Plasticization effects of dihydroxyl soybean oil improve flexibilities of epoxy-based films for coating applications

Jonggeun Sung, Yonghui Li, Xiuzhi Susan Sun

Bio-Materials and Technology Lab, Department of Grain Science and Industry, Kansas State University, 1980 Kimball Ave., BIVAP Bldg., Manhattan, Kansas 66506
Correspondence to: X. S. Sun (E-mail: xss@ksu.edu)

ABSTRACT: Novel bio-based coating materials were developed through cationic ring-opening photopolymerization of dihydroxyl soybean oil (DSO) with commercial epoxy monomers [i.e., epoxidized soybean oil (ESO) and 3,4-epoxycyclohexylmethyl-3,4-epoxycyclo-hexanecarboxylate (ECHM). The ether cross-linking and post-polymerization of the polymeric network were observed using Fourier transform infrared spectroscopy. Thermal properties of the bio-based coating materials and their copolymerization behaviors were examined using differential scanning calorimetry and a thermogravimetric analyzer. Cross-link density and molecular weight between cross-link were obtained from dynamic mechanical analysis. ECHM/DSO (1 : 1.43 weight ratio) films showed the highest elongation at break (49.2%) with a tensile strength of 13.7 MPa. After 2 months of storage, the elongation at break and tensile strength of films were 32% and 15.1 MPa, respectively. ESO/DSO films (w/w ratios of 1 : 0.1, 1 : 0.15, and 1 : 0.2) exhibited stable flexibility of 11–13% of elongation at break without significant reductions in tensile strength (2.5–4.4 MPa) during a 2-month shelf life. Optical transparencies of the films were comparable to commercial glass and polymers, and water uptake properties (0.72% and 2.83%) were significantly low. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41773.

INTRODUCTION

The most widely used coating materials in packaging applications are polyethylene, polyvinyl alcohol, and fluorocarbon which are synthesized from petroleum resources, and most of the petrochemical coating materials are not biodegradable.[1,2] Environmental regulations have been designed to reduce chemical pollutants and conserve fossil fuels, and academia and industry are seeking sustainable alternatives to petroleum-based materials.[3,4] Bio-based polymers such as proteins and polysaccharides have been researched as raw materials for packaging applications,[1] but their hydrophilic natures lead to poor water resistance.[5,6] Plant oils can be incorporated into coating materials without loss of water barrier properties[1]; moreover, plant oils also possess the advantages of intrinsic biodegradability and low toxicity.[7] Plant oils have become one of the most important sources of renewable materials in the chemical industry, making products such as surfactants, lubricants, paints, resins, adhesives, and coatings.[4,7] Epoxidation of plant oil is commonly used to produce functionalized olefin because of its economical process and significantly improved oil reactivity.[8,9]

Photopolymerization promotes quick curing and requires low energy consumption. Photoinitiated cationic polymerization is commonly used methods for making coatings, adhesives, and printing inks in the polymer industry.[10,11] It is also one of the common curing methods for epoxy resins such as epoxidized soybean oil (ESO) and 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (ECHM).[3,12–15] Compared with free radical photopolymerization, which is based mainly on acrylates, cationic photopolymerization of epoxy offers several advantages, including low shrinkage, uninhibitedness in oxygen, and post-polymerization after UV exposure stops.[10,12,16] Compared with ESO, photopolymerized cycloaliphatic resins such as ECHM have shown excellent rigidity and adhesion to substrates, and high glass transition temperature,[10,12] but the brittleness of the epoxy polymer has been a problem for making flexible packaging coatings.[17] Previous work in our lab identified that UV copolymerization of ESO, rosin ester, and soy polyols [i.e., dihydroxyl soy bean oil (DSO)] yields the flexibility, thermal stability, and optical transmittance required to create flexible coatings.[14] Soy polyols improved the softness and tackiness of ESO-based resin.[18,19] Partially crystalline polymeric diols
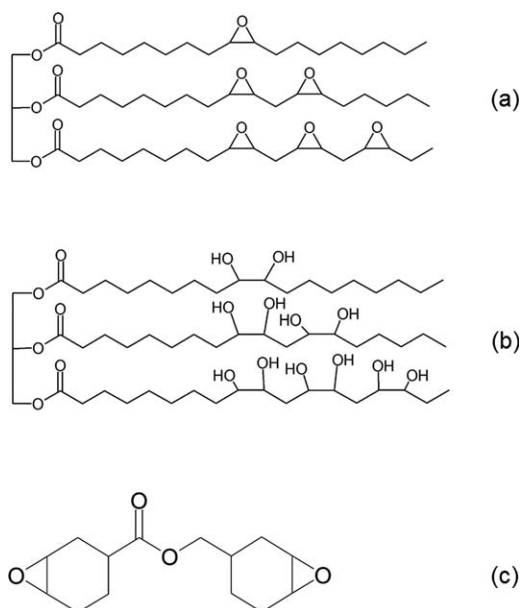
Scheme 1. (a) Epoxidized soybean oil (ESO), (b) dihydroxyl soybean oil (DSO), and (c) 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (ECHM).

[i.e., poly(e-caprolactone)] were researched to improve tensile strength and elongation of ECHM polymers using cationic thermal polymerization.[17]

In this study, ESO and ECHM were used for examples of bio-based and non-bio-based epoxy resins, respectively. In addition, DSO was formulated into the epoxy resins to improve polymer flexibility. Chemical structures of ESO, ECHM, and DSO were shown in Scheme 1. Both ESO/DSO and ECHM/DSO resins were UV-polymerized to form a copolymer which was cross-linked by ether linkage because of homo-polymerization of epoxides or co-polymerization of an epoxide and an alcohol group (Scheme 2).[11,12,15,20,21] Therefore, the objectives of this study were to develop novel bio-based coating materials via photoinitiated cationic ring-opening co-polymerization of DSO with ESO and ECHM and to characterize the structural, thermal, mechanical, shelf life, and optical properties of the polymerized films. Various characterization techniques including Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), tensile testing, dynamic mechanical analysis (DMA), UV-visible spectroscopy, and water uptake test were employed.
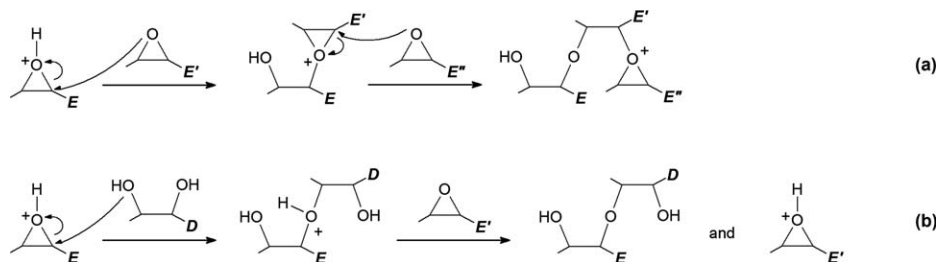
EXPERIMENTAL

Materials
ESO (Scientific Polymer Products, Ontario, NY), ECHM (Sigma-Aldrich, St. Louis, MO), and PC-2506 (Polyset, Mechanicville, NY; [4-(2-hydroxy-1-tetradecyloxy)-phenyl] phenyliodonium hexafluoroantimonate) were kindly provided by the respective companies.

Dihydroxyl Soybean Oil Synthesis
DSO was prepared according to our previous research with modifications to reduce solvent and catalyst amounts and reaction times.[14,18] Briefly, ESO (40 g, 40 mmol) was dissolved in 60 mL of tetrahydrofuran/water (40 mL : 20 mL) with 1.5% (volume of ESO) of perchloric acid, and the mixture was magnetically stirred for 5 hours at room temperature. The aqueous layer of the mixture was then separated from the organic layer in a separatory funnel by adding 60 mL of ethyl acetate. Perchloric acid in the aqueous layer was removed by water washing, and saturated sodium bicarbonate (approximately 5–6 mL) was added to neutralize the mixture. The solvent in the organic layer was removed by a rotary evaporator with a tap vacuum, then the organic layer was dried under high vacuum with a rotary evaporator to remove remaining water residues.

Preparation of UV-Cured Films
UV-curable copolymer films were prepared at various ratios of ESO and DSO and ECHM and DSO monomers. ESO and DSO were mixed at weight ratios of 1 : 0.1, 1 : 0.15, and 1 : 0.2. The mixture was heated and mixed using a heat gun and a vortex mixer. Subsequently, 3 wt % (weight of ESO) cationic photoinitiator PC-2506 was added to the mixture and mixed well using the vortex mixer and a sonicator.[12,14] Approximately 8 g of the mixture was spread over a glass plate (25.4 cm by 15.24 cm) as a substrate using a wire wound rod (#90; ChemInstruments, Fairfield, OH). The spread mixture was passed twice at a conveyor rate of 7 ft min^{-1} (radiation dose of 1.7–1.8 J cm^{-2}) through a F300 UV system (1.8 kW, 6-in (300 W in^{-1}) lamps) equipped with a LC6B benchtop conveyor (Fusion UV system, Gaithersburg, MD). The UV lamp was 10 cm above the conveyor belt. To obtain free-standing films, appropriate thicknesses of the UV-cured films were from 0.13 to 0.15 mm. ECHM/DSO films were prepared similarly at ECHM/DSO weight ratios of 1 : 1, 1 : 1.18, and 1 : 1.43 with three UV passes. The UV-cured films could not be detached from the glass substrate without cohesion failure right after UV-curing. Based on our preliminary test for making free-standing films, 3 hours is just enough to peel off the films from glass substrate without any cohesion

Scheme 2. UV-initiated cationic ring-opening polymerization of epoxides homopolymer (a) and epoxide-hydroxyl copolymer (b). E, E', and E'' are epoxy monomers such as ESO and ECHM. D is DSO.

failure. Therefore, all UV-cured films were peeled from the glass plates 3 hours after the completion of UV curing, then films were stored in the dark for 3 hours, 1 day, 5 days, 10 days, 1 month, and 2 months to obtain samples for shelf life and dark-curing effect studies.

Fourier Transform Infrared Spectroscopy

Perkin-Elmer Spectrum 400 FTIR spectroscopy (Waltham, MA) was used to verify cationic ring-opening photopolymerization of the resins and the dark-curing effect by comparing functional groups such as hydroxyl, epoxy, and ether groups. Data for non-cured resin blends and UV-cured films at 3 hours and 10 days after curing for both ESO/DSO (w/w ratio of 1 : 0.15) and ECHM/DSO (w/w ratio of 1 : 1.18) films were collected.

Thermal Properties of UV-Cured Films

A DSC (TA DSC Q200, New Castle, DE) and a TGA (Perki-nElmer Pyris 1 TGA, Norwalk, CT) were used to obtain thermal properties of the UV-cured films to determine thermal stability of the coating materials. All UV-cured samples for thermal analysis were measured within 30 min after UV curing to reduce dark-curing effect. UV-cured and noncured ESO/DSO (w/w ratio of 1 : 0.15) and ECHM/DSO (w/w ratio of 1 : 1.18) films and resins, as well as both monomers, were measured. Thermal transitions (glass transition temperature, T_g, and melting temperature, T_m) and heat of copolymerization (ΔH) were obtained. All cured and noncured samples for DSC contained 3 wt % (weight of ECHM or ESO) photoinitiator. Approximately 5–7 mg of the sample was heated from $-50°C$ to $250°C$ at a rate of $10°C$ min^{-1} under a nitrogen environment in a hermetic pan. Conventional Modulated Differential Scanning Calorimetry (MDSC) mode was used to determine accurate T_g of ESO/DSO and ECHM/DSO cured films from $-50°C$ to $200°C$ at a rate of $3°C$ min^{-1}. Thermal decomposition characteristics of 1 : 0.15 w/w ratio of ESO/DSO and a 1 : 1.18 w/w ratio of ECHM/DSO UV-cured samples were obtained using TGA and compared with the decomposition characteristics of ESO and ECHM UV-cured homopolymers, respectively, and 6–8 mg of each sample was heated from $30°C$ to $650°C$ at a rate of $20°C$ min^{-1} under a nitrogen atmosphere.

Viscoelastic Behaviors of ESO/DSO and ECHM/DSO Films

To obtain viscoelastic properties of the UV-cured films, dynamic mechanical analysis (DMA) was performed with a TA DMA Q800 (New Castle, DE) with a tension/film clamp using rectangular specimens approximately 2 cm long, 1.27 cm wide, and 0.13–0.15 mm thick. The measurements were performed at a frequency of 1 Hz, a constant amplitude of 15 μm, and a heating range of $-50°C$ to $150°C$ with $10°C$ min^{-1} increments. T_g was determined at maximum tangent delta peak, and cross-link density (v_e) and molecular weight between cross-link (M_c) were calculated from an elastic modulus (E') based on the rubbery plateau region at least $50°C$ above T_g.[22–24]

Mechanical Properties of ESO/DSO and ECHM/DSO Films

Tensile strength and elongation at break were measured according to ASTM D882-12. The UV-cured films were cropped to 20.32 cm long, 1.27 cm wide, and 0.13–0.15 mm thick according to ASTM D6287-09 using a dual-blade shear cutter (JDC Precision Cutter 10″, Thwing-Albert Instrument Company, West
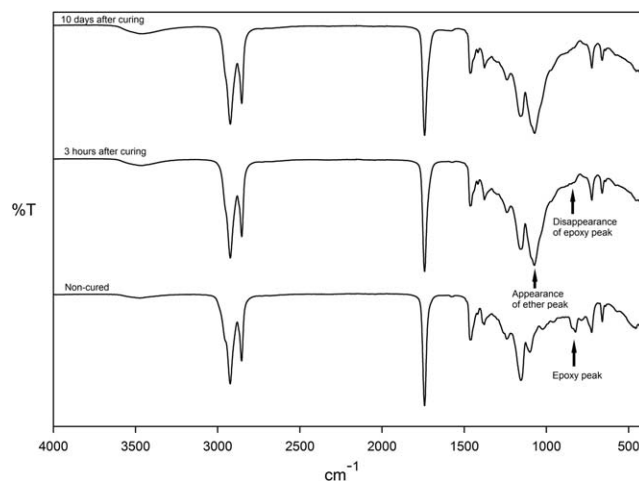

Figure 1. FTIR of ESO/DSO (weight ratio of 1 : 0.15) resin before UV curing, 3 hours after UV curing, and 10 days after UV curing.

Berlin, NJ). A strip of the film was applied on a tensile tester (TT-1100, ChemInstruments, Fairfield, OH) with 12.7 cm of initial grip separation and a rate of grip separation of 2.54 cm min^{-1}. The mechanical test was conducted at various times (1, 5, and 10 days, and 1 and 2 months) after UV curing to evaluate shelf life of the bio-based films.

Optical Transmittance

Optical transparency was measured with a UV-visible spectrometer (Hewlett-Packard 8453) with a wavelength range of 200–900 nm. The thickness of loading samples was 0.14 mm for ESO/DSO and ECHM/DSO films, and 0.91 mm for glass slides.

Water Uptake Properties

Water absorption of the UV-cured films was estimated according to 24 hours immersion test of ASTM D570-98. The loading samples were 0.14–0.15 mm thick, and 2.54 cm long and wide.

RESULTS AND DISCUSSION

UV-Polymerization

FTIR spectra were obtained to confirm functional groups of ESO/DSO and ECHM/DSO UV-cured films before and after photopolymerization (Figures 1 and 2). Epoxy peaks at 825 cm^{-1}, triglycerides at 1740 cm^{-1}, and alcohol bands around 3450 cm^{-1} were detected in the noncured ESO/DSO curve (Figure 1). After 3 hours of UV curing, the disappearance of the epoxy peak at 825 cm^{-1} and the appearance of an ether peak at 1075 cm^{-1} indicates that the reaction was completed for the polymerization of ESO and DSO (w/w ratio of 1 : 0.15)[25] (Figure 1). For ECHM and DSO (w/w ratio of 1 : 1.18), the reaction was not fully complete in 3 hours, which was confirmed by the remaining small epoxy peak at 790 cm^{-1} and the increment of the ether peak at 1070 cm^{-1} after 10 days (Figure 2). The cross-linking reaction of epoxy and alcohol leads the termination of chain propagation and the active center transferring from the polymer chain [Scheme 2(b)].[11,21] In addition, the cross-linking reaction with alcohol was dominant in ECHM/DSO copolymer because the ECHM/DSO resins contained more alcohol groups than the ESO/DSO systems. Therefore, the longer time for the post-polymerization of ECHM/
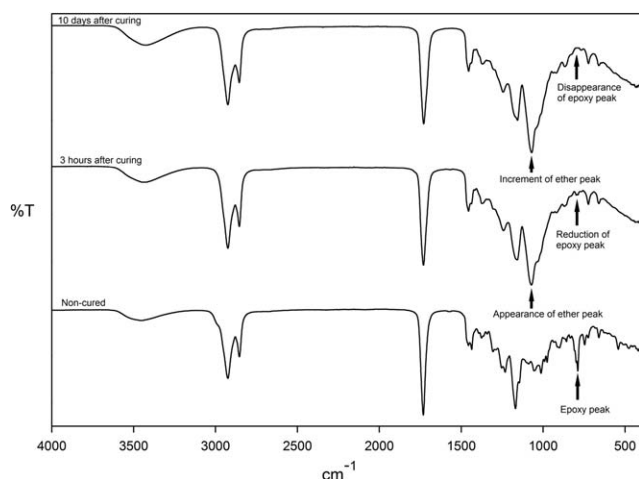
Figure 2. FTIR of ECHM/DSO (weight ratio of 1 : 18) resin before UV curing, 3hours after UV curing, and 10days after UV curing.

DSO copolymer could be caused by the new protonated epoxide monomers during the active center transferring. The increased alcohol bands around 3450 cm^{-1} after curing of both ESO/DSO and ECHM/DSO copolymers were because of the newly generated hydroxyl groups from the epoxy ring-opening polymerizations.

Thermal Analysis

ESO before UV curing had a small endothermic peak around $-6°C$ showing crystalline structures of epoxide triglycerides [Figure 3(a)]. The peak disappeared after UV curing because crystallization was impeded by cross-linking of ESO epoxides[13] [Figure 3(b)]. ESO before curing also showed a curing peak at 182°C with ΔH of 379.2 J g^{-1}. The ESO after UV curing showed a shallow and broad exothermic peak at 134.81°C with ΔH of 58.3 J g^{-1}, which was caused mainly by the cross-linking reaction of residual epoxides because the heat from DSC contributed to the cross-linking reaction following an improvement

in epoxides mobility.[12] Similarly, the ESO/DSO (w/w ratio of 1 : 0.15) after curing showed a curing peak at 136.13°C with ΔH of 87.7 J g^{-1}, and both cured ECHM and cured ECHM/DSO (w/w ratio of 1 : 1.18) also exhibited a peak of heat curing at 125.64°C with ΔH of 28.2 J g^{-1} and 77.07°C with ΔH of 33.5 J g^{-1}, respectively. The addition of DSO decreased the polymerization temperature of ESO but not ECHM. ESO and DSO have basically same backbone structures (i.e., triglyceride), and the rate of epoxy-epoxy polymerization is lower than the rate of epoxy-hydroxyl polymerization. The faster rate of epoxy-hydroxyl polymerization is because of the less steric requirements for the nucleophilic attack by a hydroxyl in compared with the attack by an epoxide. Therefore, the polymerization temperature of ESO with DSO addition was reduced. However, the polymerization temperature of ECHM was not reduced by DSO addition, because ECHM is easily polymerized itself because of its small steric hindrance of the less bulky structure in compared with a triglyceride. Therefore, DSO did not significantly affect a reduction of polymerization temperature of ECHM.

ESO and ESO/DSO showed larger ΔH than ECHM and ECHM/DSO. Ring-opening photopolymerization of ESO tended to have a lower degree of polymerization. The lower degree of cross-linking reaction of ESO could be because of epoxide steric hindrance from the bulky structure of ESO. The steric hindrance of the ESO was also considered a reason for the low degree of epoxy conversion in photoinitiated cationic polymerization.[15] In compared with ESO/DSO, ECHM/DSO showed higher degree of polymerization under UV-curing from the DSC analysis although it had longer time of post-polymerization completion using the FTIR results. Absences of melting peaks and presences of exothermic curing peaks in UV-cured films confirmed that soybean-derived coating materials were thermosetting polymers. The photoinitiator (PC2506) had melting and thermal decomposition peaks at 98.9°C and 224.1°C, respectively. T_g was determined at various weight ratios
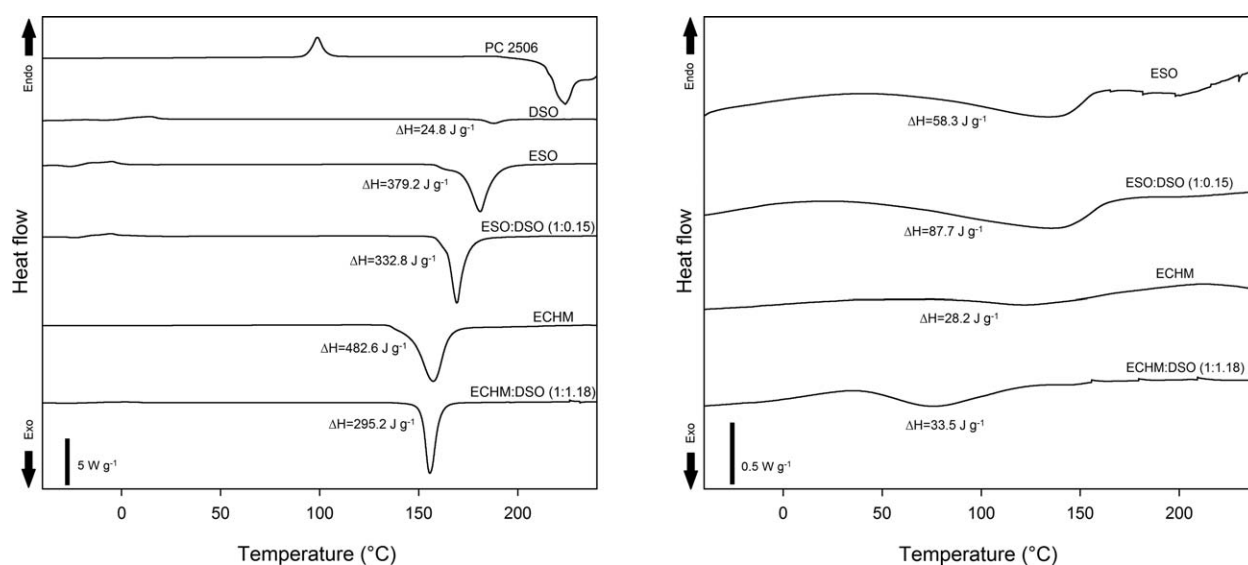

Figure 3. DSC thermograms of PC-2506, ESO, DSO, ESO/DSO (w/w ratio of 1 : 0.15), and ECHM/DSO (w/w ratio of 1 : 1.18) samples including the photoinitiator before UV curing (a) and after UV-curing (b).

Table I. Glass Transition Temperatures of Various Weight Ratios of ESO/DSO and ECHM/DSO Based on MDSC and DMA Analysis

Monomer/ratio	MDSC T_g (°C) 0 hours	DMA T_g (°C) 3 hours	10 days
ESO : DSO(1 : 0.1)	−2.8	18.5	18.8
ESO : DSO(1 : 0.15)	−4.8	16.6	17.1
ESO : DSO(1 : 0.2)	−5.4	14.0	14.9
ECHM : DSO(1 : 1)	51.0	66.7	67.1
ECHM : DSO(1 : 1.18)	36.2	60.8	58.5
ECHM : DSO(1 : 1.43)	30.8	51.2	50.8

of both ESO/DSO and ECHM/DSO films through MDSC and DMA analysis (Table I). The T_g from DMA was determined at peak loss factor (Tan δ) [Figure 5(a,b)], and that from DMA was approximately 20°C higher than that from DSC because DMA and DSC determined T_g based on different mechanisms; however, both DMA and DSC showed the same tendency toward T_g of the films as affected by DSO. T_g decreased as DSO increased because DSO acted as a plasticizer in the polymer matrix. Compared with the ESO/DSO films, ECHM/DSO films had much higher T_g, because of the rigid backbone structure of ECHM and higher reactivity of the external epoxides.

Thermal degradation of the films was measured using TGA (Figure 4). All UV-cured ESO/DSO and ECHM/DSO films had similar thermal stabilities and degraded in the temperature range of 339°C to 428°C; however, the ECHM/DSO film became more thermally stable than ECHM alone. The degradation temperatures of cured-ECHM were observed at 339°C for 5% weight loss and 408°C for 50% weight loss, and the decomposition temperatures of the ECHM/DSO (w/w ratio of 1 : 1.18) increased to 356°C for 5% weight loss and 428°C for 50% weight loss.
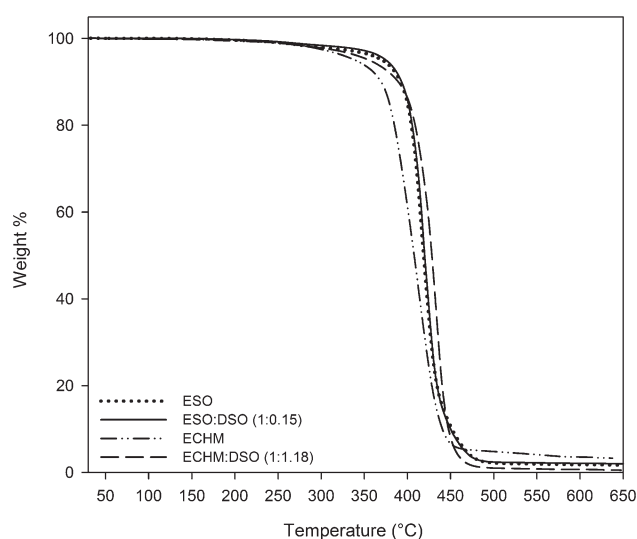
Figure 4. Thermal decomposition profiles of UV-cured samples of ESO, ESO/DSO (w/w ratio of 1 : 0.15), ECHM, and ECHM/DSO (w/w ratio of 1 : 1.18) from TGA.

Dynamic Mechanical Properties

The tensile and dynamic mechanical properties of the UV-cured samples after 3 hours and 10 days of storage are summarized in Table II. The cross-link densities (v_e) were calculated from the storage modulus (E') at 50°C greater than T_g in the rubbery plateau region [Figure 6(a,b)] following the below equation[22–24]:

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

where R is the gas constant and T is the absolute temperature. The molecular weight between chain lengths (M_c) was estimated following the below equation:

$$M_c = \frac{d}{v_e} \tag{2}$$

where d is the specific gravity of the polymer.

In Table II, the ESO/DSO films showed lower tensile strength than the ECHM/DSO films at both 3 hours and 10 days after UV curing. The apparently low mechanical strengths of the ESO/DSO films were also affected by their low T_g, which were below room temperature, whereas the tensile tests were performed at room temperature, during the samples' rubbery states.[26] The Tan δ peaks of the ECHM/DSO films at 10 days became narrower compared with those at 3 hours [Figure 5(a,b)]. This behavior could be attributed to the postpolymerization of the ECHM/DSO films because the narrower width of Tan δ peaks represented the increase in the homogeneity of polymer networks[23,24]; however, the degrees of homogeneity of the ESO/DSO polymer network did not change between 3 hours and 10 days, as indicated by the Tan δ peaks' unchanged widths [Figure 5(a,b)]. These results were in accordance with the FTIR analysis as discussed in the previous section, so the change to the more uniform polymer network of the ECHM/DSO films during postcuring could be a convincing reason for increases in their tensile strengths (Table II). Overall, less DSO led to higher cross-link densities for both ESO/DSO and ECHM/DSO films (Table II), which also could be concluded from the width and height of the Tan δ peaks in Figure 5(a,b). Broader Tan δ peak width and lower Tan δ peak height indicated larger cross-link density.[27]

E' of the ESO/DSO and the ECHM/DSO films was estimated from DMA measurements at 3 hours and 10 days after curing, respectively [Figure 6(a,b)]. E' at the glass transition region of both ESO/DSO and ECHM/ DSO films at 3 hours decreased as DSO contents increased [Figure 6(a)]. In addition, obviously lower E' was obtained at both glass transition and rubbery plateau regions for the films after 10 days of storage with more DSO additions [Figure 6(b)]. The reductions of E' and T_g with DSO additions indicated the plasticizing effects of DSO. The increase in E' at the rubbery plateau of the ESO/DSO (w/w ratios of 1 : 0.15 and 1 : 0.2) and the ECHM/DSO (w/w ratios of 1 : 1.18 and 1 : 1.43) at 3 hours after curing [Figure 6(a)] were caused by heat curing of residual materials during DMA heating.[26] No significant increases in E' of the ESO/DSO (w/w ratios of 1 : 0.1) and the ECHM/DSO (w/w ratios of 1 : 1) at 3 hours in their rubbery regions could be explained by a higher degree of polymerization during UV
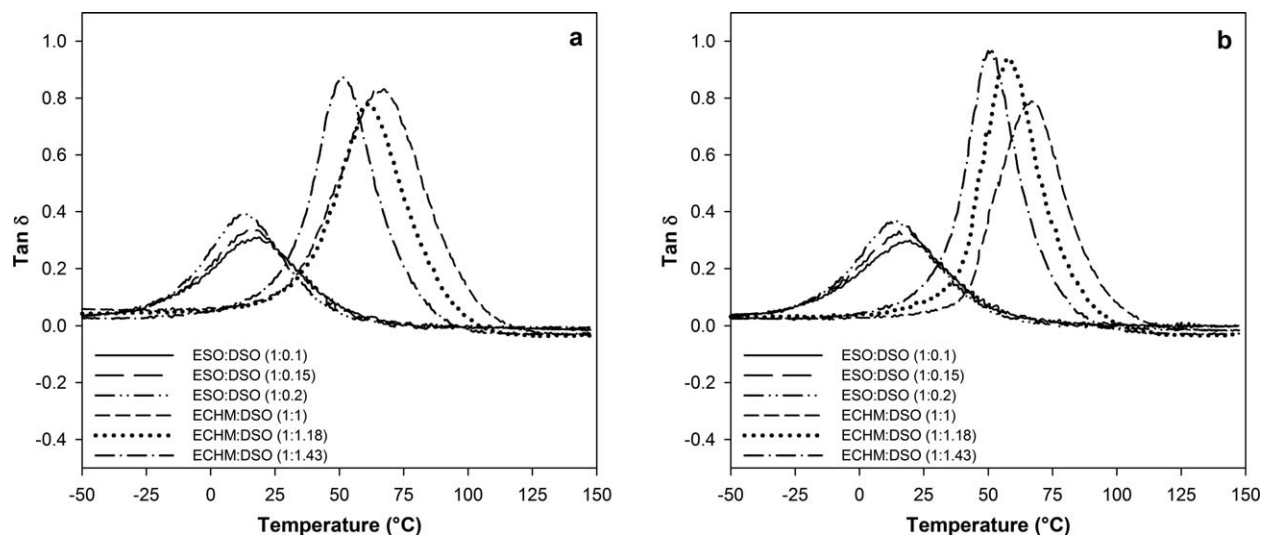
Figure 5. Loss factors of ESO/DSO and ECHM/DSO samples at 3hours (a) and 10days (b) after UV curing.

curing because of larger numbers of the epoxy sites under UV irradiation. The larger cross-link densities could effectively disturb polymer chain mobility and curing during DMA heating. E' at the rubbery plateau regions of the ESO/DSO and ECHM/DSO films at 10 days after UV curing was higher than at the rubbery region of the samples after 3 hours [Figure 6(b)]. The higher E' in the rubbery region results in the increase of cross-link densities and reductions of molecular weight between chain lengths (Table II).

Tensile Properties in Shelf Life Tests

The UV-cured ESO films at weight ratios of ESO : DSO (1 : 0.1, 1 : 0.15, and 1 : 0.2) showed a decrease in tensile strength as DSO contents increased (Figure 7). The tensile strengths of all samples increased by approximately 15–20% as storage time approached 1 month. The tensile strengths of the films (w/w ratios of 1 : 0.1 and 1 : 0.15) were slightly reduced at 2 months, but the strength of the film (w/w ratio of 1 : 0.2) remained similar. Elongation at break of the ESO-based films was not affected by DSO additions or storage times.

The tensile strength of the ECHM films of all ECHM/DSO ratios was much higher than that of ESO films and decreased significantly as DSO increased. Films' strength increased by 80–140% during the first month (Figure 8). Tensile strength decreased during the 2-month storage time. Elongations at break of the ECHM-based films increased significantly as the DSO contents increased, but decreased as storage time increased in the second month.

Overall, both the ESO- and the ECHM-based films reached maximal tensile strength by one month of storage after completion of UV curing, and the ECHM/DSO films showed much higher tensile strength compared with the ESO/DSO films at all storage times. The excellent mechanical strength of the ECHM-based films could be explained by the rigid structure of ECHM itself and the higher reactivity of the external oxiranes.[15] In addition, increased elongation at break of the ECHM-based films with larger amounts of DSO added was clearly related to the decrement in T_g of the films. A similar result was also reported by Lützen.[17] During our experiments, we found that

Table II. Summary of Cross-Link Density, Tensile Strength, Molecular Weight Between Chain Length, and Elongation of Various Weight Ratios of ESO/DSO and ECHM/DSO at 3 Hours and 10 Days After UV Curing

| Monomer/ratio	Cross-link density (mol m^{-3})		Tensile strength (MPa)		Molecular weight between chain length (g mol^{-1})		Elongation (%)	
	3 hours	10 days	3 hours	10 days	3 hours	10 days	3 hours	10 days
ESO : DSO(1 : 0.1)	1628.3	3376.9	3.9	4.0	655.2	306.7	11.2	11.5
ESO : DSO(1 : 0.15)	1145.6	1965.9	3.5	3.3	935.5	530.7	11.1	10.4
ESO : DSO(1 : 0.2)	1181.3	1598.5	3.0	2.7	884.2	658.6	10.4	11.6
ECHM : DSO(1 : 1)	459.9	584.7	26.8	34.5	2459.6	1833.0	13.4	3.7
ECHM : DSO(1 : 1.18)	339.1	425.3	19.7	29.5	3306.9	2512.4	21.1	10.3
ECHM : DSO(1 : 1.43)	332.3	372.1	11.6	15.7	3428.3	2878.1	42.2	44.1
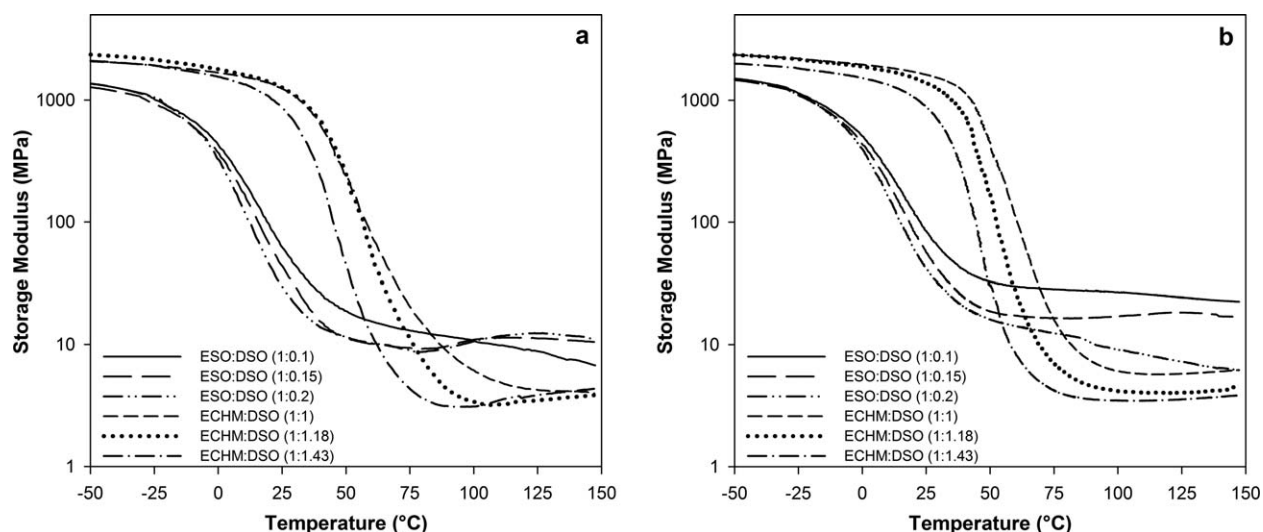
Figure 6. Storage modulus of ESO/DSO and ECHM/DSO samples at 3hours (a) and 10days (b) after UV curing.

pure ECHM film could not be peeled from the glass substrate after UV curing because of its highly brittle characteristic. DSO was an effective plasticizer of ECHM to increase the flexibility of the UV-cured ECHM polymer for flexible coating applications.

Optical Transmittance and Water Uptake Properties

The optical transmittances of the ESO/DSO (w/w ratios of 1 : 0.15) and the ECHM/DSO (w/w ratios of 1 : 1.18) were around 90% in the visible light range, their transparency was similar to microscope slide glass. In addition, 80% light transmittance of polypropylene and 60% light transmittance of polyethylene in visible ranges were confirmed from our previous research,[18] making the transparencies of the ESO/DSO and the ECHM/DSO UV-cured films comparable to glass and commercial plastics. Accordingly, the bio-based polymers could be useful in transparent coating applications.

The increases of the weights of the ESO/DSO (w/w ratios of of 1 : 0.2) and the ECHM/DSO (w/w ratios of 1 : 1.43) were $0.66 \pm 0.06\%$ and $2.83 \pm 0.2\%$, respectively, in the water uptake test during 24 hours. Both ESO/DSO and ECHM/DSO polymers exhibited good water resistance. Additionally, the lower water absorption of ESO/DSO could be related to its higher cross-link density.

CONCLUSIONS

DSO was successfully copolymerized with ESO and ECHM, respectively, to produce bio-based coating materials through UV-initiated cationic ring-opening polymerization. Photopolymerization produced ether cross-linkage polymeric networks. ECHM/DSO film was stronger than ESO/DSO film. Postpolymerization effects were confirmed by spectral, thermal, mechanical, and dynamic mechanical analyses. The ECHM/DSO (w/w ratio of 1 : 1.43) film showed excellent flexibility during the shelf life tested in this study. ESO/DSO (w/w ratio of 1 : 1)
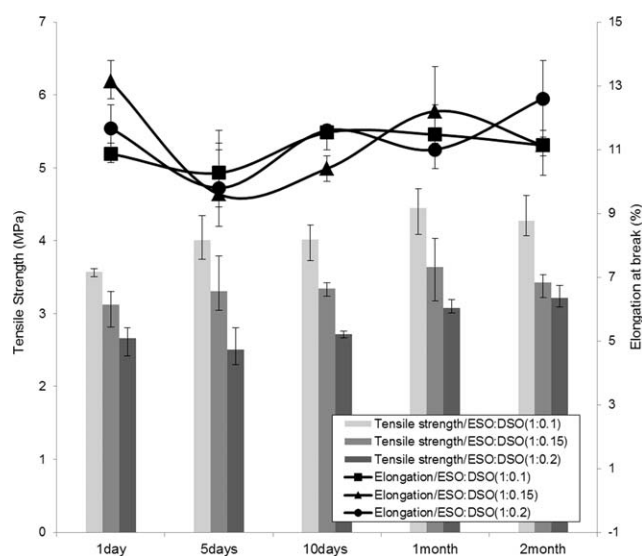

Figure 7. Tensile strength and elongation at break of ESO/DSO (w/w ratios of 1 : 0.1, 1 : 0.15, and 1 : 0.2).
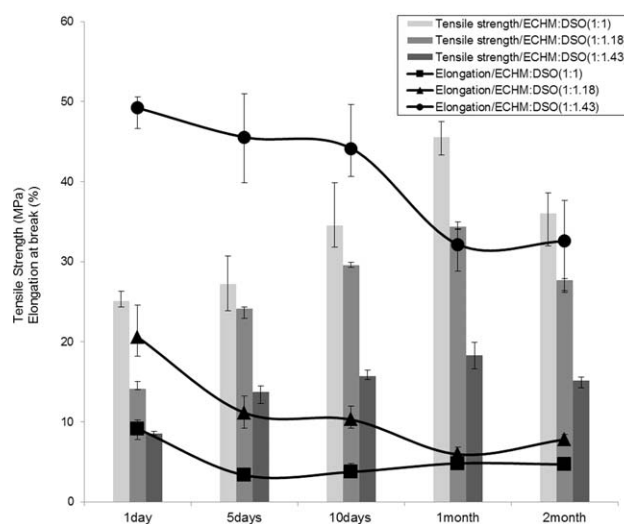

Figure 8. Tensile strength and elongation at break of ECHM/DSO (w/w ratios of 1 : 1, 1 : 1.18, and 1 : 1.43).

and ECHM/DSO (w/w ratio of 1 : 1.18) films exhibited the highest tensile strengths. Mechanical properties of these films remained stable during the 2-month shelf life. DSO was found to be an effective plasticizer for both ESO and ECHM systems. The transparencies of soybean-based UV-cured films were similar to that of microscope slide glass.

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