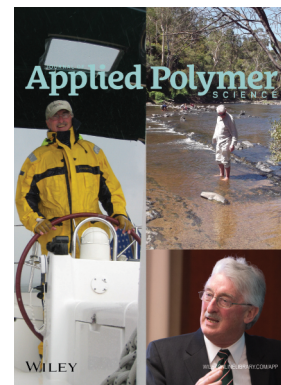


Special Issue: Sustainable Polymers and Polymer Science
Dedicated to the Life and Work of Richard P. Wool

Guest Editors: Dr Joseph F. Stanzione III (Rowan University, U.S.A.)
and Dr John J. La Scala (U.S. Army Research Laboratory, U.S.A.)



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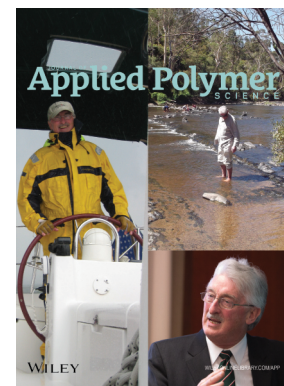
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The effect of impurities in reactive diluents prepared from lignin model compounds on the properties of vinyl ester resins

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ABSTRACT: Vinyl ester resins (VERs) often contain high concentrations of a petroleum-based reactive diluent, such as styrene. Reactive diluents that can be derived from lignin, including phenyl methacrylate (PM), 2-methoxyphenyl methacrylate (MG), and 4-propyl-2-methoxyphenyl methacrylate (M4PG), were synthesized and investigated as potential styrene replacements. A commercial VER was blended with each lignin-derived reactive diluent, and styrene, in 7:3 and 1:1 weight ratios and cured to $\geq 94\%$, based on near-IR spectral analysis. The substituents on the aromatic ring of the lignin-derived reactive diluent are shown to have small effects on viscosity, thermogravimetric, and thermomechanical properties of the cured resins, where, in general, the smaller the reactive diluent, the greater the glass-transition temperature (T_g) and the lower the viscosity. Increasing purity of the reactive diluents through chromatographic separations substantially increases the T_g and degradation temperatures of the resins. The results suggest that PM, MG, and M4PG are effective bio-based reactive diluent replacements for styrene. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43817.

KEYWORDS: biopolymers and renewable polymers; glass transition; resins; structure-property relations; thermosets

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INTRODUCTION

Vinyl ester resins (VERs) are utilized in a variety of composite applications and typically provide high thermal stabilities, moduli, strengths, glass-transition temperatures (T_g s), and chemical resistance.^{1–3} Due to their high performance characteristics and low processing costs, VERs are regularly used in the construction, marine, and transportation industries.⁴ VERs often contain a reactive diluent (RD) to both reduce resin viscosity for liquid molding processing and increase polymer performance. Incorporating reactive diluents into the polymer network allows for a higher degree of polymerization by delaying gelation.¹ However, common reactive diluents, such as styrene (St), are classified as volatile organic compounds (VOC), hazardous air pollutants (HAP), and in the case of styrene, a suspected carcinogen.⁵ Moreover, these reactive diluents are derived from petrochemical feedstocks, which are considered unsustainable resources that possess turbulent price fluctuations.⁶ Due to the environmental hazards of current petrochemical-based reactive diluents,

new, sustainable, reactive diluents with similar performances are being sought.

Previous studies have shown that methacrylated fatty acids (MFAs) derived from plant oils are a viable styrene reducer in VERs.² MFAs possess low viscosity and low volatility, while providing acceptable toughness to the polymer network; however, styrene is still needed as a reactive diluent to produce cured VERs with comparable properties to commercial products. 9–10 dibromo stearic acid glycidyl methacrylate has also been investigated as a bio-based reactive diluent in VERs; however, the resulting resins exhibited significantly increased viscosities and the cured polymers exhibited reduced values for both modulus and T_g , therefore, styrene was still required to produce polymers with acceptable properties.⁷ Bio-based methacrylated cardanol has been studied as a potential styrene replacement in VERs; however, the resulting resins have reduced values for modulus and T_g .⁸ Vinyl levulinate (VL) has also been investigated as a bio-based RD in unsaturated polyester (UPR) resins; however, due to

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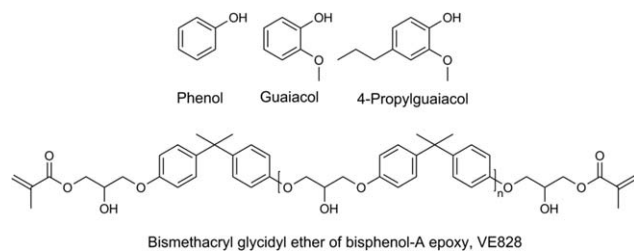


Figure 1. Structures of all LMCs and VE828.

unfavorable reactivity, unreacted VL remains inside the polymer network, and acts as a plasticizer reducing both thermal and physical properties of the cured resin.⁹ Due to the limitations of current proposed styrene replacements, more robust bio-based reactive diluents continue to be a necessity.

A renewable feedstock that has the potential to yield low molecular weight aromatic compounds is lignin, which is a highly crosslinked biopolymer that is produced in excess of 50 million tons annually.¹⁰ Most industrial lignin is produced as a waste product from the Kraft process in the pulp and paper industry and burned for energy recovery. Due to the aromaticity of lignin, it has the potential to become a feedstock for high performance polymers and fine chemicals when selectively depolymerized. Multiple studies have produced single aromatic compounds through the pyrolytic degradation of lignin, which include guaiacols, syringols, catechols, and phenols.¹¹ Some of these molecules, specifically guaiacol and eugenol individually as well as lignin-based bio-oil mimics, have been shown to be suitable VER reactive diluents when functionalized.^{6,12–14} However, there are many other phenolic derivatives that are produced during lignin depolymerization and there is a gap in knowledge on how the various substituents on the parent phenol affect the polymer properties when used as reactive diluents in VERs. If specific phenolic substituents produce polymers with desirable properties, the lignin degradation process could be tailored to produce these chemicals, significantly reducing lignin bio-oil separation and refining costs.

In this study, three lignin model compounds (LMCs), phenol, guaiacol, and 4-propylguaiacol were methacrylated and blended with a standard commercial VER (bismethacryl glycidyl ether of bisphenol A epoxy, VE828), Figure 1. These phenolic chemicals were chosen because of their relatively high abundance in lignin-derived bio-oils, as well as their representative chemical structures.^{6,10,11,15–17} Choosing phenol, guaiacol, and 4-propylguaiacol as the LMCs will provide insight into the effect of the methoxy group and the propyl group on the ability for these molecules to act as reactive diluents in VERs.

The LMCs selected for this study were methacrylated utilizing an esterification reaction and purified through aqueous washes and/or column chromatography. VE828 was blended with both pure (≥ 97.5 mol %) and impure (80–90 mol %) methacrylated LMCs (MLMCs) in 7:3 and 1:1 weight ratios that are typical for VE828:St resins.¹ The resin blends were then free radically polymerized to produce cured resins. The monomer viscosity and resin viscosity at 25 °C, extent of cure, thermogravimetric properties, and thermomechanical proper-

ties of the cured VERs are reported. In addition, styrene was utilized as a reactive diluent in VERs for comparative purposes.

EXPERIMENTAL

Materials

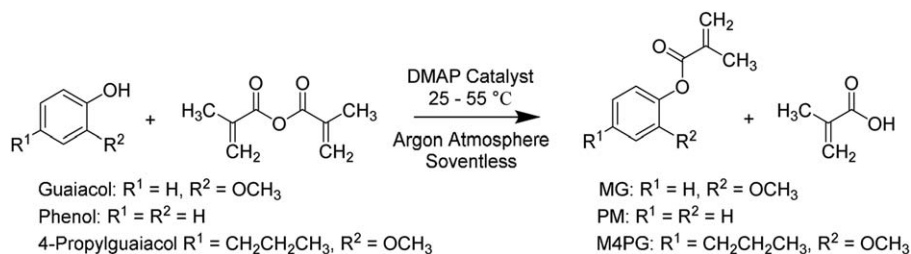
Phenol (99+ %), guaiacol (99+ %), dichloromethane (DCM) (99.9%), hexanes (99.9%), ethyl acetate (99.9%), styrene (inhibited with 10–15 ppm 4-*tert*-butylcatechol), and hydrochloric acid (32%) were purchased from Fisher Scientific (Waltham, MA). Sodium sulfate ($\geq 99\%$), 4-propylguaiacol ($\geq 98\%$), methacrylic anhydride (94%, contains 2000 ppm Topanol A inhibitor), and 4-dimethylaminopyridine (DMAP, 99%) were purchased from Sigma-Aldrich (St. Louis, MO). Deuterated dimethyl sulfoxide (DMSO-*d*₆) and deuterated chloroform (CDCl₃) were purchased from Acros Organics (Morris Plains, NJ). Compressed argon (99.998%) was purchased from Praxair (Danbury, CT). A mixture of 50% trivalent organic chromium complexes and 50% phthalate esters, AMC-2, 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). EPON 828 was purchased from Momentive (Waterford, NY). Trigonox[®] 239, which contains 45% cumene hydroperoxide, was purchased from AkzoNobel Polymer Chemicals (Chicago, IL), and utilized as a free radical initiator.

A crosslinking VER was prepared as described in the literature.^{1,2} EPON 828 was converted into bismethacryl glycidyl ether of bisphenol A and is referred to as vinyl ester 828 (VE828). Characterization methods as described in La Scala *et al.* were performed with similar results.²

Preparation of MLMCs

Phenol, guaiacol, and 4-propylguaiacol were methacrylated (Scheme 1) and purified through aqueous washes and/or flash chromatography. To a 500-mL-round bottom flask fixed with magnetic stir bar, a catalytic amount of DMAP (2 mol % of methacrylic anhydride) was added to a LMC (60 g). Prior to the addition of methacrylic anhydride (1.05 LMC equivalents), the flask was sealed and subsequently purged with argon at ambient conditions for an hour to remove moisture and oxygen. With stirring, the reaction was allowed to progress at 55 °C for a minimum of 24 h. The reaction mixture was then cooled to room temperature and diluted with dichloromethane (400 mL).

To remove methacrylic acid, unreacted methacrylic anhydride, and unreacted LMCs, two different purification methods were utilized. The first method, adapted from Stanzione *et al.*,¹² consisted of multiple aqueous washes of the organic phase (DCM) with a saturated sodium bicarbonate solution until carbon dioxide no longer evolved. The organic phase was then washed with sodium hydroxide (2.5 M), hydrochloric acid (1 M), and water. The organic phase was then dried over sodium sulfate, filtered, and concentrated under reduced pressure. The second method consisted of a single aqueous wash of the organic phase (DCM) with a saturated sodium bicarbonate solution and a single water wash. The organic phase was then dried over sodium sulfate, filtered, and concentrated under reduced pressure. Subsequent



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

flash chromatography was used to remove all other impurities. Flash chromatography was performed on a Grace Reveleris[®] X2 Flash Chromatography System using ethyl acetate and hexanes with a 0 to 20% ethyl acetate gradient. The two purification methods are further investigated to determine the effect of monomer purity on polymer properties.

VE828 and all MLMCs were characterized by ¹H NMR (400.13 MHz, 32 scans at 298.2 K) and ¹³C NMR (101 MHz, 256 scans at 298.2 K) using a Varian Mercury 400 MHz nuclear magnetic resonance system. Additionally, FTIR spectroscopy characterization was performed on a Nicolet iS50 FTIR. At room temperature, 32 cumulative scans were acquired with a resolution of 2 cm⁻¹ in absorbance mode in the mid-IR and near-IR ranges. Mass spectroscopy was performed on a Waters GCT Premier high resolution time of flight mass spectrometer (TOF MS) using liquid injection field desorption ionization. Gel permeation chromatography was also performed on VE828 using a Waters 2695 GPC fitted with Waters Styragel HR4, HR2, and HR1 columns in series using THF (1 mL min⁻¹) as the mobile phase. A Waters 2414 Refractive Index Detector was used and samples were prepared in a concentration of 2 mg mL⁻¹. VE828 was found to have a number average molecular weight of 565 g mol⁻¹ and $n = 0.18$. Spectra are provided in the Supporting Information.

Phenyl Methacrylate. ¹H NMR (DMSO-*d*₆): δ 7.46 – 7.15 (bm, 5H), 6.28 (t, 1H), 5.90 (t, 1H), 2.00 (s, 3H). ¹³C NMR (DMSO-*d*₆): δ 162.30, 150.61, 135.32, 129.54, 127.73, 125.88, 121.83, 18.08 ppm. HRMS (*m/z*, TOF FD+) Calculated: 162.0681 Found: 162.0662.

Methacrylated Guaiacol (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). ¹³C 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. HRMS (*m/z*, TOF FD+) Calculated: 192.0786 Found: 192.0775.

Methacrylated 4-Propylguaiacol (4-propyl-2-Methoxyphenyl Methacrylate). ¹H 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). ¹³C 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. HRMS (*m/z*, TOF FD+) Calculated: 234.1256 Found: 234.1246.

At the purities reported, phenyl methacrylate (PM), methacrylated guaiacol (MG), and methacrylated 4-propylguaiacol (M4PG) are clear, transparent liquids at room temperature.

VE828 is a commercial resin with a green hue. The green hue is attributed to the AMC-2 catalyst that was used in the synthesis of VE828.

Monomer and Resin Viscosity

Monomer and VE828:RD resin viscosities were obtained 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 μ m was used with an approximate sample volume of 1 gram. The shear rate was increased step-wise 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 2 seconds. The shear rate and viscosity were recorded when the shear rate stabilized to within 5% tolerance for three consecutive points.

Resin Curing

VE828 was blended with each MLMC or styrene in 7:3 and 1:1 weight ratios. Each VER was free radically polymerized using Trigonox[®] 239 (1.5 wt % of total resin mass) as the initiator. The resins were degassed until no visible bubbles remained, transferred into a silicone rubber mold, and purged with argon for 20 min. The VE828:St resins were degassed for a shorter period of time to prevent the evaporation of styrene. All resins were cured at 90 °C for 4 h with a subsequent post cure at 180 °C for 2 h in an argon atmosphere.^{6,12,18} The cured resins were allowed to cool to ambient conditions before removal from the oven. The VE828:St and VE828:MLMC cured resins resulted in visually identical, hard, and transparent cured resins with a green hue.

Extent of Cure

Near-infrared (near-IR) spectra of the uncured and cured VERs were obtained using a Nicolet iS50 FT-IR to determine the extent of cure. At room temperature, 32 cumulative scans were acquired with a resolution of 2 cm⁻¹ in absorbance mode in the near-IR range. Uncured VERs were contained in a glass vessel with a thickness of 3 mm while the cured resins typically had a thickness of 3–4 mm. The extent of cure was calculated by measuring the peak absorbance intensities of the styrenic vinyl (~6135 cm⁻¹) and methacrylate vinyl (~6165 cm⁻¹) bonds before and after curing relative to an internal standard (i.e., peak of bond(s) that are not affected by the reaction). Equations (1) and (2) were used to determine the extent of cure of the styrenic vinyl and methacrylate vinyl, respectively.

$$X(S) = \frac{\left(\frac{ABS_{6135\text{cm}^{-1}}}{ABS_{4263\text{cm}^{-1}}}\right)_{\text{unreacted}} - \left(\frac{ABS_{6135\text{cm}^{-1}}}{ABS_{4263\text{cm}^{-1}}}\right)_{\text{reacted}}}{\left(\frac{ABS_{6135\text{cm}^{-1}}}{ABS_{4263\text{cm}^{-1}}}\right)_{\text{unreacted}}} \quad (1)$$

Table I. Estimated Purity of MLMCs on the Basis of ^1H NMR after Purifications as Well as Respective Viscosities at 25 °C

Methacrylated phenolic	Methacrylated phenolic (mol %)	Unreacted LMC (mol %)	Methacrylic anhydride (mol %)	Methacrylic acid (mol %)	Methacrylated topanol A (mol %)	Viscosity at 25 °C (cP)
PM ^a	92.4 ± 3.0	— ^b	1.8 ± 1.2	1.4 ± 1.0	4.5 ± 2.6	3.1 ± 0.09
MG ^a	80.4 ± 0.4	4.5 ± 2.6	3.6 ± 2.7	3.9 ± 2.7	7.8 ± 2.8	17.1 ± 1.2
M4PG ^a	82.1 ± 1.7	6.8 ± 1.6	0.8 ± 0.2	0.3 ± 0.3	10.1 ± 0.6	36.5 ± 0.1
PM ^c	99.1 ± 0.2	— ^b	0.3 ± 0.2	0.7 ± 0.0	0	2.4 ± 0.04
MG ^c	97.8 ± 0.3	0	1.0 ± 0.1	0.4 ± 0.2	0.7 ± 0.4	14.5 ± 0.1
M4PG ^c	99.4 ± 0.1	0	0.3 ± 0.1	0.33 ± 0.0	0	29.6 ± 0.2

The viscosity of as received styrene was measured to be 0.7 ± 0.05 cP at 25 °C.

^aMLMCs post aqueous washing (Referred to as impure reactive diluents).

^bThe amount of unreacted phenolic could not be determined through ^1H NMR due to overlapping peaks in the aromatic region. Thus, the error reported for PM is potentially lower than actual.

^cMLMCs post flash chromatography (Referred to as pure reactive diluents).

$$X(M) = \frac{\left(\frac{\text{ABS}_{6165\text{ cm}^{-1}}}{\text{ABS}_{4263\text{ cm}^{-1}}}\right)_{\text{unreacted}} - \left(\frac{\text{ABS}_{6165\text{ cm}^{-1}}}{\text{ABS}_{4263\text{ cm}^{-1}}}\right)_{\text{reacted}}}{\left(\frac{\text{ABS}_{6165\text{ cm}^{-1}}}{\text{ABS}_{4263\text{ cm}^{-1}}}\right)_{\text{unreacted}}} \quad (2)$$

Polymer Properties

The thermogravimetric properties of the cured resins were measured using a TA Instruments Q500 thermogravimetric analyzer (TGA). Approximately 5 mg of sample was placed in a platinum pan and heated to 600 °C at a rate of 10 °C min⁻¹ in a N₂ atmosphere (40 mL min⁻¹ balance gas flow rate and 60 mL min⁻¹ sample gas flow rate). Thermogravimetric properties including initial decomposition temperature (*IDT*), temperature at 50% weight loss (*T*_{50%}), and temperature at maximum decomposition rate (*T*_{max}), and char content are reported.

Dynamic mechanical analysis (DMA) was performed on a TA Instruments Q800 DMA and was used to determine the thermomechanical properties of each cured resin, which includes the *T*_g, storage modulus (*E'*) at 25 °C, rubbery temperature, rubbery *E'*, and effective molecular weight between crosslinks (*M*_c). *M*_c was calculated using the theory of rubber elasticity [eq. (3)],

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

where *R* is the ideal gas constant, *T* is absolute temperature, and ρ is the sample density. The rubbery *E'* and *T* were defined as the point at which the storage modulus increases with increasing temperature and ρ was measured at 25 °C. Although the theory of rubber elasticity was derived for branched and lightly crosslinked polymer networks, literature has shown that the application of this theory to highly crosslinked polymer networks can still provide insight into polymer behavior and trends.¹⁹ The density of the polymer was determined using Archimedes' principle. Typical DMA sample dimensions were 35 × 12 × 2.5 mm³ and 35 × 12 × 1.5 mm³ with span to thickness ratios less than 10 and greater than 10 respectively in accordance with McAninch *et al.*²⁰ Thicker samples were used for the measure of rubbery *E'* and thinner samples were used for the measure of *E'* at 25 °C and *T*_g. A single cantilever geometry was used and the temperature was increased from 0 °C to

250 °C at a rate of 2 °C per min, while oscillating at 1 Hz with a 7.5 μm deflection. A Poisson's ratio of 0.35 was used.

RESULTS AND DISCUSSION

Monomer and Resin Characterization

The estimated purity of each MLMC after aqueous washing or subsection to flash chromatography is shown in Table I and all purities are based on ^1H NMR analysis. PM has an artificially high estimated purity largely due to the fact that the amount of unreacted phenol could not be determined through ^1H NMR analysis. However, it is likely that the concentration of unreacted phenol is similar to that of MG and M4PG. After aqueous purification, all MLMCs have a significant amount of methacrylic anhydride, methacrylic acid, and methacrylated topanol A, all of which possess vinyl bonds, which will react during the polymerization process. The presence of the unreacted methacrylic anhydride could result in additional crosslinking within the polymer network. The reactive diluents with purities below 97.5 mol % are referred to as impure.

All MLMCs that were purified through flash chromatography exceeded purities of 97.5 mol % and are referred to as pure. Flash chromatography removed all unreacted LMCs and greatly reduced the amount of methacrylic anhydride, methacrylic acid, and methacrylated topanol A.

The monomer viscosities of both pure and impure reactive diluents can be seen in Table I. The viscosity of styrene was measured to be 0.7 ± 0.05 cP at 25 °C. The impurities in the reactive diluents result in a marginal increase in monomer viscosity. Viscosities of the methacrylate monomers increase with molecular weight, adhering to small molecule and Rouse dynamics,²¹ and can be attributed to increasing van der Waals attractions.^{1,22} Fitting styrene to this trend is not valid as it is not a part of the homologous series of methacrylates, but styrene has the lowest molecular weight and lowest viscosity. Furthermore, because of the methoxy groups on the methacrylates that increase molecular polarity, the methacrylate monomers are expected to have higher viscosities than nonpolar derivatives of styrene of the same molecular weight.^{23,24}

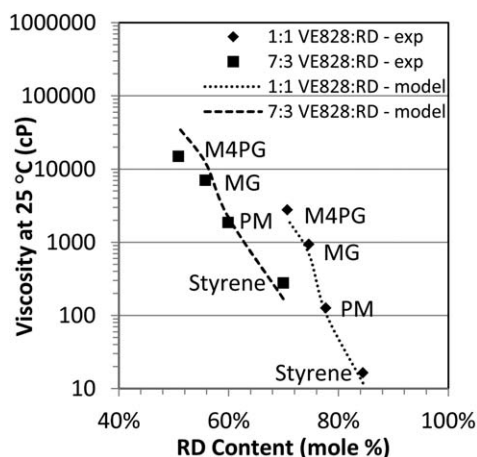


Figure 2. Vinyl ester resin viscosity as a function of reactive diluent content for the four reactive diluents and two VE828:RD ratios used.

To determine the feasibility of MLMCs as reactive diluents, the viscosities of the impure VE828:RD resins were obtained and the results are shown in Figure 2. Viscosities of the VE828:RD resins with pure MLMCs were not tested since there was negligible difference between pure and impure reactive diluent viscosities, the blended resin viscosities are anticipated to exhibit comparable viscosities to the impure blends.

All reactive diluents and VE828:RD resin blends exhibited Newtonian behavior and the viscosity at 50.5 s^{-1} was analyzed for consistency. In order for the resin to be processed using resin transfer molding techniques, a viscosity of 50 cP to 1000 cP is recommended,^{22,25} although this does not preclude the use of resins with viscosities outside of that range. The viscosities of each VE828:RD resin system decreased with increasing reactive diluent content because the reactive diluent acts like a solvent to the vinyl ester. In general, all VE828:MLMC resin blends have an order of magnitude higher viscosities compared to the VE828:St blends. In addition, the lower molecular weight methacrylates produce vinyl esters with lower viscosities than the higher molecular weight methacrylates. In fact, the viscosities of the resins are as expected based on a logarithmic simple rule of mixtures of the vinyl ester and the reactive diluent [eq. (4)]:

$$\log [\text{Viscosity}(\text{Mixture})] = \log [\text{mol fraction}(\text{VE828}) \times \text{viscosity}(\text{VE828}) + \text{mol fraction}(\text{RD}) \times \text{viscosity}(\text{RD})] \quad (4)$$

This equation effectively has one fitting parameter, as the viscosity of VE828 at 25°C is too high for accurate measurements. Based on vinyl ester monomer and resin viscosity measurements at different temperatures and as a function of diluent content for a number of diluents, a viscosity of 6×10^7 cP for the pure vinyl ester monomer is reasonable.²⁶ Thus, the trend in the viscosities as a function of reactive diluent content shown in Figure 2 is simply a function of the differences in the reactive diluent viscosities. Thus, no significant differences in the amount of hydrogen bonding is occurring between VE828:St and VE828:MLMC samples. It should be noted that part of the reason the viscosities of the resins increase with monomer molecular weight is that the samples were made with constant

VE Resin System	Viscosity at 25 °C (cP)
7:3 VE828:St	280 ± 4.0
7:3 VE828:PM	1900 ± 10
7:3 VE828:MG	7000 ± 30
7:3 VE828:M4PG	15000 ± 300
1:1 VE828:St	16 ± 2.0
1:1 VE828:PM	126 ± 3.0
1:1 VE828:MG	940 ± 10
1:1 VE828:M4PG	2760 ± 120

weight ratios of VE828:RD. Thus, as the reactive diluent molecular weight increases, the mole fraction of the reactive diluent in the resin decreases.

Extent of Cure

FTIR near-IR spectroscopy was used to determine the extent of cure of each VER. Figure 3 shows the near-IR spectra of 1:1 blends of VE828:RD uncured and cured resins that contain pure MLMCs. The VE828:RD uncured and cured resins that contain the impure MLMCs as well as all 7:3 blends have similar spectra.

The absorption bands at 6165 cm^{-1} and 4625 cm^{-1} are a result of methacrylate ($=\text{C}-\text{H}$) bonds and internal phenyl groups, respectively. It can be seen that the methacrylate band at 6265 cm^{-1} decreases during the polymerization, which is a result of the vinyl bonds polymerizing. The extent of cure after

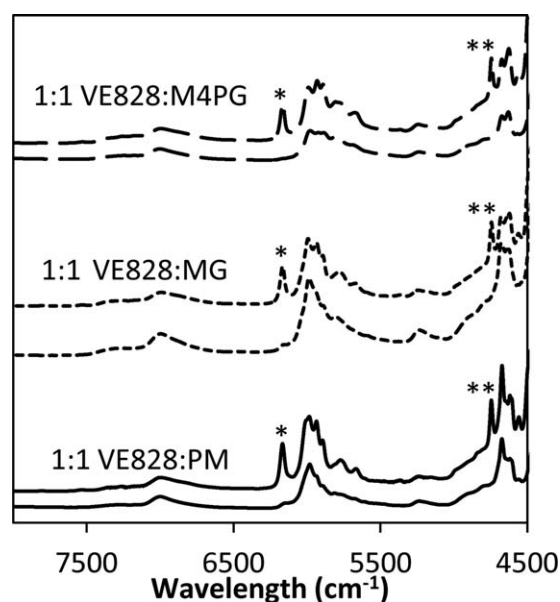


Figure 3. Near-IR spectra for 1:1 VE828:MLMC resin and cured resin. Absorptions associated with the methacrylate (*) and internal phenyl (**) are highlighted. Spectra are vertically offset for clarity, with the cured sample representing the bottom spectra.

Table II. Extent of Cure after Postcure Based on the Methacrylate for VE828:RD Cured Resins and the Bio-Based Content of the Cured Resins

VE system	Pure extent of cure (%)	Impure extent of cure (%)	Bio-based content (%)
7:3 VE828:St	99 ± 0.1	—	0
7:3 VE828:PM	94 ± 1.1	94 ± 2.7	19.0
7:3 VE828:MG	95 ± 1.1	95 ± 2.7	19.2
7:3 VE828:M4PG	99 ± 0.1	99 ± 2.7	22.2
1:1 VE828:St	99 ± 0.1	—	0
1:1 VE828:PM	95 ± 1.0	94 ± 2.7	29.7
1:1 VE828:MG	94 ± 1.4	95 ± 2.7	31.9
1:1 VE828:M4PG	99 ± 0.1	99 ± 2.7	36.6

postcure of all VE828:RD cured resins based on the conversion of the methacrylate group are shown in Table II.

The highest extent of cure is approximately 99% for the VE828:St resins and the VE828:M4PG resins. The styrenic vinyl conversions of the VE828:St cured resins are approximately 100%, and thus the vinyl ester conversion is approximately 98%. The extent of cure for the VE828:PM and VE828:MG resins are lower, which can be attributed to the lower reactivity of the methacrylate groups when compared to vinyl groups. The methoxy moiety has the potential to improve the extent of cure by destabilizing the methacrylate, thus increasing reactivity.²⁷ The effect of the methoxy is inconclusive for PM and MG due to the complexity of these blended methacrylate systems. Further investigation of the effect of the methoxy using simplified systems is recommended. Yet, the M4PG results in higher extents of cure than the PM and MG likely due to the plasticizing effect of the propyl group, which increases the extent of cure required for vitrification and reduces the ultimate T_g , allowing for increased mobility of the unreacted groups. It can be seen that the impurities (unreacted LMC, methacrylic anhydride, methacrylic acid, and methacrylated topanol A) do not have an effect on the extent of cure of the resin blends.

Polymer Properties

Based on the U.S. Food, Conservation, and Energy Act, the percent bio-based content of a compound can be defined as the amount of bio-based carbon in the material or product as fraction weight (mass) or percent weight (mass) of the total organic carbon in the material or product.²⁸ Therefore, to quantify the “greenness” of the VE828-based cured resins, this was calculated assuming that the LMCs are hypothetically derived from lignin, methacrylic anhydride is derived from petroleum, and the MLMCs were pure.^{29,30} The percent bio-based contents of the VE828-based cured resins are shown in Table II.

In general, the percent bio-based content increased with increasing MLMC content and MLMC molecular weight because the non-bio component of the MLMC, the methacrylate, is proportionally smaller as the molecular weight of the LMC is increased.

Thermogravimetric analysis was performed on all pure and impure VE828:MLMC cured resins, as well as the 7:3 and 1:1 VE828:St cured resins for commercial comparison. The thermograms of 7:3 VE828:RD and 1:1 VE828:RD with pure MLMCs can be found in Figure 4. Additional information reported from

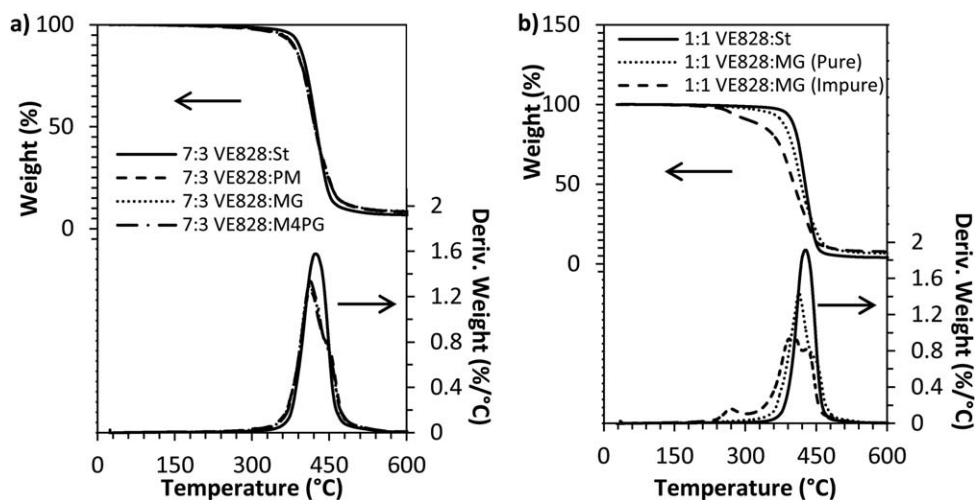


Figure 4. TGA results of (a) 7:3 VE828:RD cured resins containing pure MLMCs and styrene and (b) 1:1 VE828:MG cured resins containing pure and impure MG and styrene.

Table III. TGA Properties of VE828:RD Cured Resins Containing Pure MLMCs and Styrene (Top Half) and Impure MLMCS (Bottom Half)

VE system	IDT (°C)	$T_{50\%}$ (°C)	T_{max} (°C)	Char content (%)
7:3 VE828:St	378	425	423	6.8
7:3 VE828:PM	355	422	413	8.2
7:3 VE828:MG	361	422	412	8.6
7:3 VE828:M4PG	359	422	413	8.4
1:1 VE828:St	385	426	427	4.0
1:1 VE828:PM	348	421	417	6.7
1:1 VE828:MG	349	418	414	6.7
1:1 VE828:M4PG	352	414	414	5.4
7:3 VE828:PM	327	403	392	9.4
7:3 VE828:MG	295 ± 14	404 ± 9	399 ± 8	8.6 ± 1.3
7:3 VE828:M4PG	306	401	394	8.1
1:1 VE828:PM	296	400	394	7.5
1:1 VE828:MG	275 ± 6	400 ± 9	392 ± 6	7.7 ± 0.6
1:1 VE828:M4PG	288	396	397	6.2

TGA [including initial decomposition temperature (IDT), temperature at 50% weight loss ($T_{50\%}$), temperature at maximum decomposition rate (T_{max}), and char content] can be found in Table III.

The VE828:RD cured resins with impure MLMCs have a two stage thermal decomposition behavior, with the first stage occurring between 250 °C to 370 °C, and the second stage occurring between 370 °C and 600 °C. The first stage can be attributed to the unreacted LMCs that are not covalently connected to the polymer network and are able to volatilize and/or decompose more readily at elevated temperatures.

The VE828:RD cured resins with impure MLMCs displayed significantly lower IDT, $T_{50\%}$, and T_{max} values to those containing styrene; however, the char content is higher. The VE828:RD cured resins with pure MLMCs all exhibited comparable IDT,

$T_{50\%}$, and T_{max} values and higher char contents compared to the VE828:St cured resins. Studies by Zulfiqar *et al.*, show that poly(phenyl methacrylate) has lower thermogravimetric properties than that of polystyrene, which can be observed by comparing VE828:St and VE828:PM cured resins with pure PM.³¹ Previous studies by Harvey *et al.* show that the methoxy moiety causes electron donation to the aromatic ring, which decreases thermal stability³²; however, when comparing VE828:RD cured resins with pure MLMCs, the aromatic ring substituents do not significantly impact thermal properties. Overall, the purity of the reactive diluent has a significant impact on the thermal properties whereas the aromatic ring substituents do not.

The char contents of the VE828:MLMC cured resins were higher than that of the VE828:St cured resins. It is hypothesized that the higher char contents are due to anhydride rings forming during thermal treatment, which would interfere with polymer chains unzipping into monomers.^{33,34} Anhydride rings have been shown to suppress end-initiated and side-group depolymerizations, which, in turn, increases the dependency of monomer production to backbone scissions that often require higher temperatures, thus increasing char content.³³

Thermomechanical properties of the resins were measured using DMA. The differences in storage moduli at 25 °C (glassy moduli) were statistically insignificant for most samples. Figure 5(a) shows the storage modulus (E') and loss modulus (E'') as a function of temperature for the pure 7:3 VE828:MLMC cured resins as well as the 7:3 VE828:St cured resin. Figure 5(b) shows the E' and E'' as a function of temperature for the pure and impure 1:1 VE828:MG cured resins as well as the 1:1 VE828:St cured resin. Tables IV and V show the specific thermomechanical properties for all cured resins.

In general, all pure and impure VE828:MLMC cured resins have a E' that is comparable to the VE828:St cured resins. As anticipated, the T_g s of the VE828:RD thermosets increased with decreasing reactive diluent content because the pure VE828 T_g is approximately 180 °C while the diluents have T_g s closer to 100 °C. Also, reactive diluent purity does not have a significant

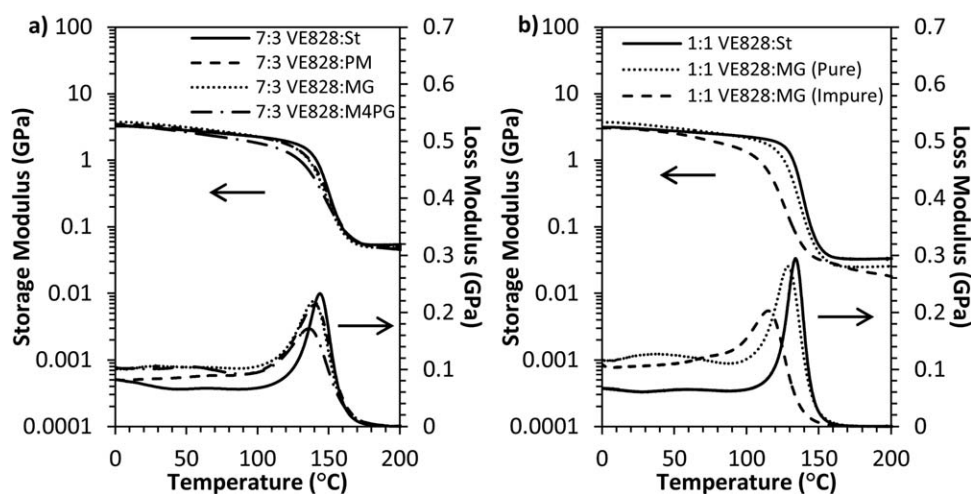


Figure 5. The storage moduli and loss moduli as a function of temperature of (a) 7:3 VE828:RD cured resins containing pure MLMCs and styrene and (b) 1:1 VE828:MG cured resins containing pure and impure MG and styrene.

Table IV. Thermomechanical Properties of Pure VE828:RD Cured Resins

VE system (Pure RDs)	E' @ 25 °C (GPa) ^a	E' (T) Inflection (°C) ^b	Peak of E'' (°C) ^c	Peak of tan δ (°C) ^d	tan δ FWHM (°C) ^e	Rubbery E' (MPa) ^f	Rubbery T (°C) ^g	eff. M_c (g mol ⁻¹)	ρ @ 25 °C (g cm ⁻³) ^h
7:3 VE828:St	3.1	143	143	154	24	53	203	264 ± 10	1.170
7:3 VE828:PM	3.2	139	140	154	28	51	200	282 ± 1	1.217
7:3 VE828:MG	3.4	136	137	151	29	48	197	299 ± 2	1.222
7:3 VE828:M4PG	2.8	136	136	151	32	58	191	239.7 ± 14	1.195
1:1 VE828:St	2.9	135	135	144	20	32	172	401 ± 39	1.137
1:1 VE828:PM	3.2	128	129	125	25	25	185	556 ± 27	1.208
1:1 VE828:MG	3.5	126	127	141	28	25	177	564 ± 43	1.221
1:1 VE828:M4PG	2.7	122	124	139	30	31	172	422 ± 13	1.174

^aMaximum standard deviation for all E' s at 25 °C = ± 0.3 GPa.

^bMaximum standard deviation for all E' (T) Inflections = ± 1.8 °C.

^cMaximum standard deviation for all Peaks of E'' s = ± 1.9 °C.

^dMaximum standard deviation for all Peaks of tan δ s = ± 2.8 °C.

^eMaximum standard deviation for all tan δ FWHM = ± 2.5 °C.

^fMaximum standard deviation for all Rubbery E' s at 25 °C = ± 3 MPa.

^gMaximum standard deviation for all Rubbery T s = ± 6 °C.

^hMaximum standard deviation for all densities at 25 °C = ± 0.006 g cm⁻³.

effect on the E' at 25 °C, with the exception of MG, which had a 0.4 GPa increase. It is expected that the methoxy group would increase the storage modulus due to increased intermolecular interactions, which can be seen if pure VE828:PM is compared to pure VE828:MG. The data suggests that the lower storage modulus of M4PG is likely due to the propyl moiety.

Tables IV and V show an increase in reactive diluent content yields an increase in M_c for all VE828:RD cured resins. This is a result of reduced crosslinker content. The pure and impure VE828:M4PG cured exhibited M_c s that were lower than that of the VE828:St blend; however, the pure and impure VE828:PM and VE828:MG cured resins had higher effective M_c s than the styrene blend. The likely cause of this was the lower extent of cure for vinyl esters using PM and MG as the reactive diluent.

Also, the high concentration of unreacted LMCs in the polymer network is anticipated to influence M_c and the overall network structure; however, the influence of unreacted LMCs on polymer network formation for VE828:RD systems is not fully understood.

The densities of the cured VERs at 25 °C did not significantly change as a function of reactive diluent content. However, it was clear that styrene-based resins and M4PG resins had the lowest density. Density is generally a function of packing in the glassy phase. The styrene resins have less intermolecular interactions due to the lower polarity of the styrene, resulting in lower densities. Conversely, the methacrylate resins have higher intermolecular interactions as a result of the ester linkages, causing an increase in density. Yet, the propyl group on the M4PG

Table V. Thermomechanical Properties of Impure VE828:RD Cured Resins

VE system (Impure RDs)	E' @ 25 °C (GPa) ^a	E' (T) Inflection (°C) ^b	Peak of E'' (°C) ^c	Peak of tan δ (°C) ^d	tan δ FWHM (°C) ^e	Rubbery E' (MPa) ^f	Rubbery T (°C) ^g	eff. M_c (g mol ⁻¹)	ρ @ 25 °C (g cm ⁻³) ^h
7:3 VE828:PM	3.4	140	140	155	29	52	200	276 ± 33	1.217
7:3 VE828:MG	3.0	130	129	148	34	48	195	298 ± 18	1.225
7:3 VE828:M4PG	2.7	130	129	149	35	59	185	230 ± 5	1.195
1:1 VE828:PM	3.0	129	129	142	26	29	190	473 ± 12	1.214
1:1 VE828:MG	3.1	118	117	134	39	25	185	564 ± 75	1.228
1:1 VE828:M4PG	2.7	111	111	129	34	33	170	421 ± 20	1.183

^aMaximum standard deviation for all E' s at 25 °C = ± 0.4 GPa.

^bMaximum standard deviation for all E' (T) Inflections = ± 3 °C.

^cMaximum standard deviation for all Peaks of E'' s = ± 4 °C.

^dMaximum standard deviation for all Peaks of tan δ s = ± 4 °C.

^eMaximum standard deviation for all tan δ FWHM = ± 4.6 °C.

^fMaximum standard deviation for all Rubbery E' s at 25 °C = ± 6 MPa.

^gMaximum standard deviation for all Rubbery T s = ± 14 °C.

^hMaximum standard deviation for all densities at 25 °C = ± 0.009 g cm⁻³.

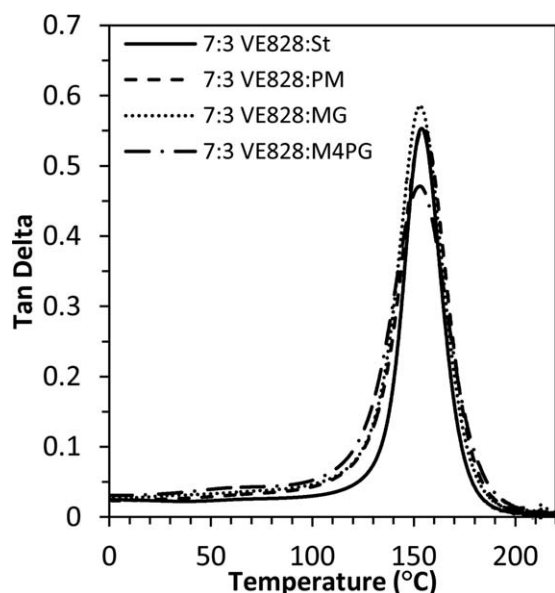


Figure 6. Tan δ of 7:3 VE828:RD cured resins with pure MLMCs and styrene as a function of temperature.

plasticizes the resin creating free volume and thereby reducing density back to values similar to that of VE828:St resins. More so, the MG has slightly higher densities than the PM vinyl esters because of the additional polarity and intermolecular interactions caused by the MG methoxy group.

Commercial cured VERs that are diluted with styrene typically have T_g s greater than 120 °C.^{1,2,35} The T_g based on the peak of the E'' thermogram is similar to that of the inflection point of the E' thermogram, which is typical among cured VERs; however, the T_g based on the tan δ curve is typically higher than that based on the E'' or E' thermograms.^{36,37} To use a more conservative value, the T_g is defined as the peak of the E'' thermogram. The VE828:MLMC cured resins with both pure and impure reactive diluents exhibit the same T_g trend; however, the impure MG and M4PG reactive diluents resulted in a substantially lower T_g , approximately 7 to 13 °C lower, than their pure analogs. The impure reactive diluents contain unreacted phenolics, methacrylic anhydride, methacrylic acid, and methacrylated topanol A. The unreacted phenolics act as plasticizers and reduce the T_g s of cured resins. Methacrylic anhydride provides additional crosslinking to the polymer network, which would increase the T_g of the polymer; however, methacrylic anhydride has the lowest concentration among all impurities in general. The impure VE828:PM has a similar T_g to that of pure VE828:PM likely due to having less unreacted LMC in the resin relative to impure MG and M4PG resins. The overall effect of MLMC purity is more distinct in the E' and E'' thermograms and becomes more apparent as the concentration of the reactive diluents is increased. Based on the pure VE828:MLMC cured resins, the use of these reactive diluents results in only a slight reduction in T_g relative to VE828:St polymers. The reasons for this reduction are a combination of reduced extent of cure, especially for PM and MG samples, and the additional free volume resulting from the methoxy group in MG and M4PG and especially the

propyl group in M4PG. Yet, the effects are small and thus the thermomechanical data suggests that PM, MG, and M4PG are effective bio-based reactive diluent replacements for styrene.

The width of the tan δ peak represents polymer network heterogeneity, where a broader peak suggests a more heterogeneous polymer and a broader glass-transition region.³⁸ According to the Twinkling Fractal Theory, an increased amount of relaxation modes present in the polymer network arises when there exists a broad distribution of solid fractal clusters that twinkle into the liquid phase on heating, thus, exhibiting heterogeneity.^{39,40} For all VE828:MLMC cured resins, the full width at half max (FWHM) of the tan δ peak increased compared to those that contained styrene, regardless of purity (Tables IV and V). The tan δ thermograms of the pure 7:3 VE828:RD cured resins are shown in Figure 6. The width of the tan δ peak appears to increase with aromatic side chain functionality on the reactive diluent indicating an increased formation of heterogeneous polymer networks.

The extent of polymer chain segmental mobility is indicated by the maximum value of the tan δ curve.³⁸ The cured resins containing M4PG exhibit the lowest chain mobility likely due to the higher crosslink density of the cured resin. Resins containing pure PM, MG, and styrene all exhibited similar maximum tan δ values, suggesting that these cured resins exhibited similar chain mobility. Also, the VE828:RD cured resins with impure MLMCs indicated that the maximum tan δ peak intensity decreased with increasing substituents and functionality on the aromatic rings of the MLMCs; however, impurities in these systems ultimately affect the results.

CONCLUSIONS

In this study, three lignin model compounds (phenol, guaiacol, and 4-propylguaiacol) were methacrylated via an esterification reaction with methacrylic anhydride. PM, MG, and M4PG were shown to be suitable reactive diluent replacements for styrene in VERs. A commercial VER (bismethacryl glycidyl ether of bisphenol A epoxy, VE828) was blended with both pure and impure lignin-based reactive diluents in 7:3 and 1:1 weight ratios. The pure lignin-based reactive diluents, when blended with VE828, produced cured resins with T_g s comparable to that of VE828 cured with styrene. The impure lignin-based reactive diluents had T_g values that were inferior to VE828 cured with styrene, with the exception of impure PM. Based on the thermogravimetric and thermomechanical data, the substituents on the aromatic ring of the reactive diluent are shown to have small effects on thermogravimetric and thermomechanical properties of the cured resins whereas purity is shown to have a more substantial effect. However, from an industrial standpoint, the overall thermomechanical properties are adequate for all cured resins. Yet, the mechanical behavior of the cured resins may be affected significantly by impurities. The thermogravimetric and thermomechanical data suggests that PM, MG, and M4PG are effective lignin-based reactive diluent replacements for styrene. Cure kinetics data and flexural and fracture properties are currently being obtained for all VE828 cured resins containing lignin-based reactive diluents to gain a more comprehensive understanding of the process-structure-property relationships of these materials.

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