

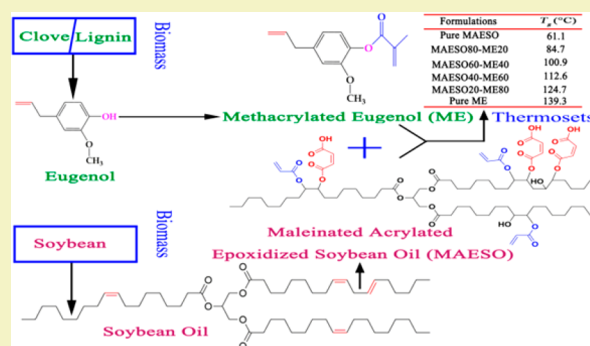
Synthesis and Characterization of Methacrylated Eugenol as a Sustainable Reactive Diluent for a Maleinated Acrylated Epoxidized Soybean Oil Resin

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S Supporting Information

ABSTRACT: This work presents a solvent-free, facile synthesis of a renewable, aromatic monomer, methacrylated eugenol (ME), from eugenol and methacrylic anhydride by the Steglich esterification reaction. The resulting ME was subsequently used as a reactive diluent to copolymerize with a commercial maleinated acrylated epoxidized soybean oil (MAESO) resin to form renewable MAESO–ME thermosets. The volatility of ME was examined, along with an analysis of viscosity and curing behavior of the MAESO–ME mixtures. The curing kinetics, thermo-mechanical properties, and thermal stabilities of the fully cured MAESO–ME thermosets with different ME proportions (0%, 20%, 40%, 60%, 80%, and 100%) were systematically investigated. The results indicated that ME monomer exhibited extremely low volatility (less than 3% mass loss after being held isothermally at 30 °C for 10 h), high biobased carbon content (BBC, 71.4%), and low viscosity (17.6 cP at 25 °C). Upon use with MAESO resin, viscosity of the system was considerably decreased. Compared with per equivalent of MAESO, ME-diluted systems exhibited higher reactivity, which resulted in improved curing extent and higher cross-link density of the MAESO–ME systems. The glass transition temperature (T_g) of MAESO–ME thermosets greatly improved from 61.1 to 139.3 °C with increasing ME loading from 0% to 100%. Overall, the developed biobased ME monomer is shown to be an effective, sustainable reactive diluent to replace styrene for commercially available MAESO resin.

KEYWORDS: Eugenol, Methacrylated eugenol (ME), Reactive diluent, Maleinated acrylated epoxidized soybean oil (MAESO), Thermosetting resins, Sustainable, Styrene replacement



INTRODUCTION

Petroleum-based thermosetting resins, such as unsaturated polyester resins and vinyl ester resins, are widely used in a variety of commercial applications because of their relatively high moduli, mechanical strengths, and T_g , as well as their light weight and low cost.^{1,2} These resins typically contain approximately 35–50% petroleum-based reactive diluents. However, because of increasing environmental concerns and the depletion of nonrenewable petroleum resources, there is an urgent need to develop biobased polymeric materials from renewable natural resources, such as proteins, carbohydrates, lignin, and vegetable oils, to name a few.^{3–5} Among them, vegetable oils (soybean, corn, tung, linseed, cottonseed, palm, peanut, rapeseed, sunflower, safflower, coconut, castor, etc.) are promising building blocks for producing biobased thermosets because of their worldwide availability, sustainability, competitive cost, and low toxicity. Soybean oil is one of the most widely investigated vegetable oils.^{6,7} Soybean oil contains more than 99% triglycerides formed by one glycerol attached to three

fatty acids, and consists of various fatty acids (23.4% oleic acid, 53.3% linoleic acid, 7.8% linolenic acid, 11% palmitic acid, and 4% stearic acid) with 0–3 carbon–carbon double bonds. However, most of the native carbon–carbon double bonds in soybean oil are nonconjugated, and thus are not sufficiently reactive to be polymerized directly.⁸ A considerable range of approaches have been employed to develop soybean-oil-based thermosetting resins, such as epoxidized soybean oil (ESO), acrylated epoxidized soybean oil (AESO), and maleinated acrylated epoxidized soybean oil (MAESO).

Among these, MAESO is one of the most promising biobased thermosetting resins to replace petroleum-based unsaturated polyester resins or vinyl ester resins. The conversion of soybean oil to MAESO consists of three reaction steps: (a) organic and inorganic peroxides together with a metal

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catalyst are used with soybean oil to convert the C=C double bonds in the fatty acid chains into oxirane rings and obtain ESO; (b) ESO is further reacted with acrylic acid to prepare AESO; (c) hydroxyl groups and residual unreacted epoxy rings in the AESO are reacted with maleic anhydride to attach maleic functionalities and form MAESO.^{9–11} However, similar to unsaturated polyester and vinyl ester resins, MAESO resin has an extremely high viscosity at room temperature and requires more than 30% reactive diluent to reduce the viscosity of the system and to copolymerize with the base resin to form a cross-linked network. Traditionally styrene has been the most widely used reactive diluent due to its low cost, low viscosity, aromatic structure, and good thermo-mechanical properties. However, new emission standards for composite manufacturing by the Environmental Protection Agency specifically target styrene as a regulated hazardous air pollutant (HAP), volatile organic compound (VOC), as well as reasonably anticipated human carcinogen.¹² Moreover, styrene is also derived from non-renewable petrochemical feedstocks.

Therefore, developing a sustainable reactive diluent with low toxicity and low volatility is receiving both industrial and academic attention. Various positive options have been reported to replace styrene. Several renewable methacrylated fatty acids, such as methacrylated lauric acid, methacrylated hexanoic, and methacrylated octanoic acid, have been evaluated as styrene replacements to copolymerize with vegetable-oil-based polymer resins.^{13–16} These methacrylated fatty acids had low viscosity and low volatility, but they showed relatively low mechanical strength, moduli, and T_g values due to the flexible, long aliphatic chains and limited reactive sites of methacrylated fatty acids. It is known that the presence of rigid moieties, such as benzene, furan, and rosin rings, in the polymeric chain contributes to an increase of the stiffness of the MAESO resins.

Sustainable resources with rigid structures, such as isosorbide (derived from starch with a rigid bicycle ring structure),^{17,18} rosin (mainly derived from pine trees),¹⁹ and cardanol (byproduct of cashew nut processing),^{20,21} have been modified to be used as reactive diluents to copolymerize with vinyl ester resin, AESO, and MAESO to formulate thermosetting resins. However, it is difficult for all of these monomers to fully replace styrene because of their complex synthesis process, high viscosity, and limited mechanical property improvement. Moreover, lignin-derived monomers with a similar structure to styrene, such as vanillin, guaiacol, eugenol, catechol, and cresols, have been reported to generate several aromatic biobased methacrylates and have served as reactive diluents.²²

Among them, vanillin can be mass-produced in industry, but methacrylated vanillin is solid at room temperature, increasing the processing complexity.²³ The availability of guaiacol, catechol, and cresol sources is not industrial mass-produced.

Eugenol is an aromatic compound derived from the essential oils of clove, nutmeg, cinnamon, basil, and bay leaf; the depolymerization or pyrolysis of lignin; or synthesis by allylation of guaiacol with allyl chloride in laboratory scale and industrial scale.²⁴ Eugenol has a relatively low cost,²⁵ making it a promising building block to synthesize biopolymer materials. The cost of eugenol has great potential to decrease with the mass-production of eugenol from lignin at industrial scale.²⁶ Eugenol is widely used in drugs, foods, perfumes, and cosmetics. However, eugenol alone is unlikely to bulk-polymerize by free-radical polymerization. This is not only because the allylic double bond of eugenol is very unreactive, but also because the phenolic hydroxyl group of eugenol would

scavenge free radicals and terminate free-radical reactions. Therefore, a variety of polymers have been prepared using chemically modified eugenol-based monomers, including thiol–ene photopolymerizations of allyl-etherified eugenol derivatives,²⁷ thermosetting bismaleimide,²⁸ methacrylated eugenol (ME),^{29–31} eugenol-based benzoxazine,^{32,33} polyesters,³⁴ and cyanate esters.³⁵ More recently, methacrylic derivatives of eugenol have been used as components of dental composites, bone cements,²⁹ and oil-absorbent microspheres.³¹ Converting the phenolic hydroxyl group of eugenol into a methacrylate group allows ME to be easily polymerized since both the methacrylic double bonds and the less reactive allylic double bonds can participate in the free-radical polymerization.

In this work, a rigid and renewable monomer, ME, was synthesized by a solvent-free reaction using eugenol and methacrylic anhydride (Figure 1), and the methacrylic

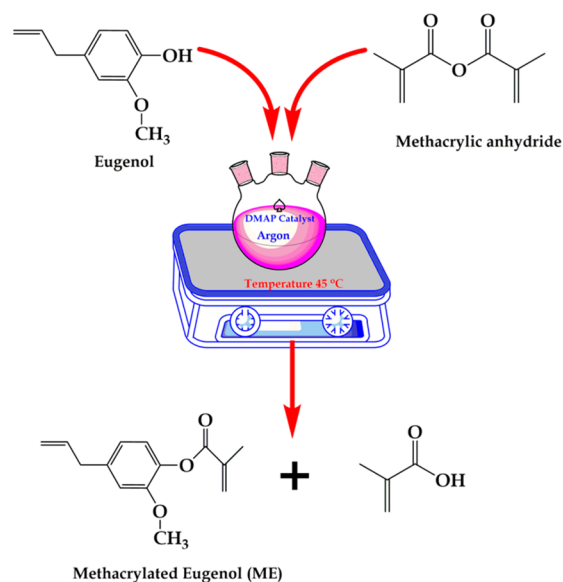


Figure 1. Schematic of the reaction between eugenol and methacrylic anhydride.

anhydride has great potential to be obtained from renewable resources.³⁶ ME was used to copolymerize with MAESO at different proportions to formulate high-performance thermosets. The volatility and viscosity of ME were analyzed. The curing behavior, curing extent, thermal stability, and thermo-mechanical properties of the fully cured MAESO–ME thermosets were also investigated.

EXPERIMENTAL SECTION

Materials. Eugenol (98%), styrene (99%, stabilized with 4-*tert*-butylcatechol), methacrylic anhydride (94%, inhibited with 2000 ppm Topanol A), 4-dimethylaminopyridine (DMAP), and Luperox P (*tert*-butyl peroxybenzoate) were provided by Sigma-Aldrich. Dichloromethane (99.6%, stabilized with amylene), sodium bicarbonate, sodium hydroxide, and anhydrous magnesium sulfate were provided by Fisher Scientific. Hydrochloric acid (36.5–38%) was provided by EMD Millipore. Dimethyl sulfoxide (DMSO- d_6) was purchased from Cambridge Isotope Laboratories, Inc. MAESO (yellow to amber viscous liquid, 1.02 g/cm³ at 25 °C, with approximately 15% maleic anhydride in MAESO) was supplied by Dixie Chemical Company, Inc. All chemicals were used as received without further purification.

Synthesis of ME. In a 100 mL round-bottom flask, 10 g (0.0609 mol) of eugenol and 0.157 g (0.0013 mol, 2% mole equivalents based on methacrylic anhydride) of DMAP were added, and then, the flask

was sealed and purged with argon gas for 2 h to remove moisture and oxygen. After that, 10.33 g (0.0670 mol, 1.1 mole equivalents based on eugenol) of methacrylic anhydride was added. The reaction mixture was slowly heated to 45 °C while being simultaneously stirred vigorously for a minimum of 24 h. The reaction solution was then diluted with dichloromethane and washed with saturated sodium bicarbonate aqueous solution repeatedly to remove the traces of unreacted methacrylic anhydride and methacrylic acid until CO₂ was no longer released. The organic layer was sequentially washed with 1.0 M NaOH aqueous solution, 0.5 M NaOH aqueous solution, 1.0 M HCl aqueous solution, and water. ME was obtained after drying over MgSO₄, filtering, concentrating under reduced pressure, and drying in a vacuum oven at 60 °C overnight. The final product is a pale yellow oil.

Formulation and Curing of MAESO–ME Thermosets.

MAESO was first heated to 70 °C for 15 min to decrease the viscosity and facilitate the processability, and then, it was blended with different weight ratios (0%, 20%, 40%, 60%, 80%, and 100%) of ME. Then, *tert*-butyl peroxybenzoate (1.5 wt % total resin mass) was added as initiator. The mixed resin system was then poured into an aluminum alloy mold and degassed in a vacuum oven until there were no visible bubbles. The mixed resin was polymerized in an argon atmosphere, curing at 90 °C for 1 h, 130 °C for 5 h, and subsequently 180 °C for 2 h. The prepared thermosets were labeled as pure MAESO, MAESO80–ME20, MAESO60–ME40, MAESO40–ME60, MAESO20–ME80, and pure ME.

Resin Characterization. Proton nuclear magnetic resonance (¹H NMR) spectra were obtained on a Varian VXR-300 NMR instrument at room temperature in the presence of DMSO-*d*₆ as the solvent.

The volatility behavior of ME and styrene was carried out on a thermogravimetric analyzer (Discovery TGA, TA Instruments). Samples (30–35 mg) were held isothermally at 30 °C for 9 h under nitrogen (flow rate: 25 mL/min).

The viscosity of the MAESO–ME systems was measured with a TA Instruments ARES-G2 rheometer. The viscosity of ME was tested using cone plate geometry (since ME had very low viscosity). For pure MAESO resin and MAESO–ME mixed resins (with ME loading of 0%, 20%, 40%, 60%, and 80%), the viscosity was evaluated using parallel plate geometry (with 25 mm diameter). All of the tests were conducted with shear rates ranging from 1 to 100 s^{−1} at 25, 30, 40, 50, 60, and 70 °C, respectively.

The polymerization behavior of ME–MAESO resins in the presence of *tert*-butyl peroxybenzoate was studied using a differential scanning calorimeter (Discovery DSC, TA Instruments) in a dynamic scan mode under nitrogen atmosphere from 30 to 250 °C at a heating rate of 10 °C/min with hermetically sealed pans. The total reaction heat (ΔH) of the curing reaction was obtained from the integrated area of the exothermic peak. For pure ME and MAESO resins, the cure kinetics was performed from 30 to 250 °C in a dynamic mode at multiple heating rates of 5, 10, 15, and 20 °C/min.

Soxhlet extraction results were used to study the curing extent of MAESO–ME thermosets. Precisely weighed samples (approximately 1.000 g, *m*₁) were extracted with dichloromethane for 24 h using a Soxhlet extractor, and finally the remaining insoluble fraction was dried at 60 °C for 24 h and weighted (*m*₂). The insoluble weight percentage was calculated as 100% × *m*₂/*m*₁.

Thermo-mechanical properties were measured on a strain-controlled rheometer (ARES-G2 rheometer) using dynamic mechanical analysis (DMA) in the torsion mode. All samples (rectangular, dimension of 30 mm length × 12 mm width × 3 mm thickness) were tested at a heating rate of 3 °C/min from −100 to 180 °C with a constant frequency of 1 Hz at a strain of 0.065%.

Thermogravimetric analysis (TGA) was performed on a TA Instruments Discovery TGA. All samples were tested from room temperature to 800 °C at a scanning rate of 10 °C/min with a nitrogen purge of 25 mL/min.

RESULTS AND DISCUSSION

ME was synthesized by means of the Steglich esterification reaction of eugenol and methacrylic anhydride with DMAP as the catalyst. The chemical structure of the synthesized ME is confirmed by the ¹H NMR spectrum (Figure 2), and the

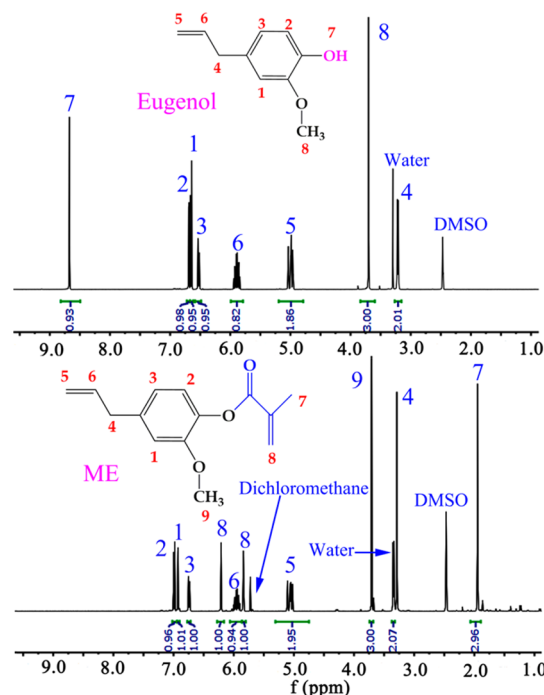


Figure 2. ¹H NMR spectra of ME and eugenol.

average yield was 81.8% after numerous aqueous extractions. The resonances at 8.65–8.70 ppm were assigned to the phenolic hydroxyl group (Ar–OH) of eugenol. After the Steglich esterification reaction, the phenolic hydroxyl group resonances disappeared in the resulting monomer, and new peaks located in the area ranging from 5.81 to 5.88 ppm, 6.16 to 6.24 ppm, and 1.92 to 1.97 ppm were observed, corresponding to the vinyl protons (C=CH₂) and methyl protons (CH₃) of the methacrylate groups, which confirms the full conversion of the phenolic hydroxyl group to methacrylate groups, and demonstrates the successful synthesis of ME.

The volatility is one of the most important parameters for developing a sustainable reactive diluent monomer for MAESO resins. As shown in Figure 3, styrene emitted extremely quickly

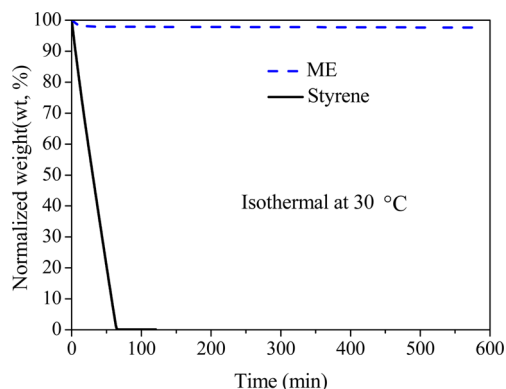


Figure 3. Evaporation behavior of ME and styrene.

and completely evaporated after isothermal exposure at 30 °C for 65 min, while ME monomer exhibited extremely low volatility with less than 3% mass loss after isothermal exposure for 10 h. This indicated that ME is a promising low VOC/HAP reactive diluent monomer.

The sustainability of the ME monomer and MAESO resin was quantified using the biobased carbon content (BBC). The BBC value was calculated by the amount of biobased carbon divided by the total amount of carbon in the polymer. Therefore, the BBC of styrene is 0 while the BBC of ME and MAESO is 71.4% and 73.1%, respectively, which greatly promotes the sustainability of the polymer material.

For an ideal reactive diluent monomer, low viscosity is necessary to dilute MAESO resin to an acceptable viscosity range to sufficiently wet the fiber for a good interfacial adhesion. The viscosity data of ME and the mixed MAESO–ME resin is plotted in Figure 4a. ME has a low viscosity of 17.6

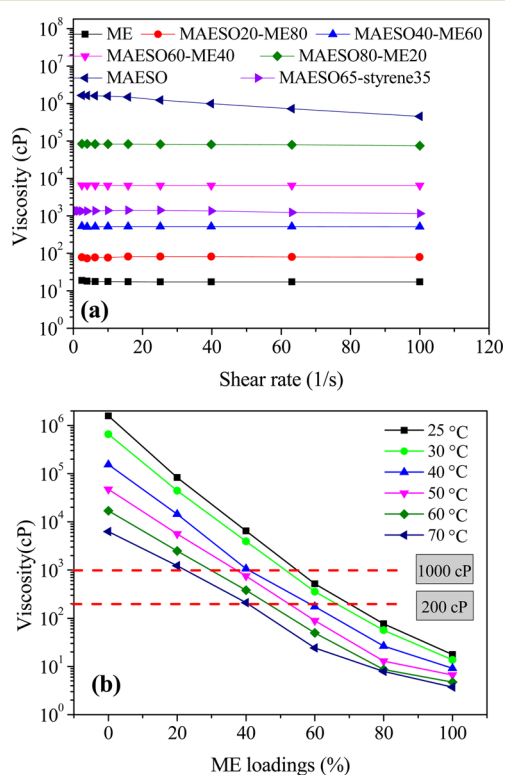


Figure 4. (a) Viscosity as a function of shear rate for the MAESO–ME resin system and MAESO65–styrene35 resin at 25 °C. (b) Viscosity as a function of ME loadings for the MAESO–ME resin system at 10 s^{−1} shear rate.

cP at 25 °C because of its low molecular weight, while MAESO resin has an extremely high viscosity up to 1.6×10^6 cP at 25

°C and exhibited some degree of shear thinning behavior due to its higher molecular weight, longer aliphatic chains, as well as presence of abundant hydrogen bonds between hydroxyl groups and ester groups. The viscosity of the MAESO–ME resin system has been found to considerably decrease with the increasing of ME concentrations, which was due to the fact that the viscosity of ME is more than 4 orders of magnitude lower than that of MAESO. The introduction of ME not only decreased the entanglement of MAESO chains, but also acted as plasticizer to break the hydrogen bonds within MAESO resin. In addition, over an order of magnitude reduction in viscosity after adding every 20% of ME in the MAESO–ME mixture system indicated good miscibility between MAESO and ME.

The preferred viscosity range for liquid molding resins is generally considered to be 200–1000 cP at room temperature in order to provide efficient flow to facilitate good processability. As shown in Figure 4b, the viscosity of MAESO–ME systems decreased to an acceptable range with increasing temperature or increasing ME content. The MAESO–ME systems possessed a viscosity of 1064.0 cP with an ME loading of 40% at 40 °C, and with further increasing ME loading to 60%, the viscosity of the MAESO–ME system decreased to 516.2 cP at 25 °C. It is worth mentioning that the MAESO65–styrene35 system had a viscosity of 1395.2 cP at 25 °C. Therefore, the viscosity of the MAESO–ME resin system can be tailored to meet the manufacturing process requirements of composites for liquid molding techniques.

The curing behavior of the MAESO–ME systems was monitored using the nonisothermal DSC scans. The peak temperature and the total heat of cure reaction (ΔH) are listed in Table 1.

In general, *tert*-butyl peroxybenzoate possesses a sensitive peroxide structure (O–O), which decomposes at high temperature. *tert*-Butyl peroxybenzoate begins to decompose at temperatures ranging from 105 to 205 °C, and reaches a maximum at 165 °C at a heating rate of 10 °C/min.³⁷ Therefore, all of the MAESO–ME resin system started curing at approximately 125 °C, and ended at 250 °C with the maximum from 158 to 168 °C (Figure 5).

It is notable that pure MAESO resin with the thermal initiator showed two distinct exothermic peaks related to the free-radical polymerization. This was because the C=C double bonds of MAESO were not completely polymerized from 135 to 185 °C (the first exothermic peak), since it is easy for the long aliphatic molecular chains of the MAESO monomer to form complex entanglement, trapping some unreacted C=C double bonds. In addition, the thermal initiator was not fully decomposed to release radicals at such conditions. With further increasing the temperature to 250 °C, more free radicals were generated, and the viscosity of MAESO was further decreased.

Table 1. Peak Temperature and Enthalpy from DSC Curing Curves

resin	peak 1 temperature (°C)	peak 1 enthalpy (ΔH , J/g)	peak 2 temperature (°C)	peak 2 enthalpy (ΔH , J/g)
MAESO	168.4	135.5	223.8	19.7
MAESO80–ME20	167.1	190.4	216.5	16.5
MAESO60–ME40	164.1	273.9	212.2	10.9
MAESO40–ME60	163.5	301.1	214.6	6.7
MAESO20–ME80	158.2	351.0	NA ^a	1.9
ME	159.3	388.8	NA	0

^aNA, not applicable.

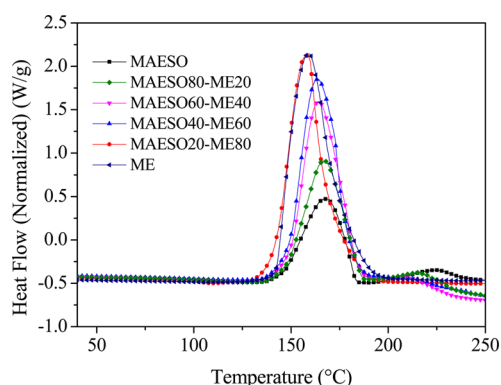


Figure 5. DSC curing curves of the MAESO–ME resin system.

This provided more spaces for the movement of radicals, monomers, and polymer chains, and finally facilitated the polymerization of MAESO resin, resulting in a second exothermic peak. In contrast, pure ME resin just had one exothermic peak.

With increasing ME loading, the exothermic peaks moved to lower temperatures with a higher intensity, which means that ME possessed higher reactivity than the pure MAESO resin. This was also confirmed by our cure kinetics analysis using both Kissinger's and Ozawa's theory.¹⁷ The activation energy of pure ME resin and pure MAESO was determined to be 120.5 and 166.0 kJ/mol, respectively. (Figures S1 and S2, in the Supporting Information). From a functional group point of view, pure MAESO resin contains both maleates and acrylates C=C bonds that could undergo free-radical polymerization; ME also possesses two types of C=C double bonds: methacrylate groups and allylic groups. Although the reactivity of allylic groups (ME) is relatively lower than that of acrylated groups and maleate groups (MAESO), and they are usually reluctant to homopolymerize, they can copolymerize with other kinds of double bonds.³¹

Therefore, the free-radical-initiated reaction in the MAESO–ME system was highly complicated, which involved MAESO homopolymerization, ME homopolymerization, and MAESO–ME copolymerization. The low viscosity of ME significantly improved mobility of the MAESO–ME reaction system, thus accelerating the curing reaction. The MAESO–ME reaction system showed increased exothermal enthalpy with increasing ME loadings. This is due to the fact that enthalpy of reaction per gram of ME resin is 2.5 times higher than that of pure MAESO resin. In other words, ME had more unsaturated C=C double bonds per gram participating in the curing reaction in comparison to MAESO resin, leading to an increased cross-linking density.

As dichloromethane is a good solvent for uncured ME and MAESO resins, we used it to perform Soxhlet extraction experiments on the fully cured resins. After extraction for 24 h with boiling dichloromethane, the remaining insoluble fractions were considered to be incorporated into the insoluble cross-linked network structure. The results in Figure 6 showed that the MAESO–ME system exhibited a higher curing degree with the increasing of ME loading. The insoluble fraction of the material increased from 91.0% to 95.6% as the ME loading was increased from 0% to 100%. This behavior is attributed to more ME monomer incorporation into the cross-linking network via free-radical polymerization increasing the cross-linking density, which is in accordance with the results from the DSC curing

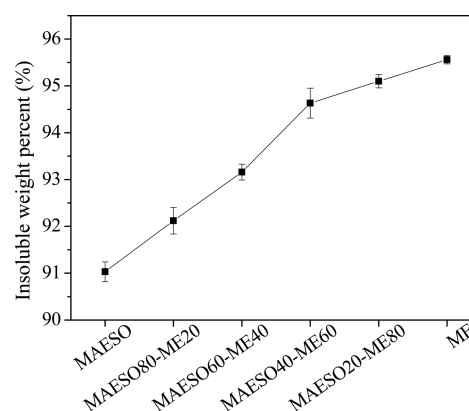


Figure 6. Insoluble weight percent for the MAESO–ME thermoset system.

experiments (Table 1). In addition, a detailed FT-IR test was used to further confirm whether there are some residual C=C bonds in the cured MAESO–ME samples. After the cure, there were only a few C=C bonds present in the pure MAESO resin because the maleate group did not readily homopolymerize. In contrast, there was almost no trace of C=C bonds present for pure ME resin and the MAESO–ME resin system (Figure S3 in the Supporting Information), which is in accordance with the Soxhlet extraction results. With more reactive ME monomer in the MAESO–ME resin system, nearly all the C=C bonds participated in the polymerization, providing further evidence for the formation of a highly cross-linked network of the MAESO–ME thermoset system.

The storage moduli and damping factor ($\tan \delta$) of the MAESO–ME thermoset system are presented in Figure 7a,b, respectively. Pure MAESO resin exhibited the lowest storage

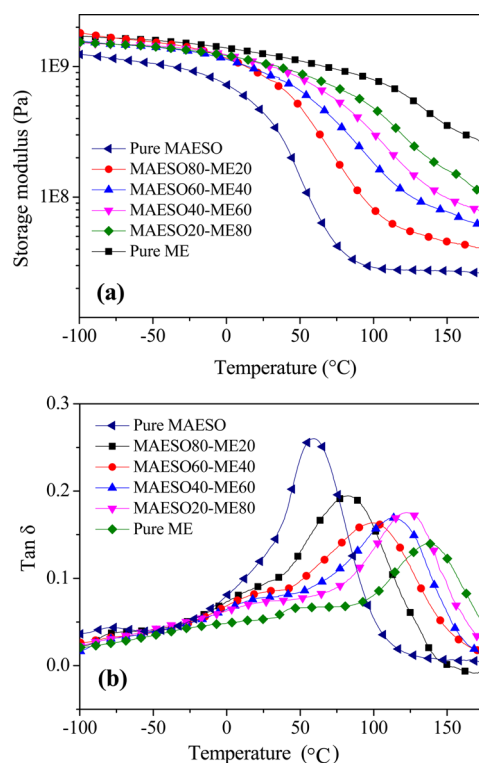


Figure 7. DMA curves of (a) storage moduli–temperature and (b) $\tan \delta$ –temperature for cured MAESO–ME thermosets.

moduli (G') of 441 MPa at 25 °C among all the MAESO–ME thermosets. The storage moduli of MAESO–ME thermosets increased with increasing rigid, aromatic ME segment, which is due to the improved cross-linking density of the MAESO–ME thermoset system, as confirmed by the improved insoluble weight percent in the Soxhlet extraction results (Figure 6) and increased curing enthalpy results (Table 1).

Pure MAESO resin showed a broad transition peak from the glassy state to the rubbery state. With the introduction of ME, the peak became even broader, possibly because of the increased heterogeneity caused by the combination of MAESO homopolymerization, ME homopolymerization, and MAESO–ME copolymerization. In addition, the height of the $\tan \delta$ peaks of MAESO–ME systems is lower than that of pure MAESO resin. Generally, a higher $\tan \delta$ peak intensity in the DMA curve indicates a more viscous behavior in a polymer network, while a lower peak intensity reveals a more elastic one. Since ME has higher reactivity and more unsaturated $C=C$ double bonds than per equivalent of MAESO, the MAESO–ME thermosets tend to be a more elastic network with more ME participating in the cross-linking reaction, leading to increased cross-linking density.

The peak of $\tan \delta$ was used as the indicator of T_g for the MAESO–ME resin systems. Pure MAESO resin exhibited the lowest T_g at 61.1 °C, while pure ME resin exhibited the highest T_g of 139.3 °C (Table 2). The T_g increased with increasing ME

Table 2. Thermo-Mechanical Properties of MAESO–ME Thermosets

formulation	T_g (°C)	storage moduli G' (25 °C, MPa)
pure MAESO	61.1	441
MAESO80–ME20	84.7	848
MAESO60–ME40	100.9	901
MAESO40–ME60	112.6	1037
MAESO20–ME80	124.7	1060
ME	139.3	1104

loadings, and reached 100.9 °C with 40% of the ME loading, which is comparable to that of MAESO–styrene systems with 33% styrene loading ($T_g = 106.0$ °C).¹⁶ This was attributed to the aromatic structure in ME, which imparts structural rigidity and limits the free volume of the MAESO–ME system network. Moreover, the increased cross-linking density with more ME loadings also contributed to a tighter cross-linked network and increased T_g .

TGA was subsequently performed to evaluate the thermal degradation behavior of the MAESO–ME thermosets (Figure 8). All of the thermosets exhibited three stages of degradation: The first degradation (150–300 °C) corresponded to the evaporation and decomposition of some low-molecular-weight portions in the cross-linked structure, such as unreacted MAESO, unreacted ME, and topanol A. It is noteworthy that pure MAESO resin degraded faster than pure ME resin in the first degradation, indicating that ME had a higher curing extent than MAESO, which is in accordance with the Soxhlet extraction results (Figure 6) and FT-IR results (Figure S3 in the Supporting Information). The second degradation (300–530 °C) was the fastest degradation stage, which was attributed to the random scission of the MAESO–ME cross-linked network structure. The decomposition temperature of MAESO–ME resin in the second stage was increased with increasing ME contents. This was attributed to the increased

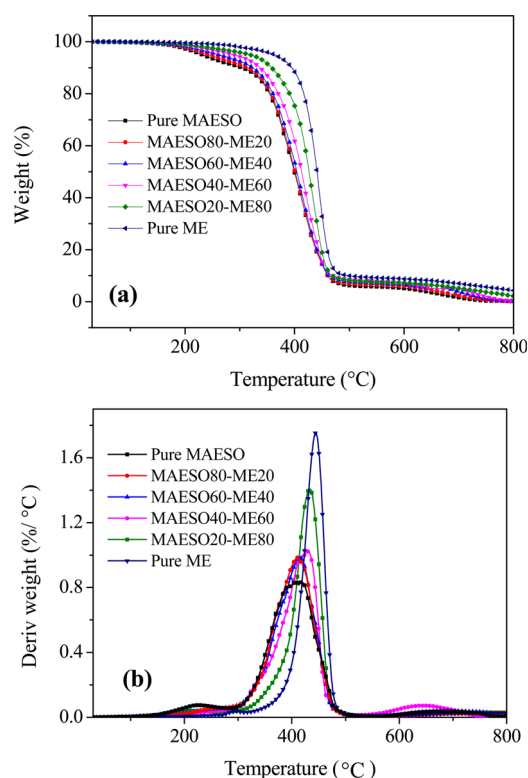


Figure 8. (a) TGA curves and (b) their derivative curves for cured MAESO–ME thermosets.

cross-linking density and inherent aromatic structure in eugenol. The third degradation (above 530 °C) was caused by the gradual degradation of the char yield. The char yield increases with the increase in ME loading, as more benzene rings in ME usually result in a higher char yield.

CONCLUSION

Eugenol was successfully methacrylated to form ME monomer using the Steglich esterification reaction. The synthesized ME monomer was then used as a sustainable reactive diluent in MAESO resin at various loadings to prepare renewable thermosetting resins with tailored properties. ME showed advantages of low viscosity, low toxicity, low VOC/HAP emissions, sustainability, and availability for free-radical polymerization. The introduction of aromatic ME into MAESO resin resulted in good processability, as well as improved T_g and storage moduli. Overall, with different ME loadings, the MAESO–ME thermosets exhibited tailored properties for applications in many diverse environmentally friendly materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b01673.

DSC results, peak temperatures and calculated activation energies of ME and MAESO based on Kissinger's theory, and FT-IR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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