Lignin-Based Bio-Oil Mimic as Biobased Resin for Composite Applications

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ABSTRACT: Lignin is an abundant renewable raw material that has the potential to yield valuable bio-oils consisting of aromatic chemicals when strategically depolymerized. In order to determine if lignin-based bio-oils can be utilized in the development of biobased vinyl ester resins without the need of extensive and costly separations, a methacrylated lignin-based bio-oil mimic (MBO) was generated and utilized as a low viscosity vinyl ester resin (30.3 cP at 25 °C) and as a reactive diluent in a standard commercial vinyl ester resin. MBO was comprised of phenol, guaiacols, and catechols that were methacrylated by esterification with methacrylic anhydride and a catalytic amount of 4-dimethylaminopyridine. Curing the resin produced hard transparent thermosets that possessed near complete conversion of free radical polymerizable groups as per near-infrared spectroscopy. Temperatures of maximum decomposition rate (≥400 °C) and initial decomposition temperatures (≥300 °C) were measured by means of thermo-gravimetric analysis (TGA). Glass transition temperatures ≥115 °C and storage moduli ≥2.5 GPa at 25 °C were measured by dynamic mechanical analysis (DMA). Overall, high-performance lignin-based thermosets were synthesized possessing comparable thermo-gravimetric and thermo-mechanical properties to commercial petroleum- and vinyl ester-based thermosets.

KEYWORDS: Lignin, Renewable resources, Vinyl ester resin, Bio-oil, Styrene replacements/alternatives, Near-IR, TGA, DMA
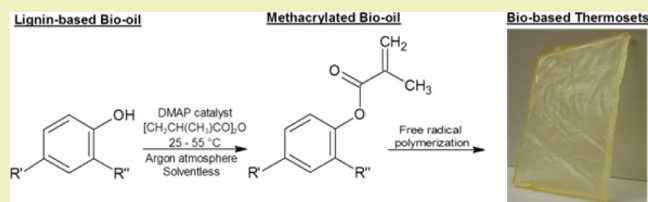
INTRODUCTION

With the uncertainty of petroleum reserves and future crude oil prices, lignocellulosic biomass is becoming an increasingly valuable resource for the sustainable production of both fuels and chemicals, including vinyl ester resins.[1,2] Petroleum-based vinyl ester (VE) resins are used to make polymer matrix composites in military and commercial applications due to their relatively high moduli, strength, and glass transition temperatures (T_gs), while maintaining low weight and cost.[3] To facilitate the use of liquid molding techniques to fabricate large scale composite parts, VE resins typically contain high concentrations (>40 wt %) of a petroleum-based reactive diluent.[4] However, the reactive diluents utilized, such as styrene (St), are oftentimes classified as hazardous air pollutants (HAPs), volatile organic compounds (VOCs), and anticipated carcinogens.[4,5] Thus, along with biobased VE resins, low viscosity, nonvolatile, renewable reactive diluents with similar performance to petroleum-based reactive diluents are being sought.

Recently, we have identified methacrylated lignin model compounds (MLMCs), namely, methacrylated versions of guaiacol and eugenol, as suitable biobased candidates to completely replace styrene as reactive diluents in liquid molding resins.[5] Lignin model compounds (LMCs) were chosen mainly due to their aromatic character. The incorporation of aromaticity in cured resins is known to provide structural rigidity (high modulus and strength) and thermal stability (high T_g) by inhibiting the rotational freedom of the polymer matrix. It is anticipated that these LMCs and others as well as a plethora of high-valued chemicals will be refined from lignin using processes that utilize techniques such as pyrolysis,[6−10] catalysis,[1,2,6,11−14] oxidation,[15,16] and fractionation[17,18] in next-generation lignocellulosic-based biorefineries. Lignocellulosic biomass typically contains roughly 15−30% lignin (nature's most abundant aromatic polymer) by weight.[19] However, only about 2% of the available lignin is used as low-value products with the remainder burned as a low-value fuel.[20] Additionally, a major bottleneck in the lignin-derived chemicals stream of future biorefineries is the separation of the individual chemicals from the anticipated lignin-based bio-oil. The aim of the work presented herein is to determine if lignin-based bio-oils can be utilized in the development of biobased VE resins without the need of extensive separations.

Jegers and Klein have reported that the pyrolysis of Kraft pine lignin (Indulin AT) at 400 °C for 7.5 min in a nitrogen atmosphere yielded a phenolic bio-oil comprised of phenols, cresols, xylenol, guaiacols, and catechols (11.43 wt % of starting lignin).[9] In this study, on the basis of weight percents and

structural characteristics, seven of the identified twenty possible phenolic compounds by Jegers and Klein[9] (83.56 wt % of the phenolic bio-oil) were chosen, methacrylated, and blended in order to generate a representative methacrylated lignin-based bio-oil mimic (Figure 1 and Table 1). The resulting
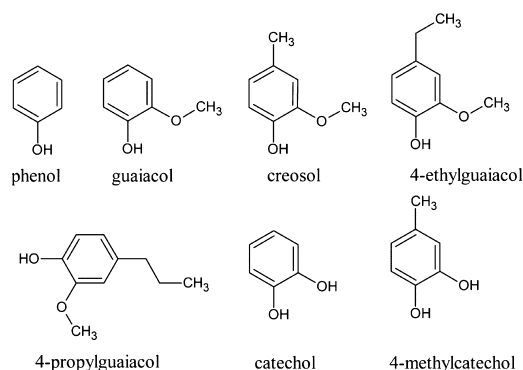

Figure 1. Chemical structures of the phenolic compounds utilized in the representative lignin-based bio-oil mimic.

Table 1. Weight Percents of Phenolic Compounds

	Jegers and Klein's pyrolysis product wt %[9a]	phenolic bio-oil wt %[9b]	phenolic bio-oil mimic wt %	methacrylated phenolic bio-oil mimic wt %[c]
phenol	0.13	1.14	1.36	1.42
guaiacol	2.6	22.75	27.23	25.50
4-methylguaiacol	2.6	22.75	27.23	24.58
4-ethylguaiacol	1.2	10.50	12.57	11.00
4-propylguaiacol	0.82	7.17	8.59	7.32
catechol	1.1	9.62	11.52	15.58
4-methylcatechol	1.1	9.62	11.52	14.60

[a]Pyrolysis product weight percents from the 7.5 min pyrolysis of Kraft pine lignin at 400 °C in a N_2 atm. [b]Total weight percent of phenolic bio-oil from the 7.5 min pyrolysis of Kraft pine lignin = 11.43 wt %. Of the 20 phenolics in the bio-oil, the listed seven (83.56 wt % of the phenolic bio-oil) were chosen to generate the representative lignin-based bio-oil mimic. [c]Weight percents after methacrylation.

methacrylated lignin-based bio-oil mimic is referred to as methacrylated bio-oil (MBO). Because four of the seven phenolics were already methacrylated in our lab with the remaining three desired to be individually methacrylated for other related studies, we decided to blend post-methacrylation. However, it is anticipated that lignin-based phenolic bio-oils can be methacrylated using traditional esterification techniques.[5] We report the synthesis of the methacrylated phenolics as well as the resin viscosities, extents of cure, and polymer properties of the MBO as a VE resin by itself and MBO as a reactive diluent (50 wt %) in a standard VE resin (bismethacryl glycidyl ether of bisphenol A, VE828). The resin viscosity, extent of cure, and polymer properties of VE828 with 50 wt % styrene are also reported for direct comparison.

■ EXPERIMENTAL SECTION

Materials. Phenol (99%), guaiacol (99+%), creosol (≥98%), 4-ethylguaiacol (≥98%), 4-propylguaiacol (≥99%), and 4-dimethylaminopyridine (DMAP, 99%) were obtained from Fisher Scientific and were used as received. Catechol (≥99%), 4-methylcatechol (≥95%), methacrylic anhydride (94%, inhibited with 2000 ppm Topanol A), methacrylic acid (99%, inhibited with 250 ppm monomethyl ether

hydroquinone), and styrene (≥99%, inhibited with 10−15 ppm 4-tert-butylcatechol) were purchase from Sigma Aldrich and used as received. Compressed argon was obtained from Keen Compressed Gas Co. (99.998%). AMC-2, which is a mixture of 50% trivalent organic chromium complexes and 50% phthlate esters, was purchased from AMPAC Fine Chemicals (Rancho Cordova, CA) and used as a catalyst in the methacrylation of diglycidyl ether of bisphenol A (Epon 828, Hexion Specialty Chemicals, Inc.). Trigonox 239 (AkzoNobel Polymer Chemicals), containing 45% cumene hydroperoxide, was purchased and utilized as a free radical initiator.

A vinyl ester cross-linking monomer was prepared as described in the literature.[3,4] Epon 828 was converted to the bismethacryl glycidyl ether of bisphenol A using standard literature procedures and is referred to as vinyl ester 828 (VE828). Characterization methods as described in La Scala et al. were performed with similar results.[4]

Preparation of Methacrylated Lignin-Based Bio-Oil Mimic. The chosen phenolics were methacrylated and purified, which included the removal of formed methacrylic acid, as described in the literature (Scheme 1).[5] The removal of methacrylic acid and

Scheme 1. Esterification Reaction Utilized To Methacrylate the Phenolic Compounds That Were Blended To Generate the Representative Lignin-Based Bio-Oil Mimic
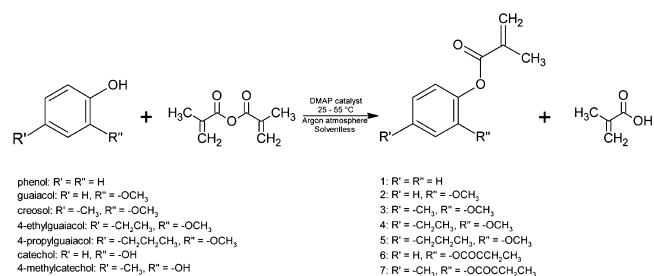
methacrylic anhydride from the phenolic products required numerous aqueous washes, including basic washes with sodium bicarbonate and sodium hydroxide, both of which resulted in the generation of sodium methacrylate.[5] However, there is potential to recover some of the methacrylic acid via proton exchange and subsequent solvent extraction. Industrially, there is potential to recover methacrylic acid via vacuum distillation. The MLMCs were then blended in appropriate ratios in accordance with the phenolic bio-oil data of Jegers and Klein[9] (Table 1).

Prior to blending, the MLMCs were characterized by means of ^1H NMR (400.13 MHz, 16 scans at 298.2K) and ^{13}C NMR spectroscopy (100.6 MHz, 32 scans at 298.2K) using a Bruker AV-400 spectrometer. The obtained spectra showed peaks in agreement with the expected chemical shifts. The MLMCs were also characterized by FTIR spectroscopy that was performed on a Perkin-Elmer Spectrum 400 FT-IR/FT-NIR Spectrometer. At room temperature, 16 cumulative scans were acquired with a resolution of 2 cm^{-1} in transmission mode in the mid-IR range.

Phenyl Methacrylate (PM). ^1H NMR (DMSO-d_6): δ 7.46− 7.15 (bm, 5H), 6.28 (t, 1H), 5.90 (t, 1H), 2.00 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 162.30, 150.61, 135.32, 129.54, 127.73, 125.88, 121.83, 18.08 ppm.

Methacrylated Guaiacol (MG) (2-Methoxyphenyl Methacrylate). ^1H NMR (DMSO-d_6): δ 7.28−6.95 (bm, 4H), 6.28 (s, 1H), 5.89 (t, 1H), 3.76 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 165.17, 151.38, 139.82, 135.49, 128.13, 127.42, 123.32, 121.03, 113.22, 56.15, 18.55 ppm.

Methacrylated Creosol (MC) (4-Methyl-2-methoxyphenol Methacrylate). ^1H NMR (DMSO-d_6): δ 6.98−6.74 (bm, 3H), 6.25 (s, 1H), 5.86 (t, 1H), 3.73 (s, 3H), 2.32 (s, 3H), 1.98 ppm (s, 3H). ^{13}C NMR (DMSO-d_6): δ 164.85, 150.52, 137.11, 136.46, 135.12, 127.51, 122.39, 120.39, 113.42, 55.60, 20.93, 18.12 ppm.

Methacrylated 4-Ethylguaiacol (MEG) (4-Ethyl-2-methoxyphenol Methacrylate). ^1H NMR (DMSO-d_6): δ 7.00−6.77 (bm, 3H), 6.24 (s,

1H), 5.86 (t, 1H), 3.74 (s, 3H), 2.6 (m, 2H), 1.98 (s, 3H), 1.20 ppm (t, 3H). ^{13}C NMR (DMSO- d_6): δ 164.87, 150.60, 142.83, 137.26, 135.11, 127.55, 122.45, 119.53, 112.34, 55.64, 28.13, 18.13, 15.66 ppm.

Methacrylated 4-Propylguaiacol (MPG) (4-Propyl-2-methoxyphenol Methacrylate). ^{1}H NMR (DMSO- d_6): δ 6.99−6.75 (bm, 3H), 6.25 (s, 1H), 5.86 (t, 1H), 3.74 (s, 3H), 2.55 (t, 2H), 1.60 (m, 2H), 0.91 ppm (t, 3H). ^{13}C NMR (DMSO- d_6): δ 164.83, 150.57, 141.23, 137.31, 135.12, 127.49, 122.34, 120.17, 112.76, 55.61, 37.21, 24.21, 18.11, 13.68 ppm.

Methacrylated Catechol (MCat) (Pyrocatechol Dimethacrylate). ^{1}H NMR (DMSO- d_6): δ 7.36 (s, 4H), 6.19 (s, 2H), 5.89 (t, 2H), 1.94 ppm (s, 6H). ^{13}C NMR (DMSO- d_6): δ 164.21, 142.08, 134.69, 128.18, 126.84, 123.60, 17.91 ppm.

Methacrylated 4-Methylcatechol (MMCat) (4-Methylpyrocatechol Dimethacrylate). ^{1}H NMR (DMSO- d_6): δ 7.23−7.13 (bm, 3H), 6.17 (s, 2H), 5.87 (m, 2H), 2.33 (s, 3H), 1.93 ppm (s, 6H). ^{13}C NMR (DMSO- d_6): δ 164.34, 164.24, 141.66, 139.71, 136.54, 134.76, 134.72, 128.05, 127.99, 127.16, 123.79, 123.09, 20.38, 17.92, 17.90 ppm.

Notable FTIR spectral peaks for all the MLMCs include the carbonyl wagging vibration, 1740 cm^{-1}, the terminal C═C wagging vibration, 1638 cm^{-1}, and the terminal C═CH$_2$ bending vibration, 946 cm^{-1}.

On the basis of the ^{1}H NMR spectra of the individual MLMCs and their respective mole percents in the MBO, the purity of the MBO was 85.8%. The impurities in the MBO include residual methacrylic anhydride (0.7%), methacrylated Topanol A (5.06%), methacrylic acid (1.02%), and unreacted LMCs (7.4%). In addition, according to the ^{1}H NMR spectra of MCat and MMCat, MCat and MMCat contain 8.37% and 8.69% monomethacrylated catechols, respectively. Despite the impurities, the MBO was used without further purification.

Monomer and Resin Viscosity. Monomer and resin viscosities were obtained on a TA Instruments ARES-G2 rheometer. Measurements were performed isothermally at 25 °C controlled by a Peltier plate (± 0.1 °C). A 20 mm 1° steel cone with a truncation gap of 25 μm and a minimum sample volume of 0.04 mL was utilized. The shear rate was increased stepwise from 1 s^{-1} to 100 s^{-1} collecting 21 data points to observe any non-Newtonian behavior. At a given shear rate, the shear stress was measured every two seconds. The shear rate and viscosity were recorded when the shear rate stabilized to within 5% tolerance for three consecutive points. Each monomer and resin was measured three times with the viscosities at 50.5 s^{-1} averaged and reported.

Resin Curing. MBO was free radically polymerized using Trigonox 239 (1.5 wt % of total resin mass) as the initiator with curing at 90 °C for 4 h and subsequent postcuring at 180 °C for 2 h. Polymerization was conducted in an argon atmosphere, whereby argon gas was purged through the oven for approximately 10 min at the beginning of cure. Prior to polymerization, MBO with initiator was degassed until no visible bubbles remained. After the 180 °C postcure for 2 h, the thermosets were allowed to cool to room temperature in the oven.

A VE828 resin containing 50 wt % MBO as the reactive diluent was prepared. Additionally, a VE828:St (50 wt % styrene) was blended for use as a standard equivalent to commercial resins for a direct comparison. The VE828 resins were polymerized in the same manner as the MBO resin with the VE828:St resin degassed for only a few minutes in order to prevent significant styrene loss.

Extent of Cure. In order to determine the overall extent of polymerization of the resins, near-infrared (near-IR) spectra of the uncured and post-cured resins were obtained on a Thermo Nicolet Nexus 870 Fourier transform infrared spectrometer in the 4000−7500 cm^{-1} range at room temperature. The near-IR spectra were acquired in absorbance mode with 64 scans at a 2 cm^{-1} resolution. The liquid or cured resin (typical thickness of 3 mm) was contained in a 3.5 mm thick glass cell (glass slides 0.25 mm thick each). The extent of cure was calculated by measuring the absorbance intensities of the styrenic vinyl (6135 cm^{-1}) and methacrylate (6165 cm^{-1}) double bonds before and after curing relative to internal standards, i.e., peaks of groups that are not affected by the reaction.[21−24] For the VE828:St resin, the peak associated with the vinyl bond of styrene is superimposed with the peak associated with the methacrylate double bonds of VE828. For the

purposes of this study, the total vinyl and methacrylate (6135−6165 cm^{-1}) bands were taken into account for a global conversion calculation. It is noted that the actual overall conversion of double bonds depends on the relative molar absorptivity of the two components. The molar absorptivity ratio of vinyl to methacrylate groups was assumed to be unity as a first approximation for the 1:1 VE828:St resin. The following equations were used to calculate the overall extents of cure for the MBO and VE828:MBO resins and VE828-St resin, respectively:

$$X = \frac{(\text{ABS}_{6165\text{cm}^{-1}}/\text{ABS}_{\text{ref}})_{\text{unreacted}} - (\text{ABS}_{6165\text{cm}^{-1}}/\text{ABS}_{\text{ref}})_{\text{reacted}}}{(\text{ABS}_{6165\text{cm}^{-1}}/\text{ABS}_{\text{ref}})_{\text{unreacted}}} \quad (1)$$

$$X = \frac{(\text{ABS}_{6135-6165\text{cm}^{-1}}/\text{ABS}_{\text{ref}})_{\text{unreacted}} - (\text{ABS}_{6135-6165\text{cm}^{-1}}/\text{ABS}_{\text{ref}})_{\text{reacted}}}{(\text{ABS}_{6135-6165\text{cm}^{-1}}/\text{ABS}_{\text{ref}})_{\text{unreacted}}} \quad (2)$$

The peak associated with phenyl groups (4623 cm^{-1}) was chosen as the internal standard.

Polymer Properties. Thermo-gravimetric behavior of the thermosets was measured using a TA Instruments Q500 Thermogravimetric Analyzer (TGA). Approximately 10 mg of sample was placed in a platinum pan and heated to 650 °C at 10 °C min^{-1} in a N$_2$ atmosphere (40 mL min^{-1} balance gas flow rate and 60 mL min^{-1} sample gas flow rate).

Thermo-mechanical properties of the thermosets were measured using dynamic mechanical analysis (DMA). Rectangular samples with approximate dimensions of 35 mm × 12 mm × 3 mm were tested using a TA Instruments Q800 DMA in single cantilever geometry. The samples were tested at 1 Hz with a deflection of 7.5 μm while ramping the temperature from 0 to 250 °C at a rate of 2 °C/min. The point at which the modulus in the rubbery plateau began to increase with increasing temperature was used to calculate the number average molecular weight between cross-links, M_C. M_C was estimated using the theory of rubber elasticity and the polymer density (measured using Archimedes' principle):

$$E = \frac{3RT\rho}{M_C} \quad (3)$$

where E is the rubbery modulus, R is the ideal gas constant, T is the absolute temperature, and ρ is the sample density.[4,25,26]

■ RESULTS AND DISCUSSION

Resin Characterization. MBO was a pale yellow transparent liquid that exhibited Newtonian behavior with a viscosity of 30.3 ± 1.0 cP at 25 °C (Table 2); a viscosity that is lower

Table 2. Average Molecular Weights and Absolute Viscosities of Styrene, MBO, and VE828 Resins[a]

resin/monomer	M_{av} (g mol^{-1})	viscosity at 25 °C (cP)
styrene	104.2	0.7 ± 0.05
MBO	216.8	30.3 ± 1.0
1:1 VE828:St	309.4	16.4 ± 1.7
1:1 VE828MBO	174.6	1593 ± 10

[a]M_{av} (molecular weight) values for the MBO and 1:1 VE828:MBO were calculated taken into account the impurities present in the MBO.

than the recommended lower limit for conventional resin transfer molding techniques but, nevertheless, a viscosity that is usable.[19] Additionally, the low viscosity allows for potential resin blending with other higher viscosity, biobased cross-linkers, such as acrylated epoxidized soybean oil (AESO) and maleinated acrylated epoxidized soybean oil (MAESO), as well as commercially available petroleum-based vinyl esters, such as bismethacryl glycidyl ether of bisphenol A (vinyl ester 828,

VE828).[4,19] Blending gives rise to the possibility of producing highly biobased thermosets that possess a wide range of tailorable properties. Furthermore, on the basis of our previous work on the volatilities of MLMCs relative to that of styrene, the MLMCs in MBO are anticipated to have considerably lower volatilities than styrene and a potential to be classified as non-VOCs and non-HAPs.[5]

Intrinsically, MBO contains 23.5 mol % cross-linking monomers. Specifically, the cross-linking monomers are methacrylated catechol and methacrylated 4-methylcatechol (6 and 7 in Scheme 1, respectively). Thus, cured MBO by itself will produce a highly biobased thermoset that could be used as a matrix in polymer composites. Additionally, because of the viscosity of MBO being only 2 orders of magnitude higher than that of styrene (0.7 cP at 25 °C) and to elucidate the ability of MBO to replace petroleum-based reactive diluents, MBO was blended (50 wt %) with a standard vinyl ester resin, VE828. Both VE828-based resins were Newtonian fluids with viscosities of 1593 ± 10 cP and 16.4 ± 1.7 cP at 25 °C for the VE828:MBO blend and VE828:St blend, respectively (Table 2).

The higher viscosity of the neat MBO compared to that of styrene is attributed to the presence of bulkier substituent groups on the phenyl rings of the MLMCs, such as methacrylate, and methoxy, methyl, ethyl, and/or propyl groups, relative to just the vinyl group on styrene. These bulkier substituent groups add molecular weight to the phenyl rings (Table 2) and, in turn, increase intermolecular interactions as van der Waals attractions are proportional to molecular weight.[3] Additionally, the bulkier substituent groups generate hindrances with regards to the ability of the molecules to easily flow passed each other, thereby, increasing the shear stress upon deformation which increases viscosity.[27]

The 1:1 VE828:MBO resin has a considerably higher viscosity than the 1:1 VE828:St resin with the viscosity decreasing with decreasing molecular weight of the reactive diluent. Similar to the 2 orders of magnitude difference between styrene monomer and MBO resin, the 1:1 VE828:MBO resin has a 2 orders of magnitude higher viscosity than the 1:1 VE828:St resin. VE828 is considered a slightly polar vinyl ester monomer due to the presence of hydroxyl groups (a minimum of two hydroxyls and a maximum of three hydroxyls per molecule).[3] In the uncured resin state, styrene is a nonpolar molecule that essentially acts as a solvent and increases the degrees of freedom and decreases the intermolecular interactions among the larger VE828 monomers.[3] On the other hand, despite MBO also acting as a solvent, MBO contains ester groups that are capable of forming hydroxyl–ester hydrogen bonds with VE828, which must be broken and reformed in order for the molecules to slide past each other. Similar behavior has been observed and shown to increase resin viscosity of other vinyl ester resin systems that contained methacrylic-based reactive diluents.[4] Typically, room-temperature liquid molding techniques used for composite layups have viscosity requirements in the range of 50−1000 cP at 25 °C in order to facilitate optimal molding and ease of construction. The 1:1 VE828:MBO resin has a viscosity slightly higher than the upper limit requirement for conventional resin transfer molding techniques. However, 1:1 VE828:MBO is still considered a highly serviceable alternative, especially if transferring is carried out at a slightly higher temperature as viscosity of most chemical species decreases exponentially with temperature.[28]

Extent of Cure. Figure 2 shows the near-IR spectra of the MBO resin and its free radically cured polymer. The absorption
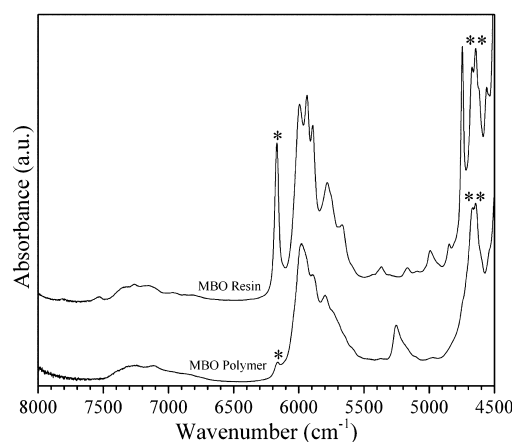

Figure 2. Near-IR spectra of MBO resin and polymer as representative uncured and cured near-IR spectra. Absorptions associated with methacrylate =C−H and internal phenyl C−H bonds are highlighted (∗) and (∗∗) at 6165 and 4623 cm^{-1}, respectively. Spectra are vertically offset for clarity.

bands associated with the methacrylate =C−H at 6165 cm^{-1} in the first overtone region and the phenyl groups at 4623 cm^{-1} in the combination region are highlighted ∗ and ∗∗, respectively. It is noted that the methacrylate =C−H also contains an absorption band at 4743 cm^{-1} in the combination region; however, reliable absorption intensity measurements were difficult to make due to the sharp baseline drop in the vicinity of the band. As shown in Figure 2 and relative to the internal standard, the absorption intensity for the methacrylate =C−H located at 6165 cm^{-1} for the MBO polymer decreased considerably compared to that of the resin.[23] The extent of cure for MBO was calculated to be 92.9 ± 0.8% (Table 3). Similar

Table 3. Extent of Cure of Thermosets as Measured by Near-IR

system	extent of cure (%)
MBO	92.9 ± 0.8
1:1 VE828:MBO	93.5 ± 0.2
1:1 VE828:St	98.9 ± 0.0

near-IR spectra to those illustrated in Figure 2 were obtained for the uncured and cured VE828 resins. The extents of cure were calculated to be 93.5 ± 0.2% and 98.9 ± 0.01% for the 1:1 VE828:MBO and 1:1 VE828:St resins, respectively. Both MBO and 1:1 VE828:MBO have lower extents of cure than 1:1 VE828:St. This is attributed to the inherent low reactivity of methacrylate groups with themselves relative to the vinyl group of styrene and to the continuing polymerization of styrene even after vinyl ester polymerization has ceased, which is a result of styrene's high mobility (i.e., low molecular weight and compact size) in a gelled resin.[4,29] It is worth noting that the extents of cure calculated from the near-IR data are higher than those that are typically reported for vinyl ester resin systems (60 to 90%; values dependent upon factors such as monomer molecular structures, resin composition, and cure times and temperatures).[4,23,29−31] Currently, in situ FTIR cure kinetics studies are being conducted in order to confirm the extents of cure obtained via near-IR.

Polymer Properties. After curing, the MBO, 1:1 VE828:MBO, and 1:1 VE828:St resins became hard polymers with qualitatively similar transparencies. The MBO polymer possessed a light yellow hue, while the VE828 polymers possessed green hues. The yellow hue of the MBO polymer is a result of the initiator utilized (Trigonox 239 is yellow in color) and the resin impurities. The green hue of the VE828 polymers is attributed to the catalyst used in order to synthesize the VE828 monomer. With achieving higher purity MBO resin and shifting to a colorless initiator and catalyst, there is potential to generate these high-performance thermosets with desired optical properties. Excluding initiator content, the biobased contents (calculation based on the amount of biobased carbon, oxygen, and hydrogen as a percent of moles of total organic product) of the MBO and 1:1 VE828:MBO cured resins were estimated to be 57.4% and 41%, respectively, with the 1:1 VE828:St containing no biobased content.

Figure 3 shows the TGA thermograms and derivative of the thermograms of the cured resins. From the TGA data, thermal
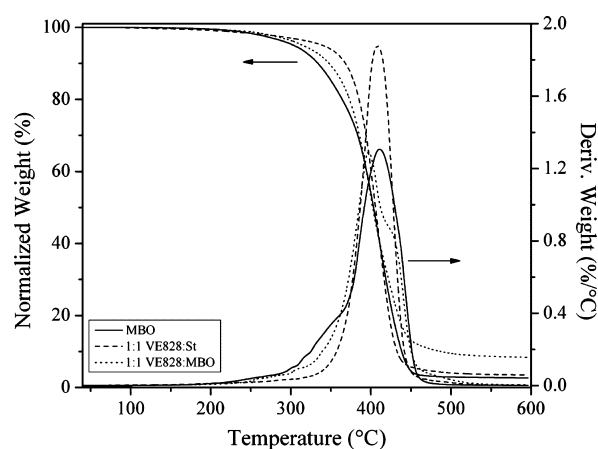

Figure 3. TGA normalized weight (left *y*-axis) and the derivative of the weight (right *y*-axis) as a function of temperature.

stability factors, including the initial decomposition temperature (5% weight loss), IDT, temperature of 50% weight loss, $T_{50\%}$, and temperature of maximum decomposition rate, T_{max} (tallest peak of the thermogram derivative), were determined and are provided in Table 4. Typical, commercially cured vinyl

Table 4. Thermo-Gravimetric Properties of MBO, 1:1 VE828:MBO, and VE828:St Thermosets

system	IDT (°C)	$T_{50\%}$ (°C)	T_{max} (°C)
MBO	306 ± 3	408 ± 7	418 ± 10
1:1 VE828:MBO	315 ± 1	409 ± 9	403 ± 8
1:1 VE828:St[a]	340	406	408

[a]Based on one TGA experiment.

ester resins possess T_{max}s and $T_{50\%}$s ≥400 °C.[32,33] The results show that the 1:1 VE828:St, which was our standard equivalent to a commercial resin, does possess a T_{max} and a $T_{50\%}$ greater than 400 °C. Additionally, the results show that the MBO and 1:1 VE828:MBO polymers are thermally stable up to roughly 300 °C with T_{max}s and $T_{50\%}$s > 400 °C. On the basis of the IDTs, the 1:1 VE828:St cured resin is more stable than the 1:1 VE828:MBO and MBO cured resins, while the 1:1 VE828:MBO resin is slightly more stable than MBO. In

relating the IDTs to the extents of cure and MBO content, a clear trend of increasing IDT with increasing extent of cure and decreasing MBO content is observed. With increasing MBO content, there is an increase in unreacted LMCs content. The unreacted LMCs are unbound to the polymer network and, thus, are able to volatilize and/or decompose more readily with increasing temperature. On the basis of these observations, the initial stage of the thermal decomposition, between 300 and 365 °C, which includes the IDTs, is believed to be mainly due to depolymerization initiated at unsaturated chain ends and unreacted LMCs decomposing and/or evolving from the polymers.[34]

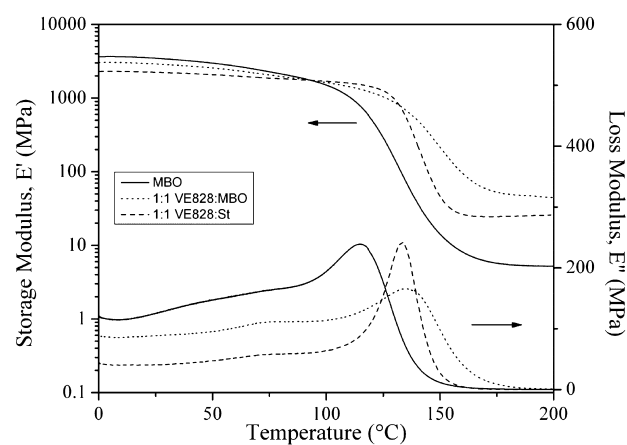Thermo-mechanical properties of the polymers were measured using DMA and are shown in Figure 4, where the

Figure 4. Storage moduli (*E′*) and loss moduli (*E″*) as a function of temperature.

storage moduli (*E′*) and loss moduli (*E″*) are plotted as a function of temperature. The stiffness of a viscoelastic material is represented by *E′* and is proportional to the energy stored during a loading cycle, while the tan *δ*, also known as the damping factor or loss tangent, is the ratio of *E″* to *E′*, where *E″* represents the energy lost as heat during a loading cycle.[35,36] Typical, commercially cured styrene-diluted vinyl ester resins possess *E′* values ≥ 2.0 GPa at 25 °C.[3,4,29,37] *E′* at 25 °C for 1:1 VE828:St was measured to be 2.2 ± 0.1 GPa (Table 5), which is in agreement with typical commercially cured styrene-diluted vinyl ester resins, while MBO and 1:1 VE828:MBO were measured to have slightly higher *E′* values at 25 °C (Table 5).

Referring to Figure 4 and Table 5, the rubbery *E′* for the MBO, 1:1 VE828:MBO, and 1:1 VE828:St thermosets were ~5.0, 40, and 25 MPa, respectively. Using the theory of rubber elasticity with the measured polymer densities, the M_C values for the MBO, 1:1 VE828:MBO, and 1:1 VE828:St were calculated to be ~2900, 360, and 520 g mol^{-1}, respectively. The MBO and 1:1 VE828:MBO polymer densities are believed to be higher than the 1:1 VE828:St polymer density due to MBO consisting of a mixture of monomers that have higher molecular weights than styrene and possess substituent groups that are capable of increasing van der Waals interactions among polymer components and that are capable of hydrogen bonding with the hydroxyl groups of VE828. Additionally, when cured, MBO contains cross-linkers that, when correctly connected to the polymer network, should result in tighter cross-linked networks (higher densities) compared to those that contain styrene. Flory's model was used to predict the expected M_C

Table 5. Thermo-Mechanical Properties of MBO, 1:1 VE828:MBO, and 1:1 VE828:St Thermosets

system	E' at 25 °C (GPa)	$E'(T)$ inflection (°C)	peak of E'' (°C)	peak of tan δ (°C)	rubbery E' (MPa)	rubbery T (°C)	M_C (g mol^{-1})	polymer density at 25 °C (g cm^{-3})
MBO	3.2 ± 0.3	116 ± 1.7	115 ± 0.3	140 ± 0.1	5.0 ± 0.4	200 ± 23	2882 ± 11	1.219 ± 0.001
1:1 VE828:MBO	2.8 ± 0.1	135 ± 0.4	135 ± 0.1	154 ± 0.7	40.0 ± 8.0	196 ± 14	358 ± 3.0	1.220 ± 0.001
1:1 VE828:St	2.2 ± 0.1	133 ± 0.1	134 ± 0.2	145 ± 0.4	24.9 ± 0.2	183 ± 3.5	519 ± 0.2	1.136 ± 0.001

values based on monomer types (monofunctional or difunctional), monomer mole fractions, resin number average molecular weight, and overall extent of cure.[38] The expected M_C values were 328 g mol^{-1} for MBO, 242 g mol^{-1} for 1:1 VE828:MBO, and 364 g mol^{-1} for 1:1 VE828:St. The fact that MCat and MMCat contained monomethacrylated catechol was taken into account in the expected M_C calculations. All experimentally determined M_C values are higher than those that were expected. Much of this is due to the fact that the Flory model was derived for lightly cross-linked elastomers and does not provide highly accurate predictions for a rigid thermosetting system without correction factors.[27] Furthermore, Flory's model assumes that all functional groups of the same type are equally reactive, that no intramolecular cyclizations occur in finite species, and that all groups react independently of each other.[38] The reactivities of VE828 and styrene have been shown to be different under roughly the same curing reaction conditions as was used in this work.[29,39] Additionally, due to styrene's mobility in a gelled resin, especially during post-curing, continued polymerization of styrene with itself may occur resulting in unpredicted long, linear chains of styrene, which in turn result in a higher than expected M_C. Because MBO and 1:1 VE828:MBO contain only methacrylates as the reactive species in free radical polymerization, equal reactivity of all functional groups is a valid first approximation, although we are currently performing in situ cure kinetics studies to validate this assumption. Methacrylated catechol (6 in Scheme 1) and methacrylated 4-methylcatechol (7 in Scheme 1) possess methacrylates that are *ortho* to each other that may result in the formation of intramolecular cyclizations during polymerization. VE828 cross-linkers have large methacrylate spacings and stiff bisphenol A cores that greatly reduce the probability of intramolecular cyclization. Thus, larger deviations in M_C from those predicted via the Flory model for MBO-based cured resins are expected due to the potential for intramolecular MBO cyclizations. Additionally, MBO and 1:1 VE828:MBO incompletely cured, resulting in chains that are not completely connected to the polymer network and/or residual unreacted monomer both of which result in increasing the apparent M_C. Interesting to note is that despite 1:1 VE828:MBO not reacting as completely as 1:1 VE828:St, there was enough of a cross-linking concentration difference between the systems (1:1 VE828:MBO contained 45 mol % cross-linkers; 1:1 VE828:St contained 16 mol % cross-linkers) and potentially enough hydroxyl-ester hydrogen bonding occurring in the 1:1 VE828:MBO at ~200 °C to result in a lower measured M_C.

Typical, commercially cured styrene-diluted vinyl ester resins possess T_gs ≥ 120 °C.[3,4,29,37] The temperature at which the peak of E'' occurs is indicative of the T_g and generally matches the temperature of the inflection point of $E'(T)$ (as in the case of the thermosets presented herein; Table 5).[26,40] Alternatively, the temperature at which the peak of the tan δ occurs has been considered the T_g for many samples, but in general, this occurs at higher temperatures relative to the inflection point of the

$E'(T)$ curve and at temperatures at which most samples are rubbery (Figure 5 and Table 5). Thus, for these reasons and to
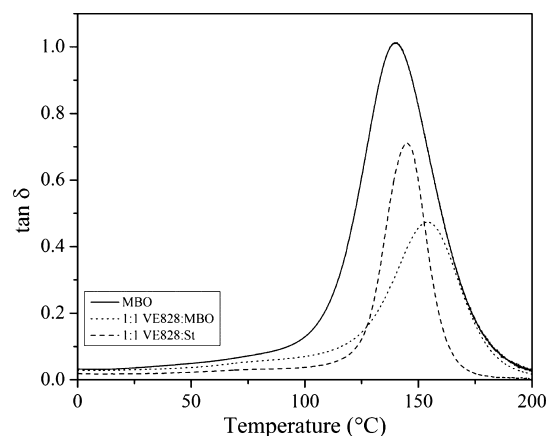
Figure 5. tan δ as a function temperature.

rely on a more conservative value, we define the T_g as the temperature at which the E'' peak occurs. According to the E'' peak, the T_g of MBO by itself was 115 °C. Polystyrene (PS) and poly(methyl methacrylate) (PMMA) are reported to have relatively high T_g values of 100 and 104 °C, respectively.[25] As anticipated, the T_g of MBO was close to that of PS and PMMA but was higher due to the formation of cross-links, which according to a new theory of the glass transition entitled the twinkling fractal theory (TFT), provides enhanced structural rigidity that rapidly slows down the twinkling fractal dynamics and, thus, increases the onset temperature of vector percolation of solid fractal clusters and fractal cavitation upon cooling.[41−43] However, because MBO contains 7.4% unreacted LMCs that act as plasticizers, the T_g of a purer MBO cured resin is anticipated to be higher. Because of the significantly higher mole fraction of cross-linkers in 1:1 VE828:MBO (45 mol %) compared to 1:1 VE828:St (16 mol %) and the ability of the MLMCs of MBO to hydrogen bond with the hydroxyls of VE828 resulting in an increase in rigidity, the T_g of 1:1 VE828:MBO was anticipated to be higher than that of 1:1 VE828:St. However, the T_g values of both VE828 polymers were ~135 °C (Figure 4 and Table 5). The T_g of 1:1 VE828:MBO is believed to be lower than expected due to the incomplete cure (93.5% as per near-IR), presence of unreacted LMCs that act as plasticizers, and potential intramolecular cyclizations, which increased M_C, reduced structural rigidity, increased the twinkling fractal dynamics, and decreased the onset temperature of vector percolation.

The width of the tan δ peak reflects polymer network heterogeneity with a broader peak implying a more heterogeneous polymer.[36] According to the 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.[41,42] In Figure 5, where the tan δ

values of the polymers are plotted as a function of temperature, the tan δ peak width of 1:1 VE828:St is considered a relatively narrow peak indicating the formation of a rather homogeneous polymer network that contains a focused distribution of relaxation modes and twinkling solid fractal clusters. On the other hand, the tan δ widths of MBO and 1:1 VE828:MBO are considered relatively broad, indicating the formation of rather heterogeneous polymer networks that contain a broad distribution of relaxation modes and twinkling solid fractal clusters. This was expected as MBO is a mixture of MLMCs of varying molecular weights and structures that results in a random mixture of pendant side groups when free radically polymerized, which increases the heterogeneity of the polymer networks formed.

The extent of polymer chain segmental mobility at the maximum tan δ peak intensity is reflected by the intensity value with higher values indicating higher energy loss and more viscous behavior, whereas lower values indicate higher elastic behavior.[36] The maximum tan δ peak intensity values (Figure 5) correlate well with the experimentally determined M_C values (Table 5), whereby tan δ peak intensity values increased with increasing M_C. Thus, the MBO exhibited a more viscous behavior indicative of a less cross-linked polymer network, while the VE828-based polymers exhibited more elastic behavior indicative of highly cross-linked polymers. For the 1:1 VE828:MBO, the viscous behavior may be further restricted and the elastic behavior enhanced by the ability of the polymer chains to hydrogen bond with each other, which may influence the relaxation dynamics of polymer and the ability of the solid fractal clusters to transition into the liquid upon heating.[41,42,44]

CONCLUSION

In this work, a methacrylated lignin-based bio-oil mimic (MBO) was generated that consisted of methacrylated versions of phenol, guaiacols, and catechols blended in appropriate ratios in accordance with the phenolic bio-oil data of Jegers and Klein.[9] Innately, MBO contained 23.5 mol % of cross-linking agents; therefore, it was cured by itself as a vinyl ester resin. Additionally, because of its low viscosity, the MBO was utilized as a biobased candidate to completely replace styrene as a reactive diluent in a standard vinyl ester resin (VE828). The VE828–MBO resin blend possessed a viscosity that was slightly higher than what was desired for typical liquid molding applications; however, it was considered still highly usable, especially since VOC/HAP components and emissions were eliminated. Curing the resin generated hard transparent thermosets that possessed near complete conversion and thermo-gravimetric and thermo-mechanical properties that were comparable to those of a standard equivalent of a commercial vinyl ester resin. Overall, this work has proved that lignin-based bio-oils can be utilized in the development of biobased vinyl ester resins without the need of extensive separations. Although this work focused on one lignin-based bio-oil with a specific composition, the ability to tailor lignin-based bio-oil compositions to achieve desired polymer properties is highly anticipated with advancements in lignocellulosic biorefinery technology.

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Notes
The authors declare no competing financial interest.

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