Biorenewable thermosetting copolymer based on soybean oil and eugenol

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Abstract

A novel biorenewable thermoset based on acrylated epoxidized soybean oil (AESO) and methacrylated eugenol (ME) was prepared via free radical polymerization. The chemical compositions of the monomers were investigated using proton nuclear magnetic resonance ($^1$H NMR) technique. The properties of this resin system were investigated using small amplitude oscillatory shear flow rheology, dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and compression testing. Soxhlet extraction was also performed on the cured thermoset to determine the percentage of monomers that are incorporated into the crosslink network. In addition, the gelation time of this resin at different curing temperature was also monitored using a rheometer. The Soxhlet extraction data indicated that more than 95% of the monomers were incorporated into the crosslink network. Gelation time study showed that this resin system can become a solid within 10 min. This resin system possesses high strength and modulus, and it is thermally stable up to 300 °C. This high biorenewable content resin system possesses good mechanical properties, high thermal stability, and fast curing speed, making it a suitable matrix resin for the pultrusion process and other composite manufacturing processes.

Graphical abstract
Keywords

- Bio-based
- Soybean oil
- Thermosets
- Rheology
- NMR
- DSC

1. Introduction

In recent years, polymeric materials derived from biorenewable resources have attracted a lot of attention due to the shortage and high price of petroleum and the increase in environmental concerns. Currently, almost all commercially available polymers are derived from non-sustainable petroleum resources. About 7% of oil and gas are used to produce plastic [1]. A wide range of biorenewable polymeric materials have been developed that utilize biorenewable resources such as sugars, polysaccharides, lignins, plant oils, pine resin derivatives, and furans [2].

Vegetable oils are one of the most abundant biorenewable materials. Their inherent biodegradability and low toxicity make them a promising starting material for polymer synthesis. Vegetable oils are composed of triglyceride molecules. Triglycerides consist of three fatty acid chains combined with glycerol through ester linkage. The length of fatty acid ranges from 8 to 22 carbon, and some of them have chemical functionalities such as hydroxyl groups, epoxide groups, and unsaturation (carbon–carbon double bond) [3]. Recently, there are many research activities focusing on using vegetable oil as partial replacement of petroleum components in plastic. Vegetable oils such as soybean oil [4], [5] and [6], linseed oil [7], [8] and [9], corn oil [10], and tung oil [11], [12] and [13] contain unsaturation sites (carbon–carbon double bonds) and have been copolymerized with petroleum-based chemicals, such as styrene (ST), divinylbenzene (DVB), dicyclopentadiene (DCPD), and acrylonitrile using cationic, free radical or thermal polymerization. The properties of the resulting thermosetting polymers range from rigid plastics to soft and flexible rubbers. However, soybean oil, corn oil, and linseed oil do not contain conjugated double bonds in their triglyceride chains, making them difficult to be incorporated into the crosslinked thermoset network. Conjugation of vegetable oils can be accomplished using catalysts containing rhodium or ruthenium [14]. On the other hand, epoxidation can be performed on vegetable oil to turn the carbon–carbon double bonds into oxirane rings [15] and [16]. The epoxidized vegetable oils (EVO) can be blended into commercially available epoxy systems to yield a new class of epoxy. Epoxidized vegetable oils have been blended with commercially available epoxy systems such as bisphenol A diglycidyl ether (DGEBA) and di-glycidyl ether of bisphenol F (DGEBF) [17] and [18]. It was found that the storage modulus at room temperature, the glass transition temperature, and the crosslink density of the epoxy blend decreased with increasing content of EVO, while fracture toughness and flexural modulus were increased with increasing amount of EVO [17], [18] and [19]. The epoxide rings of EVO can be ring-opened by alcohols [20] or acids [21] and [22] to introduce other functionalities. After the epoxide rings had been opened, hydroxyl groups were introduced, and polyurethanes with a wide range of properties can be produced by the reactions between
hydroxyl groups and diisocyanates [23]. EVO can also be ring-opened to produce molecules with acrylates to increase the reactivity of vegetable oils.

Acrylated epoxidized soybean oil (AESO) is produced by reacting epoxidized soybean oil with acrylic acid [24], and the steps of synthesizing AESO is shown in Fig. 1. AESO is commercially available under the trade name Ebecryl 860, and it can be polymerized using free radical initiators [25] and [26]. Due to the high viscosity of AESO, it has been copolymerized with styrene to increase its processibility [26] and [27]. AESO has also been combined with hemp fibers [25], cellulose fibers [28], pyrolyzed chicken feather [29], and montmorillonite clay [30] to produce composites with high renewable content. In addition, it has been proposed that AESO-based resins can be used in electronics [31] and [32] and coating applications [33].

![Fig. 1: Synthesis of acrylated epoxidized soybean oil (AESO).](image)

Eugenol is an aromatic compound found in plants such as clove, cinnamon, basil, and nutmeg. It is considered a safe additive to food and has been used as a flavoring agent in cosmetic and food products [34]. The combination of eugenol and zinc oxide has been widely used in the dental industry as a cement material [35]. Eugenol also has antibacterial property, and it has been incorporated into polypropylene to produce antibacterial plastics [36]. Qin et al. has attached epoxy groups onto eugenol to produce a biorenewable epoxy system [37]. Polyacetylene based on eugenol and propargyl chloride has also been synthesized, with molecular weight above $M_n = 30,000$ g/mol [38]. High-performance bismaleimide resin has also been synthesized utilizing eugenol and succinic acid [39]. On the other hand, even though nowadays eugenol is extracted from clove, studies have shown that eugenol can potentially be obtained from pyrolysis [40] and [41] or depolymerization [42] of lignin. Because of the low cost and abundance of
lignin, the price of eugenol can be dramatically decreased if an economical pathway of obtaining eugenol from lignin is developed.

Pultrusion is a low-cost, highly automatic manufacturing process to produce fiber reinforced composites with constant cross-section profile [43]. In the pultrusion process, fibers are impregnated with the resin, and the fibers are then pulled by a motor through a heated die with desired geometry. In the heated die, the resin (the matrix of the composites) becomes cured and fiber reinforced composites are produced. There are many studies focusing on incorporating biorenewable fibers, such as jute, hemp, and kenaf fibers into a petroleum based matrix [44], [45] and [46]; however, there are few studies focusing on developing biorenewable matrix materials suitable for the pultrusion process. Cui et al. prepared glass fiber reinforced composites using dicyclopentadiene and norbornene-modified linseed oil copolymerized by ring-opening metathesis [47]. Badrinarayanan studied the cure kinetic of soybean oil–ST–DVB copolymer system and found that this system is suitable for pultrusion due to its fast curing speed [48]. Chandrashekhara et al. used the pultrusion process on the blend of epoxidized allyl soyate (a mixture of epoxidized fatty acid ester) and Epon 9500 (a commercially available epoxy resin designed for pultrusion) to produce glass fiber reinforced composites [49]. It was found that incorporation of 10–20 wt% of epoxidized allyl soyate into epoxy yielded a material with a toughness that is much higher than pure epoxy [49]. However, the above resin systems consist of more than 50% of non-biorenewable contents; as a result, the aim of this work is to develop a vegetable oil-based thermosetting resin with high biorenewable content that is suitable for the pultrusion process.

2. Experiment details

2.1. Materials

Eugenol (98%), acrylated epoxidized soybean oil, methacrylic anhydride (94%, containing 2000 ppm topanol A inhibitor), 4-dimethylaminopyridine (DMAP), and benzoyl peroxide (BPO) free radical initiator were purchased from Sigma Aldrich (Milwaukee, WI). Methylene chloride (CH2Cl2), sodium bicarbonate, sodium hydroxide (NaOH), hydrochloric acid (HCl), magnesium sulfate (anhydrous) (MgSO4) were obtained from Fisher Scientific. Deuterated chloroform for nuclear magnetic resonance (NMR) analysis was purchased from Cambridge Isotope Laboratories, Inc. All chemicals were used as received without further purification.

2.2. Synthesis of methacrylated eugenol

The methacrylation of eugenol was performed as described in literature [50], and the synthesis route is shown in Fig. 2. 100 g of eugenol (0.61 mol) and 2.51 g of DMAP (2 mol% of methacrylic anhydride) were added into a 500 ml round-bottom flask equipped with a magnetic stir bar and a nitrogen gas inlet. After the flask had been purged with nitrogen gas for at least an hour to remove the oxygen and moisture, 98.7 g methacrylic anhydride (105 mol% of eugenol) was added into the flask. For the first three hours of the reaction, the flask was placed at room temperature. The flask was then heated to 45 °C under a nitrogen atmosphere and kept at this temperature for at least 24 h. The reaction mixture was then transferred to a 2000 mL Erlenmeyer flask, and 500 mL of CH2Cl2 was added to the reaction mixture. To remove the
methacrylic acid byproduct and unreacted methacrylic anhydride, the organic phase was washed with 1 L of saturated sodium bicarbonate aqueous solution, 1.0 M NaOH aqueous solution, 0.5 M NaOH aqueous solution, 1.0 M of hydrochloric acid, and water. Each wash was repeated at least twice. After the above washing steps, the mixture was dried with anhydrous MgSO₄ powder overnight. The mixture was then filtered to remove solid MgSO₄, and was followed by concentration under reduced pressure to remove the CH₂Cl₂.

![Fig. 2: Synthesis of methacrylated eugenol.](image)

**2.3. Free radical polymerization of AESO/ME copolymers**

Pre-weighed amounts of AESO and ME were added to a vial, followed by the addition of 2 wt% of BPO free radical initiator. The reaction mixture was stirred vigorously using a Kurabo MAZERUSTAR (Tokyo, Japan) planetary mixer until the mixture became homogeneous and all the BPO free radical initiator was dissolved. The homogeneous mixture was then degassed under reduced pressure and poured into a silicon mold. The resin was cured for 2 h at 90 °C and 4 h at 160 °C. The samples were then post-cured at 200 °C for 2 h. The heating rate for the above-stated cure schedule was set to be 1 °C per minute. The following system of nomenclature has been adopted for simplicity: AESO20–ME78 corresponds to a polymer sample prepared from 20 wt% AESO, 78 wt% ME, and 2 wt% BPO initiator.

It must be stated here that the BPO content was fixed at 2 wt% because it gives the highest degree of conversion with a reasonable curing time. The BPO can react simultaneously with both AESO and ME because both of them have similar reactivity (AESO has double bonds on the acrylate groups and ME has double bonds on the methacrylate group and in the terminal carbon position). These double bonds are very reactive. Therefore, the reaction is not competitive.
2.4. Material characterizations

Two grams of the bulk polymer sample was extracted with 400 mL of refluxing CH$_2$Cl$_2$ in a Soxhlet extractor for 24 h. After extraction, the insoluble portion of the sample was separated from the CH$_2$Cl$_2$ solvent and was dried under vacuum at 70 °C for at least 24 h before weighing.

$^1$H NMR of the synthesized ME was performed in deuterated chloroform using a Varian Unity spectrometer (Varian Associates, Palo Alto, CA) at 400 MHz. The data was obtained by averaging 32 scans.

Dynamic mechanical analysis (DMA) was carried out using a TA Q800 dynamic mechanical analyzer in tension mode. Rectangular specimen with dimensions approximating 1.0 mm thickness, 4.0 mm width, and 8.5 mm length were heated from −100 °C to 200 °C with a heating rate of 3 °C/min. All DMA measurements were performed under a frequency of 1 Hz and displacement amplitude of 5 μm.

The thermal stability of the obtained copolymers was studied using a TA Q50 thermogravimetric analyzer. Approximately 5–8 mg of sample was heated from room temperature to 800 °C in a nitrogen atmosphere with a heating rate of 20 °C/min.

The gelation process of the AESO/ME copolymerization was studied using TA AR2000ex rheometer using parallel plates with 25 mm diameter. Time sweeps at a constant shear frequency of 10 rad/s at 70 °C, 80 °C, and 90 °C were performed on the AESO/ME mixture containing 2 wt% BPO initiator. The time when the storage modulus ($G'$) and the loss modulus ($G''$) intercepted is considered the gelation time. In addition, the viscosity of the AESO/ME mixture was also measured using a steady state procedure with shear rates increasing from 10 s$^{-1}$ to 200 s$^{-1}$. The measurement was conducted at 25 °C.

Compression testing of the AESO/ME copolymers was performed according to ASTM standard D695-10 using an Instron 5569 load frame. A specimen size of 12.7 mm by 12.7 mm by 25.4 mm was used. The crosshead speed was set at 1.3 mm/min. A minimum of five samples were tested for each composition.

3. Result and discussion

3.1. Materials synthesis

A thermosetting resin for pultrusion process must possess the following characteristics: low to medium viscosity, fasting curing process, and high rigidity after cure. Unsaturated polyesters are the most commonly used resins for pultrusion application, and styrene is always added to reduce the viscosity of the unsaturated polyesters. In addition, styrene also imparts the stiffness and strength to the cured unsaturated polyesters thermostet. Eugenol is a low viscosity liquid with a viscosity value of 0.01 Pa·s at room temperature, and it also has an aromatic ring and a double bond; as a result, the molecular structure of eugenol is similar to styrene. In addition, eugenol is more environmental friendly when compared to styrene because eugenol is a bio-based chemical with low toxicity. However, unlike styrene, eugenol will not polymerize by itself by free radical
polymerization because phenol derivatives are chain breaking radical scavengers, which means that the free radicals generated by free radical initiators are trapped in the phenolic hydroxyl group in eugenol [51]. In fact, eugenol has been used as a free radical polymerization retarder [52]. Adding the methacrylate functional group onto the eugenol allows it to become a polymerizable monomer. Methacrylated eugenol is a very reactive product. By adding 2 wt% BPO free radical initiator into ME and heating the reaction mixture at 110 °C, a rigid thermoset was produced in less than two minutes. The fast reaction process of ME, combined with its low viscosity (0.02 Pa·s) and rigid aromatic structure makes ME a good candidate material for pultrusion application.

The $^1$H NMR spectra of as-receive eugenol and methacrylated eugenol are shown in Fig. 3 and Fig. 4, respectively. In the NMR spectra of the as-received eugenol, the peaks at 6.6–7.0 ppm originate from the hydrogen atoms bonding to the aromatic rings. The peaks in the range of 4.75–5.2 ppm represent the two hydrogen atoms connecting to the terminal side allylic double bond of eugenol. The multiplet in the range of 5.8–6.0 ppm comes from the hydrogen on the secondary carbon of the allylic double bond.

Fig. 3: $^1$H NMR spectrum of as-received eugenol.
Fig. 4: $^1$H NMR spectrum of methacrylated eugenol.

After the methacrylation reaction, the aromatic hydroxyl group was replaced by methacrylate group. This is evident by the presence of peaks between 6.2 ppm and 6.4 ppm, which comes from the protons on the terminal carbon of the methacrylate group. The additional peak on 2.1 ppm represents the proton found on the secondary carbon of the methacrylated group, which is not seen on the spectrum of as-received eugenol. However, there are trace amounts of impurities on the ME. The impurities come from the topanol A, which is a photodegradation inhibitor presented in the as-received methacrylic anhydride. The trace amount of impurities does not inhibit the polymerization of ME. The synthesized ME can be further purified using silica gel.

A $^1$H NMR spectrum of AESO is shown in Fig. 5. The three peaks in the range of 5.7–6.6 ppm represent the three hydrogen atoms of the acrylate function groups. The peak between 0.7 and 1 ppm comes from the hydrogen atoms attaching to the terminal carbon of the triglyceride molecules. The triplet peak between 2.1 and 2.4 ppm is related to the hydrogen atom at the alpha position of the carbonyl groups. The peaks between 4.0 and 4.5 ppm come from the protons on the primary carbon group near the center of the triglyceride. The number of acrylate groups per triglyceride molecule can be calculated by dividing the area under the acrylate peaks (5.7–6.6 ppm) by the area under the peak terminal carbon (0.7–1 ppm) and by multiplying the quotient by three. It is found that there are 3.4 acrylate groups per triglyceride molecule.
Fig. 5: $^1$H NMR spectrum of acrylated epoxidized soybean oil.

Fig. 6 depicts the crosslinking reaction between AESO and ME. ME contains two types of double bonds: the double bonds on the acrylate groups and the allylic double bonds. These two types of double bond can both participate in the crosslinking reaction [53]. On the other hand, AESO has only one type of double bonds. AESO and ME are completely miscible to each other, and the cured samples were homogeneous and transparent with a color similar to that of soybean oil. No separation was observed on all cured samples.
Fig. 6: The crosslinking reaction between AESO and ME.

Soxhlet extraction was performed to measure the content crosslinked polymer, and the data are summarized in Table 1. The soluble portion extracted from the bulk polymer consists of substances that are unreacted monomers or low molecular weight polymers. The insoluble portion of the polymer varied from 97.7% to 99.3%, indicating that the majority of AESO and ME have participated in the crosslinking reaction. The crosslinked portion in the AESO/ME system is found to be much higher than the conjugated vegetable oil–styrene–divinylbenzene system developed by Li and Larock [4]. The soluble content was analyzed by NMR to identify the unreacted components. The soluble content contained a small amount of ME, AESO, and BPO free radical initiator.

![Table 1](image)

<table>
<thead>
<tr>
<th>Polymer composition</th>
<th>Insoluble (%)</th>
<th>Soluble (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AESO0–ME98</td>
<td>99.3</td>
<td>0.7</td>
</tr>
<tr>
<td>AESO10–ME88</td>
<td>97.7</td>
<td>2.3</td>
</tr>
<tr>
<td>AESO20–ME78</td>
<td>97.7</td>
<td>2.3</td>
</tr>
<tr>
<td>AESO30–ME68</td>
<td>98.2</td>
<td>1.8</td>
</tr>
<tr>
<td>AESO40–ME58</td>
<td>97.9</td>
<td>2.1</td>
</tr>
</tbody>
</table>

### 3.2. Rheological properties

A rheometer was used to monitor the gelation time of this resin system under three different isothermal curing temperatures: 70 °C, 80 °C and 90 °C. The gelation time can be found at the intercept of storage modulus and loss modulus curves [54]. The value of the gelation time is found to be dependent on the chemical composition of the AESO/ME copolymer. Fig. 7 shows a plot of gelation time vs. AESO content at different curing temperatures. At a given curing temperature, the gelation time decreases as the AESO content increases, and this is ascribed to the fact that acrylate functional groups generally have higher reactivity than methacrylate functional groups. As the AESO content in the mixture increases, there are more acrylate functional groups (from AESO) and less methacrylate functional groups (from ME) in the mixture; as a result, the crosslinking reaction proceeded faster with higher AESO content. For a curing temperature of 90 °C, the gelation time ranges from 4.7 min (40 wt% AESO) to 6.7 min (0 wt% AESO). At this curing temperature, the mixture can become a solid gel within 10 min. The fast gelation speed of the AESO/ME system indicates that this system is a suitable candidate for pultrusion. An even shorter gelation time can be achieved by curing this resin at a temperature higher than 90 °C; however, at such a high temperature, the mixture cured almost instantaneously, making it difficult to measure the gelation time reliably with a rheometer. When the curing temperature is set at 70 °C, the gelation time ranges from 30 min to 52 min. It is evident that the chemical composition has a higher impact on the gelation time at lower temperatures. The viscosity of the AESO/ME mixture with different compositions was tested at different shear rates, and the data are shown in Fig. 8. For all compositions, the viscosity remains
almost constant with increasing shear rate, indicating that both AESO and ME are Newtonian fluids. AESO is a very viscous fluid with a viscosity value around 11 Pa·s. The viscosity of AESO is much greater than regular soybean oil. This is because the AESO contains acrylate and hydroxyl functionality, and these functional groups introduce hydrogen bonding between the triglyceride molecules and increase the viscosity of AESO. As the ME content in the mixture increased, the viscosity of the resin decreased significantly. ME acts as a reactive diluent in this resin system, making this resin easily processable. On the other hand, the viscosity of common unsaturated polyester resins for pultrusion ranges from 0.3 Pa·s to 4 Pa·s. The viscosities of the AESO/ME resin containing 0–40 wt% AESO are lower than most of the unsaturated polyester resins.

![Fig. 7: Gelation time for AESO/ME copolymers with different compositions cured at 70 °C, 80 °C, and 90 °C.](image)

![Fig. 8: Viscosity of AESO/ME mixtures as a function of shear rate.](image)
3.3. Thermal properties

Fig. 9 shows the temperature dependence of storage modulus for AESO/ME copolymers with different compositions. At extremely low temperatures (−100 °C to −50 °C), all copolymers containing 10–40 wt% AESO have similar storage moduli; however, the storage modulus of the pure ME polymer is about 800 MPa higher than those copolymers containing AESO. At a temperature range from 50 °C to 150 °C, the storage moduli of the copolymers exhibit sharp drops, indicating that glass relaxation, also called α-relaxations, occur at this temperature range. The storage moduli at room temperature for all prepared copolymers are listed in Table 2. Obviously, the storage modulus decreases with increasing AESO content because the incorporation of AESO increases the percentage of long and flexible triglyceride chains in the copolymers system. The ME acts as hard segments in the copolymers because of its aromatic structure, while the ASEO acts as soft segments. By varying the ratio between ME and AESO, the modulus of this copolymer system can be easily tailored to produce rigid thermoset plastics or softer plastics for different applications. Pure AESO polymer was also tested using the same procedure. Pure AESO polymer possesses much lower storage modulus compared to the AESO/ME copolymers.

![Graph showing temperature dependence of storage modulus for AESO/ME copolymers](image)

Fig. 9: Storage moduli for AESO/ME copolymer with different chemical compositions.
Table 2. Glass transition temperature and storage modulus at 25 °C.

<table>
<thead>
<tr>
<th>Polymer Composition</th>
<th>$T_g$ (°C)</th>
<th>$E'$ at 25 °C (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AESO0-ME98</td>
<td>149</td>
<td>1681</td>
</tr>
<tr>
<td>AESO10-ME88</td>
<td>136</td>
<td>1440</td>
</tr>
<tr>
<td>AESO20-ME78</td>
<td>130</td>
<td>1411</td>
</tr>
<tr>
<td>AESO30-ME68</td>
<td>123</td>
<td>1266</td>
</tr>
<tr>
<td>AESO40-ME58</td>
<td>122</td>
<td>1096</td>
</tr>
<tr>
<td>AESO98-ME0</td>
<td>38</td>
<td>274</td>
</tr>
</tbody>
</table>

The glass transition temperatures is obtained from the maxima of tan δ curves obtained by DMA analysis.

Fig. 10 depicts the tan δ curve of AESO/ME of different compositions. The tan δ peak is related to the alpha-relaxation of the polymer, and the peak of the tan δ curve is often regarded as the glass transition temperature ($T_g$). The peaks of the tan δ curves shifted to lower temperatures with increasing amounts of AESO in the resin, indicating that there is more free volume in the copolymer with higher AESO content. This is expected because the triglyceride chains in vegetable oil are bulky and flexible. On the other hand, the ME polymer is relatively rigid due to its aromatic structure. When the soft triglyceride chain is added into ME, the storage moduli and glass transition temperatures of the obtained copolymer are expected to be decreased. Pure ME polymer has a $T_g$ closed to 150 °C, which is comparable to most petroleum-based plastics. There is another peak on the tan δ cure of pure ME polymer at 10 °C. This peak might be associated with beta relaxation of the thermoset, which corresponds to local relaxation processes of the methacrylate side group. When the AESO content increased from 0 wt% to 10 wt%, the $T_g$ shifted about 12 °C to a lower temperature. The drop of $T_g$ is not as pronounced with high amounts of AESO: the $T_g$ only dropped 1 °C when the AESO content increased from 30 wt% to 40 wt%.

![Fig. 10: Tan δ curves for AESO/ME copolymers.](image)
Fig. 11 and Table 3 show the TGA data obtained from the AESO/ME copolymer systems. It is found that all of the copolymers are thermally stable up to 250 °C. All of the copolymers exhibit three different stages of thermal degradation above this temperature. The first stage of thermal degradation (250–330 °C) is attributed to evaporation and decomposition of some unreacted AESO, unreacted ME, or some low molecular weight portion in the crosslinked structure. The second stage from 330 °C to 500 °C is the fastest degradation stage, and this degradation stage corresponds to the degradation and char formation of the crosslinked polymer structure. The third stage (above 500 °C) corresponds to the gradual degradation of the char. The thermal stability is essentially the same before the second thermal degradation stage. The \( T_{10} \) values (the temperature corresponds to 10% weight loss) of this copolymer system ranges from 370 °C to 410 °C, and the \( T_{10} \) values decrease with an increase in the amount of AESO. The aromatic structure of ME makes ME more thermally stable than the AESO, thereby giving a lower \( T_{10} \) value when the ME content decreases. \( T_{50} \) (the temperature corresponds to 50% weight loss) and \( T_{\text{max}} \) (the maximum degradation temperature) also show the same trends as the \( T_{10} \) values, indicating that incorporating AESO into ME decreases the thermal stability at temperatures above 300 °C.

![TGA measurements for AESO/ME copolymers](image)

Fig. 11: TGA measurements for AESO/ME copolymers with different compositions at 20 °C/min heating rate under nitrogen atmosphere.

<table>
<thead>
<tr>
<th>Polymer composition</th>
<th>( T_{10} )</th>
<th>( T_{50} )</th>
<th>( T_{\text{max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AESO0–ME98</td>
<td>411</td>
<td>465</td>
<td>462</td>
</tr>
<tr>
<td>AESO10–ME88</td>
<td>387</td>
<td>456</td>
<td>458</td>
</tr>
<tr>
<td>AESO20–ME78</td>
<td>380</td>
<td>449</td>
<td>455</td>
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<tr>
<td>AESO30–ME68</td>
<td>380</td>
<td>446</td>
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<tr>
<td>AESO40–ME58</td>
<td>370</td>
<td>433</td>
<td>439</td>
</tr>
<tr>
<td>AESO98–ME0</td>
<td>368</td>
<td>422</td>
<td>421</td>
</tr>
</tbody>
</table>
3.4. Compression testing

The compressive modulus, ultimate compressive strength, compressive yield strength, and the maximum compressive strength for different copolymers are shown in Fig. 12, Fig. 13 and Fig. 14. The compressive modulus is a measure of the stiffness of the material, and it is obtained from calculating the slope of the linear region of the stress vs. strain curve. As expected, the compressive modulus increases with decreasing AESO content because the incorporation of flexible triglyceride molecules will decrease the overall stiffness of the obtained copolymers. The ME polymer possesses a compressive modulus of 2.3 GPa, while the AESO40−ME58 copolymer has a compressive modulus of 1.4 GPa. The ultimate compressive strength also follows the same trend as the compressive modulus with variation of AESO content. This is expected because the strength of the copolymers decreases with a decrease in aromatic content. The ultimate compressive strength of the copolymers ranges from 93 MPa for the ME polymer to 70 MPa for the AESO40–ME58 copolymer. The ultimate compressive strength of this bio-based copolymer system exceeds the strength of most petroleum-based thermoplastics, and it is comparable to commercially available thermosets such as epoxies and polyesters. The yield strength also follows the same trend as the ultimate strength. On the other hand, the maximum compressive strain increases with increasing AESO content, indicating that the triglyceride chains make the copolymer more flexible.

![Graph showing compressive modulus for AESO/ME copolymers with different compositions.](image-url)

Fig. 12: Compressive modulus for AESO/ME copolymers with different compositions.
Fig. 13: Maximum compressive strength and compressive yield strength of AESO/ME copolymers with different compositions.

Fig. 14: Maximum compressive strain for AESO/ME copolymers with different compositions.

4. Conclusion

High bio-content thermosetting polymers were prepared using free radical copolymerization of methacrylated eugenol and acrylated epoxidized soybean oil. To the best of our knowledge, the current manuscript presents the first study of biorenewable thermoset based on acrylated epoxidized soybean oil and methacrylated eugenol. The systematic variation in the thermomechanical properties of the thermosets with changing chemical composition is a strong evidence for the successful chemical reaction between the two monomers (see Fig. 9, Fig. 10, Fig. 11, Fig. 12, Fig. 13 and Fig. 14). Furthermore, the reaction has a high degree of conversion with little weight loss. Therefore there is no doubt about the successful bonding between the two monomers and the reaction scheme in Fig. 6 are true.

Both ME and AESO are derived from bio-based resources. These two starting materials are neither volatile nor toxic. The bio-based carbon content, which is calculated by dividing the
amount of bio-based carbon in the material or product as a weight percentage of the total organic carbon in the material or product [55], was calculated to be ranged from 70.1% (for the AESO0–ME98 sample) to 74.9% (for the AESO40–ME58 sample). All of the obtained thermosets are homogeneous and rigid. These bio-based thermosets showed excellent mechanical properties (especially the modulus and strength), a systematic variation in the glass transition temperature with different compositions, and excellent thermal stability. In addition, this resin system possesses low viscosity and fast curing speed, making it suitable for many potential applications, particularly in the pultrusion process. So far, there are very few studies that focus on developing vegetable oil-based resin for the pultrusion process. This resin system can be a green alternative to petroleum-based thermosets for various applications.

Acknowledgement

This project was sponsor by the Consortium for Plant Biotechnology Research (CPBR) under the CPBR Agreement EPA83438801-337.

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