Substantially Reinforcing Plant Oil-Based Materials via Cycloaliphatic Epoxy with Double Bond-Bridged Structure

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ABSTRACT

A diepoxide ((*E*)-1,2-di(7-oxabicyclo [4.1.0]heptan-3-yl)ethane, named DCE), possessing two cyclohexane rings bridged by a double bond was obtained via self-metathesis approach. This unique epoxy structure shows great potential in substantially overcoming the poor performances of plant oil materials in thermal and mechanical aspects. The molecular structure of DCE is more compact and regular than the commercial 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (ECHM) and was evidenced by the small-/wide-angle X-ray scattering. After conetwork was built between epoxidized soybean oil (ESO) and DCE, stiff crosslinks were created through the double bonds of DCE, which restricts the backbone rotation of ESO (P-ESO) networks. DCE-rich domains with dimensions ranging from 0.5~2 μm were observed with the increase of DCE, revealed by atomic force microscopy (AFM) phase image and voltage-distance curve. These DCE-rich domains act as micro-scale reinforcements homogenously dispersed in the ESO matrix, effectively sustaining the applied stress and preventing the chain break from high force loading. Compared to P-ESO, the co-polymerized ESO-DCE at 30 wt % DCE loading showed tensile strength of 62 MPa and glass transition temperature of 163 $^{\circ}\text{C}$ that are much higher than 4 MPa and 10 $^{\circ}\text{C}$ for P-ESO, respectively. ECHM also showed significant reinforcement effects on the thermal and mechanical properties of ESO, but DCE's reinforcement effects is doubled compared to ECHM.

KEYWORDS: plant oil; reinforcement; double bond

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INTRODUCTION

In the past decades, plant oils have been considered as a sustainable feedstock for various applications because of its widespread availability, relative low price, and advantageous versatility.¹⁻⁴ Epoxidized soybean oil (ESO) is one of the most commercially used plant oil derivatives, which has been widely used as the precursors of bio-based polyols in polyurethane field. However, polymerized ESO (P-ESO) materials are limited because of the poor thermal resistance ($T_g < 20\text{ }^{\circ}\text{C}$) and low mechanical strength (tensile strength $< 5\text{ MPa}$),^{5,6} which is mainly caused by the fatty acids crosslink structure between the triglycerides and ether groups (see supporting information Figure S1).

In this research, the P-ESO was reinforced through olefin self-metathesis pathway. Cycloaliphatic epoxy, one of the most widely used commercial cycloaliphatic epoxy, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (ECHM), was initially used to restrict the chain segment motion of ESO by the relatively stiff alicyclic epoxy rings (Figure 1). We initially co-polymerized ESO and ECHM, and found that the ECHM improved significantly not only the thermal resistance but also the mechanical strength of the ESO based resin. For example, a ESO-ECHM resin with 30 wt% ECHM loading had a glass transition T_g of 79°C and tensile strength of 30 MPa , which were much higher than the P-ESO alone resin with a T_g of only $10\text{ }^{\circ}\text{C}$ and tensile strength of 4 MPa , respectively.

Inspired by the chemical structure of ECHM, we hypothesized that the replacement of a methyl ester chain linking the alicyclic epoxy groups to a more stiff structure would further enhance the thermal and mechanical properties of ESO-based materials. Olefin metathesis has been developed in recent years as a powerful tool for the construction of defined micromolecular and polymeric architectures, including ring-opening metathesis (ROM), ring-closing metathesis

(RCM), ring-opening metathesis polymerization (ROMP), acyclic diene metathesis polymerization (ADMET), cross-metathesis, and self-metathesis.⁷⁻¹⁸ Among these reaction pathways, Self-metathesis has become an increasingly important tool in molecular design and synthesis owing to the ruthenium based catalysts developed by Grubbs and Hoveyda-Grubbs.^{19,20} The 4-ethenyl-7-oxabicyclo[4.1.0]heptanes (ECP) is one kind of alicyclic epoxy monomer bearing a terminal alkene (Figure 1). Based on the classification proposed by Grubbs et al.,²¹ ECP is considered as a type II substitute undergoing a self-metathesis with the aid of Hoveyda-Grubbs 2nd generation catalyst. Therefore, it is possible to obtain a desired compact chemical structure (named (*E*)-1,2-di(7-oxabicyclo[4.1.0]heptan-3-yl)ethane, (DCE)) in which two alicyclic epoxy rings can be firmly bridged via a double bond. Compared to the relatively flexible methyl ester chain, the newly constructed double bond would achieve a rigid conformation that strictly restricts the chain rotation between these two epoxy rings (Figure 1). Consequently, compared to the ECHM, more robust networks should be constructed via the copolymerization of ESO and DCE. It is the first time in this study, olefin self-metathesis was applied to reinforce plant oil-based materials (i.e., ESO). We expect to achieve plant oil-based materials with superior thermal resistance and mechanical strength properties suitable for engineering materials.

Figure 1. Chemical structures of 4-ethenyl-7-oxabicyclo[4.1.0]heptanes (ECP), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (ECHM), and (*E*)-1,2-di(7-oxabicyclo[4.1.0]heptan-3-yl)ethane (DCE); and synthesis route of monomer DCE from ECP via self-metathesis.

EXPERIMENTAL SECTION

Materials. The 4-ethenyl-7-oxabicyclo [4.1.0] heptanes (ECP, 98%), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (ECHM) and Hoveyda-Grubbs Catalyst 2nd Generation were purchased from Sigma-Aldrich (USA). The epoxidized soybean oil (ESO, Vikoflex® 7170) was provided by ArkemaInc., and cationic initiator (PC-2506,[4-(2-hydroxyl-1-tetradecyloxy)-phenyl], phenyliodoniumhexafluorantimonate) was kindly provided by Polyset Inc.

Synthesis of DCE. The ECP (60 mL) and Hoveyda-Grubbs 2nd Generation catalyst (400 mg) were charged into a 200 mL round bottomed flask equipped with a reflux condenser, and the mixture was stirred with a magnetic bar at 40 °C and degassed with nitrogen for 48 h. The residual ECP

was removed and collected through high vacuum rotary evaporation at 60 °C, and then the target product, (E)-1,2-di(7-oxabicyclo[4.1.0]heptan-3-yl)ethane (DCE, 9.8g), was obtained.

Networks of ESO-ECHM and ESO-DCE. Cationic photo-initiator (PC-2506, 3wt%) was added into ESO. The mixture was mixed homogenously with the aid of a Vortexmixer and sonicator, then coated onto a 15.24 cm × 25.4 cm glass plate with a film casting knife (model 4302, BYK-Gardner USA) set at 160 μm wet thickness. The resin containing photo-initiator was cured with a Fusion 300S 6'' UV system (300 W/inch power, D bulb, UVA radiation dose 1.7-1.8 J/cm²) equipped with an LC6B benchtop conveyor at conveyor speed of 213 cm/min. The corresponding cured resin was then post-cured in an oven at 170 °C for 8 h, and the product was named as P-ESO. The same procedure was used for ECHM, DCE, ESO-ECHM (80: 20 by weight), ESO-ECHM (70: 30 by weight), ESO-DCE (80: 20 by weight), and ESO-DCE (70: 30 by weight) samples respectively; and the products were named as P-ECHM, P-DCE, P-ESO-ECHM (20%), P-ESO-ECHM (30%), P-ESO-DCE (20%) and P-ESO-DCE (30%), respectively.

Characterization. FTIR, NMR, WAXS and SAXS: Fourier transform infrared (FTIR) measurements were performed with a Perkin-Elmer Frontier FT-IR/NIR spectrometer. Spectra acquisitions were based on 32 scans with data spacing of 2.0 cm⁻¹. ¹H NMR was performed using a Bruker 300 MHz spectrometer at room temperature. ¹³C NMR spectra were recorded using a Bruker 600 MHz spectrometer at room temperature. Deuterated chloroform (CDCl₃) was used as solvent for NMR tests. Small-Angle X-ray Scattering (SAXS)/Wide-Angle X-ray Scattering (WAXS) were performed at 12-ID-B station with X-ray energy of 14 keV at the Advanced Photon Source of the Argonne National Laboratory. The two-dimensional (2D) images were radically averaged to produce 1-D plots of scattered intensity I(q) versus q, where $q = 4\pi (\sin\theta) / \lambda$. A Pilatus 2M detector (Dectris Ltd.) was used to acquire scattering data with typical

exposure times in a range of 0.1-1.0 seconds.

UV-DSC: The photocalorimetric measurements of resins were performed with a TA Q200 DSC coupled to a photocalorimeter accessory (PCA, OmniCure S2000, TA instruments) equipped with a high-pressure 200-W mercury lamp. The UV wavelength was adjusted to 320–500 nm using a cut-off filter, and a light intensity of 100 mW/cm² was used. Approximately 10 mg of each resin was accurately weighed in an open aluminum pan, and an empty aluminum pan was used as reference. The sample was equilibrated at 25 °C for 0.5 min without UV, then UV-irradiated for 20 min under a nitrogen atmosphere.

AFM: Atomic Force Microscopy studies were carried out using a multimode equipped nanoscope V from Bruker AXS with a scanner type 8610 JVL. To minimize surface deformation and material removal, the experiments were performed in tapping mode using Bruker probes type RTESP. Topography and phase-shift images were simultaneously recorded in tapping mode at room temperature in air. Image analysis was performed on NanoScope Analysis software from Bruker. Tapping probes were used for cantilever deflection voltage-distance measurements because of their high spring constant (40–80 N/m), which emphasizes the sample deformation compared with cantilever deflection during the sample vertical displacement. Specific parameters for the measurement are shown in the supporting information of Figure S2.

Thermal and Mechanical Measurements: Dynamic mechanical analysis (DMA) was performed with a DMA (Q800 New Castle, DE) using a tension mode. A 5 µm amplitude was applied to guarantee the measurement was within the linear viscoelastic region. Samples were heated from -80 °C to 250 °C using a heating rate of 3 °C/min and frequency of 1Hz. Coefficient of thermal expansion (CTE) was measured by DMA (Q800 New Castle, DE) at 1Hz with tension mode and sample length of 10 mm. Heating rate was 3 °C/min under nitrogen atmosphere and

CTE values were determined at -75-200 °C range. A Thermogravimeter (TGA) was used to measure the weight loss of the samples under a nitrogen atmosphere. The samples with around 5 mg were heated by TGA (PerkinElmer, Pyris 1)) from 50 °C to 700 °C at a heating rate of 50 °C/min. Tensile strength and elongation at break were measured according to ASTM D882-12 using a tensile tester (TT-1100, Chem Instruments, Fairfield, OH) with a specimen dimension of 40 × 8 × 0.18 mm and a grip separation rate of 2.54 cm min⁻¹.

RESULTS AND DISCUSSION

DCE Structure. According to Grubb's classification, terminally unsaturated epoxides are type II olefins,²¹ prone to homodimerization through self-metathesis. Figure 1 presents the self-metathesis of ECP in the presence of the second generation Hoveyda-Grubbs catalyst (related synthesis mechanism see supporting information Scheme S1). ¹HNMR confirmed the feature structure of DCE (Figure 2a). The protons H1, H2, H15, and H16 linked to the oxirane rings were observed at 3.26-3.03 ppm, the unsaturated protons H10, H11 on the double bond –CH=CH– were observed at 5.45-5.03 ppm, and the protons H3-H9, H12-H14, and H17-H20 on cyclohexane rings were observed at 2.37-0.96 ppm. The integrated area ratios of the characteristic signals for protons were in good agreement with the theoretical values. The chiral centers on the cycloaliphatic rings led to the presence of multiple isomers as the complex splitting patterns of protons shown in Figure 2a, which was also indicated by the splitting patterns of carbon atoms C1, C2, C13, and C14 linked to the oxirane rings at 53.55-50.61 ppm and C3-C6, C9-C12 on the cyclohexane rings at 36.28-21.04 ppm (Figure 2b). The characteristic peaks at 133.38-133.01 ppm indicated the carbon atoms of C7 and C8 on the double bond –CH=CH–, demonstrating the successful self-metathesis of ECP. The self-metathesis of ECP was also confirmed by the FTIR spectra (Figure 2c). The band around 1642 cm⁻¹ corresponding to the

vinyl group of ECP monomer^{22a} disappeared after metathesis reaction. On the other hand, a new band appeared around 970 cm^{-1} , which was attributed to the formation of disubstituted alkene group^{22b}, indicating the successful connection of ECPs via self-metathesis. In general, disubstituted cis-alkene shows strong absorption at $730 \sim 665\text{ cm}^{-1}$, while disubstituted trans-alkene shows strong absorption at $980 \sim 960\text{ cm}^{-1}$ ^{22b}. In our study, the resulting DCE showed a strong absorption at 970 cm^{-1} , and no obvious band was found around $730 \sim 665\text{ cm}^{-1}$, indicating that the disubstituted trans-alkene dominated the composition.

Figure 2. ^1H -NMR (a) and ^{13}C -NMR (b) spectra of DCE. FTIR comparison of DCE and ECP (c).

DCE is capable of being self-polymerized via the opening of cycloaliphatic epoxy ring, and ECHM was used as comparison. Features of chain segment and polymeric structure were

investigated by small-wide-angle X-ray scattering (SAXS/WAXS) (Figures 3a and b). From WAXS, there are pronounced diffraction peaks appeared at $q=1.195 \text{ \AA}^{-1}$ and $1.200 \text{ \AA}^{-1}$ for P-ECHM and P-DCE, respectively, indicating P-DCE has similar structures as P-ECHM. The corresponding structural distance d ($d= 2\pi/q$) was calculated as 0.5258 nm (P-ECHM) and 0.5236 nm (P-DCE), respectively. Using the covalent radii table^{23,24}, the segment chain lengths (pink shadow paths shown in Figures 3c and d) are around 1.4081 nm for ECHM and 1.2942 nm for DCE, respectively. Considering the chain rotation and molecular conformation (steric sketch diagrams shown in Figures 3c and d), the unit size h (the size of single DCE or ECHM after polymerization as the length h illustrated in Figures 3c and d) could be shorter than the calculated segment chain length. Because the d values (0.5258 nm and 5.236 nm) derived from WAXS reflect the structural distance on molecular level^{25, 26}, it is most likely to be related to the unit size h . Compared to P-ECHM, the relatively small d value of P-DCE indicates a shorter unit due to the compact double bond in DCE monomer. From the SAXS profile, a small peak at $q=0.1$ for P-DCE (Figure 3b) indicates the formation of regular domains²⁶, and the corresponding long period L was calculated as $L= 2\pi/q= 6.3 \text{ nm}$. The regular domains were probably derived from the partially organized chain arrangements during the self-polymerization of DCE, in which the monomers connected each other via ring opening and formed some organized segments as shown in the schematic diagram (Figure 3d). However, for P-ECHM, no signal was found in the SAXS pattern, indicating a random arrangement of ECHM monomers during the polymerization process as shown in the schematic diagram (Figure 3c). Compared to the methyl ester linkage in P-ECHM, the rigid double bond achieved via self-metathesis gave P-DCE a higher compact and regular structure. Therefore, a significant improvement in thermal resistance and mechanical property

would be expected when DCE monomers are incorporated into ESO matrix to realize a copolymerization.

Figure 3. (a) WAXS and (b) SAXS patterns of P-ECHM and P-DCE, respectively. (c) Schematic representation of P-ECHM. The unit size is marked as h and a steric molecular structure is demonstrated (d) Schematic representation of P-DCE. The unit size is marked as h and a steric molecular structure is demonstrated. The long period reflecting the regular domain is marked as L .

UV-DSC Characterization. Copolymerization of ESO and dicyclic epoxy (ECHM or DCE) was conducted in the presence of the cationic initiator PC-2506 under ultraviolet (UV) light initiation using the UV-DSC. ESO alone was also polymerized by in the UV-DSC as

comparison. The generated Brønsted acid on UV radiation protonated the epoxide oxygen and initiated the chain propagation of epoxy ring²⁷. Correspondingly, the polymerization process and curing behavior were monitored and evaluated by PCA-DSC (Figure 4). Samples showed apparent exothermic peaks, indicating effective epoxy curing occurred under UV radiation. Time appearing at the exothermic peak is an indication of the curing reactivity²⁸, and shorter exothermic peak time was observed after the introduction of DCE or ECHM in ESO system. The UV initiated epoxide curing follows the cationic polymerization mechanism, in which the chain-propagation step by epoxy ring-opening dominates the overall rate of polymerization²⁹. When substituents are present on the epoxide ring, additional steric, electronic, and stereochemical effects would have a marked influence on the polymerization rate²⁹. Cycloaliphatic epoxy has a fused six-carbon ring, which is analogous to the twisted boat conformation of cyclohexene. Compared to the oxirane ring on the fatty acid chain, the pseudoaxial and pseudoequatorial protons on cycloaliphatic ring have less steric hindrance when nucleophile attacks the corresponding oxonium from the back side (inset in Figure 4, and for detailed information see Supporting Information Figure S4), which favored the epoxy ring-opening and the chain-propagation. Consequently, the introduction of DCE or ECHM accelerated the curing speed combined with a shorter exothermic peak time.

Figure 4. Exothermic behaviors of epoxy monomers containing of 3 wt% cationic initiator (PC-2506) radiated through UV light as a function of time.

Microscopic Morphology. The sample surfaces are very smooth with a height fluctuation of about $\pm 5\text{nm}$ (Figure 5 a, b, c), therefore, the impact on phase image is neglected here.³⁰ For P-ESO alone, a homogenous phase was observed (Figure 5a'). With the increase of DCE content, an obvious phase contrast appeared (Figure 5b'). At 30 wt% DCE loading, the AFM phase image of P-ESO-DCE (Figure 5c') showed a micro-phase separation with a dimension ranging from $0.5\sim 2\ \mu\text{m}$. This micro-phase separation was attributed to the incompatibility of P-DCE phase and P-ESO phase during the co-polymerization process. As discussed in the UV-DSC section, compared to ESO, the slightly steric hindrance oxonium ring of DCE accelerated the nucleophilic attack and favored the ring-opening reaction between DCE themselves. Consequently, self-polymerization of DCE occurred and uniformly dispersed in the ESO matrix.

The brighter area in phase contrast images (Figure 5b' and c') represents the more viscous component attributed by the P-ESO-rich phase (a phase consists of P-ESO, P-DCE and P-ESO-

DCE components, and P-ESO is the main component), and the darker area represents the more elastic component from the P-DCE-rich phase (a phase consists of P-DCE, P-ESO and P-ESO-DCE components, and P-DCE is the main component).³¹ This speculation was further confirmed by the cantilever deflection voltage -distance curves. As shown in Figure 5d', compared to spot D (located in the brighter area in Figure 5c'), a higher cantilever deflection voltage (CDV) was observed on the approach and retract curves of spot C (located in the darker area in Figure 5c'). As the CDV is directly related to the surface stiffness³², the higher value of spot C indicates the higher modulus in comparison with spot D. Similar phenomenon happened to P-ESO-DCE (20%) system, in which spot A (located in the darker area in Figure 5b') exhibited a higher CDV value than spot B (located in the brighter area in Figure 5b'). Moreover, compared to P-ESO-DCE (20%), a more distinct phase separation and higher CDV difference between darker phase and brighter phase (from 0.24V for P-ESO-DCE (20%) to 0.45V for P-ESO-DCE (30%)) were found in P-ESO-DCE (30%) system, indicating the higher level of microphase separation and aggregation of DCE due to its higher amounts in P-DCE-rich phase. Similar morphology evolutionary trend was also found in P-ESO-ECHM system, indicating the appearance of P-ECHM-rich phase and P-ESO-rich phase with the increase of ECHM content. However, such phase contrast in the P-ESO-DCE system is more distinct than that in the P-ESO-ECHM system, and the specific images and analysis were presented in the supporting information (Figure S3).

Figure 5. AFM height images of (a) P-ESO, (b) P-ESO-DCE (20%), and (c) P-ESO-DCE (30%). AFM phase images of (a') P-ESO, (b') P-ESO-DCE (20%), and (c') P-ESO-DCE (30%). (d) CDV-distance curves on locations A and B for P-ESO-DCE (20%). (d') CDV-distance curves on locations C and D for P-ESO-DCE (30%).

Network Thermal Mechanical Properties. Figure 6 and Table 1 present the thermal mechanical properties of P-ESO, P-ESO-DCE and P-ESO-ECHM. At temperature below -35°C , the neat P-ESO was in glassy state, with storage modulus (E') nearly constant (Figure 6a) because of the restricted fatty acid ester chains. The sudden drop of E' between -15°C and 35°C was attributed to the segment motions between cross-links which were formed via the ring-opening reactions of epoxides in ESO. As described before (Figure 3), the DCE rings were connected by rigid double bond and formed a compact chemical structure. Incorporation of DCE drastically changed the network structure and the thermal resistance of ESO system. The drop of E' at room temperature was significantly suppressed and a remarkable shift of glass transition (T_g) towards higher temperature was achieved. Similar thermal resistance improvement was also observed when ECHM was incorporated in the ESO system. However, at the same loading level,

the T_g values and E' enhancements by ECHM were much lower than those by DCE. Especially when temperature reached up to 150 °C, the E' values of P-ESO-ECHM dropped drastically and were closed to those of neat P-ESO. However, for P-ESO-DCE, the E' values were dropped but still remained as two times higher at a temperature beyond 250 °C than those of neat P-ESO. A visual thermal resistance comparison between P-ESO-DCE (20%) and P-ESO-ECHM (20%) was shown in the supporting information (Figure S5).

Coefficient of thermal expansion (CTE) is another important criteria in evaluating the thermal resistance of materials, particularly in electronic application to make sure accurate alignment of electronic components on the substrate during thermal processing³³. Compared to the neat P-ESO, CTE value was decreased obviously after the incorporation of DCE (Figure 6d), for example, the CTE was $1.56 \times 10^{-4} \text{ K}^{-1}$ for P-ESO-DCE at 30 wt% DCE loading level. ECHM has similar effects on CTE compared to DCE, but at the same loading level, CTE values of P-ESO-ECHM were relatively higher.

Figure 6. (a) Storage modulus E' and (b) loss tangent $\tan\delta$ of P-ESO and ESO matrix-based copolymers. (c-1) Weight fraction of ECHM dependent on storage modulus E' of P-ESO-ECHM at -60°C (■), 25°C (●), and 150°C (▲); (c-2) Weight fraction of DCE dependent on storage modulus E' of P-ESO-DCE at -60°C (■), 25°C (●), and 150°C (▲). (d) CTE values of P-ESO and ESO matrix-based copolymers.

Table 1. Thermal mechanical properties of P-ESO and ESO matrix-based materials

Sample	T_g (°C)	E' (MPa)			CTE ($\times 10^{-4}\text{K}^{-1}$)	Ve ($\times 10^3\text{mol mm}^{-3}$) ^a
		-60°C	25°C	150°C		
P-ESO	10	859	17	4	3.13	0.43
P-ESO-ECHM(20%)	49	931	191	5	1.86	0.47
P-ESO-DCE (20%)	100	1022	624	28	1.72	2.07
P-ESO-ECHM(30%)	79	1224	599	6	1.76	0.58
P-ESO-DCE (30%)	163	1322	1012	290	1.56	5.21

^acrosslink density ($\times 10^3\text{mol mm}^{-3}$), $Ve = E'/3RT$, where R is the gas constant and T is the absolute temperature. To ensure the cured samples were in the rubbery state, plateau modulus at $T_g + 80^\circ\text{C}$ was selected.

Schematic diagrams shown in Figure 7 exhibited the network key features of P-ESO, P-ESO-ECHM, and P-ESO-DCE, revealing the possible mechanism of DCE in thermal resistance enhancement. For the P-ESO network, there are two typical cross-linked structures: chain segments derived from the ring-opening of oxiranes (type I, highlighted by ellipse shadow), and

chain segments derived from the triglycerides of ESO (type II, highlighted by round shadow) (Figure 7). When ECHM or DCE was introduced into the P-ESO system, a third type of crosslink (type III, highlighted by rectangle shadow) was generated in P-ESO-ECHM or P-ESO-DCE systems. Different from the fatty acid chains in type II crosslink, the cycloaliphatic rings with rigid conformation in type III crosslink effectively restricted the chain rotations and segment motions, leading to higher glass transition temperatures. Relative to the flexible ester bond in ECHM, the compact double bond in DCE offered a stiff connection between cross-links, which further restricted the chain rotation. In addition, as the SAXS revealed (Figure 3), compared to the ECHM, a relatively organized segment formed during the self-polymerization of DCE; which also contribute the modulus enhancement and thermal resistance improvement.

Figure 7. Schematic diagram of the key features of the epoxy networks. Type I structure: ellipse shadow; type II structure: round shadow; and type III structure: rectangle shadow. The P-ESO-rich phase, P-ECHM-rich phase and P-DCE-rich phase are highlighted to reflect the micro-phase separation.

Thermal Decomposition. Thermal decomposition properties reflect the stability of materials under high temperature. Compared to P-ESO and P-ECHM, P-DCE is inclined to decompose when temperature reached up to 400 °C (inset of Figure 8a). This was probably attributed to the double bonds intending to form allyl radicals with the stable conjugated structure through the chain scission (inset of Figure 8b)³⁴. On the other hand, the sharp thermal decomposition behavior of P-ESO was suppressed after the introduction of DCE combined with a relatively higher residual mass. With the increase of DCE content, a minor derivative of weight (DTG) peak showed up at 530 °C in addition to the main peak at 466 °C. As the AFM images show (Figures 5b' and c'), a notable microphase separation emerged within the ESO matrix when the DCE content increased. Therefore, it was speculated the double peak appeared in the DTG curve was related to the two separated DCE-rich and ESO-rich phases. Similar to P-ESO-DCE (30%), two notable DTG peaks appeared in the P-ESO-ECHM (30%) with the increase of ECHM content, which could be related to the separated ECHM-rich and ESO-rich phases.

Figure 8. Thermogravimetry (a) and derivative thermogravimetry (b) curves of P-ESO and ESO matrix-based materials under nitrogen atmosphere.

Mechanical Properties. Incorporation of DCE substantially changed the mechanical performance of P-ESO. Figure 9 presents representative stress-strain curves for neat P-ESO, P-ESO-ECHM, and P-ESO-DCE, respectively, showing that a weak P-ESO network was significantly reinforced by DCE in mechanical strength. At 30 wt% DCE loading, for example, the P-ESO-DCE (30%) had a tensile strength of 62.3 MPa, which is more than 14-fold

enhancement compared to P-ESO with a tensile strength of only 4.2 MPa. As the AFM morphology shown in Figures 5b' and c', notable DCE-rich phases appeared after the incorporation of DCE into ESO matrix. In these phases, compact structures were built via the self-polymerization of DCE and molecule chains were firmly connected via the DCE stiff double bonds. These DCE-rich phases acting as microscale reinforcements homogeneously dispersed in the ESO matrix with a dimension ranging from 0.5~2 μm as the AFM image showed, which effectively sustained the applied stress and prevented the chain break from high force loading.

Figure 9. Stress-strain curves of P-ESO and ESO matrix-based materials.

CONCLUSIONS

A unique diepoxide monomer (DCE) with a cyclohexane ring bridged by double bond was obtained via olefin self-metathesis approach. Benefited from the double bond, the DCE possesses a more compact and regular structure than its commercial counterpart ECHM. Correspondingly, a ESO matrix-based material with high thermal resistance and superior mechanical strength were achieved. The DCE was demonstrated to reinforce the tender ESO materials into a robust

material; for example at 30 wt% DCE loading level, the tensile strength of a P-ESO-DCE resin was improved from 4 MPa to 62 MPa and T_g from 10 °C to 163 °C. AFM image revealed that the micro-phase separation exists as the DCE content increases, and the DCE-rich phases act as microscale reinforcement homogenously dispersed in the ESO matrix, sustaining the applied stress and resisting the thermal deformation. Compared to the methyl ester bond in ECHM, the double bond-bridged cycloaliphatic structure in DCE shows a greater potential in reinforcing the network of plant oil-based materials.

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