# Lignin Model Compounds as Bio-Based Reactive Diluents for Liquid Molding Resins

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Lignin is a copious paper and pulping waste product that has the potential to yield valuable, low molecular weight, single aromatic chemicals when strategically depolymerized. The single aromatic lignin model compounds, vanillin, guaiacol, and eugenol, were methacrylated by esterification with methacrylic anhydride and a catalytic amount of 4-dimethylaminopyridine. Methacrylated guaiacol (MG) and methacrylated eugenol (ME) exhibited low viscosities at room temperature (MG: 17 cP and ME: 28 cP). When used as reactive diluents in vinyl ester resins, they produced resin viscosities higher than that of vinyl esterstyrene blends. The relative volatilities of MG (1.05 wt% loss in 18 h) and ME (0.96 wt% loss in 18 h) measured by means of thermogravimetric analysis (TGA) were considerably lower than that of styrene (93.7 wt% loss in 3 h) indicating the potential of these chemicals to be environmentally friendly reactive diluents. Bulk polymerization of MG and ME generated homopolymers with glass transition temperatures ( $T_{g}$ s) of 92 and 103 °C, respectively. Blends of a standard vinyl ester resin with MG and ME (50 wt% reactive diluent) produced thermosets with  $T_{g}$ s of 127 and 153 °C, respectively, which are comparable to vinyl ester–styrene resins, thus demonstrating the ability of MG and ME to completely replace styrene as reactive diluents in liquid molding resins without sacrificing cured-resin thermal performance.

#### Introduction

Vinyl ester resins are used to produce polymer composites for commercial applications because they have relatively high moduli, strength, and glass transition temperatures ( $T_{\alpha}s$ ) while maintaining low weight and cost.<sup>[1,2]</sup> To facilitate the use of liquid molding techniques to fabricate large scale composite parts, commercial vinyl ester resins typically contain high concentrations (>40 wt%) of a reactive diluent such as styrene (St). In addition to lowering the resin viscosity, styrene is a linear chain extender. This improves the overall polymer performance by increasing the monomeric reactivity by delaying the onset of gelation and reducing diffusion limitations.<sup>[2]</sup> However, styrene has been designated a hazardous air pollutant and a volatile organic compound (VOC).<sup>[3]</sup> In 2003, with an amendment in 2005, the Federal Environmental Protection Agency (EPA) of the United States of America introduced legislation to limit styrene emissions from composite manufacturing.<sup>[1,3,4]</sup> More recently, in June 2011, the USA's Department of Health and Human Services through the National Toxicology Program in their 12<sup>th</sup> Report on Carcinogens has designated styrene as "reasonably anticipated to be a human carcinogen".<sup>[5]</sup> Moreover, not only is styrene emitted during metering, mixing, processing, and curing, but also studies have shown that up to 40% of styrene can remain unreacted after curing and continues to be released from composites during the remaining phases of their life cycle if they are not subjected to post-curing.<sup>[6]</sup> With this significant drawback, new resins are required for the continued use of polymer composites. Therefore, the development of nonvolatile reactive diluents with styrene-like performance is gaining increasing interest. Additionally, with the continued volatility of the petroleum industry and crude oil price fluctuations, the cost of styrene will eventually become a factor in the production of future resins if a suitable bio-based replacement is not identified. These significant factors give impetus for the discovery and development of renewable, bio-based reactive diluents that have styrene-like performance with minimal VOC emissions.

Previous work by La Scala et al., in conjunction with the Affordable Composites from Renewable Resources (ACRES) program at the University of Delaware, has demonstrated the potential of using methacrylated fatty acids (MFAs) as styrene replacements. These include methacrylated lauric acid (MLau), methacrylated hexanoic acid (MHex) and methacrylated octanoic acid (MOct) as styrene reducers in vinyl ester-, soybean-, and castor oil-based polymer resins.<sup>[1,7-9]</sup> These renewable, naturally occurring, methacrylated plant oil derivatives exhibit low volatilities, low viscosities (40–80 cP at 30  $^\circ$ C), and can act as acceptable chain extenders. These functionalized plant oil derivatives can also toughen polymers through their flexible, long alkyl side chains. Despite these benefits, styrene was still needed at a reduced concentration to produce cured biobased resins with thermal and mechanical performance comparable to cured, commercial vinyl ester-styrene resins.<sup>[1,7]</sup> Thus, lower viscosity, nonvolatile, renewable reactive diluents

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with styrene-like performance are still being sought, particularly reactive diluents that have similar  $T_{g}$ s to polystyrene when polymerized.

Lignin is a renewable, biobased alternative material rich in aromaticity with the capability of yielding single aromatic chemicals when selectively broken down. Lignin is abundantly available with over  $3 \times 10^{11}$  t existing in the biosphere with approximately 2×10<sup>10</sup> t generated annually and is the second most abundant natural raw material, surpassed only by cellulose.[10-12] As of 2004, the pulp and paper industry alone produced roughly 50×10<sup>6</sup> t per year of extracted lignin of which 95% was Kraft lignin.<sup>[12, 13]</sup> The Kraft process, invented in 1879 by Carl F. Dahl, is the treatment of wood chips with a mixture of sodium hydroxide and sodium sulfide, known as white liquor, which separates the lignin from celluhemicellulose.[12, 13] lose and However, only approximately 2% of the available lignin is used commercially with the remainder used as a low-value fuel to cover the internal energy needs of the pulp and paper industry.<sup>[14]</sup> Due to its very complex, 3D aromatic structure (Figure 1, top), lignin is largely intractable in its unmodified state and, therefore, is often sought to be broken down into



**Figure 1.** General chemical structure of lignin (top) with a schematic for its conversion into single aromatic chemicals (bottom).<sup>[16,19]</sup> Reprinted with kind permission from John Wiley & Sons (top) and Elsevier (bottom).

lower molecular weight aromatic components (Figure 1, bottom).

Non-degraded and chemically modified lignins have been successfully incorporated into various materials, including polymeric materials.<sup>[10,12,13,15–17]</sup> Additionally, a considerable amount of research has been conducted into selectively breaking down all types of lignin and multi-phenolic lignin model compounds (LMCs) to develop new chemicals and renewable sources of predominantly petroleum-derived chemicals.<sup>[11,14,16–24]</sup> Recently, a modest yield of vanillin (Figure 2) from Kraft lignin has been obtained using aqueous polyoxometalates in the presence of alcohols to oxidatively degrade lignin.<sup>[11]</sup> Additionally, vanillin production by Kraft lignin oxidation using a NaOH alkaline medium has been reported.<sup>[22]</sup> More-



methacrylated vanillin (MV) methacrylated guaiacol (MG) methacrylated eugenol (ME) Figure 2. Chemical structures of lignin model compounds, their derivatives, and styrene.

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over, a 70% yield of guaiacol has been achieved from the common  $\beta$ -O-4 LMCs, guaiacylglycerol- $\beta$ -guaiacyl and veratryl-glycerol- $\beta$ -guaiacyl ether, by catalytic hydrolysis using an acidic ionic liquid.<sup>[19]</sup> In 2011, Zakzeski and Weckhuysen reported 22.2 and 12% yields of guaiacol from aqueous phase reforming of a  $\beta$ -O-4 linked and a 5-5′ carbon–carbon-linked biphenyl model compound, respectively, using a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>[14]</sup> Lastly, Sergeev and Hartwig have reported yields as high as 99% of guaiacol from hydrogenolysis reactions of representative biphenyl LMCs.<sup>[24]</sup>

In the work presented herein, vanillin, guaiacol, and eugenol (Figure 2) were selected as representative LMCs for the synthesis of bio-based reactive diluents as styrene replacements in thermosetting polymers. Specifically, these LMCs were selected based on extensive studies and the potential to obtain these

chemicals in high yields from lignin, as well as from clove oil in the case of eugenol.  $^{\left[ 18,\,20,\,25\right] }$  To chemically incorporate the selected LMCs into vinyl ester resins, polymerizable carboncarbon double bonds need to be integrated onto the phenolic compounds. Methacrylated analogues of vanillin,<sup>[26,27]</sup> guaiacol,<sup>[28-31]</sup> eugenol<sup>[25, 32]</sup> and (Figure 2) have been reported in the literature, but, to date, have not been studied as styrene replacements in polymer resins. We report the synthesis, relative

4-dimethylaminopyridine (DMAP) has not been previously reported in the synthesis of phenyl methacrylates. However, methacrylations of lignins (essentially multi-phenolic macromolecules) have been performed by Thielemans and Wool by using 1-methylimidazole as the base catalyst with methacrylic anhydride as the coreactant.<sup>[34]</sup> Despite acryl anhydrides being less stable than acrylic acids, a significantly lower amount of catalyst is required than for the Steglich and acid-catalyzed esterifications. An alternative phenolic-methacrylation technique is a transesterification reaction involving methyl methacrylate catalyzed by *p*-toluenesulfonic acid with methanol, a classified green solvent,<sup>[35]</sup> as the byproduct. Currently, this reaction is being investigated as a potential scalable reaction to synthesize MLMCs. Scheme 1 depicts the synthetic route used to generate the MLMCs.



Scheme 1. Reaction of methacrylic anhydride with a lignin model compound to form a methacrylated lignin model compound monomer.

volatilities, viscosities, and polymer  $T_{g}$ s of the methacrylated lignin model compounds (MLMCs) as well as the viscosities and  $T_{g}$ s of vinyl ester resins (bismethacryl glycidyl ether of bisphenol A epoxy, VE828) copolymerized with 50 wt % MLMCs. The relative volatility of styrene and the viscosity and  $T_{g}$  of VE828 with 50 wt % styrene are also reported for direct comparison.

#### **Results and Discussion**

#### **Monomer properties**

Methacrylated versions of vanillin, guaiacol, and eugenol, which were synthesized by an acid catalyzed esterification, a Steglich esterification, or an esterification involving methacryloyl chloride, have been reported in the literature.<sup>[25–29,32]</sup> The major disadvantage of the Steglich esterification is the requirement of relatively large quantities of catalyst, 4-dimethylaminopyridine, and reagent, *N*,*N'*-dicyclohexylcarbodiimide (15.3 and 153 wt% of total reactant mass, respectively).<sup>[27]</sup> Similar to the Steglich esterification, the reported acid-catalyzed esterifications of hydroxyl groups with an acid may require relatively large quantities of catalyst.<sup>[33]</sup> Although the reactivity of acryloyl chloride is desirable, less desirable are the hazards associated with transporting and storing such unstable chemicals. The utilization of methacrylic anhydride with catalytic amounts of

Methacrylated guaiacol (MG) and methacrylated eugenol (ME) are low viscosity liquids at 25 °C. Methacrylated vanillin (MV) is a solid at 25 °C and was not used as a reactive diluent to replace styrene in this work. Average yields of  $85.5 \pm 4.5\%$ were obtained for the MLMC esterification reactions. The purities of the MLMCs were estimated to be >94% based on <sup>1</sup>H NMR spectra. The impurities are believed to arise from the methacrylic anhydride, which is typically sold with 94% purity. In the case of methacrylic anhydride, Topanol A, 2-tert-butyl-4,6-dimethylphenol, was used as the free radical inhibitor at a concentration of 2000 ppm. It is believed that, although the hydroxyl group of Topanol A is greatly hindered compared to the hydroxyl groups of the LMCs, Topanol A participated in the phenolic methacrylation reactions and was collected with the desired product. However, methacrylated Topanol A contributed to no more than 0.2 wt% of the impurities. Despite this, further purification was not pursued and, after concentration under reduced pressure, the desired product was used as collected.

To determine the volatilities of MG and ME relative to styrene, thermogravimetric analysis (TGA) evaporation studies were performed (Figure 3). Under the experimental conditions, styrene almost fully evaporated in about three hours at  $30^{\circ}$ C (only 6.3 wt% remained after three hours). Conversely, 99.04 and 98.95 wt% of ME and MG, respectively, remained after 18 h at  $30^{\circ}$ C (Figure 3, inset). This demonstrates that the



Figure 3. TGA normalized weight as a function of time for styrene, MG and ME at T = 30 °C. See inset for the MG and ME evaporation behavior. The maximum standard deviation among the styrene TGA experiments was  $\pm 0.17.$ 

MLMCs have a considerably lower volatility than styrene and a potential to be environmentally friendly and low VOC reactive diluents. The crossing of the MG and ME curves at roughly 600 min and other differences between the curves are within experimental error and not representative of the difference between the evaporation behavior of MG and ME. However, due to the structure and molecular weight similarities of MG and ME, the evaporation behavior of these MLMCs was anticipated to be similar.

To elucidate the ability of MG and ME to replace styrene as reactive diluents in resins, MG, ME, and styrene were blended (50 wt%) with a standard vinyl ester resin, VE828. The viscosities of these blends, as well as the neat viscosities of MG and ME, were evaluated. The results are shown in Table 1, where

Table 1. Viscosities of the neat MLMCs and VE828 resins. Styrene viscosity was obtained from literature (at 30 $^\circ$ C). $^{(1)}$	
System	Viscosity at 25 °C [cP]
MG	17.1±1.2
ME	$27.9 \pm 1.3$
St	0.7
1/1 VE828-MG	$937 \pm 10$
1/1 VE828-ME	1148±36
1/1 VE828–St	16.4±1.7

the viscosities at 25 °C are listed with standard deviations. Included in Table 1 is the viscosity of styrene at 30 °C as reported in the literature.<sup>[1]</sup> For all samples, the viscosities exhibited Newtonian behavior. The neat MG and ME monomers have higher viscosities than that of styrene (0.7 cP at 30 °C). This is attributed to the presence of bulkier substituent groups on the phenyl ring of the neat MLMC monomers relative to just the vinyl group on styrene as van der Waals attractions are proportional to molecular weight.[35] Accordingly, the neat ME monomer has a slightly higher viscosity than that of MG as

a result of the slightly higher molecular weight of the ME due to the allyl substituent. In addition, MG and ME have increased intermolecular attractions relative to styrene due to the presence of ester linkages.[36]

As seen in Table 1, the viscosities of each VE828-reactive diluent resin system decreased with reactive diluent molecular weight. The VE828-ME blend had a slightly higher viscosity than the VE828-MG blend, while both had significantly higher viscosities than the VE828-St blend. The observed order of magnitude higher viscosities of the VE828-MLMC resins compared to those of the VE828-St resin is attributed to the MLMC being able to hydrogen-bond with the hydroxyl groups of VE828 through the methacrylate group. Hydroxyl-ester hydrogen bonding has been shown to increase resin viscosity of similar vinyl ester resin systems that contained methacrylicbased reactive diluents.<sup>[1,2]</sup> However, resins containing 50 wt% MG and ME maintain viscosities amenable to molding applications.<sup>[12]</sup>

#### Polymer glass transition temperature

Polystyrene has a relatively high  $T_{g}$  ( $\approx 100 \,^{\circ}$ C).<sup>[37]</sup> The aromatic side chain of styrene is known to provide structural rigidity, thermal stability, limited "free volume", and brittleness through  $\pi$ -bond stacking. According to a new theory of the glass transition entitled the Twinkling Fractal Theory (TFT), the glassiness of polystyrene at room temperature is attributed to the rigid aromatic side chains rapidly slowing down the twinkling fractal dynamics and, thus, enhancing vector percolation of solid fractal clusters and ultimately fractal cavitation.<sup>[38, 39]</sup> The enhancement of vector percolation and fractal cavitation occurs despite a considerable amount of liquid-like clusters still existing, approximately 40% at 298 K.<sup>[38,39]</sup> The liquid-like clusters exhibit characteristics of "free volume", but due to the closeness of the aromatic side chains to the polymer backbone they lack the normal alkyl chain-like mobility. Thus, they contribute to the relatively high onset temperature of vector percolation,  $T_{cw}$ and fractal cavitation at  $T_{\rm q} = 100 \,^{\circ} \text{C}.^{[38-40]}$ 

The similarities between the MLMCs and styrene are evident through the aromatic ring and the presence of a reactive terminal carbon-carbon double bond. Additionally, it is interesting to note the similarities between the MLMCs and methyl methacrylate, which has a  $T_{\alpha}$  of approximately 104 °C when homopolymerized.<sup>[37]</sup> Despite the fact that there are alkyl substituents on the phenol groups that increase the bulkiness of polymer side chains, the MLMCs, when polymerized, are expected to possess  $T_{\alpha}s$  close to that of polystyrene (PS) and poly(methyl methacrylate) (PMMA) and exhibit twinkling dynamics similar to that of PS and PMMA.

Prior to methacrylation, eugenol contains a terminal allyl group in the para position relative to the hydroxyl group on the aromatic ring. However, eugenol itself is not easily polymerized due to the presence of a phenolic hydroxyl group, which acts as a free radical scavenger, and the allylic nature of the propene substituent group.<sup>[25,32]</sup> The reactivity of the allyl group of eugenol, which determines whether ME behaves as a monofunctional reactive diluent or as a cross-linker in vinyl ester resin systems, is currently under investigation.

The  $T_{g}$ s of poly(methacrylated guaiacol) (PMG), poly(methacrylated eugenol) (PME), and the cured vinyl ester resins were determined by means of differential scanning calorimetry (DSC). The DSC thermograms and the measured  $T_{g}$ s are shown in Figure 4. All of the  $T_{g}$ s of the VE828 cured resins are above



**Figure 4.** DSC thermograms of VE828 cured resins that contain 50 wt% of a reactive diluent along with DSC thermograms of PMG and PME. Thermograms are offset for clarity.

120 °C and the  $T_{g}$ s of PMG and PME are 92 and 103 °C, respectively. The 1:1 VE828–MG  $T_{g}$  is lower than the 1:1 VE828–St  $T_{g}$ , whereas the 1:1 VE828–ME  $T_{g}$  is higher than that of 1:1 VE828–St. Wesslén et al. reported a PMG (number average molecular weight,  $M_{n\nu} = 7600 \text{ g mol}^{-1}$ )  $T_{g}$  of 110 °C determined by means of DSC,<sup>[29]</sup> whereas Rojo et al. reported a low-conversion (<10 wt%) PME ( $M_{n}$ =8.1×10<sup>4</sup> g mol<sup>-1</sup>)  $T_{g}$  of 96 °C measured by DSC at a heating rate of 10 °C min<sup>-1,[32]</sup> PMG and PME were not soluble in THF indicating the preparation of high molecular weight polymers. Despite the discrepancies between the homopolymer  $T_{g}$ s reported in this paper and those reported previously, the facts that PMG and PME have similar  $T_{g}$ s to those of PS and PMMA and that the cured vinyl ester resins have similar  $T_{g}$ s to those that contain styrene are encouraging.

Glass transition broadness increased with reactive diluent molecular weight (styrene < MG < ME). This may be a result of an increased amount of relaxation modes present in the polymer, which according to TFT, arises when a broad distribution of solid fractal clusters twinkles into the liquid upon heating exists.<sup>[38-40]</sup> With increasing resin viscosity, molecular mobility is suppressed during cure leading to a greater chance of an irregular cross-linked network, and, in turn, a broader distribution of solid fractal clusters and relaxation dynamics. Unlike styrene, MG and ME contain methacrylate groups that are capable of hydrogen bonding with the hydroxyl groups of VE828. Hydrogen bonding may influence the relaxation dynamics of the cross-linked network and the ability of the solid fractal clusters to transition into the liquid. Furthermore, the irregularity of the cross-linked network may further increase due to the ability of ME to cross-link, which imparts a higher degree of rigidity and lowers molecular mobility during polymerization. Allylic monomer reactivity in the presence of methyl methacrylate has been reported to be four orders of magnitude lower than that of the comonomer.<sup>[41]</sup> Additionally, Rojo et al. have reported thermosetting-type behavior of PME, which is attributed to pendant allyl groups contributing to grafting and cross-linking when polymerization reaches high conversion.<sup>[25,32]</sup> Intentionally breaking PMG and PME specimens, PME exhibited greater qualitative brittleness compared to PMG indicating a potential degree of cross-linking. This is consistent with the fact that increased cross-linking is known to increase the breadth of the glass transition.<sup>[36]</sup> Currently, we are investigating the reactivity of the allyl group relative to the acrylic groups in the curing of vinyl ester resins by performing in situ FTIR cure kinetics studies.

#### Conclusions

In this work, lignin model compounds-vanillin, guaiacol, and eugenol-were methacrylated by esterification with methacrylic anhydride and a catalytic amount of DMAP. MG and ME, both low viscosity and nonvolatile liquids at 25 °C, were shown to be viable, bio-based candidates to completely replace styrene as reactive diluents in liquid molding resins. Bulk polymerizations of MG and ME generated polymers with  $T_{a}$ s very similar to those of polystyrene and poly(methyl methacrylate). Blends of a standard vinyl ester resin (VE828) with MG and ME produced thermosets with  $T_q$ s that were comparable to those of commercial vinyl ester-styrene based thermosets. Overall, both MG and ME were successfully utilized as low viscosity, nonvolatile reactive diluents in liquid molding resins with MG acting solely as a monofunctional monomer and ME acting as a monofunctional monomer with the potential ability to crosslink through the allyl group.

#### **Experimental Section**

#### Materials

Deuterated dimethyl sulfoxide ([D<sub>6</sub>]DMSO), 4-dimethylaminopyridine (DMAP), vanillin (99%), guaiacol (99 +%), and eugenol (99%) were purchased from Fisher Scientific and used as received. Methacrylic anhydride (94%, inhibited with 2000 ppm Topanol A), CDCl<sub>3</sub>, 2-butanone peroxide (MEKP), and styrene (inhibited with 10– 15 ppm 4-*tert*-butylcatechol) were purchased from Sigma Aldrich and used as received. Compressed argon was purchased from Keen Compressed Gas Co. (99.998%). Trigonox 239 (AkzoNobel Polymer Chemicals), containing 45% cumene hydroperoxide, was purchased and utilized as a free radical initiator.

The vinyl ester cross-linking monomer was prepared as described in the literature.<sup>[1,2]</sup> Epon 828 was converted to the bismethacryl glycidyl ether of bisphenol A epoxy (Hexion Specialty Chemicals, Inc.) using standard literature procedures and is referred to as vinyl ester 828 (VE828). Characterization methods as described by La Scala et al. were performed and similar results were obtained.<sup>[1]</sup>

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#### Synthesis of methacrylated lignin model compounds

#### To a 100 mL round-bottomed flask equipped with a magnetic stir bar, a catalytic amount of DMAP (2 mol% of methacrylic anhydride) was added to a lignin model compound (LMC, 20 g). Prior to adding methacrylic anhydride (1.2 LMC equivalents, adjustable to as low as 1.01), the flask was sealed and subsequently purged with argon gas for an hour to remove moisture and oxygen from the reaction vessel. For the first three hours with stirring, the reaction progressed at room temperature. The flask was placed in a 45 °C silicone oil bath for a minimum of 24 h. The reaction mixture was then cooled to room temperature and diluted with methylene chloride (150 mL, ethyl acetate was also used as a greener substitute). To remove unreacted methacrylic anhydride and methacrylic acid product, the organic phase was washed repeatedly with a saturated sodium bicarbonate aqueous solution (150 mL) until carbon dioxide no longer evolved. The organic phase was then washed with 1.0 M NaOH<sub>aq</sub> (150 mL), 0.5 M NaOH<sub>aq</sub> (150 mL), 1.0 MHCl<sub>aq</sub> (150 mL), and water (150 mL); dried over sodium sulfate; and then concentrated under reduced pressure.

Products were characterized by means of <sup>1</sup>H NMR (400.13 MHz, 16 scans at 298.2 K) and <sup>13</sup>C NMR spectroscopy (100.6 MHz, 32 scans at 298.2 K) by using a Bruker AV-400 spectrometer, and the spectra showed peaks in agreement with the expected chemical shifts. Additionally, the products were characterized by FTIR spectroscopy performed on a Perkin Elmer Spectrum 400 FT-IR/FT-NIR Spectrometer. At room temperature, 16 cumulative scans were acquired with a resolution of 4 cm<sup>-1</sup> in transmission mode in the mid-IR range.

Methacrylated vanillin (MV, 3-methoxy-4-methacryloyloxybenzaldehyde, mp = 55.4 °C; in agreement with literature values):<sup>[26,42]</sup> <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 9.98 (s, 1 H), 7.62–7.40 (bm, 7.62–7.40 (bm, 3 H), 6.30 (s, 1 H), 5.95 (t, 1 H), 3.86 (s, 3 H), 2.00 ppm (s, 3 H). <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 192.58, 164.74, 152.05, 144.76, 135.60, 135.07, 128.98, 124.28, 124.13, 112.32, 56.57, 18.50 ppm. Notable FTIR spectral peaks of MV: carbonyl wagging vibrations associated with the methacrylate and acetal groups,  $\tilde{\nu}$  = 1745 and 1702 cm<sup>-1</sup>, respectively; terminal C=C wagging vibration,  $\tilde{\nu}$  = 1636 cm<sup>-1</sup>; terminal C=CH<sub>2</sub> bending vibration,  $\tilde{\nu}$  = 947 cm<sup>-1</sup>.

Methacrylated guaiacol (MG, 2-methoxyphenyl methacrylate, mp =  $-59.9 \,^{\circ}C$ )<sup>[42]</sup>.<sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 7.28–6.95 (bm, 4H), 6.28 (s, 1H), 5.89 (t, 1H), 3.76 (s, 3H), 2.00 ppm (s, 3H). <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 165.17, 151.38, 139.82, 135.49, 128.13, 127.42, 123.32, 121.03, 113.22, 56.15, 18.55 ppm. Notable FTIR spectral peaks of MG: carbonyl wagging vibration,  $\tilde{\nu}$  = 1737 cm<sup>-1</sup>; terminal C=C wagging vibration,  $\tilde{\nu}$  = 1641 cm<sup>-1</sup>; terminal C=CH<sub>2</sub> bending vibration,  $\tilde{\nu}$  = 945 cm<sup>-1</sup>.

Methacrylated eugenol (ME, 4-allyl-2-methoxyphenyl methacrylate, mp =  $-58.2^{\circ}C$ ):<sup>[42]</sup> <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 7.03–6.76 (bm, 3 H), 6.25 (t, 1 H), 6.03–5.93 (bm, 1 H), 5.86 (t, 1 H), 5.14–5.05 (bm, 2 H), 3.73 (s, 3 H), 3.38 (d, 2 H), 1.98 ppm (s, 3 H). <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 165.27, 151.13, 139.29, 138, 137.91, 135.51, 128.08, 123.06, 120.73, 116.48, 113.32, 56.12, 39.96, 18.58 ppm. Notable FTIR spectral peaks of ME: carbonyl wagging vibration,  $\tilde{\nu}$  = 1741 cm<sup>-1</sup>; terminal C=C wagging vibrations associated with the methacrylate and allyl groups,  $\tilde{\nu}$  = 1638 cm<sup>-1</sup>; terminal C=CH<sub>2</sub> bending vibrations associated with the methacrylate and 916 cm<sup>-1</sup>, respectively.<sup>[25,32,43-45]</sup>

#### Monomer and resin viscosity

Monomer and resin viscosities were obtained by using a TA Instruments ARES-G2 rheometer. Measurements were performed isothermally at 25 °C controlled by a Peltier plate (+/- 0.1 °C error). A 20 mm 1° steel cone with a truncation gap of 25  $\mu$ m and a minimum sample volume of 0.04 mL was utilized. The shear rate was increased stepwise from 1 to 100 s<sup>-1</sup> and 21 data points were collected 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 viscosity was measured three times, and the viscosities at 50 s<sup>-1</sup> were averaged and reported.

#### Thermogravimetric evaporation study

The evaporation behavior of MG, ME, and styrene was measured by using a TA Instruments Q500 TGA. Approximately 50 mg of sample was placed in a platinum pan and held isothermally at  $30 \,^{\circ}$ C in a nitrogen atmosphere (40 mL min<sup>-1</sup> balance gas flow rate and 60 mL min<sup>-1</sup> sample gas flow rate). Evaporation studies of methacrylated LMCs (MLMCs) and styrene were performed for 18 and 3 h, respectively. Experiments were conducted three times to ensure reproducibility. The evaporation of MV was not measured as it is a solid at room temperature and we believe that the sublimation rate would be orders of magnitude lower than the evaporation rates of styrene, MG, and ME.

#### **Resin cure**

Homopolymers of MG, ME, polymerized MG (PMG) and ME (PME), were prepared by bulk polymerization by adding 1.5 wt% MEKP to the monomer with curing at 90 °C for 4 h and subsequent postcuring at 130 °C for two hours. Polymerizations were conducted in an argon atmosphere, whereby argon gas was purged through the oven for approximately 15 min at the beginning of cure. This purging technique was used for all subsequently described polymerizations. MV was not cured as it is a solid at standard temperature and pressure, thereby eliminating it as a reactive diluent candidate. However, curing of resins containing MV is currently under investigation.

VE828 resins containing 50 wt % MLMC monomers were prepared. VE828–St resin (50 wt % St) was blended for use as a standard equivalent to commercial resins. In an argon atmosphere, resins were cured at 90 °C using Trigonox 239 (1.5 wt % of the total resin mass) for 4 h and then post-cured at 180 °C for 2 h.

#### Polymer glass transition temperature

Thermo-physical behavior of PMG, PME, and the VE828 cured resins was measured by using differential scanning calorimetry (DSC). A TA Instruments Discovery DSC was used with 40  $\mu$ L aluminum pans as sample holders with sample masses of approximately 10 mg. With a continuous nitrogen purge at a rate of 50 mLmin<sup>-1</sup>, the samples were cooled to  $-90^{\circ}$ C and then heated to 225 °C at a rate of 10 °C min<sup>-1</sup>. The cooling-heating cycle was repeated three times to eliminate any pre-existing thermal history. The third heating cycle was used for glass transition temperature acquisition.

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### **FULL PAPERS**

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Lignin Model Compounds as Bio-Based Reactive Diluents for Liquid Molding Resins



**Glassy lignin makes good resins:** Lignin model compounds have been methacrylated and utilized as reactive diluents in a vinyl ester-based resin without the need to include the traditionally used reactive diluent styrene. The glass transition temperatures of the cured resins are comparable to those containing styrene, demonstrating the ability of these lignin model compounds to completely replace styrene as reactive diluents in liquid molding resins without sacrificing thermal performance.