Bio-based Flexible Network Polymer from Epoxidized Soybean Oil Reinforced by Poly(butyl methacrylate)

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Abstract

This study deals with the synthesis of a plant oil-based polymeric material from epoxidized soybean oil (ESO) and poly(butyl methacrylate) (PBMA). PolyESO/PBMAs were synthesized by an acid-catalyzed curing in the presence of PBMA to give a transparent bio-based polymeric material. During the reaction, the PBMA components scarcely reacted with ESO and were dispersed in the ESO polymer matrix to form semi-interpenetrating polymer network. The resulting polyESO/PBMA exhibited excellent flexibility. The incorporation of the PBMA components improved the mechanical properties of the plant oil-based network polymer. Furthermore, the polyESO/PBMA showed relatively good thermal stability. The present materials are expected to contribute to the development of bio-based polymeric materials.

Keywords: renewable resource, bio-based material, epoxidized soybeen oil, acrylic polymer

1. Introduction

Nowadays, there is a growing interest in green chemistry from the social and environmental viewpoints. A major principle in green chemistry is the use of renewable and sustainable raw materials that can introduce elements of degradability and reduced product toxicity in polymer production. Furthermore, the use of bio-based materials is highly significant for reduction of greenhouse gas and fossil resource-savings, which is one of the most promising solutions to problem concerning the global environment and energy resources (Nagarajan *et al*. 2013, Quirino *et al*. 2014, Dubé & Salehpour 2014).

Among bioresources, plant oils, such as soybean oil, palm oil, canola oil, and sunflower oil, are expected as an ideal alternative chemical feedstock, since plant oils, derived from renewable resources, are found in abundance in the world. Plant oils consist of three fatty acids which are joined to glycerol by ester linkage, and the content of fatty acids and the number of unsaturated groups are characteristic for each plant oils. Inexpensive bio-based triglyceride have been utilized extensively for coatings, inks, plasticizers, lubricants, resins, and agrochemicals in addition to their applications in food industry (Biermann *et al*. 2000, Khot *et al*. 2001, Miyagawa *et al*. 2005, Metzger & Bronscheuer 2006). However, these plant oil-based polymeric materials do not show sufficient rigidity and strength by themselves for structural applications. Therefore, plant oils were a minor component in polymeric materials; this is used solely as a modifier to improve their physical properties.

Epoxidized plant oils are found in naturally occurring oils, such as vernonia oil, and are easily synthesized from the unsaturated plant oils, such as linseed, sunflower, soybean, and palm oil, by standard epoxidation reaction. Epoxidized soybean oil (ESO) and epoxidized linseed oil are commercially available as a stabilizer and plasticizer for poly(vinyl chloride) and a modifier for coatings. Acrylates and polyols derived from epoxidized plant oils have also been used as a monomer for preparation of bio-based polymeric materials (Biresaw *et al*. 2008, Lligadas *et al*. 2010, Luo *et al*. 2011, Saithai *et al*. 2013). Furthermore, various cationic polymerization of epoxidized plant oil can be achieved by photoinitiators, latent catalysts, or acid catalysts (Chakrapani & Crivello 1998, Shibata *et al*. 2009, Wang & Schuman 2013). These epoxy compounds from renewable resources possess high potential as a starting material for bio-based thermosetting plastics (Tsujimoto *et al*. 2003, Petrović *et al*. 2005, Campanella *et al*. 2009, Gupta *et al*. 2011). Epoxidized plant oils were cured in the presence of inorganic chemicals to produce organic-inorganic hybrid materials

(Uyama *et al*. 2003, Lligadas *et al*. 2006, Tanrattanakul & Saithai 2009, Tsujimoto *et al*. 2015). Plant oil-based green composites were developed using biofiber (Williams & Wool 2000, Rakotonirainy & Padua 2001, Tran *et al*. 2006) and biopolymer (Imai *et al*. 2007, Ali *et al*. 2009, Hosoda *et al*. 2014), such as kenaf, flax, hemp, poly(lactic acid), and poly(3-hydroxybutyrate) as renewable compounds. By the incorporation of inorganic components, biofibers, or biopolymers, their mechanical strengths were effectively improved, whereas most of them showed poor flexibility due to the plant oil-based network structure.

This study deals with synthesis and properties of bio-based polymeric material from ESO and poly(butyl methacrylate) (PBMA). The resulting material exhibited excellent flexibility and relatively good transparency with increases in mechanical properties.

2. Materials and Methods

2.1 Materials

ESO was a gift from Adeka Co. PBMA was purchased from Sigma-Aldrich Co. The molecular weight of PBMA, determined by size exclusion chromatography (SEC), was 4.1×10^5. Thermally-latent cationic catalyst (a benzylsulfonium hexafluoroantimonate derivative, Sun Aid SI-60L) was provided by Sanshin Chemical Industry Co.

2.2 Synthesis of polyESO/PBMA

The synthesis of polyESO/PBMA was carried out as follows. ESO (0.5 g) and PBMA (0.5 g) were dissolved in 3.0 mL of chloroform, and a thermally-latent cationic catalyst was added to the solution. The resulting solution was poured into a Teflon mold (17 mm $\times$ 40 mm $\times$ 1 mm), and then, the solvent was allowed to evaporate at room temperature. The residual mixture was kept at 150 ℃ for 2h to produce polyESO/PBMA (50/50 wt%).

The polyESO/PBMAs with different feed ratio of ESO and PBMA were prepared by similar procedure.

2.3 Measurements

[1]H nuclear magnetic resonance (NMR) spectrum was recorded on a Bruker Biospin DPX-400 instrument. SEC analysis was carried out by using a Tosoh SC8020 apparatus with a refractive index detector at 40 ℃ under the following conditions: Tosoh TSKgel G4000 column and chloroform eluent at a flow rate of 1.0 mL min^{-1}. The calibration curve was obtained using polystyrene standards. Fourier-transform infrared spectroscopy (FT-IR) was measured by a Perkin-Elmer Spectrum One. Dynamic viscoelasticity analysis (DMA) was performed by using an IT Instruments DVA-200 with a frequency of 1 Hz at a heating rate of 3 ℃ min^{-1}. Tensile properties were measured by a Shimadzu EZ Graph with a cross-head speed of 5 mm min^{-1}. The sample was cut into a plate shape of 10 mm $\times$ 20 mm $\times$ 1 mm. Thermogravimetric (TG) analysis was performed using a Hitachi High-Tech Science TG/DTA7200 at a heating rate of 10 ℃ min^{-1} under nitrogen.

3. Results and Discussion

3.1 Synthesis of polyESO/PBMA

In this study, a bio-based polymeric material was synthesized from ESO and PBMA. The number of oxirane groups per an ESO molecule, determined by ^{1}H NMR, was 3.2. PBMA is one of acrylic polymers, which is an amorphous polymer with relatively low glass transition temperature. PBMA exhibits a flexible property and has been used for coating, adhesive, and sizing agent for paper. The crosslinking of ESO was carried out in the presence of PBMA using a thermally-latent acid as a catalyst to produce the bio-based polymeric material with high transparency (Figure 1). During the reaction, the oxirane groups of ESO reacted with each other to form the plant oil-based network structure. The resulting polyESO/PBMAs showed good transparency and flexibility, indicating that the PBMA components were dispersed in ESO polymer matrix.
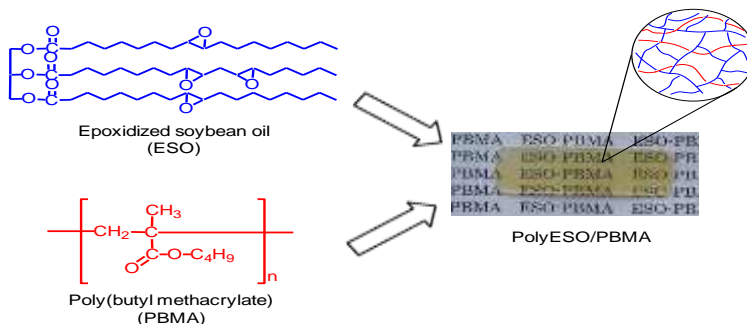

Figure 1. Synthesis of polyESO/PBMA.

Figure 2 shows the FT-IR spectra of ESO, neat PBMA, and the polyESO/PBMA (50/50 wt%). In the FT-IR spectrum of the polyESO/PBMA (50/50 wt%), a characteristic peak at approximately 820 cm^{-1}, ascribed to C-C antisymmetric stretching of the oxirane groups of ESO, decreased, and a broad peak centered at 3400 cm^{-1} due to O-H vibration newly appeared. These data indicate that the oxirane groups of ESO react with each other to form plant oil-based network structure. On the other hand, the peaks at 1723 and 1741 cm^{-1} hardly changed. These peaks were derived from carboxyl groups of PBMA and ESO, respectively. The polyESO/PBMAs were immersed in chloroform for 24 h, and the residue was washed with chloroform. The residual weight was close to the feed weight of ESO, because the PBMA components dissolved in chloroform. These results strongly suggest that the PBMA components scarcely reacted during the curing of ESO, and that semi-interpenetrating polymer network is formed.
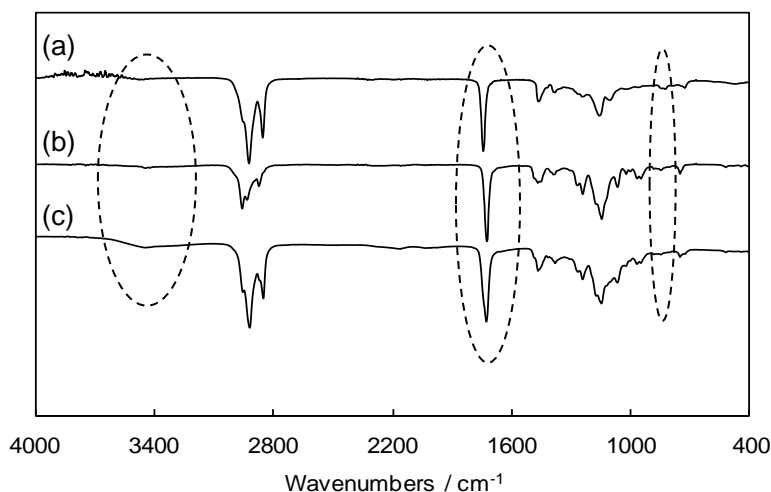

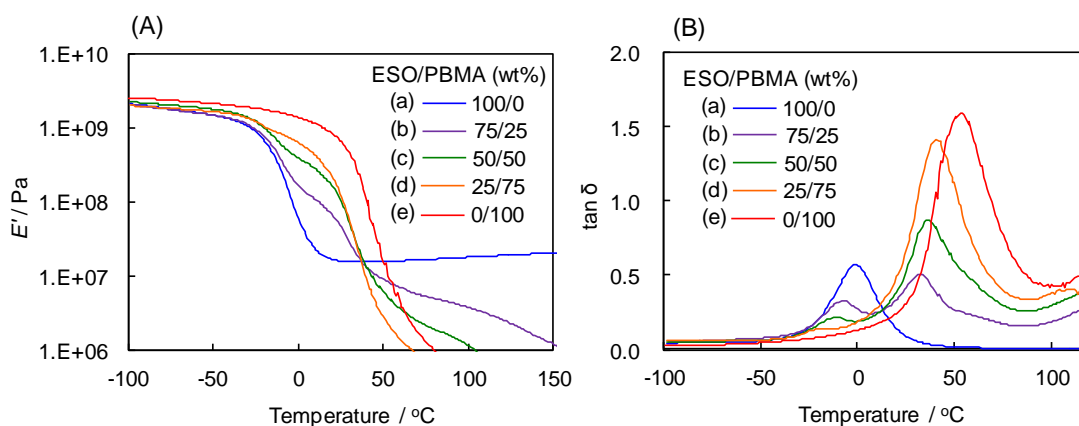Figure 2. FT-IR spectra of (a) ESO, (b) neat PBMA, and (c) polyESO/PBMA

Figure 3. Dynamic viscoelasticity of (A) storage modulus, and (B) loss factor; (a) ESO homopolymer, (b) polyESO/PBMA (75/25 wt%), (c) polyESO/PBMA (50/50 wt%), (d) polyESO/PBMA (25/75 wt%), and (e) neat PBMA

3.2 Mechanical and Thermal Properties of polyESO/PBMA

In order to investigate the effect of the incorporation of PBMA on the mechanical properties of the plant oil-based network polymer, the dynamic viscoelasticity analysis was carried out. Figure 3 shows storage moduli and loss factor curves as a function of temperature for the ESO homopolymer, the polyESO/PBMAs, and neat PBMA. For all samples, the storage moduli remained almost constant between -100 and -40 ℃. The storage modulus of the ESO homopolymer decreased rapidly at -25 ℃, due to the glass transition of ESO-based network polymer. The storage modulus in rubbery region was constant with 10 MPa, suggesting the quantitative consumption of the oxirane groups of ESO. On the other hand, the storage modulus of neat PBMA dropped at 30 ℃, and PBMA became molten state. The storage moduli of polyESO/PBMAs decreased stepwise at approximately -10 and 30 ℃, which were attributed to the glass transition of the ESO polymer and the PBMA component, respectively. The storage modulus of the polyESO/PBMAs at room

temperature increased as the PBMA content increased, indicating effective reinforcement of the incorporation of the PBMA components. In loss factor curves of the polyESO/PBMAs, two peaks at approximately -10 and 35 ℃ were observed. This result indicates that the PBMA components are immiscible with ESO polymer. Furthermore, the peak with the lower temperature, which was derived from the glass transition of ESO polymer, shifted to lower temperature region. This may be because the incorporation of the PBMA components decreases the crosslinking density of the ESO-based network polymer.

To evaluate the reinforcement effect of the PBMA components, a tensile test was performed. The mechanical properties, such as tensile modulus, stress at break, and elongation, are summarized in Table 1. The ESO homopolymer was brittle, and fractured at low stress and strain, due to the ESO-based network structure. On the other hand, the polyESO/PBMAs exhibited ductile behaviors. The tensile modulus and the stress at break depended on the PBMA content, and they increased with increase in the PBMA content. The incorporation of the PBMA components also increased the elongation, and the elongation at break of the polyESO/PBMA (25/75 wt%) was larger than that of neat PBMA. This is due to the plasticization effect of ESO. Furthermore, the polyESO/PBMAs showed excellent flexibility and could be easily bent (Figure 4). This characteristic property of the polyESO/PBMAs may be derived from the fine dispersion of the PBMA components in ESO matrix and the decrease of the crosslinking density of ESO-based network polymer.

Figure 4. Photograph of flexible polyESO/PBMA (50/50 wt%)

Table 1. Tensile properties of polyESO/PBMA

Sample code	Tensile modulus[a] / MPa	Stress at break[a] / MPa	Elongation[a] / %
ESO homopolymer	7.2	0.4	7
PolyESO/PBMA (75/25 wt%)	12.1	1.3	37
PolyESO/PBMA (50/50 wt%)	56.6	2.5	47
PolyESO/PBMA (25/75 wt%)	73.8	2.7	305
neat PBMA	324.4	6.3	163

[a] Determined by tensile test.

The thermal stability of the polyESO/PBMA was evaluated by thermogravimetry (TG) under nitrogen. Figure 5 shows TG traces of the ESO homopolymer, neat PBMA, and the polyESO/PBMA (50/50 wt%). The weight of the ESO homopolymer and neat PBMA decreased at approximately 370 and 250 ℃, respectively. The polyESO/PBMA (50/50 wt%) was stable at a temperature lower than 280 ℃ and decomposed at around 300 ℃. Temperature at 5% weight loss of the ESO homopolymer, neat PBMA, and the polyESO/PBMA (50/50 wt%) were 350, 237 and 299 ℃, respectively. These data indicates relatively good thermal stability of the polyESO/PBMAs.
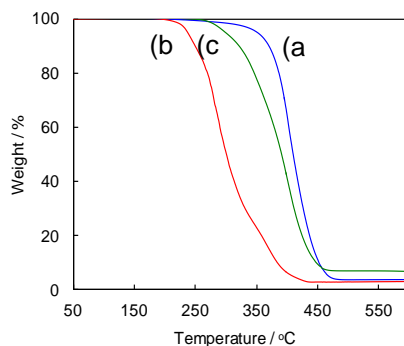

Figure 5. TG traces of (a) ESO homopolymer, (b) neat PBMA, and (c) polyESO/PBMA (50/50 wt%).

4. Conclusion

In this study, a new class of bio-based material from renewable plant oil was developed. The acid-catalyzed curing of epoxidized soybean oil in the presence of PBMA produced the transparent polymeric material with semi-interpenetrating network structure. The dynamic viscoelasticity analysis showed the reinforcement effect by the incorporation of the PBMA component. The tensile modulus and stress of the polyESO/PBMAs were larger than those of the ESO homopolymer. The elongation at break was also improved by the incorporation of PBMA components, and the polyESO/PBMAs exhibited excellent flexibility. Furthermore, the polyESO/PBMAs showed relatively good thermal stability.

Natural plant oils are renewable, nontoxic, and inexpensive materials. Thus, plant oil-based polymers and composites have large potential for industrial applications due to the low cost and the amorphous properties. This study provides new methodology of the preparation of high-performance bio-based polymeric materials.

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