Bio-based Polymeric Materials from Epoxidized Triglyceride and Rosin Derivatives

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Abstract

In this study, bio-based polymeric materials have been developed from plant oil and rosin derivative. An acid-catalyzed curing of epoxidized soybean oil (ESO) in the presence of rosin derivative produced the transparent bio-based materials. The resulting polyESO/rosin derivatives exhibited excellent flexiblity. Dynamic viscoelasticity analysis presented the formation of the homogeneous structure of ESO polymer and rosin components. The incorporation of the rosin components improved the thermal properties and increased elongation at break. Furthermore, the present materials showed high adhesion property. The development of the bio-based materials from inexpensive renewable resources, plant oil and rosins, is expected to contribute to global sustainability systems.

Keywords: Renewable resource, Crosslinking, Epoxidized soybean oil, Rosin, Adhesion property

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Introduction

Bio-based polymers are now moving into the mainstream and may soon be competing with commodity plastics [1-3]. Using biomass as a starting material for plastics is highly significant for reduction of greenhouse gas and fossil resource-saving in social viewpoints, which is one of the most promising solutions to problems concerning global environment and energy resources. Among them, triglyceride oils are expected as an ideal alternative chemical feedstock, since triglyceride oils, derived from plant source, such as soybean, palm, canola, and sunflower, are found in abundance in the world [4,5]. Inexpensive plant oils have been extensively used for various applications such as coatings and inks as a binder [6-11]. However, these oil-based materials did not show properties of rigidity and strength required for various applications by themselves. In some cases, triglyceride was a minor component in the polymeric materials; this was used solely as a modifier to improve their physical properties [12-18].

Epoxidized plant oils are easily synthesized from the more common unsaturated oils, such as linseed, sunflower, and soybean oil, by standard epoxidation reaction [19]. Epoxidized soybean oil (ESO) and epoxidized linseed oil (ELO) are commercialized in large volumes, and have been used as an environment-conscious plasticizer for poly(vinyl chloride), chlorinated rubber, and poly(vinyl alcohol) emulsions to improve stability and

flexibility. The polyols and acrylates converted from epoxidized plant oils were developed as a starting material for bio-based functional polymers [20-22]. Furthermore, epoxidized plant oils have been polymerized by ring-opening polymerization using photoinitiators, latent catalyst, and acid catalyst to produce plant oil-based network polymer [23-26].

Recently, organic-inorganic green nanocomposites were developed by an acid-catalyzed curing of ESO in the presence of a silane coupling agent or an organic clay [27-31]. The mechanical properties of these plant oil-based nanocomposites increased by incorporating the inorganic moieties. Bio-based green composites were synthesized using biofiber such as kenaf, flax, and hemp as renewable compounds. Their mechanical strength was effectively improved by the incorporation of biofiber, whereas most of them showed poor flexibility due to the plant oil-based network structure [32-34].

Rosin is one of bio-based materials and is obtained from the exudation of pines and conifers, which contains approximately 90% of abietic acid and its isomer. Rosin exhibits excellent solubility for organic media and compatibility with a variety of synthetic resins. Rosin and its derivatives have been used as adhesive tackifiers, and are still mainly used in those markets. In addition, they have also found other applications in printing, varnishes, paints, sealing wax, some soaps, paper sizing, etc. [35-41].

In this study, bio-based polymeric materials were synthesized from ESO and rosin derivatives. The effects of rosin derivatives on the thermal and mechanical properties of the ESO-based network polymer were examined.

Experimental Method

Materials

Epoxidized soybean oil (ESO) was gifted from Adeka Co. (Tokyo, Japan). Rosin-modified phenolic resin (Tamanol 803L, RMPR) and rosin pentaerithritol ester (Ester Gum HP, RPE) were kindly donated from Arakawa chemical industries, LTD. (Osaka, Japan). Thermally-latent cationic catalyst (a benzylsulfonium hexafluoroantimonate derivative, Sun Aid SI-60L) was gifted from Sanshin Chemical Industry Co. (Yamaguchi, Japan).

Synthesis of polyESO/rosin compound

The following procedure was typically used in the synthesis of the polyESO/RMPR. ESO (0.5 g) and RMPR (0.5 g) were mixed with gentle stirring at 50°C, and then a thermally latent catalyst (1.0 wt% for the sample) was added to the mixture. The obtained mixture was poured into a Teflon mold (40 mm × 17 mm × 1 mm) and was kept at 100°C for 12 h to produce polyESO/RMPR (50/50 wt%).

The polyESO/RPE was synthesized by a similar procedure.

Evaluation of adhesion strength

The sample was attached with a contact area of 2.5 × 1.4 cm between polished stainless steel panels, and a weight of 1000 g was ridden for 5 minutes. The measurement was carried out with a crosshead speed of 5 mm·min^{-1} at room temperature. The adhesion strength was evaluated as shear force per unit area of testing.

Measurements

^{1}H nuclear magnetic resonance (^{1}H NMR) spectrum was measured by a DPX 400 instrument (Bruker BioSpin Co., MA, USA). Fourier-transform infrared spectroscopy (FT-IR) was recorded on a Spectrum One (Perkin-Elmer Inc., MA, USA). Dynamic viscoelasticity analysis (DMA) was performed by using a DMS6100 (Hitachi High-Tech Science Co., Tokyo, Japan) with a frequency of 1 Hz at a heating rate of 3°C·min^{-1}. Tensile properties and adhesion strength were measured by a Shimadzu EZ Graph (Shimadzu Co., Kyoto, Japan). The sample was cut into a plate shape of 5 mm × 20 mm × 1 mm. The measurement was carried out with a crosshead speed of 5 mm·min^{-1} at room temperature.

Results and Discussion

Synthesis of polyESO/rosin compounds

The oxirane number of ESO used in this study was 3.4 per a molecule, determined by ^{1}H NMR spectrum. The curing of ESO was carried out by using a thermally latent acid catalyst in the presence of rosin-modified phenolic resin (RMPR) at 100°C for 12 h to produce the transparent brown polyESO/RMPR **(Figure 1)**. During the curing, the oxirane groups of ESO reacted with each other to form a plant oil-based network polymer. The feed ratio of RMPR was 20 or 50 weight%. The polyESO/rosin pentaerithritol ester (RPE) was synthesized by a similar procedure.

In FT-IR spectra of the polyESO/RMPR, a peak at approximately 830 cm^{-1} ascribed to C-C anti-symmetric stretching of the oxirane groups of ESO disappeared, and a broad peak centered at 3400 cm^{-1} due to O-H vibration increased. These data indicate that the oxirane groups were consumed to form a hydroxy-terminated ESO-based network polymer. On the other hand, the peaks which are derived from RMPR hardly changed. Extraction test of the samples was examined. For chloroform, the ESO homopolymer was insoluble, whereas RMPR was soluble. The polyESO/RMPRs were immersed in chloroform at room temperature for 24 h, and the residue was washed with chloroform. The rosin components in the polyESO/RMPR dissolved in chloroform, and the residue weight was close to the feed weight of ESO. These results suggest that the RMPR scarcely reacted during the crosslinking of ESO due to the low reactivity of the hydroxyl groups of RMPR and that the RMPR components are dispersed in the ESO matrix.

The resulting polyESO/rosin compounds, especially polyESO/RPEs, exhibited high flexibility, and these materials could be bent as shown in **Figure 2**. In contrast, the ESO homopolymer readily broke by bending. This behavior of the polyESO/rosin compounds may be because of the increase in the crosslinking distance of the ESO-based network polymer by the incorporation of rosin moiety.

Properties of polyESO/rosin compounds

In order to evaluate the effect of the incorporation of RMPR, dynamic viscoelasticity analysis as a function of temperature was performed. The storage modulus and loss factor of the ESO homopolymer and polyESO/RMPR are shown in **Figure 3**. The storage modulus of the ESO homopolymer at lower temperature region was almost constant at approximately 2.5 GPa and
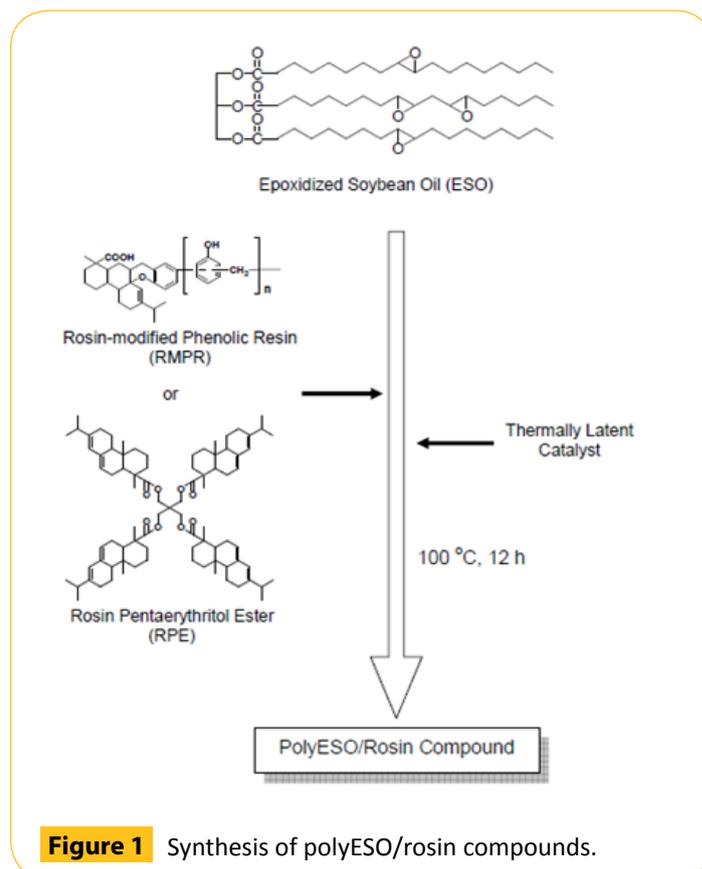
Figure 1   Synthesis of polyESO/rosin compounds.

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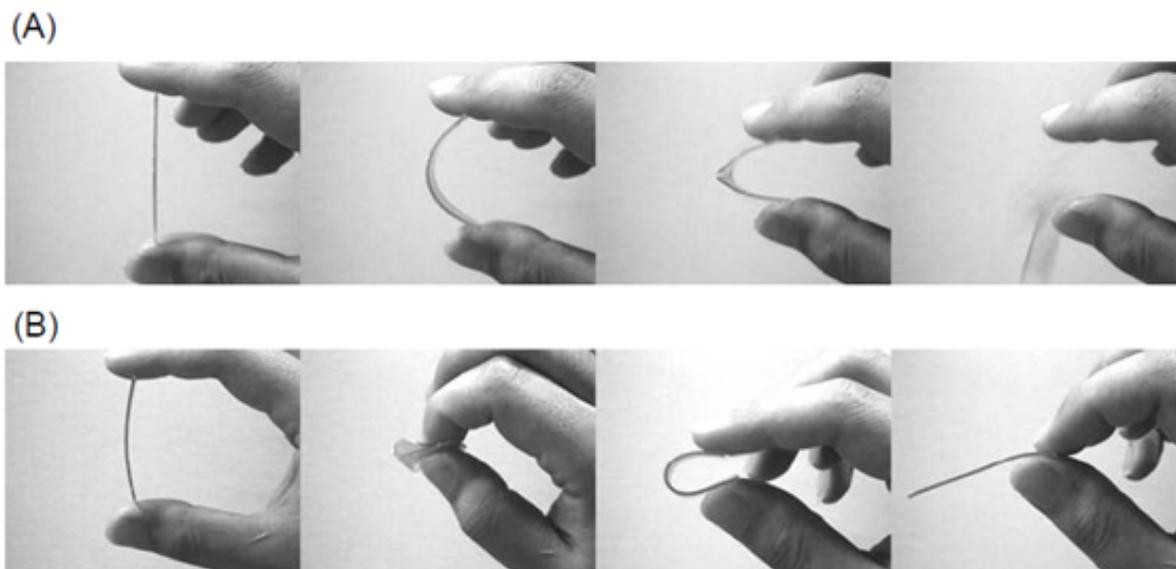
Figure 2 Photographs of bending test; (A) ESO homopolymer and (B) polyESO/RPE (50/50 wt%).
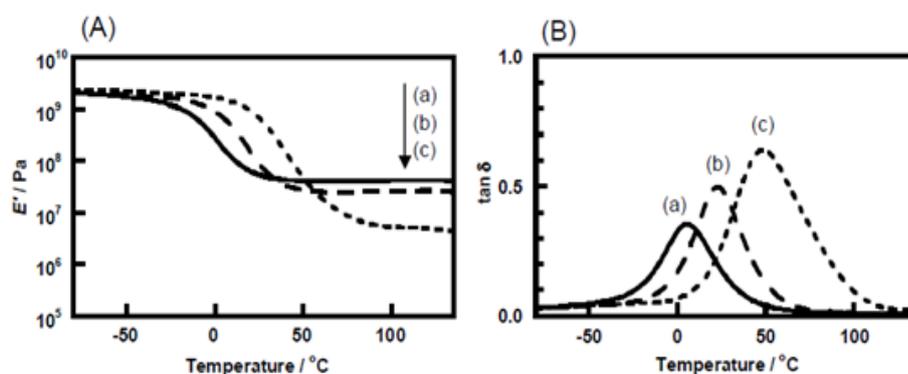
Figure 3 Dynamic viscoelasticity of (a) ESO homopolymer, (b) polyESO/RMPR (80/20 wt%), and (c) polyESO/RPMR (50/50 wt%): (A) storage modulus, and (B) loss factor.

gradually decreased at around 0°C, which is derived from glass transition of ESO-based network polymer. In the rubbery region, the storage modulus of the polyESO/RMPR was lower than that of the ESO homopolymer, and the storage modulus depended on the RMPR content. This result indicates that the incorporation of the RMPR components decreases the crosslinkink distance of the ESO-based network polymer. This behavior was contrast with that of ESO/silica or ESO/clay composites; the storage modulus of these organic-inorganic composites increased as a function of the inorganic content **[27-31]**. The storage moduli of the ESO homopolymer and the polyESO/RMPR were almost constant in the rubbery region, suggesting the quantitative consumption of the oxirane groups of ESO.

In loss factor curves of the polyESO/RMPRs, only a broad peak was found and the peak shifted to the higher temperature region with increase in the RMPR content. The intensity of loss factor peak also increased as a function of the RMPR content. These results suggest that RMPR components are miscible with the ESO

polymer and that the interface in nanometer scale between ESO polymer and RMPR components is formed.

Figure 4 shows the storage modulus and loss factor curves of the ESO homopolymer, polyESO/RMPR (50/50 wt%), and polyESO/RPE (50/50 wt%). It is found that the dynamic viscoelasticity of the polyESO/RPE is similar to that of the polyESO/RMPR. The storage modulus of the polyESO/RPE rapidly dropped at approximately 20°C due to the glass transition, and the storage modulus in rubbery region was lower than that of the ESO homopolymer and the polyESO/RMPR. The loss factor peak of the polyESO/RPE was sharper and larger compared with that of the ESO homopolymer and the polyESO/RMPR; the peak top was more than 1.5. These data suggest that the RPE components enhance the friction in the interface between ESO polymer and rosin moiety.

In order to evaluate the mechanical properties of the polyESO/ rosin components, tensile test was carried out. The strain-stress curves of the ESO homopolymer, polyESO/RMPR (50/50 wt%), and polyESO/RPE (50/50 wt%) were shown in **Figure 5**, and the
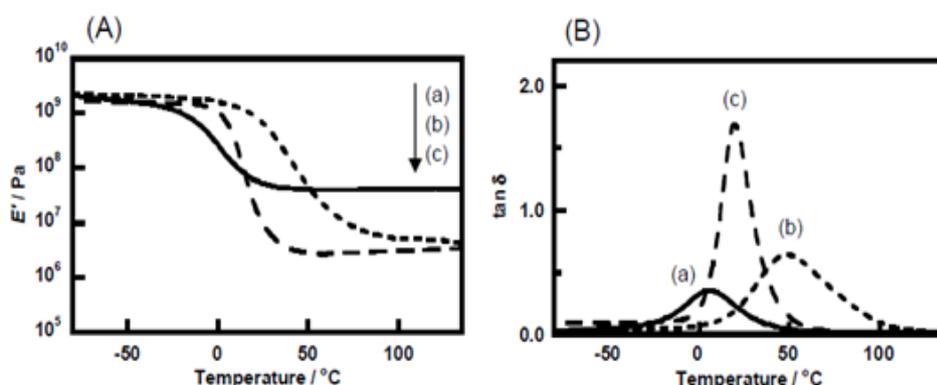
Figure 4 Dynamic viscoelasticity of (a) ESO homopolymer, (b) polyESO/RMPR (50/50 wt%), and (c) polyESO/RPE (50/50 wt%): (A) storage modulus, and (B) loss factor.
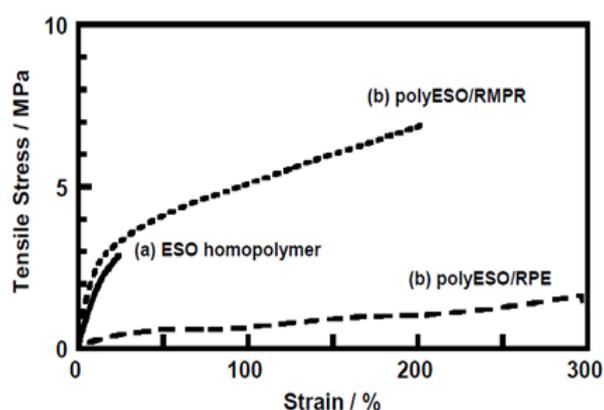
Figure 5 Strain-stress curves of (a) ESO homopolymer, (b) polyESO/RPMR (50/50 wt%), and polyESO/RPE (50/50 wt%).

Figure 6 Adhesive strengths of ESO homopolymer, polyESO/RPMR (50/50 wt%), and polyESO/RPE (50/50 wt%).

thermal and mechanical properties were summarized in **Table 1**. The ESO homopolymer fractured at low strain due to the network structure, whereas the polyESO/RMPR and the polyESO/RPE exhibited ductile behaviors. These data are related to the good compatibility between rosin components and ESO polymer and the increase in the crosslinking distance of the ESO polymer by the incorporation of the rosin components. Moreover, the tensile strength of the polyESO/RMPR was improved by the incorporation of RMPR component.

The crosslinking density was calculated using the following equation **[42]**:

$$\sigma = \frac{E'}{3RT}$$

where σ is the appearance crosslinking density of elastically effective network chains, E' is the storage modulus at glass transition temperature (T_g) + 40°C, R is the gas constant, and T is T_g + 40. The crosslinking density decreased as a function

of the amount of rosin component, whereas elongation at break increased. Furthermore, the glass transition temperature increased with increase in the rosin content.

Adhesive property of polyESO/rosin compounds was evaluated by lap share strength test. The sample was attached between stainless steel panels. The adhesion strength of the ESO homopolymer was 1.2×10^2 N·cm^{-2} and the ESO homopolymer did not show adhesive behavior. On the other hand, the adhesion strength of polyESO/RMPE (50/50 wt%) and polyESO/RPE (50/50 wt%) were higher than that of the ESO homopolymer and the polyESO/RMPR (50/50 wt%) and the polyESO/RPE (50/50 wt%) exhibited good adhesion property. These results indicate that the incorporation of rosin components is obviously effective in improvement of adhesion properties of the ESO-based network polymer. Especially, the polyESO/RPE (50/50 wt%) achieved a noteworthy improvement of adhesion properties, and the adhesion strength was higher approximately six times than that of ESO homopolymer **(Figure 6)**.

Conclusions

In this study, bio-based materials were developed from plant oil

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and rosin derivatives. An acid-catalyzed crosslinking of epoxidized soybean oil in the presence of rosin derivatives produced the bio-based materials with high flexibility. In the resulting polyESO/ rosin compounds, the ESO polymer was compatible with the rosin components, and the rosin components scarcely reacted with ESO and were dispersed in the plant oil-based network polymer in nano-meter scale. By the incorporation of rosin components, the thermal properties of the ESO polymer were improved and the elongation at break of polyESO/RMPE and polyESO/RPE remarkably increased with increase in the rosin content. Furthermore, the resulting materials exhibited excellent adhesion properties.

Plant oil and rosin are found in abundance in all over the world, making them an ideal alternative chemical feedstock. The present study provides new molecular design of high-performance plant oil-based polymeric materials by combination of inexpensive renewable resources.

Acknowledgement

Table 1: Thermal and mechanical properties of polyESO/ rosin compound.

Rosin	Amount [a] / wt%	T_g [b] / °C	Crosslinking density [b] / mol·m^{-3}	Tensile modulus [c] / MPa	Tensile strength [c] / MPa	Elongation at break [c] / %
-	0	6	5.1	20	2.9	26
RMPR	10	15	4.0	14	2.9	37
RMPR	20	23	2.9	32	4.3	84
RMPR	50	49	0.7	86	7.1	202
RPE	10	8	3.6	15	2.4	38
RPE	20	9	2.2	11	2.3	59
RPE	50	20	0.3	3	1.6	296

[a] Amount of rosin component.
[b] Determined by dynamic elastic analysis.
[c] Determined by tensile test.

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