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Soybean Oil-based Thermosetting Resins with Methacrylated Vanillyl Alcohol as Bio-based Reactive Diluent

Yuehong Zhang[a,b], Vijay Kumar Thakur[a,c], Yuzhan Li[a], Thomas F Garrison[a,d], Zhenhua Gao[b], and Michael R Kessler[a*]

[a] *School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164, USA*

[b] *College of Material Science and Engineering, Northeast Forestry University, Harbin, 150040, China*

[c] *Enhanced Composites and Structures Center, School of Aerospace, Transport and Manufacturing, Cranfield University, Bedfordshire MK43 0AL, UK*

[d] *Department of Chemistry, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*

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ABSTRACT:

A novel, bio-based, aromatic monomer (methacrylated vanillyl alcohol, MVA), was synthesized using vanillyl alcohol and methacrylic anhydride in the absence of solvents. The resulting MVA was characterized and used as a sustainable reactive diluent to replace styrene in a maleinated acrylated epoxidized soybean oil (MAESO) resin to produce novel thermosetting resins via free radical polymerization. The influence of MVA loading (10 - 40%) on the viscosity, gelation time, curing extent, thermo-mechanical properties, and tensile properties of the MAESO-MVA copolymer was investigated. The synthesized MVA exhibited very low volatility relative to styrene, which is beneficial for the development of construction material with low or zero emission. With 40 wt% of MVA content in MAESO, a significant reduction of system viscosity (over an order of magnitude) was achieved. Increasing the MVA content accelerated the crosslinking reaction rate and improved thermal and mechanical properties of the MAESO-MVA system. The glass transition temperature increased with increasing MVA content. Soxhlet extraction experiments showed that more than 90% of the components were incorporated into the crosslinking network. The effect of MVA purity on the properties of the resulting copolymer was also investigated. MAESO-MVA copolymers prepared using high-purity MVA exhibited higher degree of crosslinking.

KEYWORDS: *Vanillin; Methacrylated vanillyl alcohol (MVA); Reactive diluent; Maleinated acrylated epoxidized soybean oil (MAESO); Thermosetting resin; Sustainable; Styrene replacement*

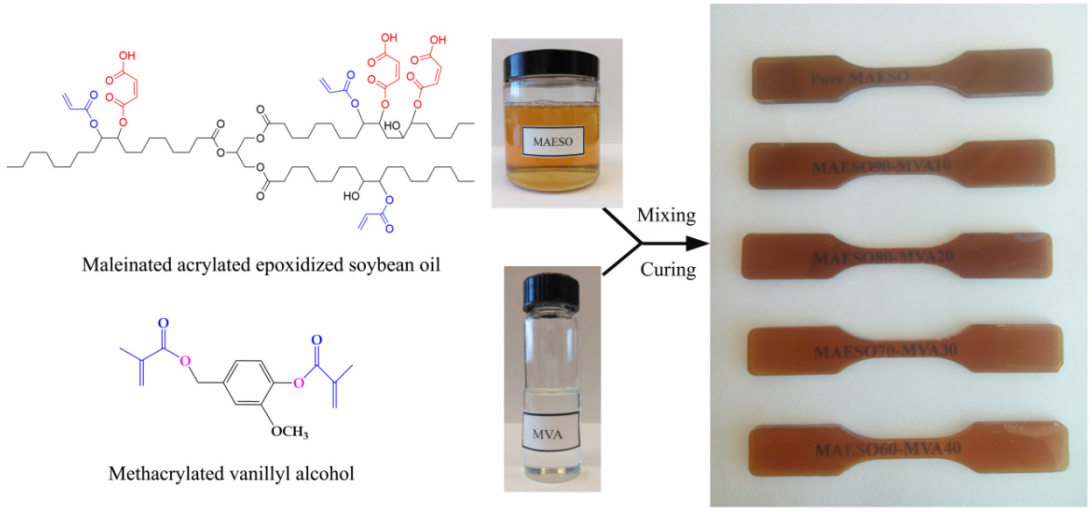
HIGHLIGHTS:

- MVA was used as reactive diluent for MAESO and showed advantages in terms of low volatility, sustainability, environmental friendliness, good processability, and improved glass transition temperature.
- MVA showed promising results as a bio-based reactive diluent component for MAESO resins. Bio-based MVA-MAESO

thermosetting copolymers were produced for the first time and their properties were evaluated comprehensively.

- Both MVA and MAESO resin were derived from bio-based, renewable resources.
- A bio-based, high-purity MVA monomer was obtained using silica gel column chromatography.

GRAPHICAL ABSTRACT



Schematic for the preparation of MAESO-MVA copolymers

1. INTRODUCTION

Petroleum-based thermosetting polymers, such as unsaturated polyester resins (UPR) and vinyl ester resins (VER), 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 non-sustainable 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 non-conjugated 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 **Fig. 1.** First, the carbon-carbon double bonds in soybean oil are epoxidized by a peroxy acid to form epoxidized soybean oil (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 acrylated epoxidized soybean oil (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 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

approximately 33% of low-viscosity styrene as a reactive diluent 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 (HAP) and a volatile organic compound (VOC). It is also classified as a potential human carcinogen, as well as being derived from non-renewable petroleum resources. Therefore, the development of a low-viscosity, nonvolatile, renewable aromatic-based reactive diluent has become of great interest.[17-19]

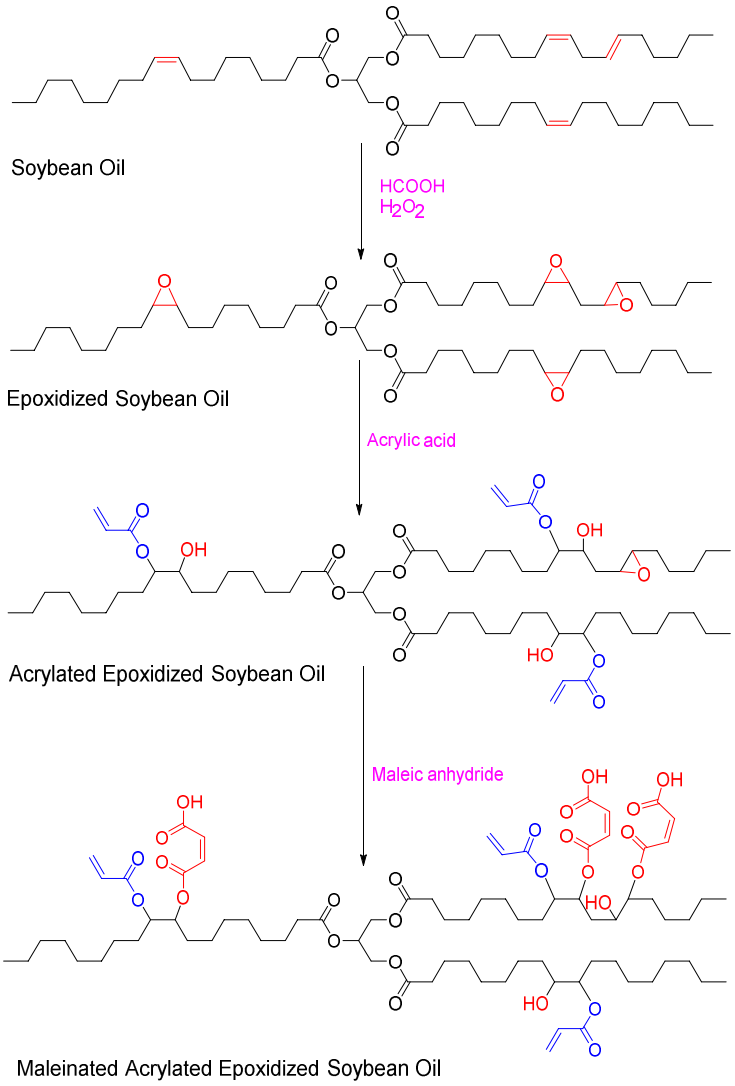


Fig. 1 Schematic for the synthesis of maleinated acrylated epoxidized soybean oil (MAESO)

Vanillin is one of the bio-based aromatic chemicals that are 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 biobased 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 biobased thermosetting polymer.[17] Moreover, Renbutsu *et al*. successfully prepared MV via a Steglich esterification of vanillin with methacrylic acid to create a coating for electroless plating of non-conductive materials.[29] However, pure MV is solid (with a melting point of approx. 54 °C) at room temperature, and it is a mono-functional monomer (just one methacrylate group available for radical copolymerization). Other vanillin derivatives are also commercially available, including vanillyl alcohol and vanillic acid shown in Fig. 2.[30, 31]

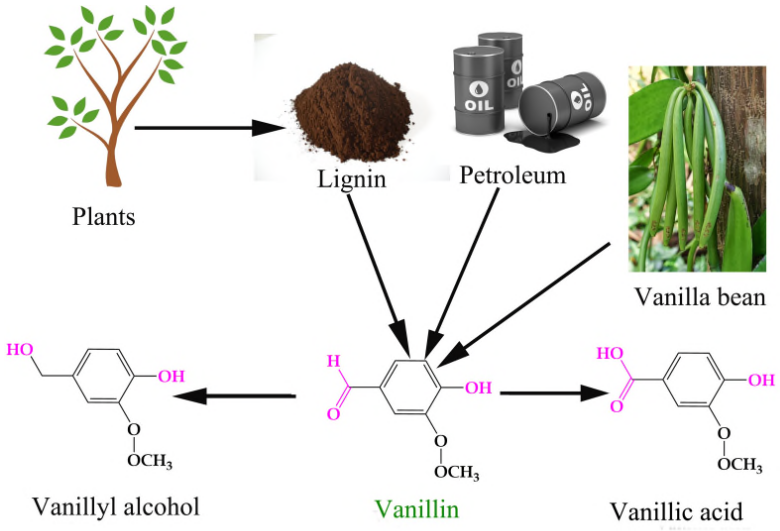


Fig. 2 Chemical structures and preparation of vanillin derivatives

In recently work, we developed methacrylated vanillyl alcohol (MVA), a new monomer, using vanillyl alcohol and methacrylic anhydride

(Fig. 3). 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. To date, MVA has not been used as a bio-based reactive diluent to replace styrene in functionalized soybean oil-based thermosetting resins.[28]

This work highlights the possibility of using MVA as the reactive diluent for MAESO to produce bio-based thermosetting polymers with improved thermal and mechanical properties. The chemical structure and purity 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, thermo-mechanical properties, and tensile properties of the MVA-MAESO 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%), methacrylate 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. All materials were used as received without further purification.

2.2 Synthesis of Methacrylate Vanillyl Alcohol (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 washed seven times with sodium bicarbonate solution, 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.

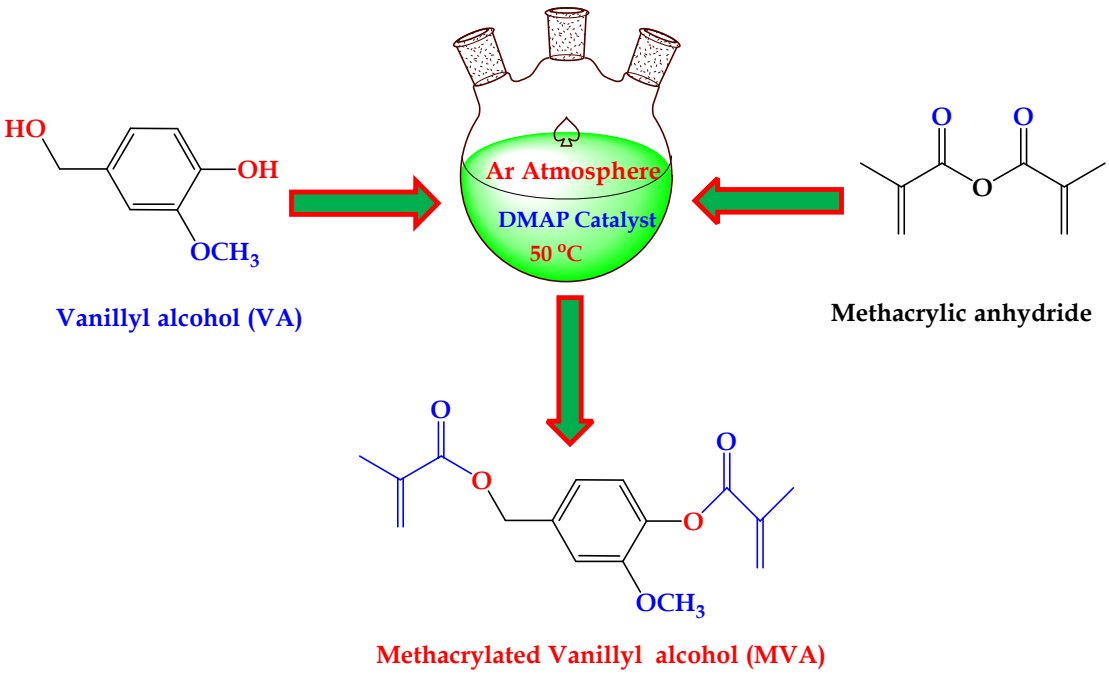


Fig.3 Synthesis of methacrylated vanillyl alcohol (MVA)

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 to 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 at 170 °C for 2 h. The prepared thermosetting copolymers were labeled as pure MAESO, MAESO90-MVA10, MAESO80-MVA20, MAESO70-MVA30, and MAESO60-MVA40. In addition, in order to study the effect of MVA purity on thermo-mechanical properties of the copolymer, three copolymers with 35 wt% of high-purity MVA (HP-MVA), as-synthesized MVA (AS-MVA),

and styrene were prepared and labeled as MAESO65/HP-MVA35, MAESO65/AS-MVA35, and MAESO65/Styrene35.

2.4 Resin Characterization

The volatility of both MVA and styrene was measured using a TA instruments Discovery thermogravimetric analyzer (TGA). Approximately 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.

The gelation test was performed on an ARES G2 rheometer using parallel plates with 25 mm diameter 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 °C.

Soxhlet extraction tests were conducted to analyze the crosslinking degree of the MAESO-MVA copolymers. Approximately 1.000 g of MAESO-MVA copolymer sample was 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.

The dynamic mechanical properties of the MAESO-MVA copolymers were evaluated using a strain-controlled rheometer (ARES G2, TA Instruments) in 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, a strain of 0.15%, and an oscillation frequency of 1 Hz. The DMA of MAESO resin with 35 wt% of three different reactive diluents (HP-MVA, AS-MVA, and styrene) was carried out in the torsion rectangular mode with a strain of 0.065%, a constant frequency of 1 Hz and a heating rate of 3 °C/min in the temperature range of −100 to 180 °C.

Tensile tests were performed in accordance with ASTM D638 using an universal testing machine (INSTRON 4466) with a crosshead speed of 0.1 in/min. Standard 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 copolymers 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 under a nitrogen atmosphere.

Dynamic DSC scans were conducted using a differential scanning calorimeter (Discovery DSC, TA Instruments) under a nitrogen purge of 20 ml/min with a ramp rate of 10 °C/min in the temperature range of 30 to 200 °C.

3. RESULTS AND DISCUSSION

3.1 Diluent Volatility

The volatility of a reactive diluent 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 (Fig. 4). The results confirmed that styrene was highly volatile, as it completely evaporated (only 0.26% 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.[32] In contrast, MVA exhibited significantly lower HAP/VOC emissions with a weight loss of less than 5% after isothermal 9 h at 30 °C, confirming that bio-based MVA is a promising reactive diluent monomer with low VOC.

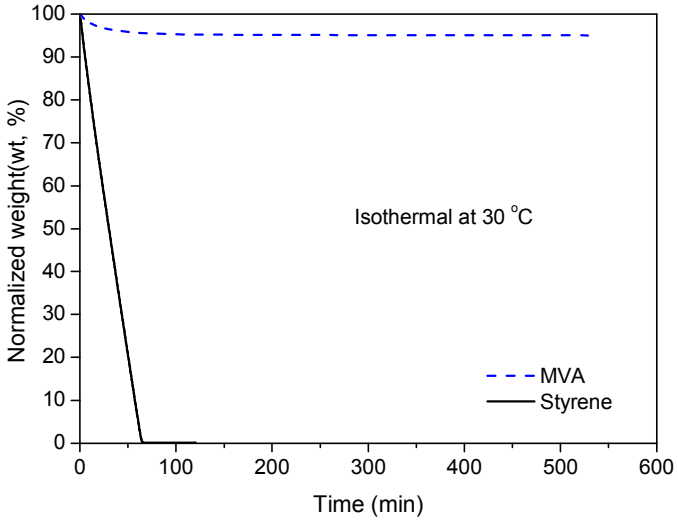


Fig. 4 Weight loss as a function of time for MVA and styrene

3.2 Viscosity, Gelation Time and Curing Extent of MAESO-MVA Copolymers

The viscosity data of the MVA monomer and MAESO-MVA mixtures with various MVA loadings are shown in Fig. 5. The MVA monomer

exhibited a higher viscosity (97.4 cP @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 non-polar, small molecule that behaves like a solvent. Pure MAESO resin exhibited extremely high viscosities, up to 7.88 $\times 10^5$ cP at 25 °C, caused by the presence of abundant hydrogen bonds between hydroxyl and ester groups. Pure MAESO also exhibited shear-thinning behavior because hydrogen bonds and the entanglements within the system can be destroyed at higher shear rates. With the introduction of MVA, the viscosity of the MAESO-MVA system significantly decreased (more than an order of magnitude), resulting in a viscosity of 2.4 $\times 10^4$ cP with a MVA loading of 40%. However, the viscosity of the MAESO-MVA resin systems was still higher than that of MAESO-styrene resins (1000-1500 cP) as the reactive diluent loading reached 35%. 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.

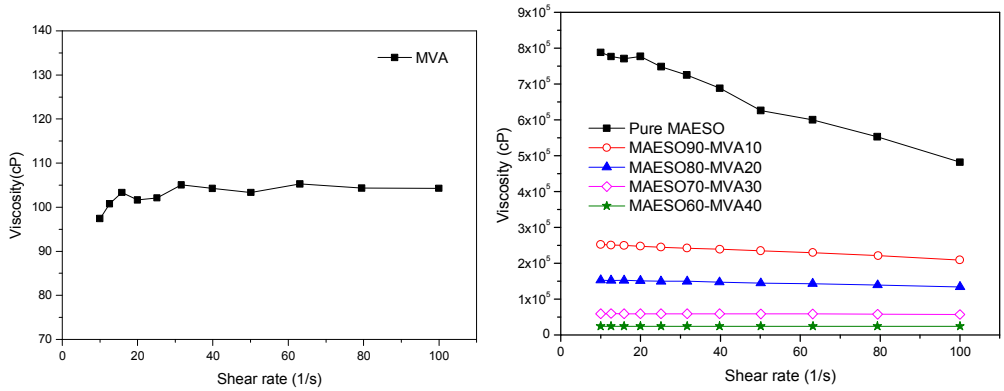


Fig. 5 The viscosity of MVA monomer (left) and MAESO-MVA systems with various MVA loadings (right)

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 (Fig. 6), and it decreased from 16.9 min to 10.8 min as the MVA loading increased from 10 to 40% (Table 1), indicating that the introduction of MVA accelerated the crosslinking reaction. This acceleration was attributed to two factors: (1) The introduction of MVA 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. The maleate groups in MAESO do not easily homopolymerize, but they can copolymerize with MVA[14]. The combination of MAESO homopolymerization, MVA homopolymerization, and MAESO-MVA copolymerization contributed to the final gelation. With increasing MVA loading, 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.

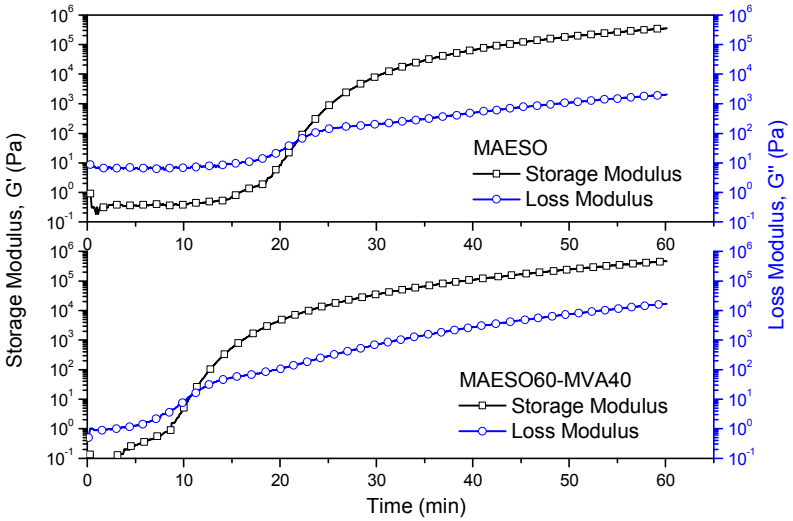


Fig.6 Time dependence of G' and G" for MAESO-MVA copolymer with different MVA loadings

Table 1. Gelation time for MAESO-MVA copolymers 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

In order to further evaluate the degree of curing of the crosslinked MAESO-MVA copolymers, Soxhlet extraction was performed for 24 h using dichloromethane as a solvent. Table 2 shows the weight percent of crosslinked polymer remaining after Soxhlet extraction. The insoluble content of the resin increased from 90.63 to 93.83% 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 proton nuclear magnetic resonance (^{1}H NMR).

Table 2. Insoluble weight percent for MAESO-MVA copolymer systems

Formulations	Insoluble weight percent (%)
Pure MAESO	90.63 ± 0.11
MAESO90-MVA10	91.30 ± 0.15
MAESO80-MVA20	92.24 ± 0.09
MAESO70-MVA30	93.46 ± 0.22
MAESO60-MVA40	93.83 ± 0.04

3.3 Thermo-Mechanical Properties

Fig. 7 shows storage modulus (left) and tan δ (right) of copolymers with different MVA loadings. The storage modulus of the resin at room temperature (30 °C) increased from 0.85 to 1.45 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. 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. According to the twinkling fractal theory (TFT), 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.[33] 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. 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 63.27 °C, while MAESO-MVA copolymers with 40% MVA content showed a T_g of 78.48 °C. This was not only attributed to the rigid aromatic nature of MVA compared to the long flexible MAESO chains, but also to a higher crosslinking degree of the resin system. As anticipated, the rubbery modulus (storage modulus @150 °C) of the copolymer also showed an increase from 56.1 to 132.9 MPa with the MVA loading increased from 10 to 40%, suggesting a tighter crosslinked network (high degree of crosslinking). Increasing crosslinking degree restricts chain mobility, leading to improved storage modulus and T_g.

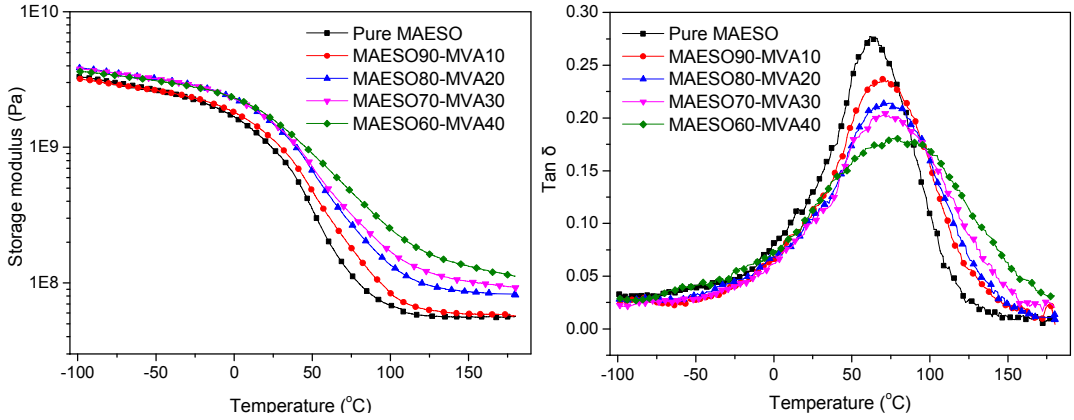


Fig. 7 Storage modulus (left) and tan δ (right) as functions of temperature for MAESO-MVA copolymers

Table 3. Thermo-mechanical properties of copolymers of MAESO and MVA

Formulations	T_g [a] (°C)	Storage modulus (30 °C, MPa)	Rubbery modulus (150 °C, MPa)

Pure MAESO	63.27	847.08	56.1
MAESO90-MVA10	69.15	1004.77	59.1
MAESO80-MVA20	71.20	1325.50	86.2
MAESO70-MVA30	72.24	1357.42	102.5
MAESO60-MVA40	78.48	1452.91	132.9

[a]The glass transition temperatures (T_g) is obtained from the maxima of the tan δ curves obtained by DMA analysis

3.4 Tensile Properties

Table 4. Mechanical properties for copolymers of MAESO and MVA

Formulations	Tensile strength (MPa)	Young's modulus (MPa)
Pure MAESO	23.73 ± 1.23	569.93 ± 21.09
MAESO90-MVA10	26.52 ± 1.11	633.93 ± 29.65
MAESO80-MVA20	27.71 ± 1.56	719.13 ± 37.45
MAESO70-MVA30	29.24 ± 0.69	840.76 ± 32.65
MAESO60-MVA40	31.53 ± 1.42	885.14 ± 48.96

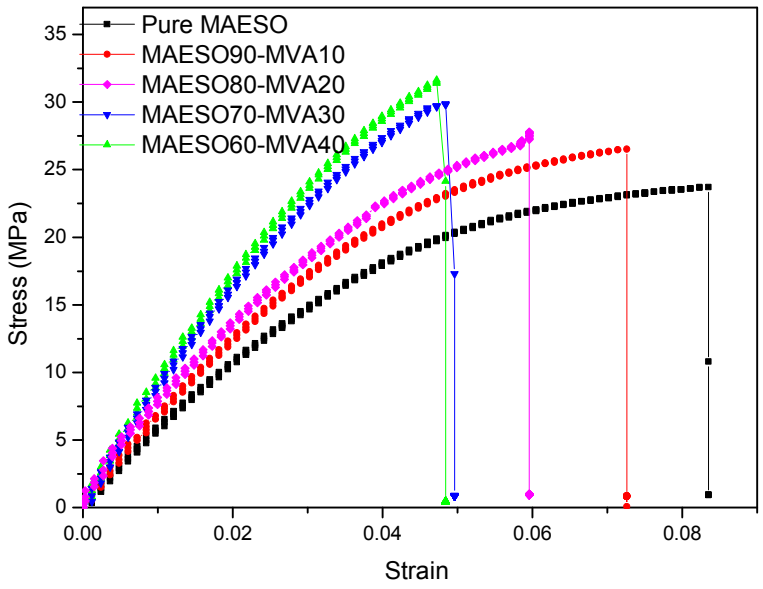


Fig. 8 Stress/strain curves of MAESO-MVA copolymer systems

Table 4 shows tensile strength and Young's modulus of MAESO-MVA copolymers. Pure MAESO homopolymer exhibited a tensile strength of 23.73 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 31.53 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 (Fig. 7). Elongation decreased with increasing MVA content because the aromatic MVA component resulted in a more brittle material compared to the flexible MAESO component (Fig. 8).

3.5 Thermal Stability

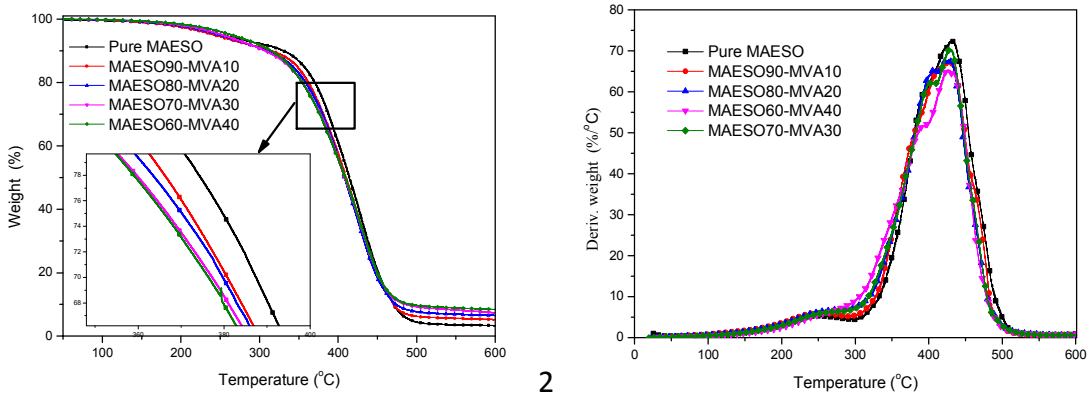


Fig. 9 Thermal degradation curves of MAESO-MVA copolymer systems

Fig. 9 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 2). 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 degradation occurred between 350 and 450 °C and was the fastest degradation stage. MAESO homopolymer was more stable than MVA-MAESO copolymers because of the tri-ester structure of MAESO. 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.

3.6 Effect of MVA Purity on Thermo-Mechanical Properties of MVA-MAESO Copolymers

In order to determine the purity of the as-synthesized MVA, ultra-performance liquid chromatography (UPLC) was performed. The UPLC results indicated that the purity of the as-synthesized MVA (AS-MVA) was limited (81.24%, Supplementary Fig.S1 and S2) and three major impurities were present in the AS-MVA. Column chromatography was used to purify and separate MVA with the impurities. The separated impurities were investigated using gas chromatography-mass spectroscopy (GC-MS). The results showed that the impurities included two kinds of partially reacted vanillyl alcohols (phenolic hydroxyl group converted vanillyl alcohol and aliphatic hydroxyl group converted vanillyl alcohol), and Topanol A, which was an inhibitor in the starting material methacrylic anhydride (Supplementary Fig.S3 and S4). In order to understand the effect of MVA purity on the final properties of the copolymer, high-purity MVA (HP-MVA) was obtained using silica gel column chromatography and was used to prepare MAESO-MVA copolymers. After purification, a clean ^{1}H NMR spectrum was obtained (Supplementary Fig.S5), which was in agreement with the TLC results (Supplementary Fig.S2). UPLC experiments determined that the purity of HP-MVA was 96.30% (Supplementary Fig.S6).

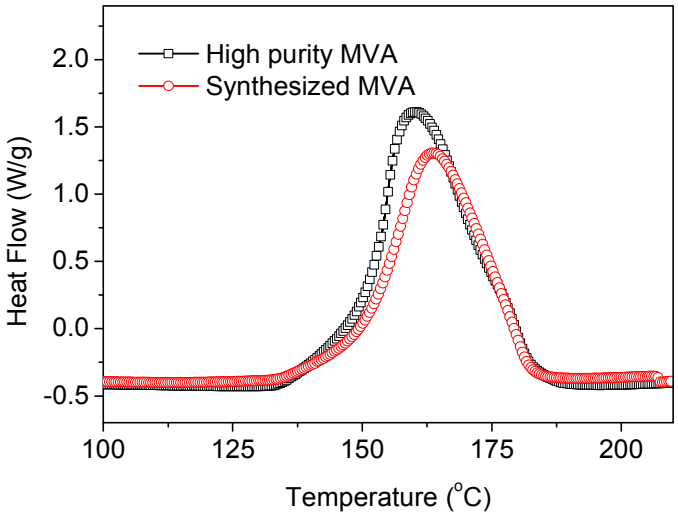


Fig. 10 Dynamic DSC curing scans of HP-MVA and AS-MVA

Dynamic DSC scans were used to determine the curing behavior of

HP-MVA and AS-MVA in the presence of 1.5% tert-butyl peroxybenzoate initiator (Fig. 10). Methacrylate groups (C=C double bonds) of MVA can undergo free radical polymerization at elevated temperature, resulting in an exothermic peak. The enthalpy of reaction per gram of sample was calculated by integration of the DSC curve. The results show that the exothermic enthalpy for HP-MVA (271.22 J/g) was higher than that of the AS-MVA (217.30 J/g), indicating that more methacrylate groups (C=C double bonds) participated in the curing reaction. This can be attributed to the removal of impurities, such as Topanol A and partially reactive vanillyl alcohol, which would otherwise have acted as polymerization inhibitors by trapping the generated free radicals.

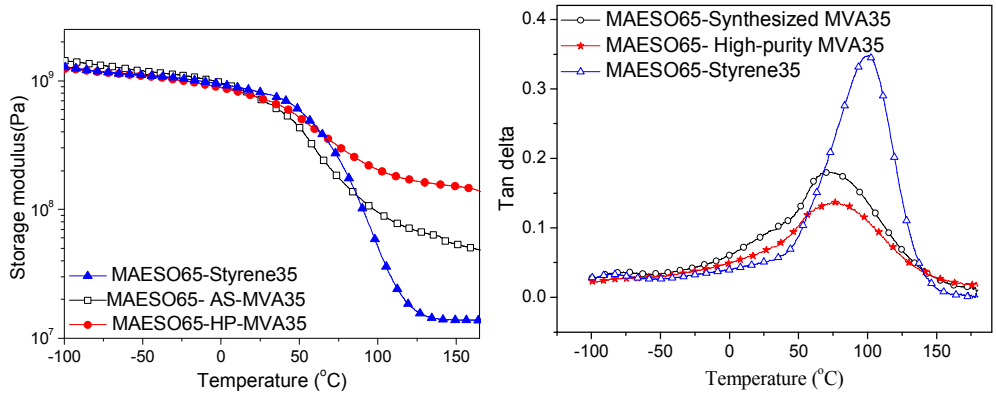


Fig. 11 Storage modulus (left) and tan δ (right) as functions of temperature for MAESO with 35% of HP-MVA, AS-MVA, and styrene as benchmark

Purification completely removed the inhibitor Topanol A and the partially reacted vanillyl alcohol. We discovered that HP-MVA is a white solid with a low melting point of 44.7 °C (Supplementary Fig. S7), exhibiting slow crystallization rates. MAESO65/HP-MVA35 copolymers exhibited a slightly higher T_g (76.6 °C) than MAESO65/AS-MVA35 copolymers (73.7 °C), and showed a lower T_g than styrene diluted MAESO resin (100.8 °C), as shown in Fig. 11. The tan δ peak height of three copolymers was in the order of MAESO65/HP-MVA35 copolymer < MAESO65/AS-MVA35 < MAESO65/Styrene35, which indicated the MAESO65/HP-MVA35 copolymer possessed the highest elasticity because of the increased crosslinking degree. This agrees well with the exothermic enthalpy results shown in Fig. 10. The copolymers prepared using HP-MVA also exhibited a significant increase in rubbery modulus, which confirmed the increased crosslinking reaction. In the MAESO65/styrene35 resin systems, styrene has just one reactive group,

causing a decrease in crosslinking degree and rubbery modulus.

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 reactive diluent 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 copolymers prepared using commercial styrene resin. Therefore, MVA can be used as a reactive diluent for MAESO resin.

ASSOCIATED CONTENT

Supporting information

UPLC results of AS-MVA (Fig. S1); TLC picture of AS-MVA and HP-MVA (Fig. S2); GC-MS results of Topanol A impurity (Fig. S3); GC-MS of partially reacted vanillyl alcohol impurity (Fig. S4); ^{1}H NMR of AS-MVA (Top) and HP-MVA (Bottom, Fig. S5); UPLC and Melting point results of HP-MVA (Fig. S6 and S7)

AUTHOR INFORMATION

Corresponding Author

* PO Box 642920, Pullman, WA, 99164-2920; Phone (509) 335-8654;
Email: MichaelR.Kessler@wsu.edu

Notes

The authors declare no competing financial interest.

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Zhang, Yuehong; Thakur, Vijay Kumar; Li, Yuzhan; Garrison, Thomas F.; Gao, Zhenhua ...

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