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High Performance Thermosets with Tailored Properties Derived from Methacrylated Eugenol and Epoxy-Based Vinyl Ester

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Abstract:

A renewable chemical, eugenol, is methacrylated to produce methacrylated eugenol (ME) employing the Steglich esterification reaction without any solvent. The resulting ME is used as a low viscosity comonomer to replace styrene in a commercial

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epoxy-based vinyl ester resin (VE). The volatility and viscosity of ME and styrene are compared. The effect of ME loadings and temperatures on viscosity of the VE-ME resin is investigated. Moreover, the thermo-mechanical properties, curing extent， and thermal stability of the fully cured VE-ME thermosets are systematically examined. The results indicate that ME is a monomer with low volatility and low viscosity, and therefore the incorporation of ME monomer in VE resins allows significant reduction of viscosity. Moreover, viscosity of the VE-ME resin can be tailored by adjusting ME loadings and processing temperature to meet commercial liquid molding technology requirements. The glass transition temperatures of VE-ME thermosets range from 139 to 199 °C. In addition, more than 95% of the monomer is incorporated and fixed in the crosslinked network structure of VE-ME thermosets. Overall, the developed ME monomer exhibits promising potential to replace styrene as an effective low viscosity comonomer. The VE-ME resins show great advantages for use in polymer matrices for high performance fiber-reinforced composites. This work showed great significance to the vinyl ester industry by providing detailed experimental support.

KEYWORDS: methacrylated eugenol (ME); comonomer; vinyl-ester (VE);

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thermosets; styrene replacement.

INTRODUCTION

Vinyl ester (VE) resins are one of the most widely used thermosetting polymer matrices for fiber-reinforced composites in diverse applications, including civil infrastructure, marine, aerospace, and automotive, due to their superior mechanical properties, easy processing, excellent thermal stabilities, light weight, and low cost.[1-5]

Commercialized epoxy-based VE resins are commonly prepared by the reaction of diglycidyl ether of bisphenol A (DGEBA) and an unsaturated carboxylic acid such as acrylic or methacrylic acid,[6] as shown in Figure 1. VE resins have two terminal reactive double bonds, which could easily polymerize into a cross-linked network structure by free-radical polymerization.[7-8] However, the viscosity of pure VE resins is too high to be used for common processing technologies. Therefore, VE resins typically need 35-50 wt% of styrene as a low viscosity comonomer to decrease viscosity of the resin formulation and copolymerize with VE resin.[9-11] However, new emission standards for composite manufacturing by the Environmental Protection Agency specifically target styrene as a volatile organic compound (VOC), hazardous

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air pollutants (HAP), and a potential human carcinogen. Moreover, styrene is derived from non-renewable petrochemical feedstocks.[12]

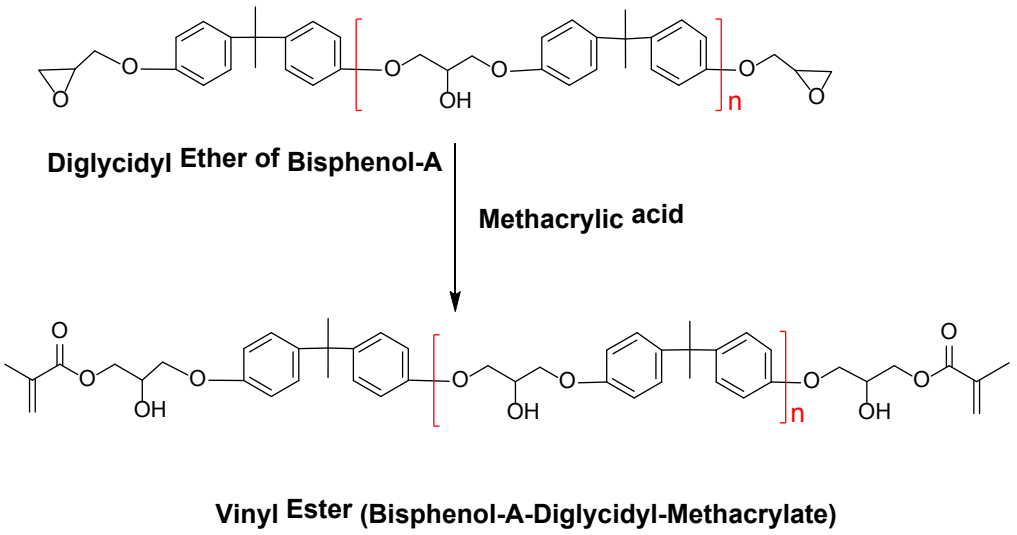

Figure 1. Schematic for the synthesis of VE resins

Therefore, there is a great need for the development of low viscosity, low volatility, and green comonomers due to the growing environmental concern and negative health impacts of using styrene.[13] So far, significant research has been focused on the development of bio-based comonomers bearing methacrylate or acrylate groups from renewable resources. Aliphatic methacrylated fatty acids have been evaluated as low viscosity comonomers to replace styrene for vinyl ester resins, such as methacrylated lauric acid, methacrylated stearic acid, methacrylated oleic acid, and methacrylated linoleic acid. All the methacrylated fatty acids exhibited

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advantages of lower volatility but showed higher viscosity (48-58 cP at 30 °C) than that of styrene (0.7 cP at 30 °C). The cured VE-methacrylated fatty acids showed lower glass transition temperatures (ranged from 79-94 °C) and storage moduli (1.6-1.9 GPa at 35 °C and 35% comonomer) than that of VE-styrene benchmark systems (150 °C and 3.0 GPa) due to the high molecular weight and inherent long, aliphatic flexible chains of fatty acids.[14]

Aromatic biobased methacrylates have also been used as comonomers of VE resins. [15-16] Cardanol can be obtained from cashew nut shell liquid and is a potential alternative to petrochemicals derived from phenols. Bio-based methacrylated cardanol has been reported to replace styrene in VE resins. The resulting VE-methacrylated cardanol resin exhibited improved thermal stability. However, cured VE-methacrylated cardanol resin system showed lower thermal stability, glass transition temperature, and storage modulus than that of VE-styrene resin systems.[16]

Lignin-derived monomers, such as vanillin, eugenol, guaiacol, syringols, and catechols, were methacrylated to serve as low viscosity comonomers in VE resins. Among them, methacrylated vanillin is a solid at room temperature, which leads to processing issues. The availability of guaiacol, syringols, and catechols is not

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industrial.[17-18]

Eugenol is an aromatic, inexpensive, and renewable molecule, which can be extracted from certain clove essential oils (nutmeg, cinnamon, basil, bay leaf), by lignin depolymerization or pyrolysis, or by allylation of guaiacol with allyl chloride. Moreover, eugenol exhibits several pharmacological properties, such as antibacterial and antioxidant properties because of the presence of phenol groups, rendering its utilization in perfumes, cosmetic, and flavorings applications. [19,20] So far numerous studies have used eugenol as a building block for the synthesis of bio-based polymers, such as benzoxazines resins,[21-23] allyl-etherified eugenol,[24-26] polyesters resins,[27] cyanate ester resins,[28] bismaleimide,[29] epoxy resins,[30-32] and ME etc.[33] Among them, ME, prepared by incorporation of a polymerizable methacrylate group to eugenol, shows promising potential to be used as a replacement for styrene in VE resins because both methacrylate groups and allyl groups can participate in the free radical polymerization. In our previous work, it was demonstrated that ME is an effective comonomer in an acrylated epoxidized soybean oil (AESO) resin.[34] However, AESO resin still has not been commercially mass produced. In contrast, epoxy-based VE resins are widely used in industry with styrene as a reactive diluent. Therefore, there

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is great need to evaluate the possibility of using ME as a comonomer for commercially available epoxy-based VE resins. Although literatures have reported the use of ME as a comonomer for VE resins, the mass ratio of ME to VE was fixed at a single value.[11, 35] Several significant aspects, especially the effect of ME loading were not sufficiently investigated to provide enough information to the industrial community. As an ideal comonomer for VE resin, the monomer is not only required to offer good processability by decreasing the viscosity of VE resin for common liquid molding techniques, but also required to be reactive enough to homopolymerize and copolymerize with the C=C double bonds of VE resin to improve overall properties. Therefore, the viscosity and the curing behavior (curing extent and crosslinking degree) of VE-ME system with various ME loadings need to be systematically investigated to provide experimental support to facilitate the commercialization of ME to replace styrene for VE resins.

The objective of our work was to systematically investigate the potential use of ME to completely replace styrene for a commercially available vinyl ester resin. The volatility of ME was evaluated. The viscosity, extent of cure, thermal stability, and thermal-mechanical properties of VE-ME resins with ME loading ranging from 0 to

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100% were systematically investigated as well.

EXPERIMENTAL

Materials

The commercial styrene-free VE resin (bisphenol a diglycidyl methacrylate) was supplied by Polynt Composites USA, Inc. Eugenol (98%), styrene (99%), methacrylate anhydride (94%, inhibited with 2000 ppm topanol A), 4-dimethylaminopyridine (DMAP), and tert-Butyl peroxybenzoate were obtained from Sigma-Aldrich. Hydrochloric acid was provided by EMD Millipore. Methylene chloride, sodium bicarbonate, anhydrous magnesium sulfate and sodium hydroxide were purchased from Fisher Scientific. Dimethyl sulfoxide (DMSO-d_6) was purchased from Cambridge Isotope Laboratories, Inc. All chemicals were used as received without further purification.

Synthesis of ME Monomer

First, 10 g of eugenol and 0.16 g (2% mole equivalents based on methacrylic anhydride) of DMAP were added into a 100 mL sealed flask equipped with a magnetic stir bar and an inert gas inlet. Argon gas was purged for 2 h to remove

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moisture and oxygen. After that, 10.33 g of methacrylated anhydride was introduced (1.1 mole equivalents based on eugenol). The mixture was heated at 45 °C while stirring for 24 h. After the reaction, the mixture was diluted with methylene chloride and washed with saturated $NaHCO_3$ solution, 1.0 M NaOH aqueous solution, 0.5 M NaOH aqueous solution, 1.0 M HCl aqueous solution, and water to remove the traces of unreacted methacrylic anhydride and methacrylic acid. The organic phase was then dried over sodium sulfate, filtered, concentrated under reduced pressure, and dried in a vacuum oven at 60 °C overnight (Figure 2).

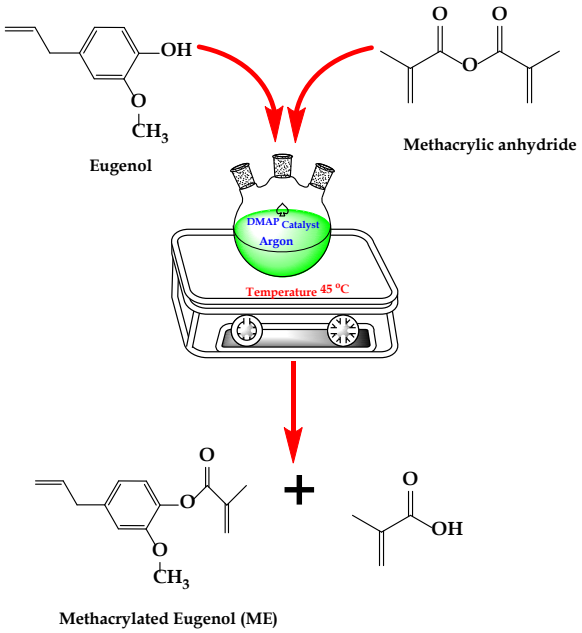

Figure 2. Schematic of the reaction between eugenol and methacrylic anhydride

Formulation and Curing of VE-ME Resins

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VE resins were initially placed in a glass beaker and heated to 70 °C for 10 mins, and then mixed thoroughly with 0, 20, 40, 60, 80, 100% (by weight percent) of ME, respectively. Tert-Butyl peroxybenzoate (1.5 wt% of total resin mass) was then added as a free radical initiator. The mixed resin system was then poured into an aluminum alloy mold and degassed in a vacuum oven to eliminate visible bubbles. The mixed resin was subjected to a three-step curing procedure in an argon atmosphere using the cure schedule: 90 °C for 1 h, 130 °C for 5 h, and subsequently 180 °C for 2 h. The prepared thermosetting resins were labeled as pure VE, VE80-ME20, VE60-ME40, VE40-ME60, VE20-ME80, and pure ME.

Characterization

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Varian VXR-300 NMR instrument at 25 °C using DMSO-d_6 as a solvent. The volatility behavior was studied using a thermogravimetric analyzer (TGA) (Discovery TGA, TA Instrument). Samples were isothermally heated at 30 °C for 10 h under nitrogen flow (25 mL/min). The viscosity was measured using a strain-controlled rheometer (ARES-G2, TA Instruments). Measurements were performed isothermally in a parallel-plate geometry (25 mm diameter) with shear rates ranging from 1 to 100 s^{-1} at

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25, 30, 40, 50, 60 °C, respectively. Dynamic mechanical analysis (DMA) was carried out on the ARES-G2 rheometer in DMA mode with a torsion geometry. Samples were ramped at 3 °C/min from -100 to 180 °C, with a strain of 0.065%, and a constant frequency of 1 Hz. Soxhlet extraction was used to measure the gel content of VE-ME thermosets. The cured specimens were precisely weighted (approximately 1.000 g, m_1) and extracted using dichloromethane as a solvent for 24 h. The extracted resins were dried in vacuum oven and weighted (m_2). Gel content was calculated as 100% × m_2/m_1. Thermogravimetric behavior of the VE-ME resin was investigated on a Discovery TGA from TA Instrument. All samples were tested from room temperature to 600 °C at a heating rate of 10 °C/min under nitrogen flow (25 mL/min).

RESULTS AND DISCUSSION

Eugenol was reacted with methacrylate anhydride in the presence of DMAP catalyst under mild conditions by one pot Steglich esterification reaction to obtain ME monomer. The average yield was 81.8% after aqueous washing. The chemical structure of the synthesized ME was confirmed by ^{1}H NMR spectrum (Figure 3); the chemical shift ′ (ppm) was observed as follow: 6.99, 6.92, 6.74 (2.94H, Ar-H), 6.21,

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5.84 (2H, -C=CH_2), 5.95 (1H, =CH-), 5.06 (1.95H, CH_2=), 3.71 (3H, -OCH_3), 3.34 (2.07H,-CH_2-), 1.95 (2.96H, -CH_3). No observable phenolic hydroxyl group peaks and the presence of methacrylate groups (7 and 8 peaks), confirming that the phenolic hydroxyl group was fully methacrylated.

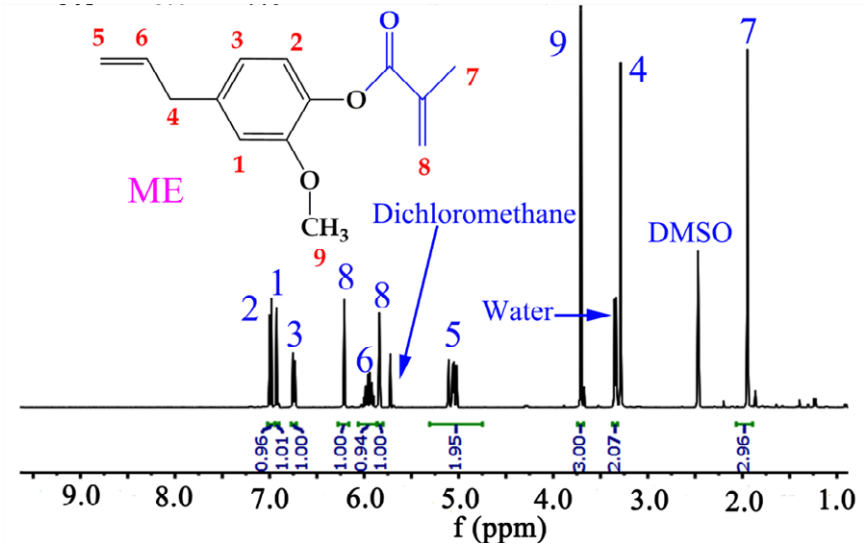

Figure 3. ^{1}H NMR spectrum of ME monomer

In order to evaluate the resin's volatility, the mass loss of ME and styrene as a function of time at 30 °C was measured. Styrene has much higher vapor pressures (666 Pa at 25 °C), leading to a full evaporation in 65 min at 30 °C. In contrast, ME monomer is less volatile with more than 97% remaining after isothermal exposure at 30 °C for 10 h (Figure 4).

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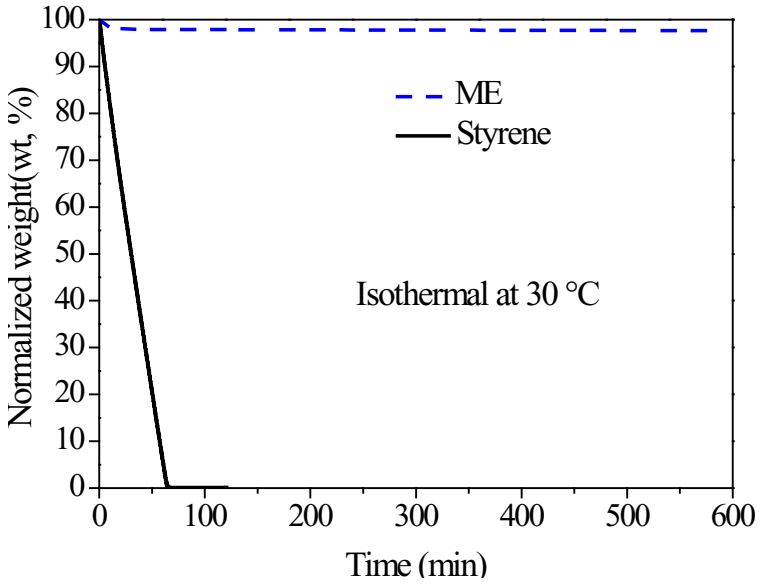

Figure 4. Evaporation behavior of ME and Styrene

The viscosity of VE-ME resin system is a key parameter since it has great influence on the processability. Pure VE resin showed an extremely high viscosity of 5.93 $\times 10^5$ cP (Figure 5 (a)) at 25 °C due to its high molecular weight, long molecular chains, and the presence of abundant hydrogen bonds between hydroxyl groups and ester groups. Since viscosity is a measurement of resistance to flow, it is strongly related to the dissipation of internal energy. High molecular weight, long molecular chains, and abundant hydrogen bonds made the dissipation of internal energy of VE resin difficult. Pure VE resin also showed a shear thinning behavior due to the deformation and alignment of the flexible molecules under high shear rate. In contrast, ME monomer exhibited a significantly lower viscosity of 17.6 cP at 25 °C. With the

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introduction of 20 wt% ME monomer to VE resin, a reduction in viscosity of VE-ME system over an order of magnitude was obtained, indicating a good miscibility between ME and VE resin. VE-ME system with 40% ME loading showed a viscosity of 1543 cP at 25 °C. Further increasing ME loading to 60% resulted in a VE-ME system with a viscosity of 226 cP. Moreover, the viscosity of VE-ME resin system was highly sensitive to temperature. With the temperature increased from 25 to 60 °C, the viscosity of VE-ME resin system was greatly decreased (Figure 5(b)). However, with high ME loadings, the viscosity of the VE-ME resin system became less dependent on temperature. VE-ME system with 40% ME loading showed a viscosity of 847.5 and 304.9 cP at 30 and 40 °C, respectively. It is noteworthy that the viscosity of VE-styrene resin system (used as benchmark resin) was obviously lower than that of VE-ME system with the same comonomer loadings and at the same temperatures in Figure 5(c). This is mainly due to the fact that the viscosity of ME monomer is 20 times higher than that of styrene. In general, in composite processing, the viscosity requirement for liquid molding resins is between 200-1000 cP. Therefore, the viscosity of VE-ME resin system can be tailored by adjusting ME loading and processing temperature to meet the composites manufacturing requirements for liquid

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molding techniques.

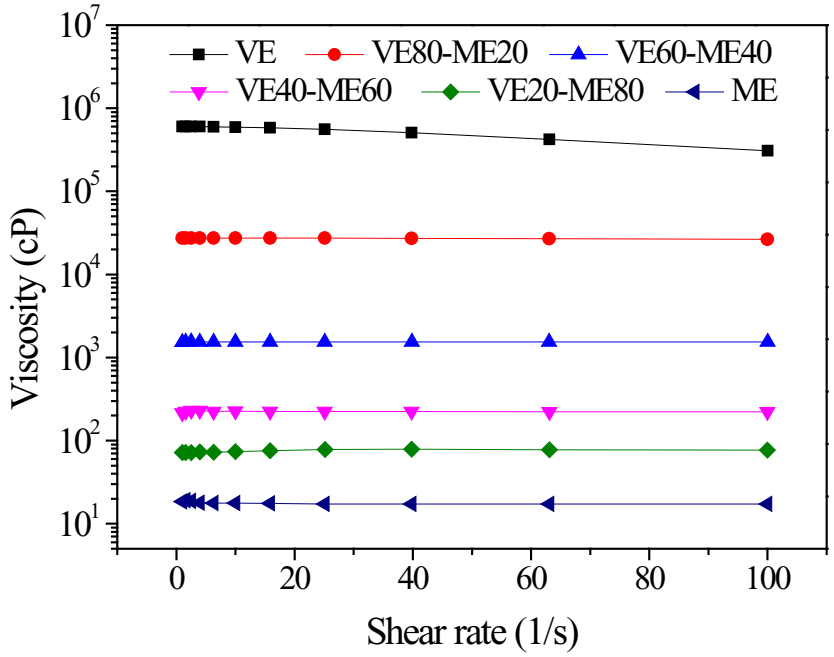

Figure 5(a). Viscosity as a function of shear rate for the VE-ME resin system at 25 °C

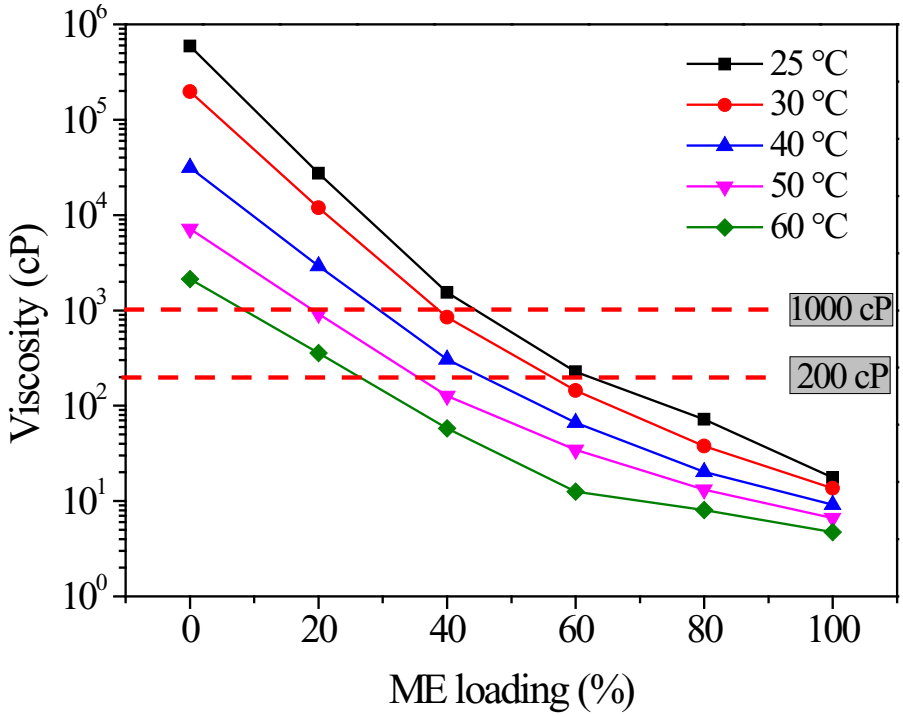

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Figure 5(b). Viscosity as a function of ME loadings for the VE-ME resin system at 10 s^{-1} shear rate

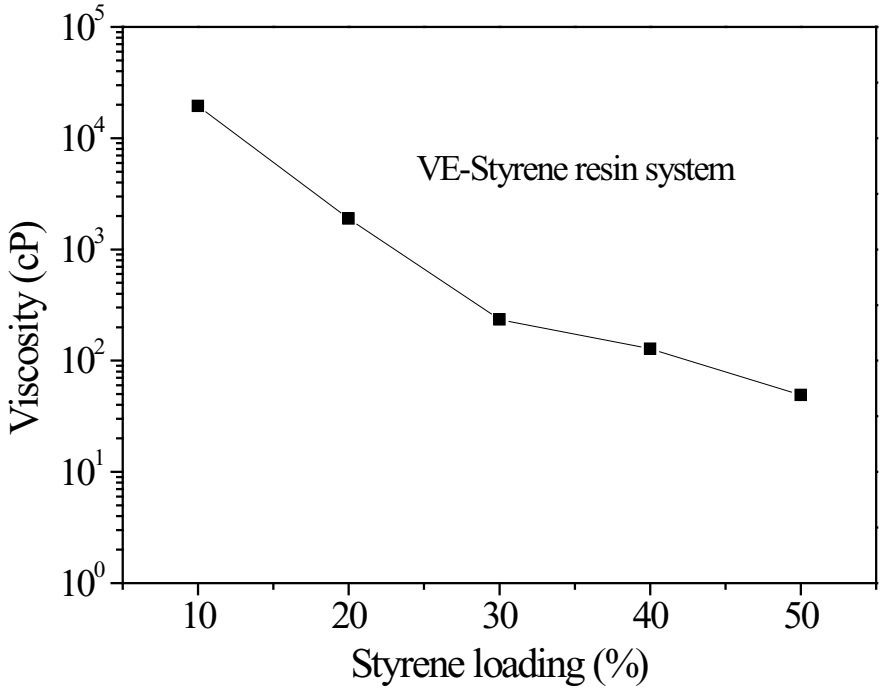

Figure 5(c). Viscosity as a function of styrene loadings for the VE-Styrene resin system at 10 s^{-1} shear rate at 25 °C

The polymerization between VE and ME is mainly based on their methacrylate group. VE molecule contains two terminal reactive methacrylate double bonds and ME monomer contains one methacrylate double bond and one allylic double bond. Although the allylic double bond is difficult to be homopolymerized, it can copolymerize with methacrylate groups. Therefore, VE resins with ME monomer as a

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comonomer can be readily polymerized by free radical polymerization to form a crosslinked network structure. The gel content of VE-ME systems was evaluated by Soxhlet extraction using dichloromethane as solvent since it is a good solvent for uncured VE, and uncured ME. After polymerization, the VE-ME thermosets were considered to form a crosslinked network structure that is insoluble in dichloromethane. All the VE-ME thermosets exhibited a high gel content ranging from 95 to 99% (Table 1), which indicated most of the monomer is incorporated and fixed in the crosslinked network. The curing extent of the VE-ME system increased with increasing ME loading and reached the highest with 60% of ME loadings. Further increasing ME loading, more allylic double bonds with low reactivity were available in the reaction system, leading to decreased gel content.

Table 1. Gel content for VE-ME thermosets

Formulations	Gel content (%)
VE	95
VE80-ME20	96
VE60-ME40	98
VE40-ME60	99
VE20-ME80	97
ME	97

The storage modulus and tan ´ as a function of temperature for cured VE-ME

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thermosets were evaluated and the results are shown in Figure 6 (a) and Figure 6(b). All the VE-ME thermosets exhibited high storage modulus (more than 1 GPa) at the glass state. Pure VE resin showed a storage modulus (G') of 1.22 GPa at 25 °C. This was attributed to a high rigidity of VE segment (bisphenol structure) compared to that of ME (benzene ring). Pure ME also showed a high storage modulus of 1.10 GPa at 25 °C, which was attributed to its high crosslink density. When normalized with their molecular weight, ME had more double bonds than that of VE. In general, a higher tan ′ peak indicates a more viscous behavior of a polymer network and a lower crosslinking degree, while lower peak intensity reveals a more elastic one and a higher crosslinking degree. The tan ′ peak intensity in Figure 6(b) also confirmed that ME resin had higher crosslinking degree than that of VE.

The initial introduction of ME monomer to VE resin resulted in an increase in crosslinking degree of the VE-ME thermosets. The crosslinking degree reached a maximum value with 60% ME loading, and then decreased gradually with further increases of ME. This was mainly attributed to a balanced homopolymerization and copolymerization of the C=C bonds from ME and VE molecules, which was confirmed by both Soxhlet and DMA experiments. Moreover, VE40-ME60

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thermosets exhibited the widest tan ′ peaks among all the VE-ME thermoset systems, indicating the complexity and heterogeneity of the crosslinked network.

The peak of tan ′ was used as an indicator of T_g for the VE-ME resin systems. Pure ME resin showed a T_g at around 139 °C, while pure VE resin showed a T_g of 191 °C. The T_g of VE-ME thermosets increased gradually with decreasing ME loadings. Structure rigidity and crosslinking degree both contributed to the T_g of VE-ME thermosets. VE resin contributed more on rigidity than that of ME to the VE-ME thermosets，and the presence of methoxy groups in ME have been reported to cause a drop in T_g ;[36-37] while ME monomer offered improving crosslinking degree than that of VE in VE-ME thermosets. VE80-ME20 thermosets showed a similar T_g with that of VE60-ME40, and both of their T_g were higher than that of pure VE resin, confirming that both the higher rigidity (VE) and higher crosslinking degree (ME) contributed to the T_g of VE-ME thermosets. The T_g of VE-ME thermosets was mainly depended on the structural rigidity of VE resin with more than 40% ME.

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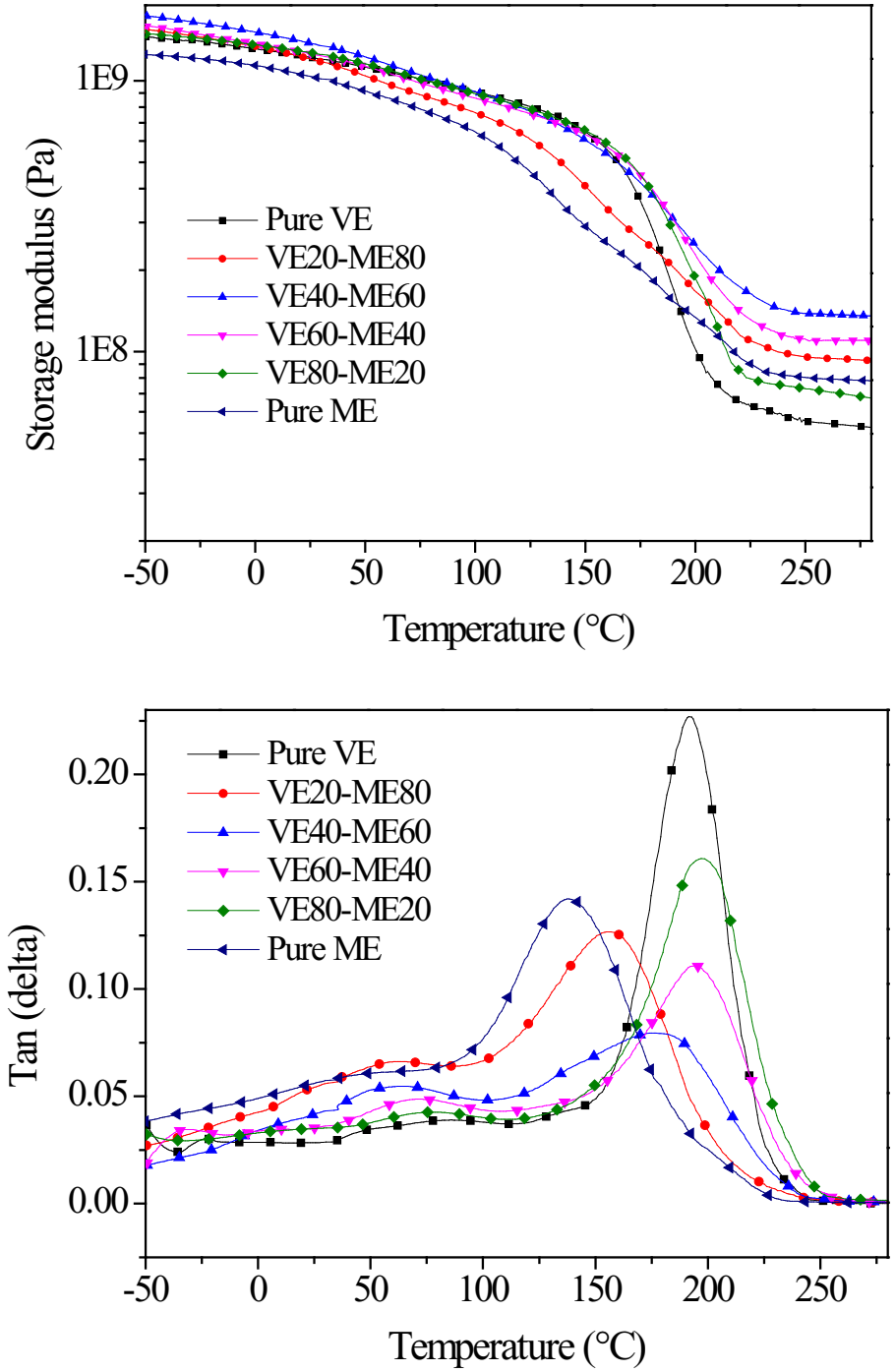

Figure 6. Storage modulus (a) and tan ´ (b) versus temperature for cured VE-ME thermosets

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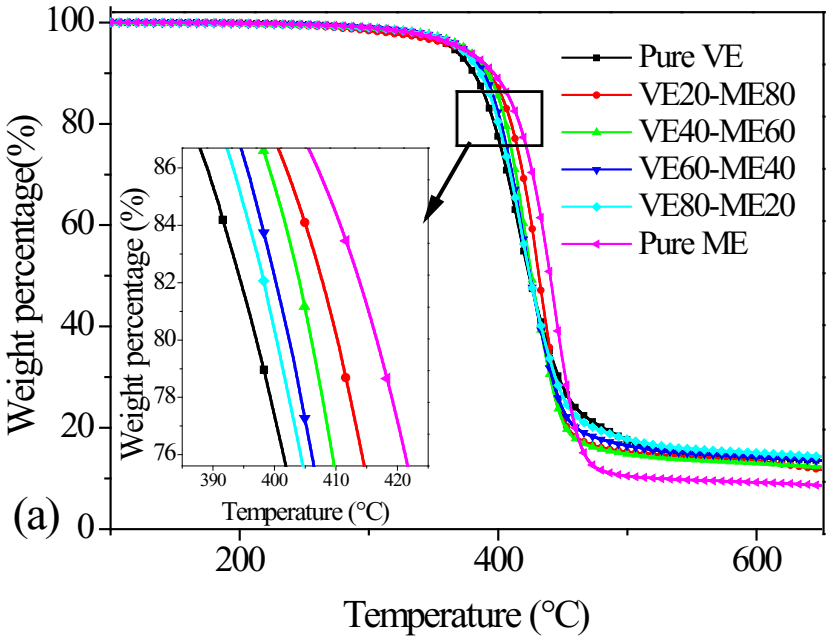
Table 2. Thermo-mechanical properties of VE-ME thermosets

Formulations	T_g (°C)	Storage modulus G' (25 °C, GPa)
Pure VE	191	1.22
VE80-ME20	199	1.27
VE60-ME40	197	1.26
VE40-ME60	178	1.38
VE20-ME80	157	1.20
ME	139	1.10



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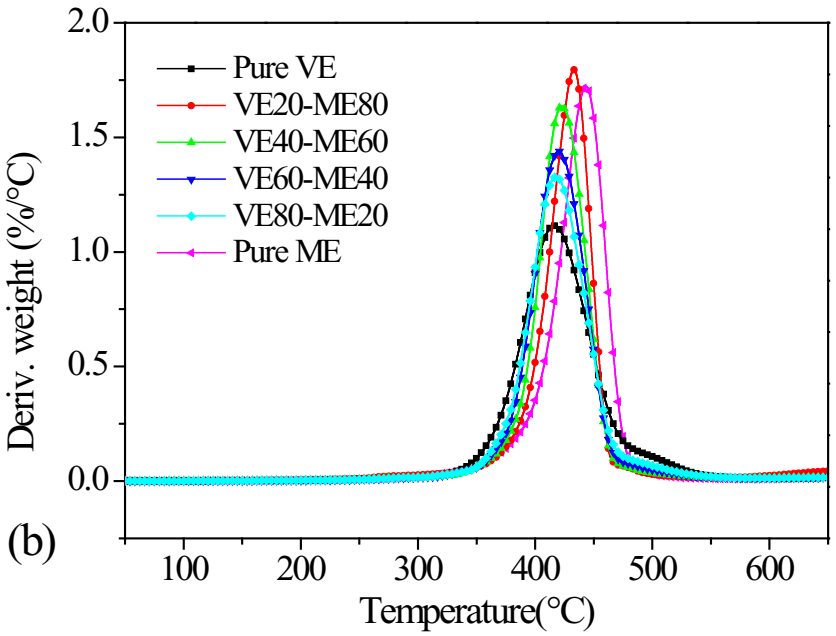

Figure 7. TGA curves (a) and their derivative curves (b) of the cured VE-ME resins

The TGA curves of the VE-ME thermosets under nitrogen atmosphere are shown in Figure 7(a) and Figure 7(b). As can be seen, all the VE-ME thermosets exhibited one major thermal decomposition peak between 300 to 530 °C, corresponding to the random scission of VE-ME crosslinked network structure. The thermal stability of VE-ME thermosets is directly related to crosslink degree and chemical structure of the network. ME monomer showed improved thermal stability than that of VE monomer. This is not only due to the high crosslinking density of the ME resin, as confirmed by

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the DMA analysis (Figure 6), but also the high tendency of thermal decomposition of the methylene ((-O-CH_2)$_2$-CHOH) segment in VE resin at elevated temperature. These two factors contributed to the final thermal stability behavior of the VE-ME thermosets. Moreover, the char yield of the VE-ME thermoset at 600 °C increased with increasing VE loading. This higher char yield is attributed to more phenyl groups present in the VE resin than the ME monomer, as more phenyl groups usually results in a higher char yield.

CONCLUSIONS

Biorenewable eugenol was successfully methacrylated to form ME monomer via Steglich esterification. ME was then incorporated into VE resin at various loadings (from 0 to 100 %) to produce VE-ME thermosets by free radical polymerization. The effect of ME loadings on properties of the VE-ME resin was systematically investigated. ME monomer showed extremely low VOC/HAP emissions compared to styrene. With the introduction of low viscosity ME into VE resin, the VE-ME resin system showed significantly reduction of viscosity, which would be suitable for common liquid molding processes. Moreover, VE resins and ME monomer can be

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polymerized to form crosslinked networks with high crosslinking degree. The T_g of VE-ME thermosets ranged from 139 to 199 °. Therefore, ME showed great advantages to replace styrene as a green comonomer in VE resin.

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