



Tuneable Shape-Memory Property of Composite based on Nanoparticulated Plant Biomass, Lignin, and Poly(ethylene carbonate)

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In this article, we propose a thermally responsive shape-memory polymer (SMP) consisting of poly(ethylene carbonate) and non-deteriorated lignin nanoparticles. This SMP was obtained readily by thermal kneading and melt molding without requiring any chemical reaction. The shape-recovering properties of the SMP can be tuned by changing the feed ratio of the components. The estimation of viscoelasticity, thermal and mechanical properties of the SMP reveals that the stepwise structural transitions in the SMP rendered the dynamic shape-recovering behavior.

Introduction

Shape-memory polymers (SMPs) are an important class of smart polymers able to revert to their original shape upon external stimulation despite being deformed mechanically and fixed to a temporary shape.¹⁻⁶ Some common stimuli are heat, light, and electric/magnetic field. Thermoresponsive SMPs have been actively studied, and will be presented in this paper. Over the last decades, there have been several advances in SMPs for use in various applications such as medicine⁷ and aerospace.⁸

Here, lignin, a polyphenol in plants, was used as a component of the SMP. Because lignin is one of non-edible plant biomasses, its use is essential in contributing to sustainable social development, i.e., moving away from petroleum-based resources to renewable biomass resources.^{9,10} Lignin has been mainly used as a supplemental additive for the modification of petroleum materials such as a reinforced filler^{11,12} and the hard segment of SMPs.¹³ However, heterogeneous chemical reactions involving toxic reagents are needed for the design of lignin-based useful materials. Furthermore, lignin is commonly extracted from plants using a treatment with strong chemicals at a high temperature.¹⁴ This process prevents the use of lignin in an industrial or commercial scale due to the environmental load and the nature of lignin, which deteriorates during the extraction process.

To date, a number of physicochemical techniques have been reported for the isolation of polysaccharides and lignin from

plants, such as kraft¹⁵ and organosolv¹⁶ pulping methods, γ -valerolactone-based process,¹⁷ alkaline cooking¹⁸ and glycerol thermal processing.¹⁹ Recently, we proposed a physicochemical process that employed simultaneous enzymatic saccharification and comminution (SESC) of plant materials to isolate non-deteriorated plant biomass as a sugar solution and a colloidal lignin dispersion.²⁰ In principle, the SESC allowed the extraction of lignin under extremely mild conditions (i.e., 50 °C, pH 5.0 and 1 psi) without the requirement for strong and toxic chemicals. In this case, the lignin was obtained as a colloidal dispersion in water containing particles with diameters of several tens of nanometers. The obtained lignin (later denoted as SESC lignin) exhibited high purity, and the extraction ratio of its aromatic components by nitrobenzene oxidation indicated that it did not deteriorate during the extraction process. The SESC lignin could then be mixed with ordinary synthetic polymers by merely kneading without further chemical processing. We also reported an excellent heat tolerance property of small amount of SESC lignin in poly(ethylene carbonate) (PEC); by the addition of only 5 wt% of SEC lignin, the decomposition temperature of PEC increased from 198 °C to 265 °C.²¹

In this paper, we propose a novel lignin-based SMP consisting of SESC lignin and PEC. The conventional lignin-based SMPs were precisely synthesized using hyperbranched smart elastomeric copolymers utilizing lignin as the hard segment.¹³ In contrast, the lignin-based SMPs presented here were obtained only by thermal kneading and melt molding of the mixture of SESC lignin and PEC. Therefore, it seems that the function of SMPs, e.g., shape-recovering ratio/speed, could be easily controlled by changing the feed ratio of the components. Furthermore, the detailed molecular mechanism in the shape memory/recovery of lignin-based SMPs became apparent from the estimation of their viscoelastic, thermal, and mechanical properties because of their simple composition.

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Experimental

Materials. Ultrapure water was used throughout the study and obtained using a Milli-Q® Advantage A10® system (Millipore™, Eschborn, Germany). Poly(ethylene carbonate) (PEC; $M_n = 39,000$) was purchased from Empower Materials, Inc. (New Castle, USA). Other reagent-grade chemicals were purchased from Tokyo Kasei Chemicals, Wako Pure Chemical Industries, and DuPont™ Genencor® Science and used as received. Cedar wood was powdered (10 $\mu\text{m}\phi$) by dry grinding and jet milling for several seconds.

Simultaneous enzymatic saccharification and comminution (SESC) of plant materials. The SESC treatment followed the procedure described previously.^{20,21} Briefly, a mixture of degreased plant powder (50 g), OPTIMASH XL (containing cellulase and xylanase) and OPTIMASH BG (containing xylanase and β -glucosidase) (1:1 ratio, 10 g) and 100 mM phosphate buffer (pH 5.0, 440 g) was ground by bead milling (Labstar® LMZ015; Ashizawa Finetech Ltd., Japan) at a peripheral velocity of 14.0 m s^{-1} at 50 °C. To prevent damage to the enzyme, the inner wall of the LMZ015 vessel was covered with a ceramic lining because stainless steel inactivates the enzyme. Following bead milling for 2 h using 0.5 $\text{mm}\phi$ zirconia beads, the obtained mixture was centrifuged at 10,000 $\times g$ for 30 min. The saccharide-containing supernatant was then collected, and the precipitate was milled once more under the same conditions and buffer strength, but using 5 g of the enzyme mixture and smaller zirconia beads (0.1 $\text{mm}\phi$). Following this second milling process, further saccharification of the generated slurry was performed at 50 °C for 48 h. The final slurry was centrifuged at 10,000 $\times g$ for 30 min, after which the supernatant was recovered, and the lignin-rich precipitate was washed twice by mixing it with an equal amount of ultrapure water before another centrifugation under the same conditions described above.

Preparation of non-deteriorated lignin and PEC composites.

Defined amounts of powdered SESC lignin and melted PEC pellets were mixed and kneaded at 120 °C by an injection molding machine (IMC-A300, Imoto Machinery Co., Ltd. Japan). The obtained composites were hot-pressed at 3–5 MPa for 10 min at 120 °C to mold into films.

Dynamic viscoelasticity measurements. The dynamic viscoelasticity measurements of the cast films were performed using a dynamic viscoelastometer (DMS210, SII NanoTechnology Inc., Japan) under the following test conditions: applied distortion = 0.05%, driving frequency = 0.1 Hz, temperature range = 0–85 °C (for the composite film) or 0–60 °C (for the neat PEC film) at 2 °C min^{-1} . The test strip dimension was 2 mm wide, 20 mm long, and typically 0.1 mm thick.

Thermomechanical analysis (TMA) for quantitative estimation of shape-recovering behavior. TMA measurements were performed using Thermo plus EVO2 TMA (Rigaku, Japan). A striped sample (10 mm wide, 5 mm long, and typically 0.1 mm thick) was used for measurements. The method for quantitative estimation of the shape-recovering behavior is

described as follows: First, the sample was elongated to add 40% strain at 25 °C. After cooling at 1.7 °C min^{-1} to 0 °C to fix the shape, the sample was heated at 1.7 °C min^{-1} to 25 °C to recover the shape. Then, the sample was left to stand for 15 min to recover its shape. The shape-recovering temperature (T_r) was defined as the temperature at which the decreasing ratio of strain was maximum until heating. From the residual strain after standing, the shape-recovering ratio (R_r) was determined according to the following equation:

$$R_r = (1 - (\text{residual strain}/\text{initial strain})) \times 100.$$

The shape-recovering speed (S_r) was determined as follows:

$$S_r = (\text{initial strain} - \text{residual strain}) / (\text{time deformation stopped} - \text{time deformation started})$$

Differential scanning calorimetry (DSC) measurements. DSC measurements were performed using Rigaku Thermo Plus DSC 8230 under nitrogen flow at 10 °C min^{-1} .

Tensile stress-strain measurements. Tensile stress-strain measurements of the composite films were performed using an OZ502 system (Sentec Co., Japan) at 25 °C. Dumbbell-shaped samples (2 mm inner wide, 14.5 mm gage long and typically 0.1 mm thick) were prepared using a cutting machine (Dumb Bell Co., Ltd, Japan). The tensile stress-strain responses were then measured using a load cell at 7 mm min^{-1} head speed. The measurable maximum strain of our experimental system is 600%.

Results and discussion

Thermoresponsive shape-memory behavior of PEC-SESC lignin composite film. PEC is soft elastomer that is synthesized from epoxides and carbon dioxide.²² Recently, due to the novel ionic conductive property of the PEC-Li mixture, it has been an attractive candidate for polymer Li salt electrolytes.²³ In the previous study, we prepared a composite consisting of PEC and SESC lignin by thermal kneading in which the SESC lignin was finely dispersed in the PEC matrix in nanometer order.²¹ By introducing a small amount (several wt%) of SESC lignin into PEC, Young's modulus and the thermal decomposition temperature increased, i.e., the PEC-SESC lignin composite film was stiffer than the neat PEC film. Since an analogous polymer

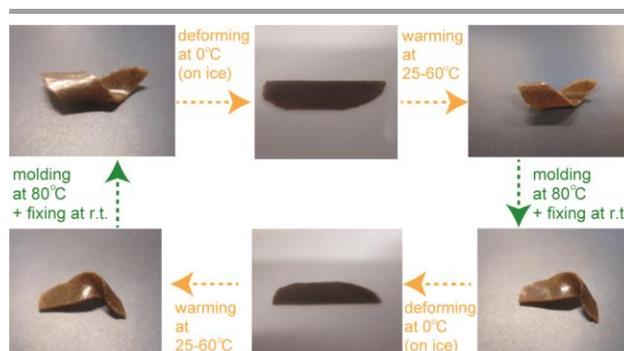


Fig. 1 Noticeable thermoresponsive shape memory behavior of the PEC-SESC lignin composite film. PEC : SESC lignin = 8 : 2 (wt/wt).

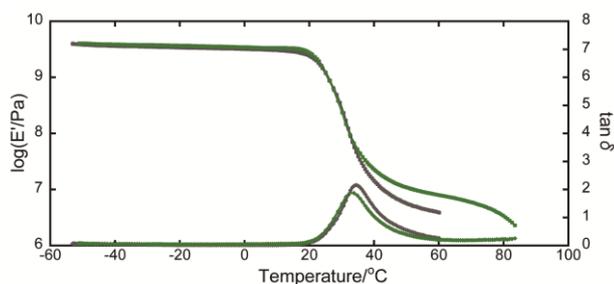


Fig. 2 Dynamic viscoelasticity measurements of the PEC-SESC lignin composite film (green curves, PEC : SESC lignin = 8 : 2) and the neat PEC film (black curves).

of PEC, such as poly(trimethylene carbonate), exhibited shape-memory behavior via its copolymerization with the hard segment,²⁴ it seems that the PEC-SESC composite also exhibited similar shape-memory behavior whereby PEC and lignin acted as the soft and hard segments, respectively.

In this article, we report noticeable thermoresponsive shape-memory behavior of the PEC-SESC lignin composite films, as shown in Fig. 1. The composite film acquired its shape (hereinafter referred to as the original shape) by molding the film at a high temperature (i.e., 80 °C) and cooling afterwards. Thereafter, following deformation and shape fixing at a low temperature (i.e., 0–10 °C), the shape of the composite film still reverted to its original shape at a medium temperature (i.e., 25–60 °C). Molding of different original shapes of the composite film at high temperature could be repeated at least several tens of times. The shape recovery of the composite film was noticeable, and the cycle finished within 1 min (Movie S1). As a comparison, the neat PEC film also exhibited similar thermoresponsive shape-memory behavior; however, the deformation rate was slower, and the composite did not fully revert to its original shape.

The nature of thermoresponsive shape memory of PEC-SESC lignin composite film. To reveal the structural origin of the shape-memory nature of PEC-SESC lignin composite film, we estimated the dynamic viscoelasticity of the film. On elasticity-temperature curves of the dynamic viscoelasticity of the PEC-SESC lignin composite film (Fig. 2), two shoulders were observed around 20 °C and 80 °C, i.e., there are two different structural

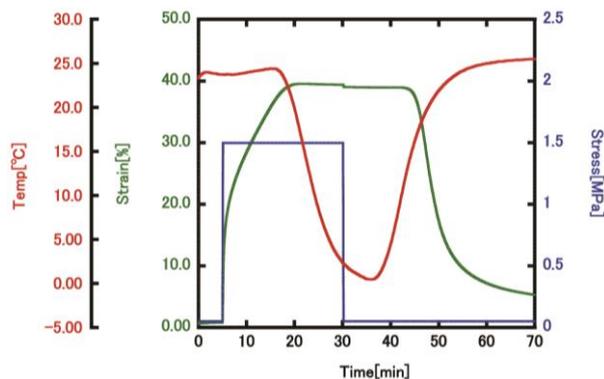


Fig. 3 Strain change of the PEC-SESC lignin composite film (PEC : SESC lignin = 8 : 2) as a function of temperature under elongation.

Table 1 Parameters in thermomechanical analysis (TMA) of the shape recovering behaviour of the composite films.

PEC : lignin	R_f (%)	T_r (°C)	R_r (%)	S_r (%strain min ⁻¹)
100 : 0	98.6	13.8	79.2	2.8
95 : 5	99.0	19.5	83.3	29
90 : 10	99.0	20.1	85.9	7.8
80 : 20	98.5	19.7	86.6	5.4
70 : 30	98.9	21.5	81.4	3.5

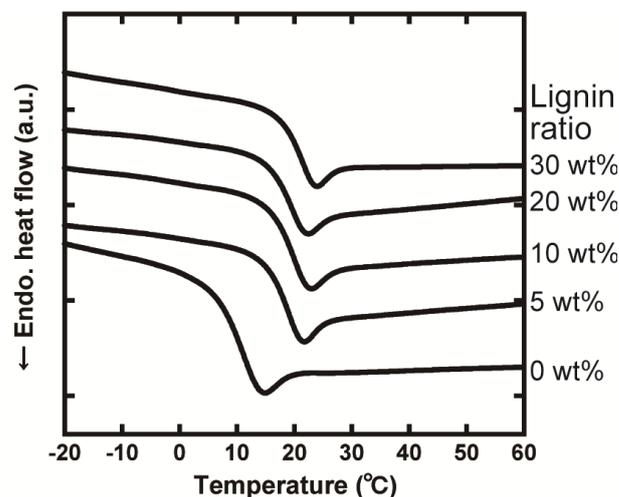


Fig. 4 DSC curves of the PEC-SESC lignin composite film with various lignin ratios. The T_g values (estimated from the inflection point of the curves) of the composite film at 30 wt% and 0 wt% of lignin are 18 °C and 6 °C, respectively.

transitions of the composite following temperature changes. Meanwhile, the neat PEC film exhibited only one shoulder at about 20 °C. The neat PEC film was too soft to withstand the heat and subsequently failed to retain its shape above 60 °C; hence, its elasticity could not be measured. Due to the viscoelastic nature of the films, it seems that the stepwise structural transitions in the composite film as the temperature changes cause the fast shape-memory behavior, i.e., the original shape was easily molded at high temperature due to the rubbery state of PEC and lignin; then the temporary shape fixing by a subsequent cooling process was due to the glass transition of PEC and lignin, and finally, the shape recovery at medium temperature was due to the rubber transition of PEC only. Here, the lignin acted as a framework for speedy and full shape recovery when the composite film was molded at the rubbery state of lignin.

Different thermoresponsive shape-recovering behavior of PEC-SESC lignin composite film depending on feed ratio of lignin. Hereinafter, the shape-recovering behavior was estimated quantitatively using TMA. According to the previous reference,²⁵ the strain values of films under elongation at different temperatures were plotted (Fig. 3). The TMA results indicate that the PEC-lignin composite film is dual-SMP. The shape-fixing ratio (R_f) of the initial temperature change (at minute 20 – red line) to the start of shape recovery (at minute 45 – red line) was 99% as shown in Table 1, regardless of the feed ratio of lignin in the range of 0–30 wt%, which was higher

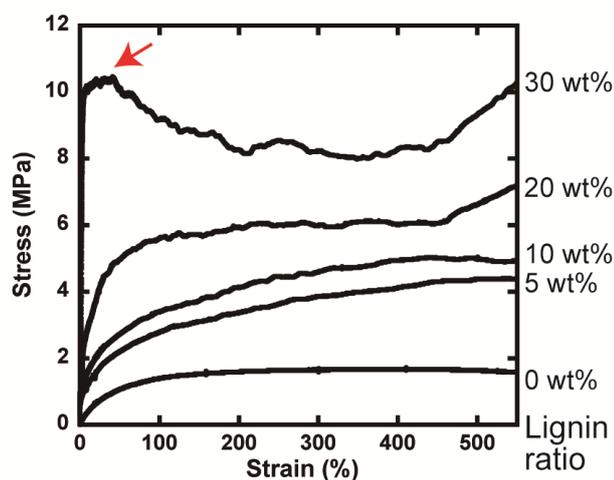


Fig. 5 Typical tensile stress-strain curves of the PEC-SESC lignin composite film with various lignin ratios. At 30 wt% lignin ratio, a definite yielding point (indicated by red arrow) was observed.

than previous lignin-based SMPs.²⁶ As shown in the Experimental part, the shape-recovering behavior was also analyzed in terms of shape-recovering temperature (T_r), shape-recovering ratio (R_r) and shape-recovering speed (S_r).

The shape-recovering behavior of the lignin-PEC composite film changed according to the feed ratios of SESC lignin, as shown in Table 1. The T_r value increased with the lignin ratios because T_r was only tuneable by changing the feed ratios of lignin, as previously reported.²⁶ The nature of lignin as the hard segment in the composite caused this phenomenon, supported by increasing glass transition temperature (T_g) as the lignin ratios increased (Fig. 4).

At 20 wt% lignin ratio, the R_r of the composite film was maximum. However, as shown in Fig. 5, the composite film with 30 wt% lignin ratio exhibited a clearer yielding point (red arrow) at lower tensile strain because the plastic deformation of the composite only occurred up to the TMA measurement (20 wt%) at high lignin ratios. This brittle nature of the composite film with high lignin ratio resulted in the low shape-recovering behavior.

Meanwhile, the maximum S_r value was achieved with 5 wt% lignin ratio, indicating an optimum lignin content rendering the stiffness and elasticity for excellent shape-recovering behavior of the film. From this result, it is speculated that the SESC lignin in the composite acted as a nucleating agent for PEC. This nucleating effect, i.e., as aggregating force for dispersing SESC lignin in PEC in a nanometre order,²¹ led to the increase in T_g , high lignin ratio, and fast shape recovery of the film. In contrast, excess lignin nanoparticles (above 5 wt%) in the composite could decrease the S_r of the composite film.

As shown in Table 1, the neat PEC (PEC : lignin = 100 : 0) also showed some extent of shape recovery under a temperature stimulus. However, its R_r and S_r values were smaller than those of any PEC-SESC lignin composite films. Especially, the shape recovery rate of the neat PEC was much slower than that of the composites, causing slow, partial, and subtle shape-recovering behavior.

According to the above experimental results and previous studies,^{3,27} the PEC itself behaved like thermosetting polymers.³

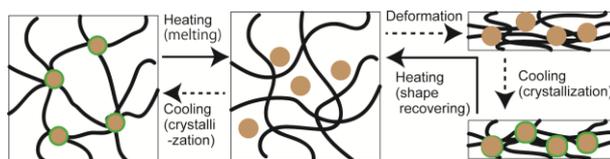


Fig. 6 Schematic depiction of the molecular transformation during a shape-memory/recovery cycle of the PEC-SESC lignin composite film. In illustration, black lines, brown circles and green circles are PEC chains, SESC lignin nanoparticles and aggregation points of PEC chains, respectively.

We assumed that the neat PEC chains formed non-covalent bonding (e.g., hydrogen bonding via carbonate groups) by cooling that induced the shape memory/recovery. The SESC lignin in the composite film forms assemblies with several hundred nanometer size.²¹ These assemblies consisting of SESC lignin should work as tacks and/or nuclei for aggregating PEC chains as illustrated in Fig. 6 that causes dynamic recovering of overall shape of the composite film. The cooperative aggregation and melting of the PEC chains by SESC lignin assemblies resulted in the dynamic shape-recovering behavior of the composite films relative to neat PEC films.

Conclusions

In this study, we prepared the SMPs consisting of SESC lignin and PEC only by kneading without any toxic reagents and chemical modification. The dynamic viscoelastic measurement of the SMPs indicates that the stepwise structural transition according to temperature changes in the SMPs led to the dynamic shape-memory behavior of the composites. The shape-recovering properties depend on the feed ratio of the components, namely lignin and PEC. The estimation of the thermal and mechanical properties of the film suggests that the nucleating effect of lignin on PEC increased the shape-recovering temperature, the shape-recovering ratio, and the shape-recovering speed.

The lignin presented here was prepared using an environmentally friendly process via SECS of the plant materials. Therefore, the use of lignin in SMPs could have a positive impact because it not only uses plant biomass as a high-value industrial material, but also reduces the environmental load by avoiding toxic petroleum-based resources (e.g., fluorocarbons) in the preparation of SMPs.²⁵ Furthermore, PEC is also an environmentally friendly polymer because it originates from carbon dioxide.²² From this point, we believe that the utilization of PEC and lignin as SMPs would contribute to the realization of a low-carbon society.

Conflicts of interest

There are no conflicts to declare.

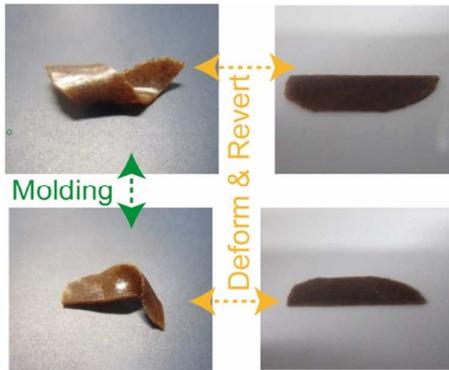
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A shape-memory polymer consisting of lignin and poly(ethylene carbonate) only by kneading was obtained without any toxic reagents.