

Full Biobased Polymeric Material from Plant Oil and Poly(lactic acid) with a Shape Memory Property

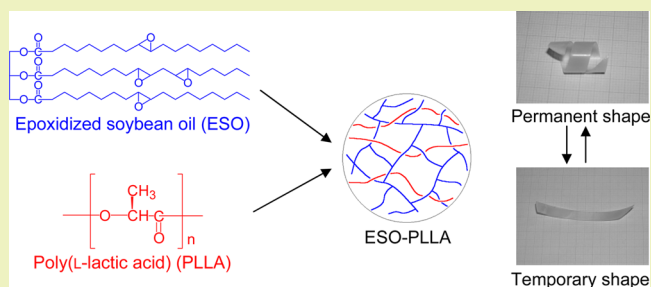
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S Supporting Information

ABSTRACT: This article deals with the synthesis of biobased polymeric material with a shape memory property from epoxidized soybean oil (ESO) and poly(L-lactic acid) (PLLA). PolyESO/PLLAs were synthesized by an acid-catalyzed curing of ESO in the presence of PLLA. PLLA was scarcely reacted with ESO during the reaction and was dispersed in the ESO-based polymer network. The Young's modulus and maximum tensile stress of the polyESO/PLLA increased as the PLLA content increased. On the other hand, the strain at break of the polyESO/PLLA was larger than that of the ESO homopolymer and neat PLLA. The polyESO/PLLA exhibited excellent shape memory-recovery behaviors, and the ability depended on the feed ratio of ESO and PLLA. Because the present materials are prepared from renewable resources by a simple preparation method, this study is highly significant to provide biobased intelligent materials.

KEYWORDS: Renewable resource, Epoxidized soybean oil, Poly(L-lactic acid), Shape memory



INTRODUCTION

Recently, growing interest in the exploitation of renewable resources in the areas of energy and materials has been one of the major scientific and technological issues. Biobased materials are made from biomass feedstock fixed with carbon dioxide from the atmosphere. The use of biobased materials allows a decrease in oil consumption and CO₂ emissions to the atmosphere, compared to the use of petroleum-based commodity plastics.^{1,2}

Poly(L-lactic acid) (PLLA) is a biodegradable thermoplastic, which is produced from lactic acid derived from the fermentation of corn, potatoes, and so on.³ Due to its good mechanical strength and excellent biocompatibility, PLLA exhibits great potential applications in many fields, such as packaging, automotive industries, and biomedical devices.^{4–8} Plant oils are also one of the cheapest and most abundant biomass available in large quantities and, hence, are expected to be an ideal alternative chemical feedstock.⁹ Plant oils, such as linseed, sunflower, soybean, and palm oil, have been extensively used for various applications such as coatings, inks, agrochemicals, etc.^{10–13} These plant oil-based polymeric materials, however, do not show the properties of rigidity and strength required for structural applications by themselves. In some cases, therefore, triglyceride was a minor component in polymeric materials; this is used solely as a modifier to improve their physical properties.

Epoxidized soybean oil (ESO) is manufactured by the epoxidation of the double bonds of soybean oil, and they have been used as a plasticizer for poly(vinyl chloride), chlorinated rubber, and poly(vinyl alcohol) emulsions to improve stability

and flexibility.¹⁴ In recent years, extensive work has been done to develop the polymers from epoxidized triglycerides or epoxidized fatty acids. The cationic polymerization of epoxidized plant oils has been investigated using photo-initiators, latent catalysts, and acid catalysts to produce biobased epoxy resins.^{15–21} Epoxidized plant oils were cured in the presence of inorganic chemicals to produce organic–inorganic materials. The acid-catalyzed curing of epoxidized plant oils with a silane coupling agent produced the nanocomposite with excellent mechanical properties and transparency.^{22–24} The curing of epoxidized plant oils in the presence of an organophilic clay produced the triglyceride–clay nanocomposites with homogeneous distribution of the clay, in which silicate layers of the clay were intercalated and randomly distributed in the polymer matrix.^{25–27} The triglyceride–clay composites sometimes showed a good water vapor barrier property.

Shape memory polymers (SMPs) have a sensitive response to the external stimuli, such as temperature, pH, humidity, chemo, light, and electricity. Among shape memory materials, thermoresponsive SMPs have drawn great interest because of their good processability, low cost, and high recovery ability at relatively low temperature.^{28–37} Thermoresponsive SMP is first processed to receive a permanent shape. Afterward, above a given temperature range (a switching temperature), SMP can be easily deformed into a temporary shape that is fixed by fast

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cooling under stress. When reheated above the switching temperature without stress, the permanent shape is regained. Because of the sensitivity to environmental conditions, SMPs have found various applications, such as actuators, smart fabrics, heat shrinkage tubes for electronic packaging, and biomedical devices. Recently, considerable efforts have been expanded to develop SMPs, and excellent shape memory behaviors were observed in many polymers including polynorbornene, poly(ϵ -caprolactone), polyurethanes, their copolymers, etc.^{38–45} Although SMPs derived from biomass have been also studied, most of them were the block copolymers that were prepared from glycerol, glycolide, or lactide by means of a two-stage synthesis or coupling method.^{46–52}

In this study, we synthesized a biobased polymeric material from epoxidized soybean oil (ESO) and poly(lactic acid) (PLLA) and investigated the thermal and mechanical properties and shape memory-recovery behaviors of the resulting polyESO/PLLAs.

EXPERIMENTAL SECTION

Materials. ESO and a thermally latent cationic catalyst (benzylsulfonium hexafluoroantimonate derivative, Sun-Aid SI-150L) were gifts from Adeka Co. (Tokyo, Japan) and Sanshin Chemical Industry Co. (Yamaguchi, Japan), respectively. PLLA (product 4032D) was obtained from Nature Works LLC. (MN, U.S.A.). Other reagents and solvents were commercially available and were used as received.

Synthesis of PolyESO/PLLA. The following procedure was typically used in the synthesis of polyESO/PLLA. A mixture of ESO (0.5 g) and PLLA (0.5 g) was dissolved in 3 mL of chloroform, and a thermally latent catalyst was added to the solution. The obtained solution was coated using an applicator with slit thickness of 400 μm on a glass plate, and then the solvent was allowed to evaporate at room temperature. The residual mixture was kept at 150 $^{\circ}\text{C}$ for 2 h to produce the polyESO/PLLA.

Measurements. The ^1H nuclear magnetic resonance (^1H NMR) spectrum was recorded on a Bruker DPX-400 instrument (Bruker Biospin Co., MA, U.S.A.). Fourier-transform infrared spectroscopy (FT-IR) was measured by a PerkinElmer Spectrum One (PerkinElmer, Inc., MA, U.S.A.). The film properties of the sample were evaluated by using a Fischerscope H100VS microhardness tester (Fisher Instrument Co., Sindelfingen, Germany) with a test force of 40 mN. The thermal properties of the sample were investigated under nitrogen atmosphere by using a DSC6020 differential scanning calorimeter (DSC) (Hitachi High-Tech Science Co., Tokyo, Japan). The sample was melted at 180 $^{\circ}\text{C}$ for 5 min and then cooled to -50 $^{\circ}\text{C}$ at a cooling rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$. The temperature was maintained for a duration of 5 min, and the sample was reached to 200 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$. Dynamic mechanical analysis (DMA) was performed by using an EXSTAR6000 (Hitachi High-Tech Science Co., Tokyo, Japan) with a frequency of 1 Hz at a heating rate of 3 $^{\circ}\text{C}\cdot\text{min}^{-1}$. Tensile properties were measured by a Shimadzu EZ Graph (Shimadzu Co., Kyoto, Japan) with a cross-head speed of 5 $\text{mm}\cdot\text{min}^{-1}$ (strain rate: 50% min^{-1}). The sample was cut into a plate shape of 10 mm \times 5 mm \times 0.2 mm.

Shape memory properties were evaluated by the end-to-end distance of the sample to determine the strain fixity and the shape recovery. The sample was heated at 80 $^{\circ}\text{C}$ and loaded to the predetermined strain (ϵ_m), followed by cooling and unloading at 20 $^{\circ}\text{C}$. Upon unloading, a part of the strain was instantaneously recovered, leaving an unloading strain (ϵ_u). Then, the sample was reheated at 80 $^{\circ}\text{C}$ to recover the strain, leaving a permanent strain (ϵ_p). The strain fixity and shape recovery are defined as follows.

$$\text{Strain fixity (\%)} = \epsilon_u / \epsilon_m \times 100$$

$$\text{Shape recovery (\%)} = (\epsilon_m - \epsilon_p) / \epsilon_m \times 100$$

RESULTS AND DISCUSSION

Synthesis of PolyESO/PLLA. The oxirane group number of ESO used in this study was 3.7 per molecule, as determined by ^1H NMR spectroscopy. The cross-linking of ESO was carried out in the presence of PLLA using a thermally latent acid catalyst as a catalyst to produce the biobased polymeric material (Figure 1). During the cross-linking, the oxirane

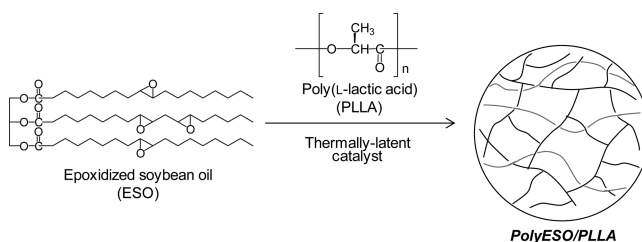


Figure 1. Synthesis of polyESO/PLLA.

groups of ESO were reacted with each other to form the plant oil-based polymer network structure. PLLA was dispersed in the ESO-based polymer network (Figure S1, Supporting Information). In the FT-IR spectrum of the resulting material, a characteristic peak at 824 cm^{-1} , ascribed to the C–C antisymmetric stretch of the oxirane groups of ESO, was not observed, and a broad peak centered at 3400 cm^{-1} arising from the O–H stretch appeared. On the other hand, the peaks derived from PLLA were hardly changed (Figure S2, Supporting Information). The polyESO/PLLA was immersed in chloroform at room temperature for 24 h, and the weight of the residue was close to the ESO content. These results strongly suggest that PLLA is scarcely reacted in the curing of ESO and semi-interpenetrating polymer network is formed.

Thermal and Mechanical Properties of PolyESO/PLLAs. The thermal and mechanical properties of the polyESO/PLLAs were examined. Figure 2 shows the relationships between the feed ratio and film properties of the polyESO/PLLAs determined by indentation hardness test. The Young's modulus of the polyESO/PLLAs increased as a

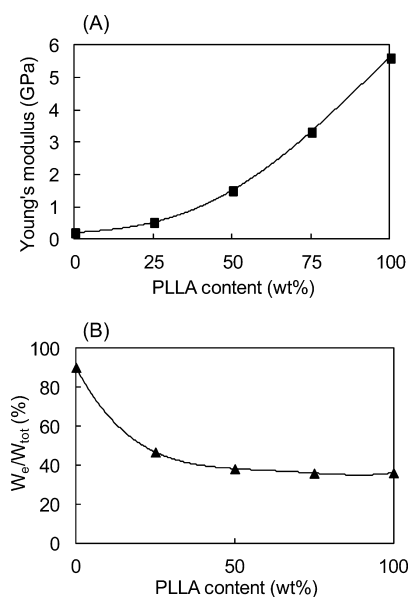


Figure 2. Relationships between feed ratio of PLLA and film properties of polyESO/PLLA: (A) Young's modulus, (B) W_g/W_{tot} .

function of the PLLA content (Figure 2A). In this study, W_e/W_{tot} was evaluated as an indicator as flexibility of the sample (W_e , work volume of elastic deformation; W_{tot} , total work volume). The W_e/W_{tot} values of the polyESO/PLLAs decreased by the incorporation of PLLA, and the values were almost 40% (Figure 2B).

The DSC curves of the ESO homopolymer, neat PLLA, and polyESO/PLLAs with different compositions are shown in Figure 3, and the thermal and mechanical properties are

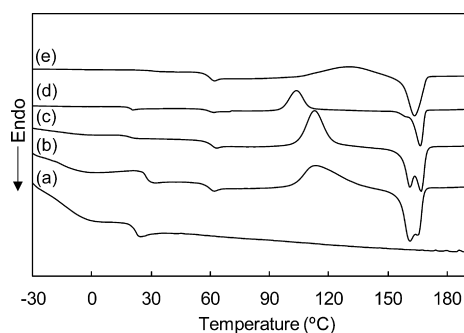


Figure 3. DSC thermograms of (a) ESO homopolymer, (b) polyESO/PLLA (75/25 wt %), (c) polyESO/PLLA (50/50 wt %), (d) polyESO/PLLA (25/75 wt %), and (e) neat PLLA.

summarized in Table 1. In the curves of the ESO homopolymer and neat PLLA, a glass transition was observed at 17 and 57 °C, respectively. On the other hand, two glass transitions attributed to the ESO homopolymer ($T_{g(\text{ESO})}$) and PLLA ($T_{g(\text{PLLA})}$) were observed in polyESO/PLLAs, and $T_{g(\text{PLLA})}$ decreased slightly. These data indicate that the ESO polymer and PLLA are immiscible at the molecular scale. Plant oils and epoxidized plant oils are often used as a plasticizer for common polymers such as poly(vinyl chloride) and polypropylene.^{53,54} It is shown that the cold crystallization temperature (T_{cc}) of the PLLA component decreased by the incorporation of ESO. This may be due to the increase in the segmental mobility of PLLA chains by the plasticization effect of ESO. The polyESO/PLLAs exhibited two melting peaks, demonstrating the melting–recrystallization–melting process, and the intensity of the lower melting peak of the bimodal endotherms increased as the PLLA content decreased.

Figure 4 shows the strain–stress curves of the ESO homopolymer, neat PLLA, and polyESO/PLLAs. The ESO homopolymer and neat PLLA fractured at low strain, whereas the polyESO/PLLAs exhibited ductile behavior. The tensile modulus and maximum stress of the polyESO/PLLAs increased as the PLLA content increased. The strain at break of the polyESO/PLLAs was larger than that of the ESO homopolymer and neat PLLA due to the local plasticization of plant oil. The strain at break depended on the PLLA content, and the

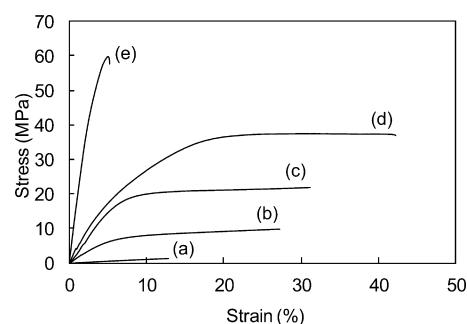


Figure 4. Strain–stress curves of (a) ESO homopolymer, (b) polyESO/PLLA (75/25 wt %), (c) polyESO/PLLA (50/50 wt %), (d) polyESO/PLLA (25/75 wt %), and (e) neat PLLA.

largest strain at break was found in polyESO/PLLA (75/25 wt %).

The temperature-dependent storage modulus and loss factor ($\tan \delta$) of the ESO homopolymer, neat PLLA, and polyESO/PLLA (50/50 wt %) are shown in Figure 5. In general, the

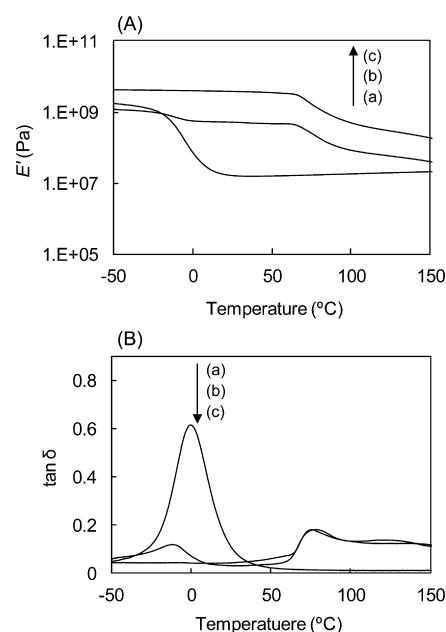


Figure 5. Temperature dependence of (A) storage modulus (E') and (B) loss factor: (a) ESO homopolymer, (b) polyESO/PLLA (50/50 wt %), and (c) neat PLLA.

modulus below the switching temperature governs the strength of the SMPs, whereas the modulus above the switching temperature determines the recovery force. At lower temperature ($T < T_{g(\text{ESO})}$), the polyESO/PLLA (50/50 wt %) was glassy with a storage modulus above 1.0 GPa. The storage

Table 1. Thermal and Mechanical Properties of PolyESO/PLLA

sample code	$T_{g(\text{ESO})}^a$ (°C)	$T_{g(\text{PLLA})}^a$ (°C)	T_{cc}^a (°C)	$E'_{20}{}^{b,c}$ (MPa)	maximum stress ^d (MPa)	strain at break ^d (%)
ESO homopolymer	18	—	—	17	1.2	12.9
polyESO/PLLA (75/25)	24	54	111	320	9.7	27.1
polyESO/PLLA (50/50)	17	56	110	518	21.8	31.1
polyESO/PLLA (25/75)	17	56	102	1348	36.9	42.2
PLLA	—	57	129	3717	59.7	5.0

^aDetermined by DSC. ^bDetermined by DMA. ^cStorage modulus at 20 °C. ^dDetermined by tensile test.

modulus of the polyESO/PLLA (50/50 wt %) slightly dropped at around $T_{g(\text{ESO})}$, giving rise to the first rubbery state. The initial drop of the storage modulus became larger as the PLLA content decreased (Table 1). At about 60 °C, which was attributed to $T_{g(\text{PLLA})}$, the storage modulus dropped again to yield the second rubbery state. Correspondingly, two peaks were found in the loss factor curve. This is in agreement with the DSC results. Upon further heating, the plateau gradually decayed, as is typical for most semicrystalline polymers approaching the melting point. In the secondary rubbery region, the storage modulus of the polyESO/PLLA (50/50 wt %) was about 80 MPa.

Shape Memory-Recovery Behaviors of PolyESO/PLLAs. An investigation of shape memory-recovery behaviors of the polyESO/PLLAs was performed. A thermoresponsive SMP is easily deformed to a temporary shape under external force above the switching temperature. When the deformed shape is cooled below the switching temperature, the temporary shape is fixed without loading, and the deformed shape can be kept well. When the operation temperature rises above the switching temperature again, the SMP returns to the initial shape (permanent shape). In this study, the shape memory-recovery behaviors were activated by changing temperature above and below $T_{g(\text{PLLA})}$ as a switching temperature. The polyESO/PLLA in spiral shape was prepared as a permanent shape, which was obtained by the curing wrapped around a Teflon rod. Figure 6 shows typical shape memory behaviors of

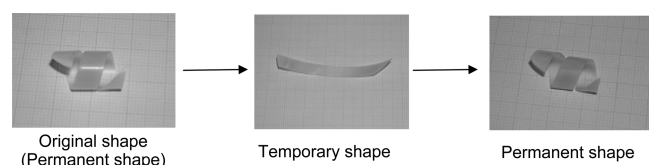


Figure 6. Shape memory-recovery behaviors for polyESO/PLLA (50/50 wt %).

the polyESO/PLLA (50/50 wt %). Above $T_{g(\text{PLLA})}$, the polyESO/PLLA (50/50 wt %) behaved as a soft rubbery material. The sample was deformed to the stretching shape by unwinding and was fixed by the subsequent cooling to 20 °C. Upon reheating at 80 °C, the spiral shape (permanent shape) was quickly and completely recovered. The plausible shape memory-recovery mechanism is as follows. The driving force of shape recovery is the elastic force of the plant oil-based polymer network generated during the deformation. At the higher temperature ($T > T_{g(\text{PLLA})}$), the polyESO/PLLA is easily deformed because both the ESO polymer and PLLA are in a rubbery state (second rubbery state). After the subsequent cooling, PLLA component becomes glassy, and the temporary shape is fixed with the internal stress of the ESO-based polymer network. Upon reheating above the switching temperature, the mobility of PLLA chains becomes larger, and the shape of the sample returns to the original shape by the entropy elasticity of the ESO-based polymer network.

The abilities of shape memory and recovery, evaluated by the end-to-end distance of the samples, are summarized in Table 2. The ESO homopolymer could not be deformed due to the brittleness. Although the deformed shape of neat PLLA was prepared above $T_{g(\text{PLLA})}$, neat PLLA was not returned to the original shape by reheating. The polyESO/PLLAs showed good shape memory-recovery behaviors, and all of the shape recovery was more than 90%. However, the strain fixity decreased as the

Table 2. Shape Memory-Recovery Properties of PolyESO/PLLA

sample code	ESO content (wt %)	PLLA content (wt %)	strain fixity ^a (%)	recovery rate ^a (%)
ESO homopolymer	100	0	–	–
polyESO/PLLA (75/25)	75	25	10	100
polyESO/PLLA (50/50)	50	50	99	100
polyESO/PLLA (25/75)	25	75	99	93
PLLA	0	100	96	4

^aDetermined by the end-to-end distance of sample.

PLLA content decreased. This poor fixing characteristic may be attributed to the increase in inner stress of the ESO-based polymer network. These data strongly indicate that the shape recovery from the deformed shape to the original shape derives from the relaxation of the internal stress of the ESO-based polymer network. Furthermore, the shape memory-recovery processes of the polyESO/PLLAs were recyclable, and similar results on the strain fixity and shape recovery were obtained with even more than five cycles (Figure S3, Supporting Information).

CONCLUSIONS

In this paper, a new class of full biobased shape memory materials was developed from plant oil and PLLA. An acid-catalyzed curing of ESO in the presence of PLLA was performed at 150 °C for 2 h to produce a biobased polymeric material. PLLA components were scarcely reacted in the curing and dispersed in the ESO-based polymer network. The mechanical properties such as tensile modulus and stress were improved by the incorporation of PLLA. The strain at break of the polyESO/PLLAs was larger than that of the ESO homopolymer and neat PLLA due to the plasticization effect of plant oil. Furthermore, the polyESO/PLLAs exhibited excellent shape memory-recovery properties, and the strain fixity depended on the feed ratio of ESO and PLLA.

Because the present biobased polymeric material consists of renewable resources, this will more greatly contribute to the development of sustainable society. We think that the polyESO/PLLA prepared by a relatively simple method is an intelligent polymeric material with potential applications in many fields.

ASSOCIATED CONTENT

Supporting Information

TEM image of polyESO/PLLA (Figure S1). FT-IR spectra of ESO, neat PLLA, and polyESO/PLLA (Figure S2). Recyclability of shape memory-recovery behaviors of polyESO/PLLA (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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