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Soybean-Oil-Based Thermosetting Resins with Methacrylated Vanillyl Alcohol as Bio-Based, Low-Viscosity Comonomer

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A novel, bio-based, aromatic monomer (methacrylated vanillyl alcohol, MVA) is synthesized using vanillyl alcohol and methacrylic anhydride in the absence of solvents. The resulting MVA is used as a sustainable comonomer to replace styrene in a maleinated acrylated epoxidized soybean-oil (MAESO) resin to produce novel thermosets via free radical polymerization. The influence of MVA loading on the viscosity, gelation time, curing extent, thermomechanical properties, and tensile properties of the MAESO–MVA thermoset is investigated. The synthesized MVA exhibits very low volatility, which is beneficial for the development of construction material with low or zero emission. The viscosity of the MAESO–MVA system can be tailored to meet the commercial requirements. Increasing the MVA content accelerates the crosslinking reaction rate and improves thermal and mechanical properties of the MAESO–MVA system. The glass transition temperature increases with increasing MVA content. Soxhlet extraction experiments show that more than 90% of the components are incorporated into the crosslinking network. Overall, the developed MVA monomer shows promising properties to be used as an effective, green comonomer to replace styrene.

1. Introduction

Petroleum-based thermosetting polymers, such as unsaturated polyester resins (UPR) and vinyl ester resins, have been widely used in aerospace, automotive, marine, and structural applications because of their relatively high mechanical properties, such as modulus and strength, glass transition temperatures (T_g), good processability, light weight, and low cost. However, increasing environmental concerns, progressive depletion of nonsustainable fossil fuel reserves, and future crude oil prices have stimulated both academia and industry to develop bio-based materials from renewable and sustainable resources.[1–5]

Renewable natural resources, such as lignin, starch, protein, and plant oil, offer advantages in terms of environmental friendliness and resource abundance.[6] Among these candidates, soybean-oil is one of the most promising starting materials owing to its sustainability, low toxicity, availability, and relative low cost. Soybean-oil is composed of more than 99% triglycerides formed from glycerol and three fatty acids. These triglycerides contain mainly nonconjugated carbon–carbon double bonds that are not sufficiently reactive to facilitate free radical polymerization. Therefore, various chemical modifications have been explored to improve their reactivity and produce soybean-oil-based thermosetting polymers with tunable properties.[7,8]

Epoxidation of soybean-oils and the following ring-opening of the oxirane rings is one of the most important pathways to synthesize triglyceride-based monomers, such as acrylated epoxidized soybean-oil (AESO).[9–11] The synthesis process is shown in **Figure 1**. First, the carbon–carbon double bonds in soybean-oil are epoxidized by a peroxy acid to form ESO, then acrylic acid is used to initiate the ring-opening reaction, incorporating the acrylated functional groups to produce AESO.[12–14] AESO contains both hydroxyl groups and residual unreacted epoxy rings, both of which can further react with maleic anhydride to introduce more double bonds, forming maleinated AESO (MAESO). The resulting MAESO-based thermosets exhibit improved properties compared to the corresponding AESO-based thermosets because of the increased number of reactive sites (more double bonds available). However, pure

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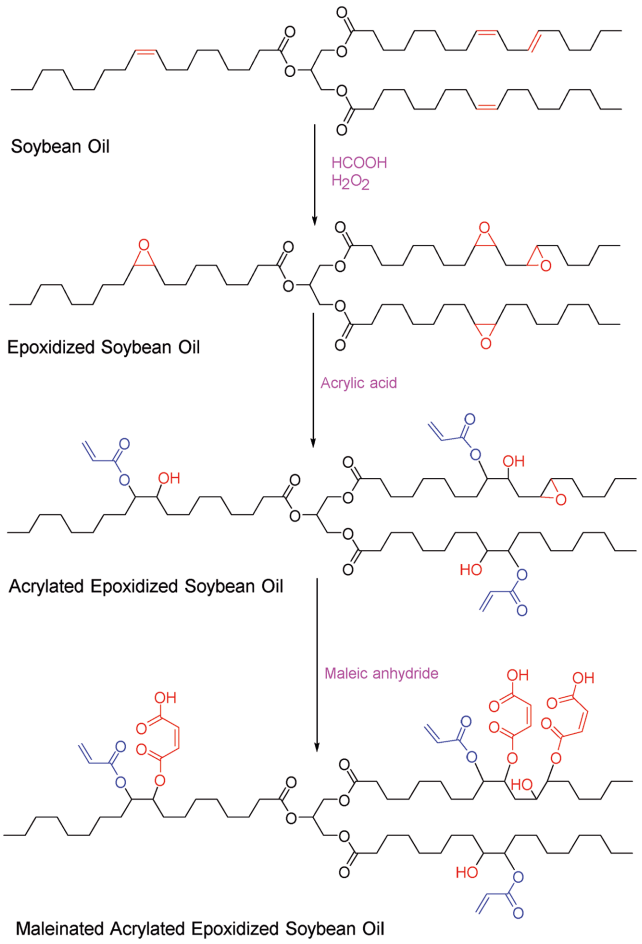

Figure 1. Schematic for the synthesis of MAESO.

MAESO resins exhibit extremely high viscosities at room temperature, which makes it difficult to use common processing technologies.[15,16] Therefore, MAESO resins typically require ≈33% of low-viscosity styrene as a comonomer prior to curing by free radical polymerization. The introduction of styrene not only imparts good processability by lowering resin viscosity, its rigid, aromatic structure also improves the overall polymer performance. However, styrene is considered as a hazardous air pollutant and a volatile organic compound (VOC). It is also classified as a potential human carcinogen, as well as being derived from nonrenewable petroleum resources. Therefore, the development of a low-viscosity, nonvolatile, renewable comonomer has become of great interest.

A series of bio-based methacrylated fatty acids, such as methacrylated lauric acid, methacrylated hexanoil, and methacrylated oatanoil acid,[1,13,15,17] have been reported and used as comonomers for vegetable-oil-based polymer resins. These methacrylated fatty acids offered the advantage of low viscosity and low volatility, but the resulting resins exhibited relatively low moduli, mechanical strength, and glass transition temperatures due to the flexible, long aliphatic chains, and limited reactive sites of the methacrylated fatty acids. The incorporation of the rigid aromatic structures, such as a benzene ring, a furan ring, and a rosin ring, is anticipated to impart improved structural rigidity and thermal stability of the polymer resins.

Isosorbide, derived from starch, with a highly rigid bicycle ring structure, has been used to synthesize methacrylated isosorbide to serve as comonomer of vinyl ester. The resulting resin exhibited excellent thermal and mechanical properties with a T_g greater than 240 °C and a main degradation temperature of ≈400 °C. However, the viscosity of methacrylated isosorbide (157 cP) was still much higher than that of St (0.7 cP). Therefore, the potential use of methacrylated isosorbide as a comonomer in MAESO was limited because the increased viscosity negatively affected the processability of MAESO resin and difficult to ensure good wetting of fibers.[18]

Moreover, lignin-derived monomers with similar structure to styrene have been reported to generate several aromatic bio-based methacrylates as comonomers, such as vanillin, guaiacol, eugenol, catechol, and cresols.[19] Among them, vanillin is the only bio-based aromatic chemical which has been produced on an industrial scale. It is mainly used as a flavoring, fragrance ingredient, and in pharmaceuticals.[20] Vanillin can be produced from petroleum-derived phenol (85%), by lignin depolymerization (15%), or by extraction of vanilla beans (0.2%). Borregaard Company, the second largest vanillin producer in the world, employs an ultrafiltration technology to produce vanillin from lignin,[21–24] making vanillin a promising bio-based building block monomer. Functionalization with methacrylate groups is among the most common strategies employed to polymerize vanillin using free radical polymerization.[25,26] In previous work, we synthesized methacrylated vanillin (MV) using an esterification reaction of vanillin with methacrylic anhydride. The synthesized MV was used to copolymerize with AESO at different ratios to develop novel biorenewable polymers. The resulting bio-based copolymers exhibited glass transition temperatures ranging from −4 to 103 °C, increasing with increasing MV content.[27,28] Stanzione III et al. used the same methods to prepare MV, followed by copolymerization with glycerol dimethacrylate to obtain a bio-based thermosetting polymer.[19] Moreover, Renbutsu et al. successfully prepared MV via a Steglich esterification of vanillin with methacrylic acid to create a coating for electroless plating of nonconductive materials.[29] However, pure MV is solid (with a melting point of ≈54 °C) at room temperature, and it is a monofunctional monomer (just one methacrylate group available for radical copolymerization). Other vanillin derivatives are also commercially available, including vanillyl alcohol and vanillic acid (**Figure 2**).[30,31]

In recent work, we developedmethacrylated vanillyl alcohol (MVA), a new monomer, using vanillyl alcohol and methacrylic anhydride (**Figure 3**). The reactant, methacrylic anhydride, has great potential to be obtained from renewable resources in the future.[32] Vanillyl alcohol is commercially prepared by reduction of vanillin, and it contains phenol and aliphatic hydroxyl reactive sites. Both hydroxyl groups can be converted to methacrylate groups for free radical polymerization.[28] To date, MVA has not been used as a bio-based comonomer to replace styrene in functionalized soybean-oil-based thermosetting resins.

This work highlights the possibility of using MVA as the comonomer for MAESO to produce bio-based thermosetting polymers with improved thermal and mechanical properties.

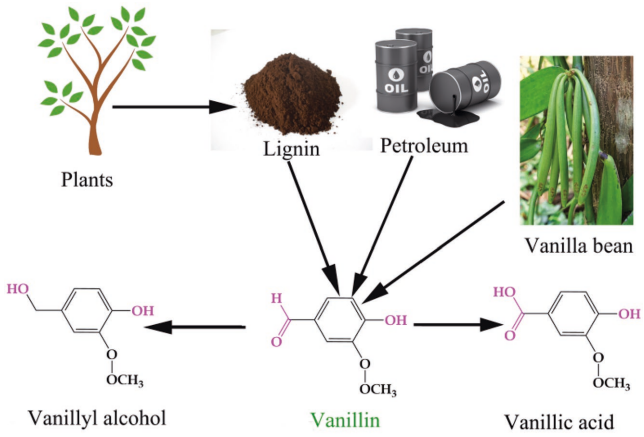

Figure 2. Chemical structures and preparation of vanillin derivatives.

The chemical structure of the synthesized MVA was characterized. The volatility of styrene and MVA was compared using isothermal thermogravimetric analysis (TGA). MVA was then incorporated into MAESO at various ratios. The viscosity, gelation time, curing extent, thermomechanical properties, and tensile properties of the MAESO–MVA systems were investigated.

2. Experimental Section

2.1. Materials

Vanillyl alcohol (4-hydroxy-3-methoxybenzyl alcohol, 98%), styrene (containing 4-*tert*-butylcatechol as stabilizer, 99%), methacrylic anhydride (containing 2000 ppm topanol A as inhibitor, 94%), 4-dimethylaminopyridine (DMAP), and *tert*-butyl peroxybenzoate were purchased from Sigma-Aldrich. Dichloromethane (stabilized with amylene, 99.6%), sodium bicarbonate ($NaHCO_3$), and anhydrous magnesium sulfate ($MgSO_4$) were purchased from Fisher Scientific. Dimethyl sulfoxide (DMSO-d_6) was purchased from Cambridge Isotope Laboratories, Inc. MAESO was supplied by Dixie Chemical Company, Inc. (1.02 g cm^{-3} at 25 °C, the level of maleic functionality was 1.45, and the acrylate group was 3.16). All materials were used as received without further purification.

2.2. Synthesis of MVA

Vanillyl alcohol (10.00 g) and 0.35 g of DMAP (2 mol% of methacrylic anhydride) were added to a 100 mL two-necked flask equipped with a magnetic stir bar, and then the flask was sealed and purged with argon gas for 2 h to remove moisture and oxygen from the reaction flask. Subsequently, 22.00 g methacrylic anhydride (the mole ratio of the hydroxyl group and the anhydride group was 1:1.1) was added. Then, the flask was placed in a silicone oil bath preheated at 45 °C for 24 h. The reaction mixture was cooled to room temperature and diluted with methylene chloride. Saturated sodium bicarbonate aqueous solution was added to the mixture until carbon dioxide no longer evolved to remove unreacted methacrylic anhydride and methacrylic acid byproducts. 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, dried with anhydrous $MgSO_4$, and filtered. Methylene chloride was removed by rotary evaporation, and the resulting liquid was dried in a vacuum oven at 50 °C for 12 h.

2.3. Preparation of MAESO–MVA Copolymers

MAESO was heated to 70 °C for 20 min to decrease the viscosity before different weight ratios (10–40 wt%) of MVA and free radical initiator *tert*-butyl peroxybenzoate (1.5 wt% of total amount of MVA and MAESO) were introduced. After vigorous stirring, the mixture was poured into an aluminum alloy mold and placed in a vacuum oven to remove gas bubbles. The mixture was then purged with nitrogen gas for 30 min and cured at 90 °C for 1 h, 130 °C for 5 h, and subsequently 170 °C for 2 h. The prepared thermosetting copolymers were labeled as pure MAESO, MAESO90-MVA10, MAESO80-MVA20, MAESO70-MVA30, and MAESO60-MVA40.

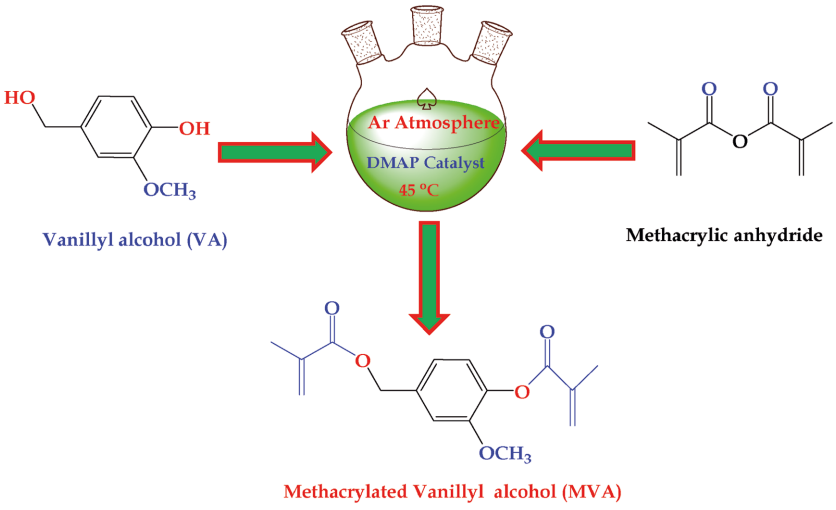

Figure 3. Synthesis of MVA.

2.4. Resin Characterization

The chemical structure of MVA was characterized by means of proton nuclear magnetic resonance (^{1}H NMR). The ^{1}H NMR spectra of MVA was obtained by means of a Varian VXR-300 NMR instrument at room temperature in the presence of DMSO-d_6 as the solvent.

Fourier transform infrared spectroscopy (FT-IR) were recorded using a NEXUS 670 FTIR spectrometer in attenuated total reflectance mode.

The volatility of both MVA and styrene was measured using a TA Instruments Discovery

thermogravimetric analyzer. ≈30 mg of sample was placed in a platinum pan and held isothermally at 30 °C for 9 h under a nitrogen purge of 25 mL min^{-1}.

The gelation test was performed on an ARES G2 rheometer using 25 mm diameter parallel plates with time sweeps at a constant shear frequency of 1.0 Hz at 120 °C. In addition, the viscosity of the MAESO–MVA mixtures was measured using a steady-state procedure with shear rates increasing from 10 to 100 s^{-1} at 25, 30, 40, 50, and 60 °C, respectively.

Soxhlet extraction tests were conducted to analyze the curing extent of the MAESO–MVA thermosets. Approximately 1.000 g of MAESO–MVA thermoset sample was weighted (m_1) and extracted with 250 mL of refluxing methylene chloride in a Soxhlet extractor for 24 h. The remaining insoluble fraction was dried under reduced pressure and weighed (m_2). The insoluble weight percentage was calculated as $100\% \times m_2/m_1$.

The dynamic mechanical properties of the MAESO–MVA thermosets were evaluated using a strain-controlled rheometer (ARES G2, TA Instruments) in a dynamic mechanical analysis (DMA) mode. The MAESO–MVA copolymer samples (MVA content ranging from 0 to 40 wt%) were tested with linear film tension geometry (rectangular samples, 0.25 mm thickness × 4.0 mm width) in a temperature range from −100 to 180 °C at a heating rate of 3 °C min^{-1}, a strain of 0.15%, and an oscillation frequency of 1 Hz. The crosslinking density was estimated using the rubber elasticity theory. Since the rubber modulus with a crosslinked network structure is proportional to the cross-link density (μ, mol m^{-3}) according to the following Equation (1).

$$E' = 3\mu RT \quad (1)$$

where E' is the rubbery modulus, R is the ideal gas constant (8.314 J $(mol\ K)^{-1}$), and T is the absolute temperature (K). The temperature and the rubbery modulus of the resins at T_g + 60 °C were used for the calculation in Equation (1) because the MAESO–MVA copolymers behaved as rubbers at such temperature.

Tensile tests were performed in accordance with ASTM D638 using a universal testing machine (INSTRON 4466) with a crosshead speed of 0.1 in. min^{-1}. Standard ASTM type V dog-bone samples were used for testing. At least three samples were tested for each sample.

The thermal stability of the MAESO–MVA thermosets was evaluated using a TA Instruments Discovery TGA. Approximately 10 mg of sample were heated from room temperature to 600 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere.

3. Results and Discussion

3.1. Monomer Properties

MVA was synthesized by direct Steglich esterification reaction between vanillyl alcohol and methacrylic anhydride using DMAP as the nucleophilic catalyst under mild conditions with a product yield of 78.4%. The chemical structure of MVA and vanillyl alcohol was characterized by ^{1}H NMR and is displayed in **Figure 4**. The peaks at 8.75 and 5.00 ppm belong to the phenolic hydroxyl group (Ar—OH) and aliphatic hydroxyl group ($-CH_2-OH$) of vanillyl alcohol, respectively. After reacting with methacrylic anhydride, these hydroxyl group peaks disappeared, and new multiple peaks emerged at 5.70–6.24 ppm and 1.90–1.97 ppm, which were attributed to methyl proton ($-CH_3$) and vinyl proton ($-C=CH_2$) of the methacrylate groups, confirming that both hydroxyl groups were converted to methacrylate groups and demonstrating that MVA had been successful synthesized.

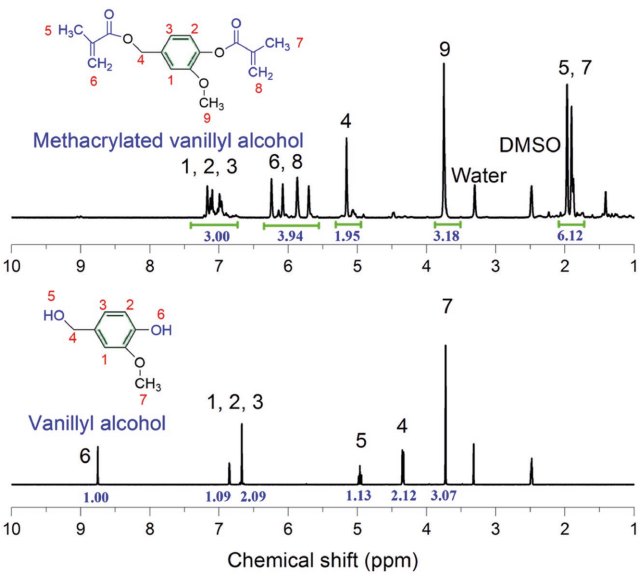

Figure 4. ^{1}H NMR of MVA and vanillyl alcohol.

The UPLC results indicated that the purity of the as-synthesized MVA (AS-MVA) was 81.2% (Figures S1 and S2, Supporting Information), we also obtained high-purity MVA (HP-MVA, 96.3%; Figure S3, Supporting Information) using silica gel column chromatography. It was found that MAESO65/HP-MVA35 copolymers exhibited a slightly higher T_g (76.6 °C; **Figure 5**) than MAESO65/AS-MVA35 copolymers (73.7 °C). Therefore, the purity of AS-MVA did not have great influence on the final properties of MAESO–MVA system. Considering the high cost of purification, we used AS-MVA as the low-viscosity comonomer of MAESO resin.

The volatility of a comonomer for MAESO resin is very important because of its potential negative environmental and health impacts. To determine the volatility of MVA and to compare it to that of styrene, the mass loss of MVA and styrene over time was measured using TGA (**Figure 6**). The results confirmed that styrene was highly volatile, as it completely evaporated (only 0.3% remained) in about 65 min at 30 °C, which was in agreement with Sylvain, Cousinet et al., who worked on replacing styrene with bio-based methacrylates for UPR.[33] In contrast, MVA exhibited significantly lower HAP/VOC emissions with a weight loss of less than 5% after isothermal for 9 h at 30 °C, confirming that the synthesized MVA is a promising comonomer monomer with low VOC.

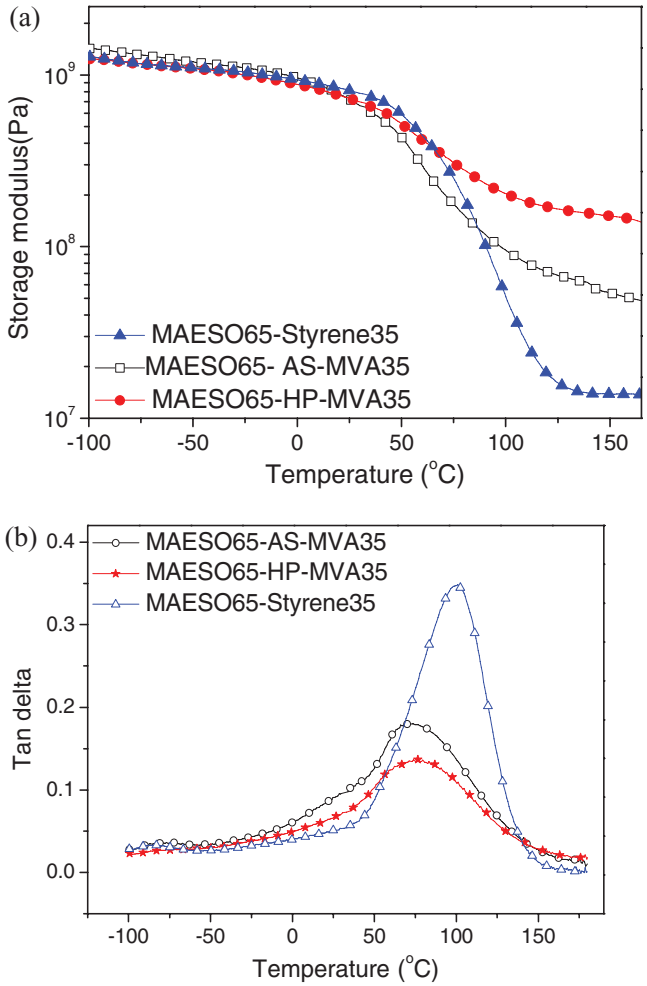

Figure 5. a) Storage modulus and b) tan δ as a function of temperature for MAESO with 35% of HP-MVA, AS-MVA, and styrene.

3.2. Viscosity, Gelation Time, and Curing Extent of MAESO–MVA Resins

The viscosity data of the MVA monomer and MAESO–MVA mixtures with various MVA loadings are shown in **Figure 7**. The MVA monomer exhibited a higher viscosity (43.9 cP at 10 s^{-1}, 25 °C) than styrene (0.7 cP at 30 °C) caused by the higher van der Waals attractions of MVA. The higher viscosity also reflected increased intermolecular interactions in the MVA monomer compared to styrene because MVA contains methoxy–ester groups that can induce the formation of hydrogen bonds, while styrene is a nonpolar, small molecule that behaves like a solvent. Pure MAESO resin exhibited extremely high viscosities, up to 1.7×10^6 cP at 25 °C, caused by the presence of abundant hydrogen bonds between hydroxyl and ester groups, as well as high molecular weight. Pure MAESO also exhibited shear-thinning behavior because hydrogen bonds and the entanglements within the system can be destroyed at higher shear rates (Figure 7A).

The preferred viscosity range for resins used for manufacturing composite materials by liquid molding approaches is generally between 200 and 1000 cP at room temperature. The

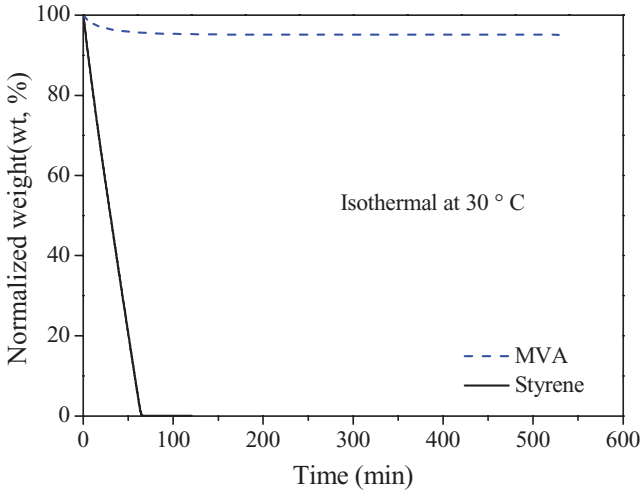

Figure 6. Weight loss as a function of time for MVA and styrene.

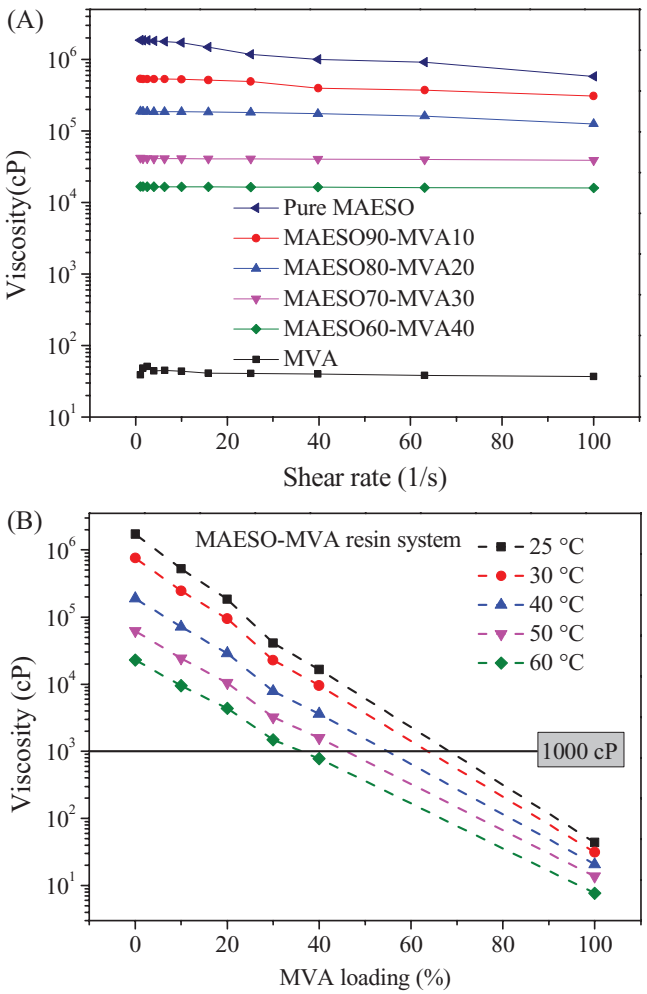

Figure 7. A) Viscosity as a function of shear rate for the MAESO–MVA resin systems at 25 °C. B) Viscosity as a function of MVA loadings for the MAESO–MVA resin systems at 10 s^{-1} shear rate.

Table 1. Viscosity of MAESO–MVA system at 25 °C and Arrhenius parameters.

Formulations	η[Pa s, 25 °C]	η_0 [Pa s]	R_2	$E\eta$ [kJ mol^{-1}]
Pure MAESO	1719.0	2.48×10^{-15}	0.9967	101.6
MAESO90-MVA10	526.9	1.39×10^{-14}	0.9978	94.4
MAESO80-MVA20	185.2	5.62×10^{-14}	0.9980	88.4
MAESO70-MVA30	41.0	7.01×10^{-13}	0.9980	78.4
MAESO60-MVA40	16.5	3.41×10^{-12}	0.9981	72.3
Pure MVA	0.04	5.67×10^{-9}	0.9923	39.3

viscosity of MAESO–MVA system was significantly decreased with increasing MVA loadings. With the MVA loading of 40%, the viscosity of the MAESO–MVA system was significantly decreased (by more than two orders of magnitude), to 1.7×10^4 cP at 25 °C. Moreover, the viscosities of MAESO–MVA system decreased in an exponential manner with increasing temperature (Figure 6B), which was supported by the Arrhenius Equation[13]

$$\eta = \eta_0 \exp\left(E_\eta/(RT)\right) \tag{2}$$

where η is the apparent viscosity, η_0 is the prefactor, E_η is the activation energy for the viscos flow, R is the ideal gas constant, and T is the absolute temperature. As shown in **Table 1**, E_η decreased from 101.6 to 72.3 kJ mol^{-1} with increasing MVA loading to 40% in the MAESO resin, because that MVA had lower molecular weight and polarity than that of MAESO resin. Further increasing the processing temperature to 55 and 60 °C, the MAESO–MVA system with 40% of MVA showed a viscosity of 1090 and 775 cP, respectively, which can match with the viscosity of MAESO–styrene resin (1000–1500 cP at 25 °C) with 33% of styrene loadings. The hydrogen bonds between hydroxyl groups of MAESO and ester groups of MVA also contributed to the increased viscosity of the MAESO–MVA system compared to MAESO–styrene systems. Therefore, the viscosity of MAESO–MVA resin system can be tailored by adjusting MVA loading or processing temperature to meet the composites manufacturing process requirements for liquid molding techniques, such as sheet molding compounds , bulk molding compounds, or vacuum-assisted resin transfer molding.

To evaluate the curing behavior of MAESO–MVA systems, MVA was blended with MAESO at different weight ratios (0–40%) and isothermally cured at 120 °C. Excellent miscibility was observed between MAESO and MVA. Before curing, the storage modulus (G') of the MAESO–MVA mixture was significantly lower than the loss modulus (G'') due to the viscous characteristic. While both G' and G'' increased with increasing curing time, G' increased faster than G'', which was attributed to the crosslinking reaction that turned the liquid mixture into solid gel. The gelation time was determined as the crossover point of the G' and G'' curves. The gelation time of pure MAESO resin was determined as 21.9 min (**Figure 8**), and it decreased from 16.9 to 10.8 min as the MVA loading increased from 10 to 40% (**Table 2**), indicating that the introduction of MVA accelerated the crosslinking reaction. This acceleration was attributed to two factors: (1) The introduction of MVA

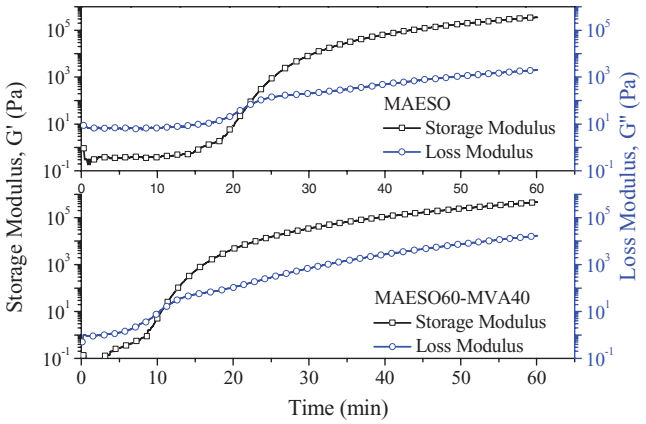

Figure 8. Time dependence of G' and G'' for MAESO–MVA thermosets with different MVA loadings.

reduced the viscosity of the reacting system, resulting in a faster chain-growth crosslinking reaction, and (2) for pure MAESO resin, only the MAESO homopolymerization crosslinking reaction was involved in the gelation process, and the maleate groups in MAESO do not readily homopolymerize, but they can copolymerize with MVA.[14] With increasing MVA loading, the combination of MAESO homopolymerization, MVA homopolymerization, and MAESO–MVA copolymerization contributed to the final gelation, more reactive methacrylate functional groups (from MVA) and less maleate groups and acrylate groups (from MAESO) with carbon–carbon double bonds were available in the reaction system, thus accelerating the crosslinking reaction.

In order to further evaluate the curing extent of the crosslinked MAESO–MVA thermosets, Soxhlet extraction was performed for 24 h using dichloromethane as a solvent. **Table 3** shows the weight percent of crosslinked polymer remaining after Soxhlet extraction. The insoluble content of the resin increased from 90.6 to 93.8% with increasing MVA loading, confirming that most of the MAESO and MVA were incorporated into the crosslinking network constituted. The unreacted MVA, MAESO, and *tert*-butyl peroxybenzoate initiator constituted the soluble content as analyzed by ^{1}H NMR. In addition, a detailed Mid-FTIR study has been carried out to investigate the curing extent of MAESO–MVA samples (**Figure 9**). After cure, there were some uncured C=C bonds (1638 cm^{-1}) present in the MAESO–MVA resin system. MVA resin had more uncured C=C bonds than that of MAESO resin, and the uncured C=C bonds were increased with increasing MVA loading in the MAESO–MVA resin system, which resulted in lower extent of cure of the system. It was observed that pure MVA resin had

Table 2. Gelation time for MAESO–MVA thermosets with different MVA loadings.

Formulations	Gelation time [min]
Pure MAESO	21.9
MAESO90-MVA10	16.9
MAESO80-MVA20	12.5
MAESO70-MVA30	12.3
MAESO60-MVA40	10.8

Table 3. Insoluble weight percent for MAESO–MVA thermosets systems.

Formulations	Insoluble weight percent [%]
Pure MAESO	90.6 ± 0.1
MAESO90-MVA10	91.3 ± 0.2
MAESO80-MVA20	92.2 ± 0.1
MAESO70-MVA30	93.5 ± 0.3
MAESO60-MVA40	93.8 ± 0.1

more unreacted methacrylate functionality available at 945 cm^{-1} (attributed to the out of plane bending of the methacrylate vinyl groups). After one of the methacrylate groups of MVA tied to the network, it was difficult for the other to react because of a reduced mobility of the molecule especially after vitrification of the resin. As a result, these unreacted methacrylate groups cannot be cured properly. With the introduction of more than 60% MAESO resin to MVA resin system, all the methacrylate groups within MVA were polymerized (Figure 9b).

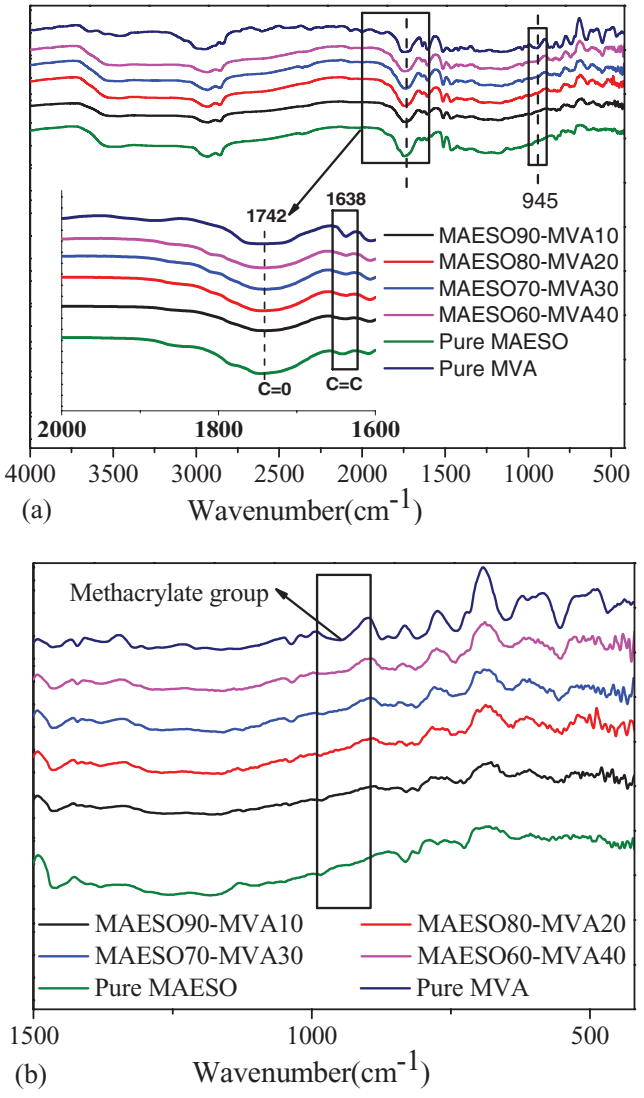

Figure 9. FT-IR of cured MAESO–MVA thermosets in the a) 400–4000 cm^{-1} and b) 400–1500 cm^{-1} region.

3.3. Thermomechanical Properties

Figure 10 shows (a) storage modulus and (b) tan δ of thermosets with different MVA loadings. The storage modulus of the resin at room temperature (30 °C) increased from 0.8 to 1.5 GPa with increasing MVA loading (from 0 to 40%) as a result of the introduction of rigid aromatic MVA chain segments. The storage modulus decreased with increasing temperature because of the increased mobility of the chain segments of the MAESO–MVA resin at high temperatures.

Pure MAESO polymer exhibited a broad glass transition peak (from −50 to 150 °C). This was attributed to the complex and bulky alkyl chain of the MAESO resin. Generally, the breadth of the T_g increases and height of the peak (E'' or tan δ) decreases as crosslinking increases. With increasing MVA loading, the tan δ peak became broader because of the heterogeneity of the crosslinked network structure consisting of MAESO and MVA homopolymers, and MAESO–MVA copolymer, and increasing crosslinking degree. According to the twinkling fractal theory, an increased amount of relaxation modes present in the polymer network arises when there exists a broad distribution of solid fractal clusters that twinkle into the liquid upon heating, thus, exhibiting heterogeneity.[34] In addition, the height of the tan δ peak of MAESO–MVA copolymers decreased with increasing MVA loading. Higher tan δ peaks reflect a more viscous behavior in a polymer network, while lower peaks indicate a more elastic behavior, indicative of a highly crosslinked polymer network. The incorporation of the rigid, difunctional MVA resulted in a more elastic polymer network and a higher degree of crosslinking, as confirmed by the increasing crosslinking degree from 5786 to 14 089 mol m^{-3}. Furthermore, the presence of hydrogen bonds between MVA (containing methacrylate groups) and MAESO (with available hydroxyl groups) also contributed to the improved elastic behavior.

The glass transition temperature was defined as the temperature at which tan δ reached its maximum. Pure MAESO resin exhibited a T_g of 63 °C, while MAESO–MVA copolymers with 40% MVA content showed a T_g of 79 °C. This was not only attributed to the rigid aromatic nature of MVA compared to the long flexible MAESO chains, but also to an improved crosslinking degree of the resin system. As anticipated, the rubbery modulus (storage modulus @ T_g + 60 °C) of the copolymer also showed an increase from 57.2 to 144.6 MPa with the MVA loading increased from 10 to 40%, confirming a tighter crosslinked network. Increasing crosslinking degree restricted chain mobility, leading to improved storage modulus and T_g (see **Table 4**).

In addition, MAESO65-HP-MVA35 copolymers showed a lower T_g (76.6 °C) than styrene diluted MAESO resin (100.8 °C), as shown in Figure 5. The tan δ peak height of two copolymers was in the order of MAESO65-HP-MVA35 copolymer < MAESO65/Styrene35, which indicated that the MAESO65-HP-MVA35 copolymer possessed the highest elasticity because of the increased crosslinking degree. The FT-IR results (Figure 9)

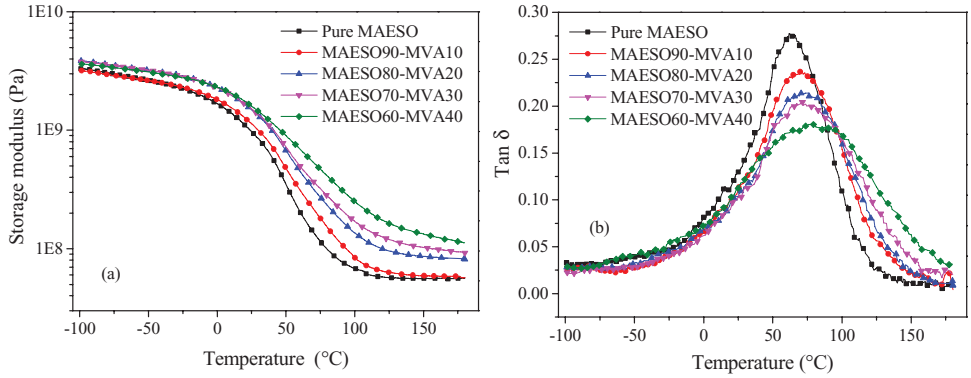

Figure 10. a) Storage modulus and b) tan δ as functions of temperature for MAESO–MVA thermosets.

indicated that low extent of cure for the MVA resulted in the low T_g of the purified MVA–MAESO. The MVA molecules with methacrylates group served as chain extenders just like styrene, but methacrylates groups (MVA) do not react as well with maleates as styrene does. In addition, the high degree of crosslinking of MVA–MAESO resin system resulted in overall lower extent of cure compared with styrene–MAESO resin system, leading to a decreased T_g than that of styrene–MAESO system.

3.4. Tensile Properties

Table 5 shows tensile strength and Young's modulus of MAESO–MVA copolymers. Pure MAESO homopolymer exhibited a tensile strength of 23.7 MPa. Both tensile strength and Young's modulus increased with increasing levels of MVA content. When the MVA loading reached 40%, the tensile strength increased to 31.5 MPa, which can be attributed to the increase in the number of rigid, aromatic MVA rings incorporated into the crosslinked copolymer network and the increased crosslinking degree, as confirmed by DMA analysis (Figure 10). As shown in **Figure 11**, elongation at break decreased with increasing MVA content because of the lower extent of cure with increasing MVA loading, as confirmed by FT-IR results (Figure 9). In addition, the aromatic MVA component resulted in a more brittle material compared to the flexible MAESO component.

Table 4. Thermomechanical properties of thermosets of MAESO and MVA.

Formulations	T_g [°C]	Storage modulus [30 °C, MPa]	Rubbery modulus [T_g + 60, MPa]	Crosslinking degree [mol m^{-3}]
Pure MAESO	63.3	847.1	57.2	5786
MAESO90-MVA10	69.2	1004.8	62.2	6197
MAESO80-MVA20	71.2	1325.5	92.1	9129
MAESO70-MVA30	72.2	1357.4	132.6	13117
MAESO60-MVA40	78.5	1452.9	144.6	14089

Table 5. Mechanical properties for thermosets of MAESO and MVA.

Formulations	Tensile strength [MPa]	Young's modulus [MPa]
Pure MAESO	23.7 ± 1.2	569.9 ± 21.1
MAESO90-MVA10	26.5 ± 1.1	633.9 ± 29.7
MAESO80-MVA20	27.7 ± 1.6	719.1 ± 37.5
MAESO70-MVA30	29.2 ± 0.7	840.8 ± 32.7
MAESO60-MVA40	31.5 ± 1.4	885.1 ± 49.0

3.5. Thermal Stability

Figure 12 shows the TGA curves of MAESO–MVA copolymer systems. Generally, the degradation of the copolymers occurred in three stages, and all copolymers were stable up to 200 °C. In the first stage of degradation (ranging from 200 to 300 °C), unreacted MVA, MAESO monomer and oligomers were thermally degraded, as documented in the earlier Soxhlet extraction tests (Table 3). As the MVA loading increased, the number of unsaturated carbon–carbon double bonds increased, resulting in a decrease in thermal stability of the copolymer in the first degradation stage from 200 to 300 °C. The second stage of

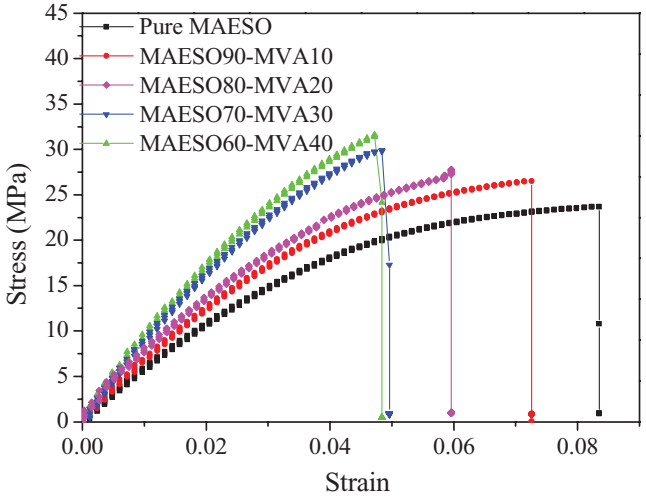

Figure 11. Stress/strain curves of MAESO–MVA thermosets systems.

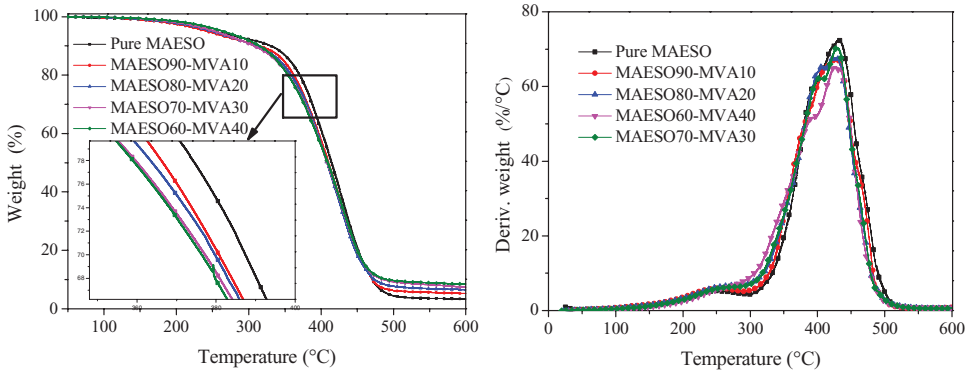

Figure 12. Thermal degradation curves of MAESO–MVA thermosets systems.

degradation occurred between 350 and 450 °C and was the fastest degradation stage. MAESO homopolymer was more stable than MVA–MAESO copolymers because MAESO had higher extent of cure. The curing extent was decreased with increasing MVA loading, as confirmed by the FT-IR test (Figure 9). In the third stage of degradation, the copolymers started to degrade rapidly because of the random scission of polymers chains. With higher MVA content, the copolymers were relatively more stable and exhibited a higher residual weight due to the increased crosslinking degree and the increased rigid aromatic structure of MVA, as char formation is generally promoted by aromatic structures.

4. Conclusion

Vanillyl alcohol was functionalized with a methacrylate group using an esterification process to form a low-viscosity and low-volatile MVA monomer. The synthesized MVA was used as a green comonomer in a MAESO resin to produce a novel, sustainable thermosetting polymer via free radical polymerization. The MAESO–MVA copolymer showed improved thermal and mechanical properties and improved processability with significantly decreased viscosity, while maintaining low VOC/HAP emissions, sustainability, and environmental friendliness compared to thermosets prepared using commercial styrene resin. Therefore, MVA can be used as a comonomer for MAESO resin to replace styrene.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

comonomer, maleinated acrylated epoxidized soybean-oil (MAESO), methacrylated vanillyl alcohol (MVA), styrene replacement, thermosetting resin

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