. The composite plates were manufactured in a 100 mm × 200 mm compression mold. To ensure the resin was uniformly distributed throughout the fibers, each layer of fiber fabric was pre-soaked by matrix and then stacked up on each other. The initiators, promoter, resin, and styrene were blended thoroughly. Upon compression, the resin started to flow from the center of the mold to the corners. The compression molding was done for 12 hours at room temperature at 110 kN on a press to obtain partial curing of the resin. To complete the curing reaction the composite was subsequently post-cured at 150 ºC for one hour, 175 ºC for one hour, and 200 ºC for 4 hours. The fiber/resin ratio was about 50:50 by volume. Five specimens of each series were prepared. The samples were conditioned at room temperature and tested.

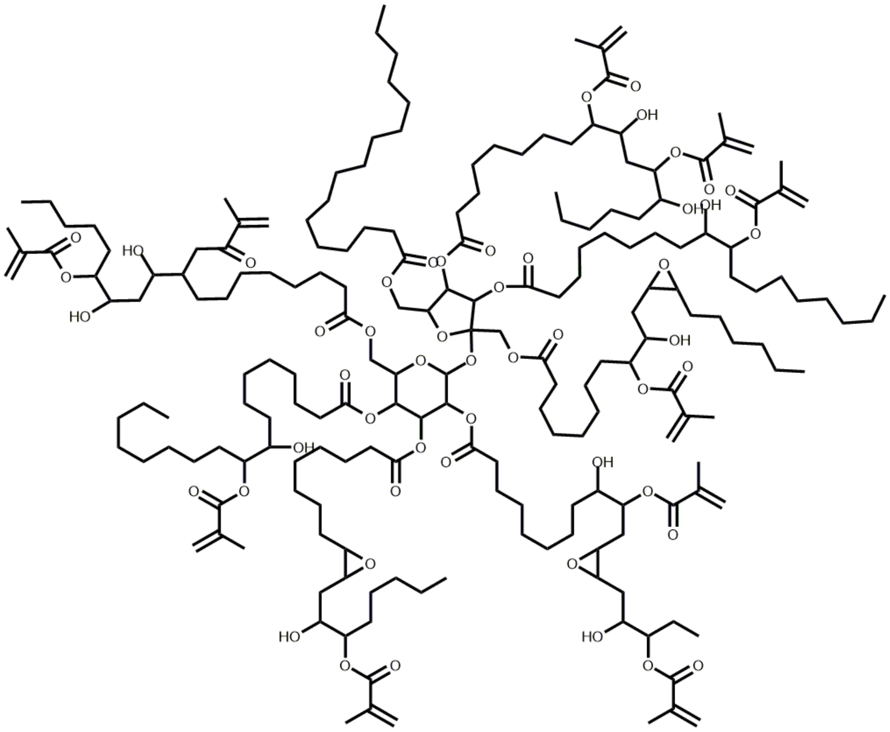


Figure 1: Representative structure of methacrylated epoxidized sucrose soyate (MAESS) [18].

2.2. Characterization

Modulated differential scanning calorimetry (MDSC) experiments using a Q1000 from TA Instruments was employed in this study as an advanced high performing version of traditional DSC. Besides providing information about the heat flow of DSC, MDSC provides required information about the non-reversing and reversing features of thermal functions. MDSC was used to ensure that the composite samples were fully cured and measured glass transition temperature. In materials such as highly crystalline thermoplastics in which the reduction of amorphous content occurs, variation of properties upon glass transition will usually decrease [25]. The smaller signal changes decrease the sensitivities of the DSC technique to the glass transition, though MDSC technique has value in measuring the T_g by separating non-reversing transitions such as volume relaxation and curing from the glass transition which is impossible by traditional DSC. Small size samples from different locations of MAESS composite and VE composite samples (9.5 mg) were heated from 0 °C up to 250 °C at a ramping rate of 3 °C/min using an amplitude of modulation of ± 0.3 °C and a period of 40 s under nitrogen flow of 50 ml/mins.

Density of composite plates was calculated by a Mettler Toledo 33360 density determination kit at room temperature. Weight fraction of fiber in the E-glass reinforced composite plates, (W_f), was measured by resin burn-off method [D2584]. The composite samples were burnt in a furnace at 600 °C until only fibers remained. Void contents in the composite were measured according to ASTM D2734. Tensile, flexural, and interlaminar shear strength were determined using Instron 5567 machine test in accordance with ASTM D3039, ASTM D790 and ASTM D2344, respectively. Izod impact strength of notched specimens were evaluated using Tinius Olsen impact testing instrument in accordance with ASTM D256. All mechanical tests were conducted at ambient temperature and minimum of five test specimens were tested for each material for each test.

To study the adhesion between the fiber and the matrix, fracture surfaces of tensile specimens were examined using a JEOL JSM-6490LV scanning electron microscope

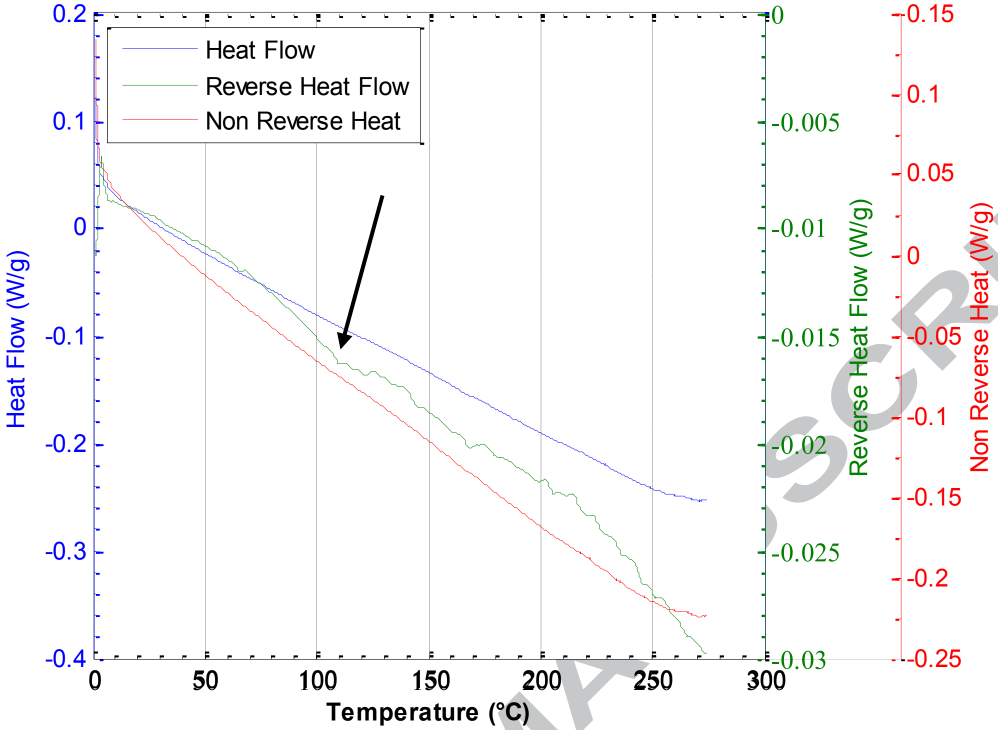
(SEM). Dynamic Mechanical Analysis was carried out on a Q800 DMA from TA Instruments to measure the glass transition temperature and Heat Distortion Temperature (HDT) of the composites according to ASTM D7028 and ASTM D648 respectively. To measure the glass transition temperature a dual cantilever fixture was used with a fixed frequency of 1 Hz with a strain rate of 0.01% and a heating rate of 5 °C/min from 30 to 180 °C. The sample dimensions were (60 mm × 12.5 mm × 3 mm). Heat Distortion Temperature usually denotes the highest temperature to which a polymer may be used as a rigid material in application where the material is able to support a load for some considerable period of time. The DMA is used in the three-point bending mode and the force equivalent to 1.82 MPa is applied on the samples. The samples were heated from 25 °C to 300 °C at the rate of 3 °C/min at which the DMA sample deflects by 0.121% strain is the HDT.

3. Results and Discussion

3.1. Curing analysis of MAESS/E-glass composite

Figure 2 shows an MDSC scan for (a) the E-glass/VE and (b) E-glass/MAESS composites. Samples were machined from different parts of a cured composite panel. The T_g was determined from the reversing heat flow runs (green lines). The total heat flow from the conventional DSC method (blue line) does not show any inflection points to indicate glass transition temperature (T_g) of composite samples. As mentioned earlier, with the MDSC method, the signal of the heat flow is converted into a reversing and a non-reversing signal through Fourier transformation deconvolution. Briefly, the reversing signals are those which are heat capacity events such as the glass transition and melting. The non-reversing components of heat flow signals refer to kinetic reactions such as decomposition, crystal reorganization and perfection, and cure [26]. As indicated in Figure 2, the non-reversing curves (red line) do not show any exothermic peak which indicate that the VE and MAESS resins are fully cured or its conversion is high. On the other hand, the reversing curve (green line) shows heat capacity events such as the glass transition temperature (T_g) sensitive to heating rate the resulting T_g, is distinguishable at reversing curve which is sensitive to heating rate. The glass transition temperature (T_g) are noted by the sudden decrease in the heat flow of cured samples. The DSC software figures out the Tg at around 109 °C and 126 °C in MAESS/E-glass and E-glass/VE composites respectively as was shown by arrows in reversing curve (green line) in Figure 2 (a) and Figure 2 (b).

(a): E-glass/MAESS



(b): E-glass/Vinyl ester

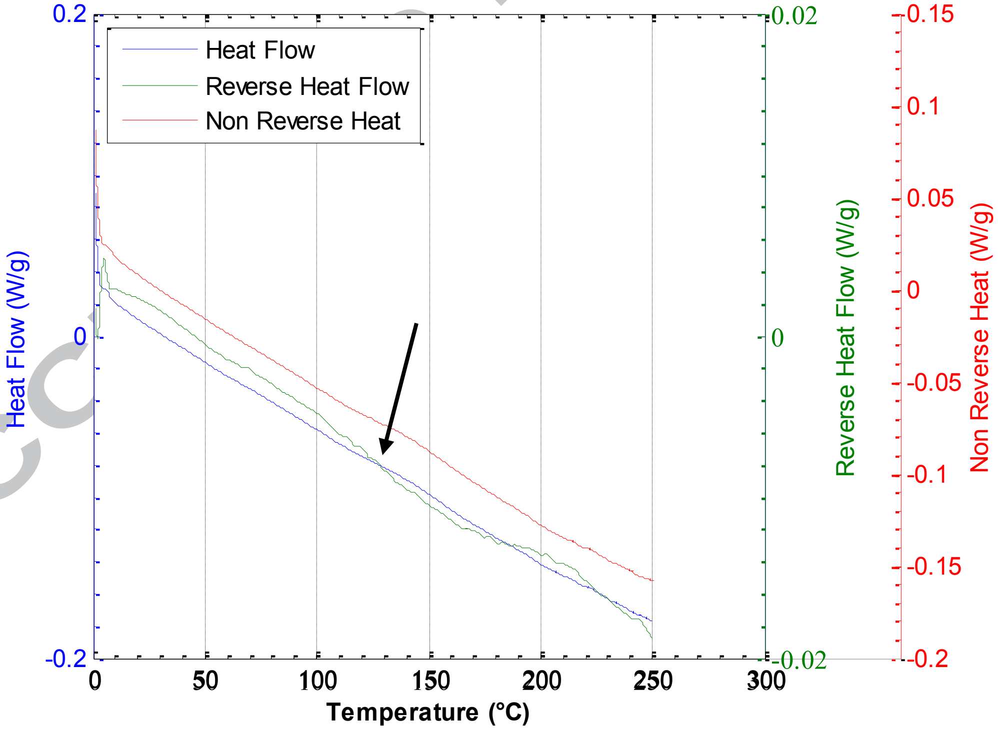


Figure 2: MDSC scans of (a) cured E-glass/MAESS and (b) cured E-glass/VE composites.

3.2. Mechanical Testing

3.2.1. Tensile and flexural test

The physical properties of the composite plates are reported in Table 1.

Table 1: Physical properties of the E-glass reinforced composites.

Composite	Density (g/cm^3)	Fiber Volume Fraction (%)	Fiber Weight Fraction (%)	Void content (%)
E-glass/VE	1.74	50	71.72	4.11
E-glass/MAESS	1.76	50	71.10	2.69

Tensile and flexural strength and modulus of MAESS based neat resin and E-glass fiber reinforced MAESS and VE composite plates were measured and the results are shown in Table 2. Measured mechanical properties of E-glass/VE and E-glass/MAESS are compared in Figure 3. Composite samples using the MAESS thermoset as the matrix have comparable properties with the corresponding E-glass/VE composites. E-glass/MAESS showed only comparable tensile strength and only 10% decrease in tensile modulus, when the results were compared with E-glass/VE. Comparison of the results between E-glass/MAESS and E-glass/VE reveals that when E-glass/MAESS is under tensile deformation, they showed comparable modulus and strength, since the E-glass fibers are able to support the majority of the load, while, when they are under flexural deformation, which has both tensile and compression deformation, the polymer supports the majority of the load. Therefore, this decrease in flexural modulus can be attributed to the lower compression modulus of MAESS resin than VE. High mechanical properties of E-glass/MAESS in this study are believed to be due to the compact and rigid chemical structure, as well as the elevated functionality of the oligomers in MAESS thermoset resin.

Table 2: Mechanical Properties of Neat MAESS, 50 vol. % E-glass/MAESS/, and 50 vol. % E-glass/VE Composites.

Sample	Tensile Properties [a]		Flexural Properties [a]		ILSS [a]	Impact Strength[a]
	Strength (MPa)	Modulus (GPa)	Strength (MPa)	Modulus (GPa)	(MPa)	Notched (kJ/m^2)
Neat MAESS	32.01 (0.10)	1.45 (0.02)	55.96 (3.47)	1.50 (0.14)	--	14.54 (1.82)
E-glass/VE	536.07 (13.86)	36.40 (1.02)	432.68 (12.38)	37.18 (0.66)	22.47 (2.47)	191.04 (18.14)
E-glass/MAESS	531.81 (25.10)	36.79 (2.31)	459.25 (4.76)	33.73 (1.68)	25.12 (0.96)	236.84 (7.95)

[a] Values in parentheses are standard deviations

3.2.2. Interfacial Properties

As adhesion between fiber and matrix plays a key role in transferring the stress from the matrix to the reinforcement, better interlaminar shear properties will enhance the overall performance of the composite [1, 27]. Results of the short beam shear test of E-glass/MAESS and E-glass/VE composites are presented in Figure 3 and Table 2. Furthermore, SEM images were taken from fracture surface of the composite samples in order to investigate the adhesion between fiber and matrix.

The SEM images of the fracture surfaces for E-glass/VE and E-glass/MAESS are shown in Figure 4a and Figure 4b. As can be seen, there are several fiber bundles which have been pulled out together from the other half of the sample at both E-glass/VE and E-glass/MAESS composites. Observing the SEM images taken from the fracture surface of E-glass/MAESS composites shown in Figure 4a, there are remnants of matrix resin sticking to the surface of fibers, which also confirms strong adhesion between fiber and matrix in bio-based composite. This can be the result of good wetting of the fiber by the resin as well as better adhesion between the fiber and the matrix resin in E-glass/MAESS composites. Due to the high number of hydroxyl groups in the MAESS thermoset resin, the likelihood of hydrogen bond formation in the interphase region of fiber in E-glass/MAESS composites is high [28].Therefore the higher ILSS of E-glass/MAESS composite compared to E-glass/VE comes from better wetting of fibers and stronger adhesion between E-glass fibers and the MAESS thermoset resin.

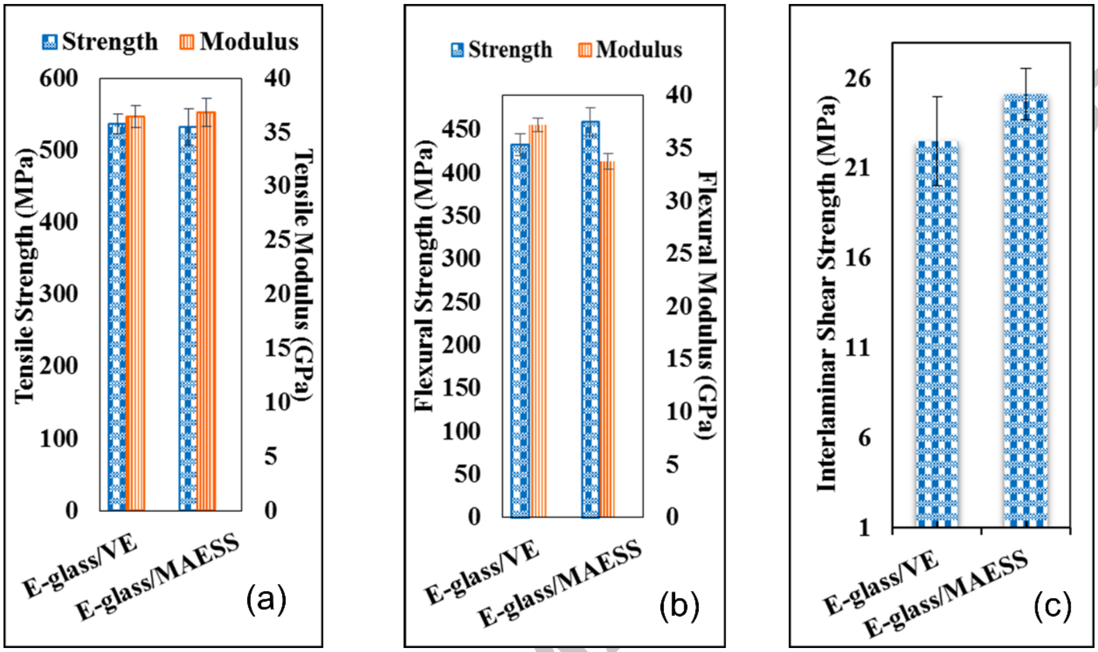
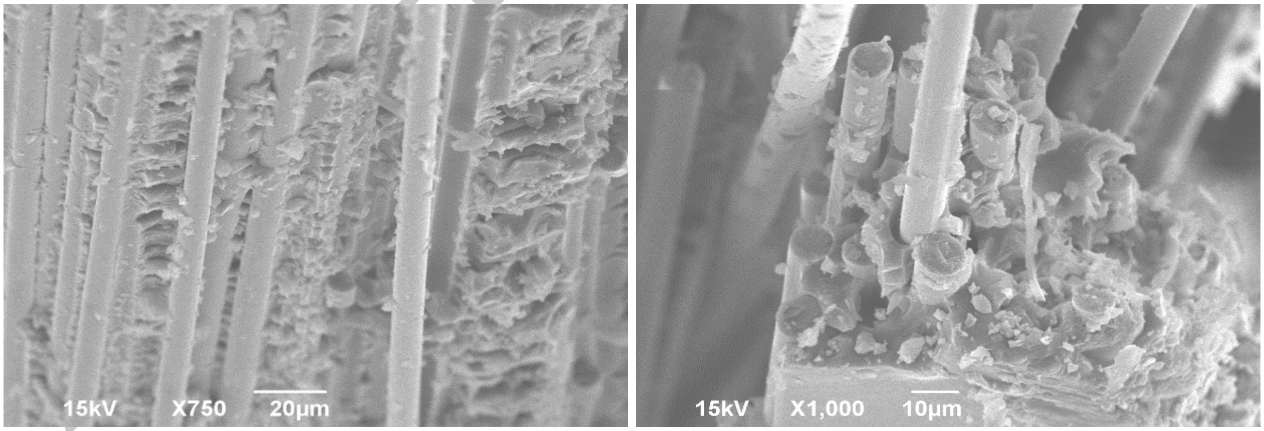
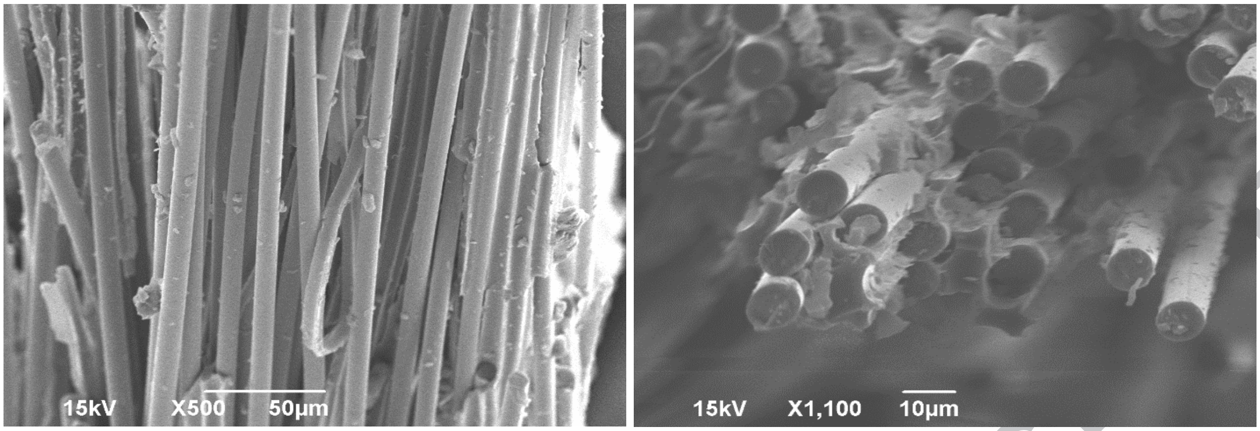


Figure 3: (a): Tensile strength and modulus, (b): Flexural strength and modulus, (c): interlaminar shear strength of 50 vol. % E-glass/MAESS and E-glass/VE composites



(a)



(b)

Figure 4: SEM photograph of (a): E-glass/MAESS and (b): E-glass/VE

3.2.3. Izod Impact Test

The Izod impact tests show a high impact strength for the E-glass/MAESS composite, and lower impact resistance for the E-glass/VE composites, as reported in Table 2. The notched Izod impact strength of MAESS thermoset resin increased from 14.54 kJ/m^2 to 236.84 kJ/m^2 when E-glass fibers are inserted as reinforcement. In composites crack initiates and then peeling along the fibers leads to fiber breakage or fiber pull out depending on the adhesion between fiber and matrix, but in resin cracks initiate and propagate freely in the neat resin. Comparing impact strength of E-glass/MAESS with E-glass/VE composite 25% higher impact strength is observed in bio-based composite. The impact strength of notched specimens was found to be higher for MAESS based composite samples in comparison with that of VE based composite samples. It is expected that replacing petroleum based VE resin with MAESS results in increase of impact properties [29]. This increase is due to the long aliphatic chains originally from the soybean oil, which contribute to the toughness of the composite. Similar trends were observed for other similar resin system [30]. Higher cross linking density of the cured bio-based resin along with higher concentration of dangling chains in the molecular structure have improved modulus as well as impact properties of current E-glass/MAESS composite [31]. Also, as mentioned most of the impact energy is dissipated by debonding, fiber and/or matrix fracture, and fiber pullout, therefore the impact response of the fiber composites is vastly affected by the interfacial bond strength and the matrix and fiber properties [32]. As discussed earlier, current E-glass/MAESS has exhibited greater interfacial bonding compared to E-glass/VE composites. This is also another reason for greater impact properties of the bio-based composite.

3.3. Thermal properties

DMA is another thermal analysis technique which is used to characterize the glass transition temperature (T_g). DMA detects the T_g by monitoring the mechanical strength and energy loss [33, 34]. Tan δ is defined as the ratio of the loss modulus to the storage modulus E''/E', which combines the viscous and elastic components into a single term. Tan δ method was applied to measure T_g of MAESS thermoset resin and its subsequent composite. Log storage modulus, E', and tan δ of the composites were recorded over shown temperature range at the heating rate of 3 °C/min in Figure 5.

As seen in Figure 5a, up to 78 °C the E-glass/MAESS and E-glass/VE composites behaved the same. The broader transition from the glassy to the rubbery region for the E-glass/MAESS composite is characteristic of materials having a wider distribution of crosslinking density and lower homogeneity of these networks [35]. However, at higher temperature, MAESS composites show higher storage modulus, which might attributed to reinforcing action due to improvement of wetting or surface energy that occurs at the interface region between E-glass fiber and MAESS resin. This ultimately contributes to improved modulus of the composite at high temperatures.

The glass transition temperature is determined using the tan δ peak. Variations of tan δ of the resin and the subsequent composite as a function of temperature are presented in Table 3. Tan δ value is higher for the neat resin compared to E-glass/MAESS composite. Based on Dwan'isa *et al.* [36] this is due to higher net volume of resin and also less mobility of chains in the composite. Upon fiber incorporation no significant change in T_g value was observed. Take into account that E-glass fibers may also participate in the curing process by reaction of some possible reaction of E-glass fiber sizing with the styrene at lower temperature before all epoxy groups react at high temperature curing, and in turn alter the MAESS matrix network structure. This resulted in slight decrease of T_g.

Figure 5b compares the tan δ curve for E-glass/MAESS and E-glass/VE composites. The tan δ curve is slightly broader for E-glass/MAESS composite. This suggests that the bio-based composite has a broadened glass transition region because of more heterogeneity of the materials compared to E-glass/VE composites. Since vegetable oils have usually a broad molecular weight distribution that generally results in broad peak of tan δ curve than that of the petroleum-based composite [35, 37]. High values of T_g for neat resin as well as ensuing composites are attributed to great structural rigidity and high functionality of the sucrose molecule which is the core of sucrose soyate. Rigidity of sucrose molecule has been shown to give more rigid thermosets in previous studies [16, 38]. The crosslink density (v_e) was evaluated using Equation 1, an expression derived from the rubber elasticity's theory:

$$E' = 3v_eRT \qquad \text{Equation 1}$$

where E' is the storage modulus in the rubbery plateau above T_g. The rubbery plateau region was peaked 40 °C above glass transition temperature at 153°C, 169 °C, and 150 °C for neat MAESS, E-glass/VE, and E-glass/MAESS composites respectively. R is the gas constant (8.314 J K^{-1}/mol^{-1}), and T is the temperature in Kelvin. Using Eqn. (1), v_e is calculated and reported at Table 3.

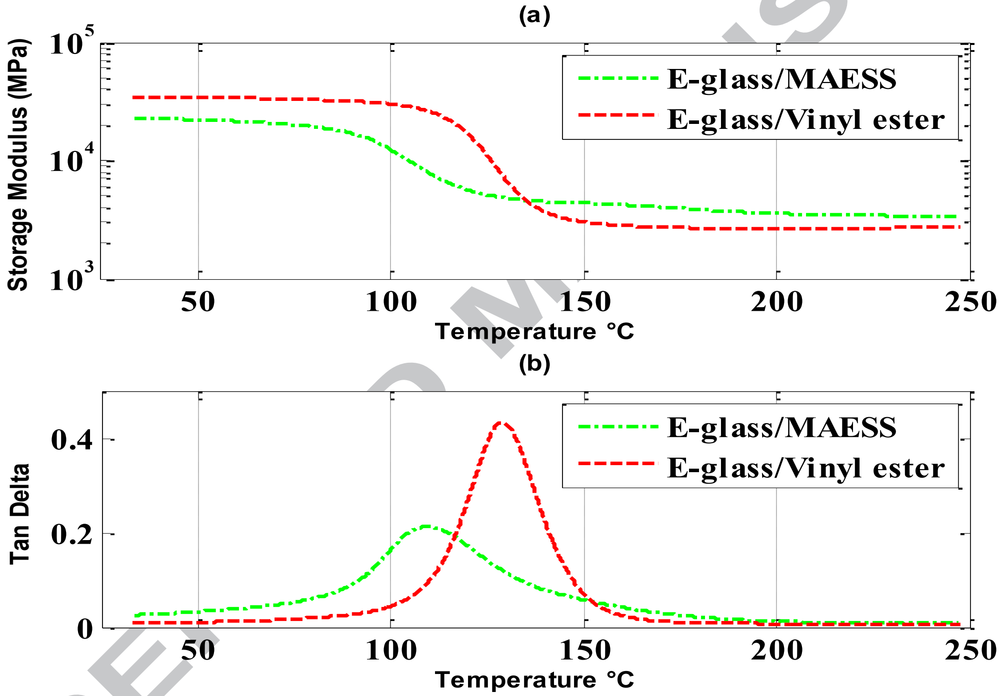


Figure 5. Temperature dependence of (a): storage modulus (E'), and (b): glass transition temperature (T_g) of E-glass/MAESS and E-glass/VE reinforced composites.

The HDT or softening point of polymer-based materials is another important property for designing industrial products. Table 3 reports HDT values for MAESS rein, E-glass/MAESS, and E-glass/VE composite. The HDT value of pure MAESS resin is 51°C. It should be mentioned that a significant increase in the HDT by incorporating fibers is due to the high modulus of E-glass fibers as well as the high interfacial adhesion and crystallinity of the MAESS. HDT results for E-glass/MAESS, and E-glass/VE composite are 340 °C and 375 °C, respectively, confirming relatively comparable HDT results for both bio-based and petroleum based composites.

Table 3. Thermal properties for 50 vol. % E-glass/MAESS and E-glass/VE composites.

Composite	DSC T_g(°C)	DMA				HDT (°C)
		T_g (°C)	E' at 40°C (GPa)	$E'_{rubbery\ plateau}$ (GPa)	v_e (× 1000 mol/m^3)	
Neat MAESS	112.88	113 (1.50)	2.44	0.08 @ T_g+40°C	7.71	51.01 (3.82)
E-glass/VE	126.50	129.01 (0.59)	34.42	2.74 @ T_g+40°C	248.45	375.88 (3.71)
E-glass/MAESS	109.34	109.81 (0.25)	22.59	4.44 @ T_g+40°C	420.87	340.45 (3.90)

[a] Values in parentheses are standard deviations

4. Conclusion

A bio-based composite was manufactured with a compression-molding technique. A novel highly-functional bio-based resin methacrylated epoxidized sucrose soyate (MAESS) was used as a matrix, and E-glass fibers were used as reinforcements. The fiber/resin ratio was 50:50 by volume. The prepared bio-based composites were characterized by tensile, flexural, and impact strength testing. Scanning electron microscopy and interlaminar shear strength (ILSS) were examined to study the fiber–matrix interface behavior. To highlight the performance of the bio-based MAESS resin in composites, the results of the E-glass/MAESS composite were compared against E-glass/VE as a control. The tensile strength and modules of MAESS and VE resins reinforced with E-glass fibers are 532 MPa, 36.79 GPa and 536 MPa, 36.40 GPa, respectively. The flexural strength and modules of MAESS and VE resins reinforced with E-glass fibers are 459 MPa, 34 GPa, and 432 MPa, 37 GPa, respectively. The impact strength of the composites with MAESS resin reinforced with E-glass fibers was 237 kJ/m^2, whereas that of the VE resin reinforced with same E-glass fiber was 191 kJ/m^2. Results of SEM images along with flexural strength, interlaminar shear strength and impact tests revealed better wetting of fibers by the matrix, stronger adhesion between fiber and matrix and greater interfacial bonding compared to corresponding E-glass/VE composites. The composite using MAESS were hard and ductile with high modulus and exhibit excellent interface and mechanical properties due to high functionality, rigid and compact chemical structures of MAESS oligomers in thermoset resin. These bio-based composites have potential uses in variety of composite applications both in low and high temperature uses and make this resin a great alternative to current bio-based and petroleum-based resins.

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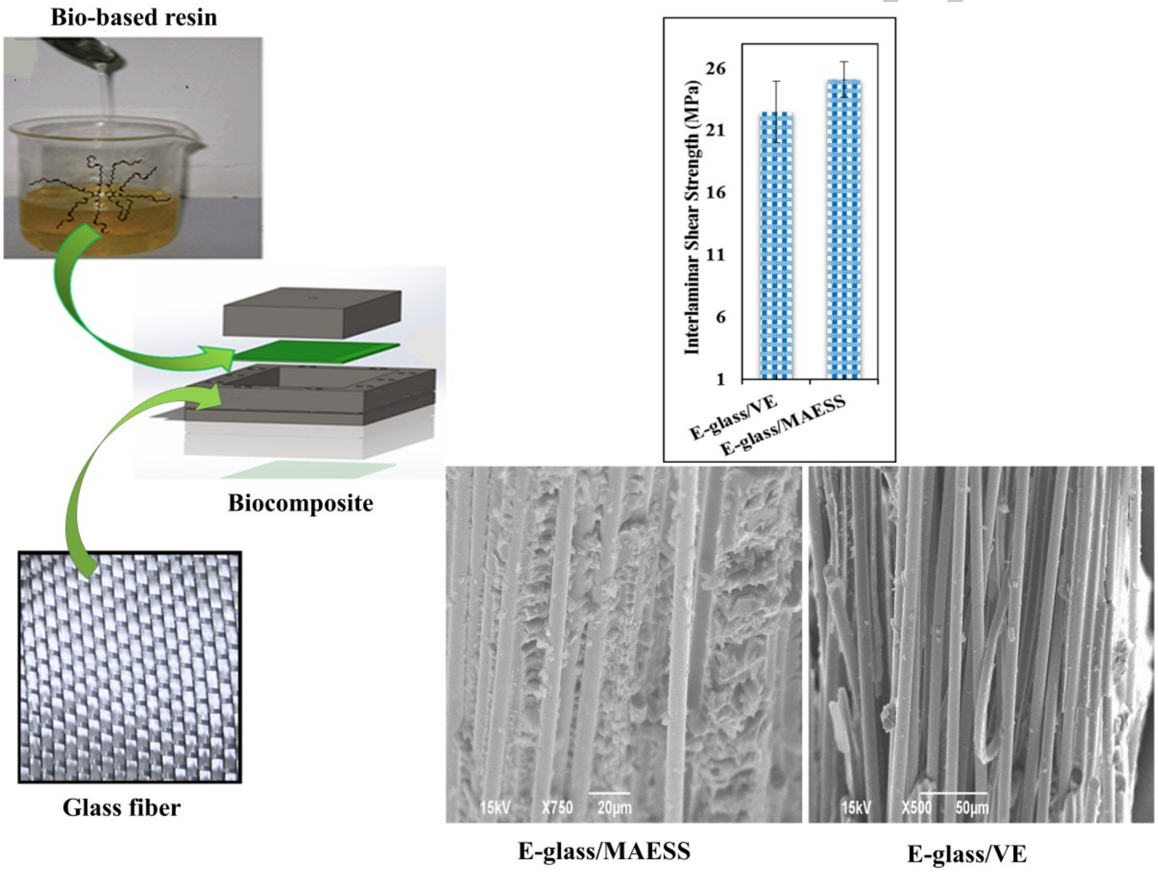
Graphical abstract



Highlights

Highly-functional bio-based methacrylated epoxidized sucrose soyate (MAESS) were developed.
MAESS was used as a matrix for compression molding E-glass composites.
High bio-based content composites were found to outperform petrochemical based counterparts.
SEM of fractured composites revealed improved wetting of fibers enhancing interfacial bonding.