Renewable Myrcene-based UV-curable Monomer and its Copolymers with Acrylated Epoxidized Soybean Oil: Design, Preparation, and Characterization

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An innovative myrcene-based ultraviolet curable vinyl ester monomer was synthesized, and its molecular structure was analyzed with Fourier transform infrared spectroscopy and nuclear magnetic resonance (^{1}HNMR and ^{13}CNMR) analysis. A series of copolymers were also prepared by mixing the myrcene-derived monomer with another vinyl ester monomer, acrylated epoxidized soybean oil, under ultraviolet light. The curing process was monitored using Fourier transform infrared spectroscopy. Ultraviolet curing analysis showed that all the mixed systems had high curing rates and were fully cured within the first 30 seconds. When the weight ratio of myrcene-derived monomer to acrylated epoxidized soybean oil was 50/50, the ultimate double bond conversion reached 94.08%. Dynamic mechanical analysis showed that the storage modulus and glass transition temperature of the cured resins both increased with increasing content of myrcene vinyl ester monomer because the molecular structure of myrcene-derived vinyl ester monomer was more rigid and stronger than that of acrylated epoxidized soybean oil. Thermogravimetric analysis indicated that the main thermal initial decomposition temperatures were all above 360 °C, demonstrating that the copolymers had modest thermal stability.

Keywords: Myrcene; Acrylated epoxidized soybean oil; Bio-based vinyl ester resin; UV curable; Copolymers

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INTRODUCTION

Vinyl ester resin (VER), a well-known thermosetting resin, is widely used in marine, transportation, construction, aerospace, and automotive industries due to its excellent mechanical properties, thermal stability, and high corrosion resistance (Rosu *et al.* 2009). Ultraviolet (UV) curing VER has become more popular due to its advantages of being a cleaner more efficient method with lower costs compared with other curing methods. Generally, the UV curing mechanism includes cationic polymerization and free radical polymerization (Decker 2001). The cationic polymerization mechanism usually initiates polymerization of monomers such as epoxies and vinyl ethers; however, the free radical polymerization usually initiates the polymerization of acrylate-based resins (Esposito Corcione *et al.* 2010). The UV curing process usually utilizes free radical polymerization, and the photoinitiators for free radical polymerization accounts for more than 90% of commercial photoinitiators (Endruweit *et al.* 2006). Free radical polymerization typically involves three steps named initiation, propagation, and termination. In the initiation step, a photoinitiator is decomposed to produce free radicals containing unpaired electrons. After the initiation, the radical can combine with a monomer to produce another radical; then the active center continuously reacts with another monomer resulting in growth of the polymer chain. The propagation continues until the growing chain radical is deactivated by chain termination (Endruweit *et al.* 2006).

Cationic polymerization is commonly used to prepare curing systems that are not sensitive to the free radical photoinitiators. Like free radical polymerization, cationic polymerization process also contains the three stages of initiation, propagation, and termination. Although such systems have the advantages of low shrinkage and not being influenced by oxygen inhibition, the cationic polymerization kinetics are complex and strongly affected by resin formulation. In addition, lacking of suitable UV-sensitive cationic photoinitiators and lower reactivity of cationic copolymerization all limit its wide application (Esposito Corcione *et al.* 2004).

UV curing allows fast, almost instant, transformation of liquid resin into solid material. Thus it is commonly used for curing thin polymer films in application such as fast drying of varnishes, paints, printing inks and adhesives, as well as in the stereolithographic process (Esposito Corcione *et al*. 2006). Additionally, the UV-cured polymers are widely used for the protection of Cultural Heritage artworks (Esposito Corcione and Frigione 2012) due to their ability to form water repellent and optically clear coatings.

Traditional VER is commonly obtained from the petroleum-derived bisphenol A. However, with the reduction of availability of petroleum-based resources and increasing environmental concerns, it has become necessary to explore novel materials using renewable resources as raw materials for the chemical industry (Reddy *et al.* 2013). For instance, plant oils, starch, cellulose, and their derivatives will substitute traditional petroleum-based feedstock (Biswas *et al.* 2006). Therefore, using renewable resources as raw materials to synthesize VER also has been a topic of interest.

Epoxidized soybean oil (ESO, Fig. 1) is obtained by epoxidizing the double bonds in soybean oil (SO). ESO is expected to be an ideal alternative to chemical feedstock because of its low price, abundance in nature, and low toxicity (Kiatsimkul *et al.* 2006). The acrylated epoxidized soybean oil (AESO, Fig. 1) also has potential for use in many fields, such as resin, coating, adhesive, and composites (Ahn *et al.* 2011). However, the inherent flexibility of the aliphatic chains in SO results in low rigidity and strength, which limits its application in some areas. In general, a small amount of petroleum-based reactive diluent is added to acquire desired properties. However, the diluents are volatile and harmful to the environment (Işın *et al.* 2009). Therefore, many efforts have been made to develop bio-based monomers to copolymerize with AESO to prepare fully bio-based products.

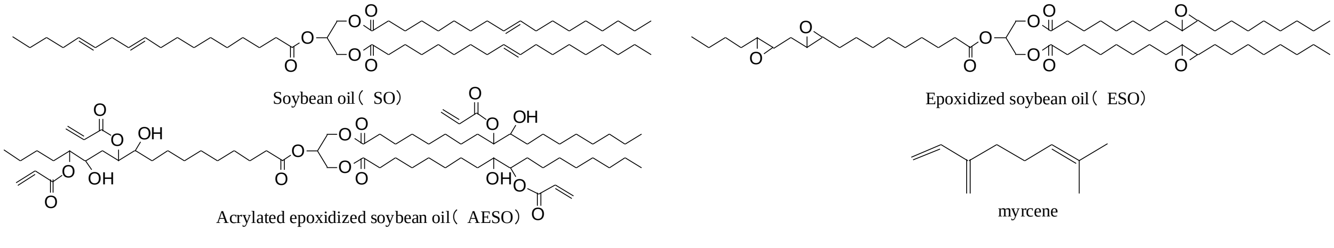

Fig. 1. The molecular structure of SO, ESO, AESO, and myrcene

Myrcene is an oily liquid extracted from the essential oils of many plants. In industry it is mainly obtained from the pyrolysis of β-pinene (Kolicheskia *et al.* 2007), which is produced from the distillation of pine tree oil and is already used in many industrial processes. The chemical structure of myrcene (Fig. 1) contains three highly reactive double bonds, including one conjugated double bond and a single one which act as reactive sites in the applications (Robles-Dutenhefner *et al.* 2005). Traditionally, myrcene is used as synthetic fragrance and a pharmaceutical intermediate (Behr *et al.* 2012). Myrcene is rarely used as raw material in the VER field, which hinders its further processing and utilization. In this work, the aim is to prepare a VER monomer from a Diels-Alder reaction, glycidylation, and epoxy ring-opening esterification of myrcene with maleic anhydride, epichlorohydrin, and an acrylic monomer. The VER monomer is then copolymerized with AESO monomer to form fully bio-based VER copolymers. In this study, the comprehensive properties of the copolymers with different weight ratios of the two bio-based VER monomers are also explored.

EXPERIMENTAL

Materials

Myrcene was purchased from Jiangxi Kaiyuan spices Co., Ltd. as a technical product containing about 75% (weight ratio) of myrcene. Acrylated epoxidized soybean oil (AESO) was prepared in the laboratory. Hydroquinone (stabilized, 99.5%), benzyltriethylamine chloride (≥98.0%), acrylic acid (≥99.0%), calcium oxide (99.5%), and epichlorohydrin（≥99.0%) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Sodium hydroxide (≥98.0%) was purchased from Shanghai Zhanyun Chemical Co., Ltd. Dimethoxybenzoin (99%) was purchased from Aladdin Industrial Corporation. All reagents were used as received.

Methods

Preparation of diglycidyl ester of maleinized myrcene modified with acrylic acid (A-DGEMYM)

First, 100.0 grams (g) (0.51 mol) of maleic anhydride were charged to a 1000 milliliter (mL) flask equipped with a magnetic stirrer, a thermometer, a dropping funnel, and a reflux condenser. The temperature was raised to 55 ^{o}C and maintained until maleic anhydride melted completely. Then 200.0 g (0.55 mol) of myrcene were added drop-wise with the dropping funnel while the temperature was maintained at 55 to 60 ^{o}C. After the addition of myrcene, the mixture was heated to 70 ^{o}C and reacted for 4 hours (h). Next, the crude product was developed through vacuum distillation and the fraction at 190 to 195 ^{o}C was collected. Finally, maleinized myrcene was obtained as a light yellow liquid.

Then 46.8 g (0.2 mol) of maleinized myrcene and 4.5 g (0.25 mol) of distilled water were added into a 1000-mL flask. Next the mixture reacted at 70 to 80 ^{o}C for 2 h until complete hydrolysis had occurred. After that, 185.0 g (2.0 mol) of epichlorohydrin and 0.9 g (0.004 mol) of benzyltriethylamine chloride were added to the flask. Then the mixture was heated to 100 ^{o}C and the reaction continued at this temperature for 2 h. After the mixture was cooled to 60 ^{o}C, 16.0 g (0.4 mol) of sodium hydroxide and 22.4 g (0.4 mol) of calcium oxide were added and reacted at this temperature for 3 h. Finally, the products were filtered with celite, and the filtrate was collected. After the excess epichlorohydrin was distilled via rotary vacuum evaporation, a light yellowish viscous liquid, *viz.* diglycidyl ester of maleinized myrcene (DGEMYM) was obtained.

Then 20 g (0.55 mol) of DGEMYM, 0.14 g benzyltriethylamine chloride and 0.085 g of hydroquinone were added to a flask. After the temperature was raised to 100 °C, 7.93 g (0.11 mol) of acrylic acid was added slowly through the dropping funnel. The mixture reacted at 100 °C for 3 h, and then a yellow viscous resin (A-DGEMYM) was obtained. The synthesis route is shown in Fig. 2

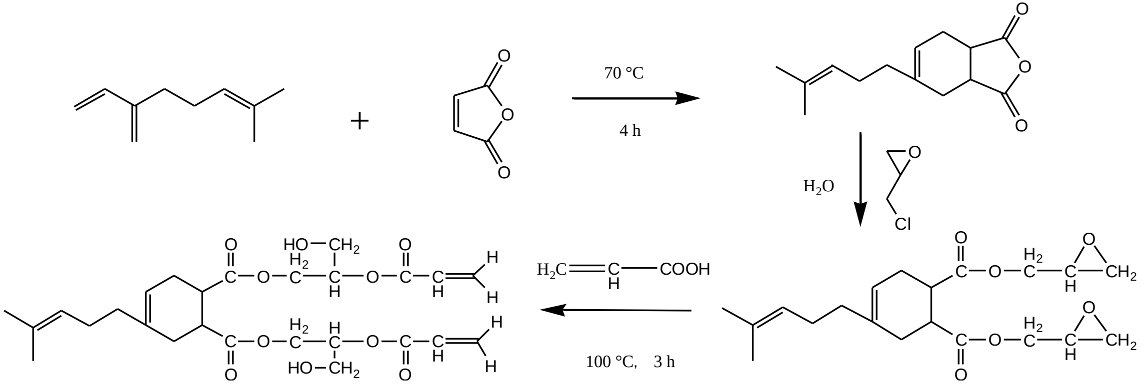

Fig. 2. The synthesis route of A-DGEMYM

Copolymerization of ADGEMYM with AESO

AESO and A-DGEMYM were mixed uniformly by different weight ratios of 0%/100%, 30%/70%, 50%/50%, 70%/30% and 100%/0%, respectively. Then, 3% (on the basis of total weight of resins) of dimethoxybenzoin was added as the photoinitiator. Cured polymer samples were prepared by casting the mixture into molds with dimensions of 80×10×4 cubed millimeters (mm^3) and 7.62×3.18×0.5 mm^3. Then, curing was performed in the Intelli Ray 400 UV light curing box for 20 minutes with the irradiation intensity of 100 milliWatts per square centimeter (mW/cm^2). The copolymers were labeled as follows: A-DGEMYM30/AESO70 denotes a mixture of 30 wt% of A-DGEMYM and 70 wt% of AESO.

UV curing behaviors of the resins

The mixtures prepared as above were evenly spread on the clean glass plates with a 50 μm obliterator and cured under UV light of 100 mW/cm^2 intensity. Each sample was collected at 10, 20, 30, 60, 120, and 240 seconds (s), respectively. The cured behaviors were investigated by FTIR analysis. The absorption peak intensities of the double bonds at about 1635 cm^{-1} and of the carbonyl group at about 1730 cm^{-1} were calculated, respectively. The conversion of double bond can be obtained by contrasting the integral area of the two peaks.

Characterization and properties testing

Fourier transform infrared (FTIR) analysis was performed using an IS10 spectrometer (Nicolet, America) by an attenuated total reflectance method. Each sample was scanned from 4000 to 400 cm^{-1}. ^{1}HNMR and ^{13}CNMR spectra (300 MHz) were recorded on an ARX300 spectrometer (Bruker, Germany). The chemical shifts relative to that of deuterated chloroform (d 7.26) were recorded.

Tensile property was measured following ASTM D638-03 and GB/T 1043-1993 respectively using a CMT4303 universal test machine (SANS, China) with the test speed of 1 mm/min. To be able to quantify the precision, five replicates were measured and the average values were obtained. All the samples were tested at 25 °C.

Dynamic mechanical analysis (DMA) was performed with a Q800 dynamic mechanical thermal analyzer (TA, America) in three-point bending mode with a frequency of 1 Hz. All samples had dimensions of 60×10×4 mm^3 and were swept from -40 to 120 °C at a heating rate of 25 °C/min. Thermogravimetric analysis (TGA) was performed using a 409PC thermogravimetric analyzer (Netzsch, Germany). Each sample was tested from 25 to 800 °C at a heating rate of 15 °C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

FTIR Analysis

The FTIR spectra of the myrcene based VE monomer and its intermediates are shown in Fig. 3. For the spectrum of myrcene, the two absorption peaks at 1644 and 1594 cm^{-1} corresponded to the symmetric and asymmetric coupled vibration absorption of the conjugated double bonds, respectively. The absorption peak of the isolated double bond of myrcene also appeared at 1644 cm^{-1}. The weak absorption peak at 3089 cm^{-1} corresponded to the asymmetric stretching vibration absorption of C-H on the terminal vinyl group. The absorption peak at 1796 cm^{-1} was assigned to the frequency doubling absorption of the terminal vinyl group. The appearance of the above peaks verified the existence of the conjugated double bond and isolated double bond in the structure of the myrcene. All above absorption peaks clearly verified the chemical structure of myrcene.

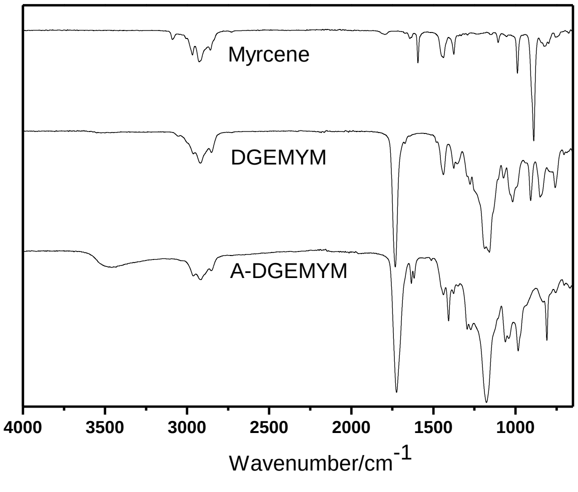

Fig. 3. FTIR spectra of myrcene-derived VER monomer and its intermediates

For the spectrum of DGEMYM, the characteristic peaks of cyclic anhydride at 1834 and 1768 cm^{-1} disappeared and a new intensity absorption peak corresponding to the carbonyl group of the ester appeared at 1732 cm^{-1} after the reaction between maleinized myrcene and epichorohydrin. The absorption peaks at 1439 and 1176 cm^{-1} were assigned to the asymmetric and symmetric vibration absorption of C-O-C bonds, respectively. The peak at 908 cm^{-1} was attributed to the characteristic absorption peak of an epoxy group. In the spectrum of A-DGEMYM, the absorption peak of an epoxy group at 908 cm^{-1} disappeared and the peak of a free hydroxyl group at 3460 cm^{-1} appeared. The characteristic peak of a double bond at 1635 cm^{-1} and the multiple absorption peaks of an ester carbonyl conjugated with a vinyl group also appeared. The changes in the appearance of the groups demonstrated that the acrylic acid had already reacted with DGEMYM via ring-opening esterification.

^{1}HNMR and ^{13}CNMR of A-DGEMYM

The ^{1}HNMR spectrum of A-DGEMYM is shown in Fig. 4-1. The chemical shift from 5.70 to 6.53 parts per million (ppm) was attributed to the protons in the acrylic acid part. The chemical shift from 4.89 to 5.46 ppm was assigned to the protons of –CH= in the myrcene part. In addition, the chemical shift from 3.40 to 4.46 ppm corresponded to the protons of glycidyl ester which were produced after ring-opening esterification between acrylic acid and the glycidyl group. The appearance of the peak at around 3.70 ppm further indicated the occurrence of ring-opening esterification. The peaks at 2.90 and 2.33 ppm corresponded to the protons in the hexatomic ring which confirmed the occurrence of the Diels-Alder reaction. The evidence in the ^{1}HNMR spectrum of A-DGEMYM verified the chemical structure of the A-DGEMYM monomer.

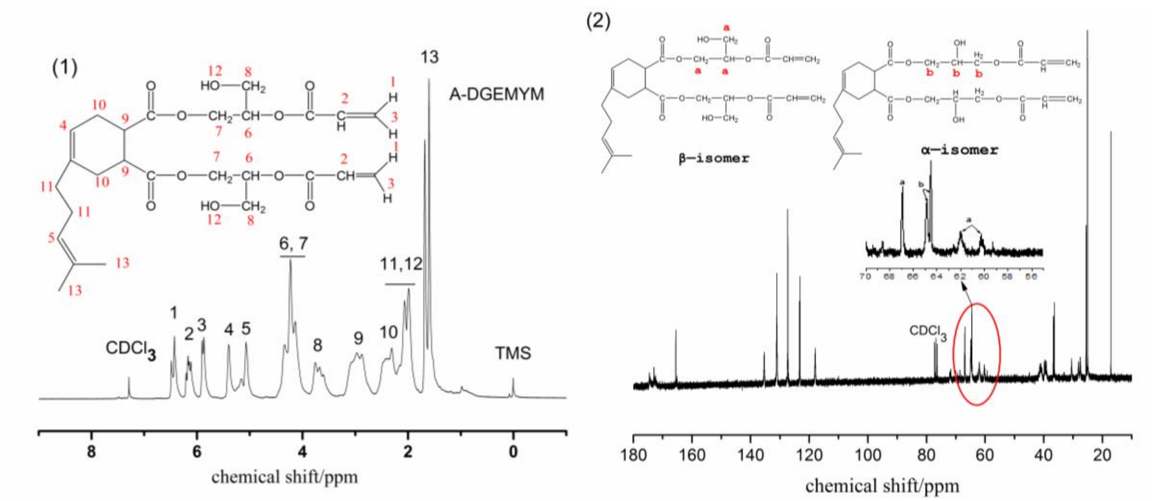

Fig. 4. ^{1}HNMR and ^{13}CNMR spectra of A-DGEMYM

It is well known that two isomers (α and β-isomer) are usually formed during the ring-opening of epoxides by acids. The ratio of the two isomers depends on the structure of the epoxide and the catalyst used (Steinmann 1989). For asymmetric epoxy compounds, the epoxide ring-opening reaction catalyzed by acid followed the mechanism of unimolecular nucleophilic substitution (S_N1), and the C-atom connecting to more substituents is attacked preferentially. Thus the β-isomer was expected to be the main product in the reaction of interest.

The ^{13}C-NMR spectrum of the A-DGEMYM is shown in Fig. 4-2. The three peaks at 67, 62, and 60 ppm were assigned to the C-atoms of β-isomer. The two peaks at around 64.9 and 64.5ppm were attributed to the b C-atom of α-isomer. Additionally, one can calculate the integral areas of the hydrogen peaks in the spectrum of ^{1}H-NMR, and the ratio of β-isomer is approximately 89.5%. Thus it can be concluded from the NMR results that the product was a mixture of the two isomers, with β-isomer being the main product.

UV Curing Behaviors of the Resins

The UV-curing behaviors of the copolymers with different weight ratios of A-DGEMYM/AESO are shown in Fig. 5. Clearly, the ultimate double bond conversions of all cured resins were above 83% after curing for 240 s. This ultimate double bond conversion was higher than that of the cured system of VE 65/ methacrylated lauric acid 35 (Campanella *et al.* 2011). The double bond conversion increased sharply and reached the ultimate curing degree within 30 s, which indicated the high copolymerization activity of the two monomers. The curing rate increased slowly after 30 s, due to the decrease of the double bond density and the increased viscosity of the cure material. Compared with pure AESO resin, A-DGEMYM had higher copolymerization ability, while the mixture of the two resins was more reactive than either of the two pure cured resins. Despite the presence of many long fatty acid chains in AESO, the long chains were not beneficial to the curing process or the curing kinetics (La Scala *et al.* 2004). Thus, the pure AESO had the lowest curing ability compared to other cured resins.

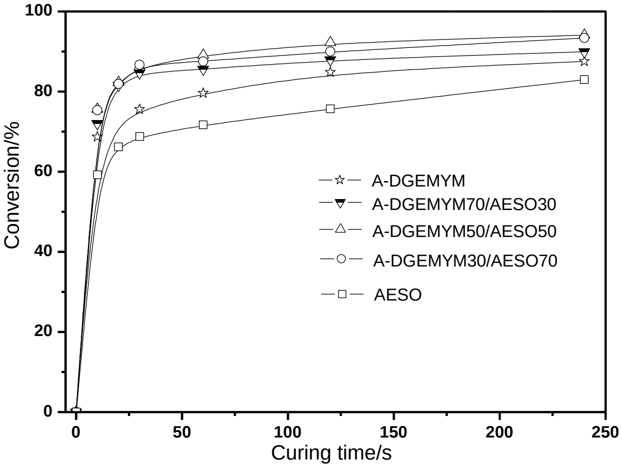

Fig. 5. UV-curing behaviors of VER monomers with different weigh ratios

For copolymers, the curing rates were very close to each other within the first 20 s. With increasing AESO content, after 20 s the curing rates varied and the ultimate double bond conversion first increased and then decreased. This phenomenon can be explained by the steric hindrance of alicyclic structures in A-DGEMYM and the free volume in AESO.

Long fatty acid chains in AESO introduce more free volume to the curing system, which enables the double bonds to move more freely. When the two effects were balanced with the changing weight ratio, the curing rate and the ultimate double bond conversion both reached high levels. In the A-DGEMYM/AESO curing system, when the weight ratio of A-DGEMYM/AESO was 50/50, the curing was up to 94% within 240 s.

Tensile Properties

Figure 6 shows the stress-strain curves of cured resins with different weight ratios of A-DGEMYM/AESO. All of the cured resins exhibited rigid tensile behaviors without a yield point. The breaking elongation of all samples was below 10%, indicating that the copolymers possessed the characteristics of rigid materials.

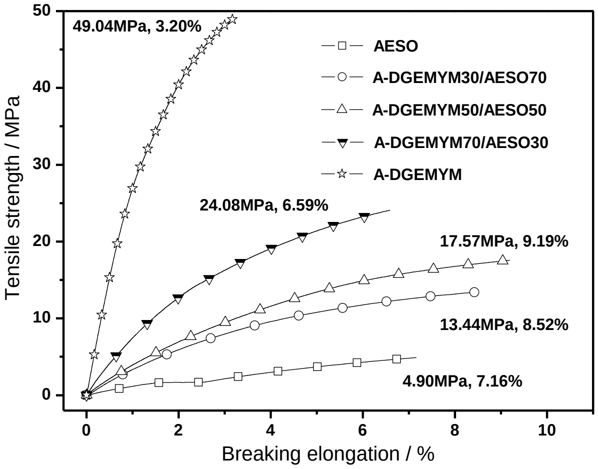

Fig. 6. Tensile stress-strain curves of copolymers with different weight ratios

The tensile strength of the copolymers was enhanced with increasing A-DGEMYM content, and the breaking elongation first increased and then decreased. Generally, the tensile property of a cured resin is influenced by its chemical structure and the cross-linked state (Li *et al.* 2014), but the structure of A-DGEMYM has rigid alicyclic structures, which gives the cured products high strength. In addition, the aliphatic chain that could enhance the flexibility of the cured resin is much shorter in A-DGEMYM than in AESO. Thus, the pure cured A-DGEMYM showed the highest tensile strength (49.04 mega Pascals (MPa)) and lowest breaking elongation (3.20%). As explained above, the pure cured AESO resin should have the highest elongation as its molecules have long flexible aliphatic chains, but no stiff chemical structure. However, this was not the case in Fig. 6. The major explanation is that the double bond conversion of pure cured AESO is lower (Fig. 5) than other cured resins and the interaction between the long aliphatic chains also hinders AESO from forming a good cross-linked system. With the incorporation of 50% A-DGEMYM, the tensile strength reached 17.57 MPa, which was much higher than that of the pure AESO (4.90 MPa). The breaking elongation reached 9.19%, which was also much higher than that of the traditional vinyl ester resin that had a breaking elongation that was generally lower than 5%. These changes can be ascribed to the synergistic effect of the alicyclic structures in A-DGEMYM and long aliphatic chains in AESO, which give the cured resins excellent strength and elongation, respectively.

Dynamic Mechanical Analysis (DMA)

Figure 7 depicts the storage modulus (E') and loss factor (tanδ) curves of cured resins with different A-DGEMYM/AESO ratios. The peak temperature of tanδ corresponded to the glass transition temperature (T_g). All cured resins showed a similar changing trend and all the tanδ curves had one clear single T_g, demonstrating that all the cured systems were homogenous and compatible. With increasing A-DGEMYM content, the E' in the glassy state increased monotonically, mainly because the alicyclic structure in the A-DGEMYM monomer bestowed the cured resin with high stiffness, as discussed before. The tanδ curves also show that the tanδ peak became more intense and less broad with increasing A-DGEMYM content. Aside from the chemical structure, the T_g peak intensity increased probably because cross-linked network and hyperbranched structures were formed well (Karger-Kocsis *et al.* 2004; La Scala and Wool 2005). The alkyl chains in AESO are much longer than those in A-DGEMYM, and thus there are more possible relaxation modes in AESO, which resulted in a broader T_g peak with the increasing AESO content. When the A-DGEMYM/AESO ratio was 70/30, the *E'* value reached 3500 MPa and the T_g was 68.06 ^oC, which was very close to the T_g (71.2 ^oC) of bio-based VE resin reported by Campanella *et al.* (2009), in whose study 35 wt% of styrene was used as the comonomer to copolymerize with AESO. Thus, it can be inferred that the copolymer of A-DGEMYM and AESO is a potential material in the VER area.

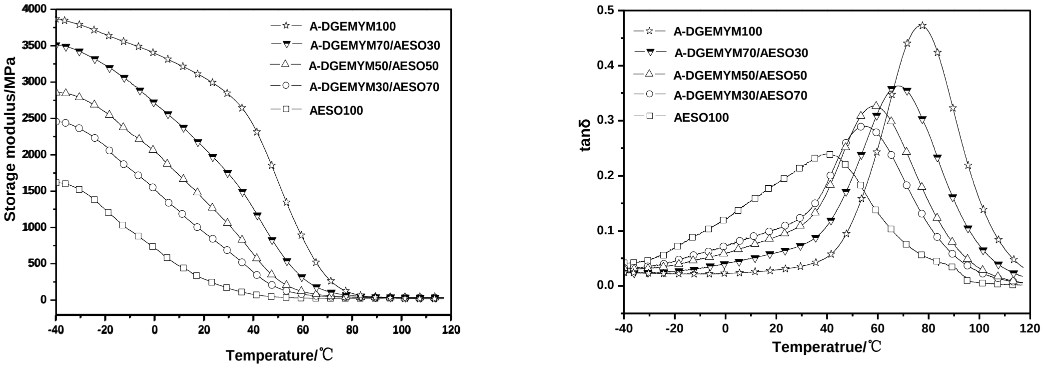

Fig. 7. DMA curves of copolymers with different weight ratios

The cross-link density (v_e) helps to explain the effects of comonomers on the mechanical properties. Thermosets behave as a rubbery substance when the temperature is above T_g, and at small deformation, the *E*' of the elastomer with a network structure is proportional to the cross-link density. Thus, v_e can be calculated by using the rubber elasticity theory listed as follows (Asif *et al.* 2005),

$$v_e = E'/3RT \tag{1}$$

where *E*' is the storage modulus of the rubbery state. *R* is the gas constant and *T* is the absolute temperature.

The value of *E*' at T_g+20 ^oC was taken to ensure the cured resins were in the rubbery state, and the calculated v_e is listed in Table 1. Clearly, the cross-link density of the copolymer was higher than that of pure cured A-DGEMYM and AESO. The results of v_e in copolymers with different A-DGEMYM and AESO contents were very close. Generally, higher *E*' corresponds to higher v_e, but the results do not agree. The reasons may be that in this curing system AESO contains longer alkyl chains than A-DGEMYM. In this case, the chemical structures affect the mechanical properties more severely than the cross-link density. Thus, the cured copolymer with increasing A-DGEMYM content showed superior mechanical properties.

Table 1. Crosslinking Density of Copolymers with Different Weight Ratios

SAMPLE	T_g/ °C	E' at T_g+20 °C/MPa	v_e/(mol/m^3)
A-DGEMYM	77.10	35.70	3866
A-DGEMYM70/AESO30	68.06	45.61	5063
A-DGEMYM50/AESO50	58.42	44.80	5109
A-DGEMYM30/AESO70	54.24	44.10	5090
AESO	40.50	28.86	3468

Thermogravimetric Analysis (TGA)

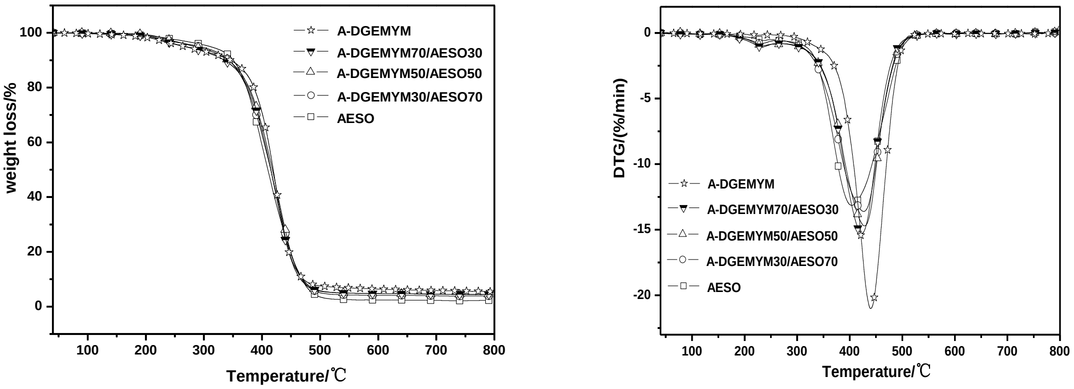

Fig. 8. TGA curves of copolymers with different weight ratios

All samples exhibited one-step thermal degradation. Clearly, all of the cured resins were thermally stable at temperatures lower than 200 ^oC. As the temperature increased to around 228 ^oC, the cured resins containing AESO monomer experienced a slight weight loss of about 5%. This small weight loss was probably due to the small volatile component in AESO, such as the part of the ester group in the acrylate moiety and the unreacted acrylic in AESO. The second degradation step occurred above 360 ^oC for the copolymers, but at 402.9 ^oC for the pure A-DGEMYM. The temperatures were slightly lower than that of the VE/AESO system reported by Grishchuk (approximately 400 ^oC) as it formed an Interpenetrating Polymer Network (IPN) in VE/AESO (Grishchuk and Karger-Kocsis 2011). The catastrophic degradation was attributed to the complete decomposition of the cross-link system, which included the rupture of the cross-link sites and the fracture of the molecular chains. When the temperature exceeded 420 ^oC, the decomposition rates were maximized because numerous high-volatility components were generated. The char yield of the copolymers at the end of the TGA was higher than the pure cured A-DGEMYM and AESO resins, which was ascribed to the good cross-link structures of the copolymers. According to the TGA, the copolymers of A-DGEMYM and AESO were modestly thermally stable as they had lower weight loss below 200 ^oC and the main initial thermal degradation temperature was above 360 ^oC.

Table 2. Thermal Degradation Data of Cured Resins with Different Ratios

SAMPLE	T_i (℃)	T_{max} (℃)	Char yield (%)
A-DGEMYM	402.9	439.8	0.3
A-DGEMYM70/AESO30	369.0	422.8	4.50
A-DGEMYM50/AESO50	368.0	428.4	4.49
A-DGEMYM30/AESO70	361.8	426.7	3.85
AESO	356.7	403.7	2.30

T_i: initial degradation temperature
T_{max}: temperature corresponding to the maximum degradation rate

CONCLUSIONS

1. A myrcene based VER monomer was synthesized *via* a Diels-Alder reaction, glycidylation reaction, and ring-opening esterification. FTIR, ^{1}HNMR, and ^{13}CNMR characterization demonstrated that the monomer had been successfully synthesized. Properties tests showed that cured pure A-DGEMYM resin was a rigid material.
2. UV curing analysis indicated the mixed VERs (AESO and A-DGEMYM) had high curing rates within the first 30 s and the ultimate double bond conversion could reach 94.08% when A-DGEMYM/AESO weight ratio was 50/50. The tensile strength, T_g, and storage modulus increased with the increasing content of A-DGEMYM. The main initial thermal decomposition temperatures of prepared copolymers were all above 360 °C.
3. The use of myrcene and SO to prepare VER-based copolymers is a promising strategy to develop fully bio-based thermosetting materials. It is a potential alternative to petroleum-based resin in some areas, which makes this an important contribution to the development of green chemistry.

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