

A Slow Shape-Recovery Polymer Based on Polylactic Acid

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ABSTRACT: Shape-recovery materials are expected to have numerous applications as ductile structural compounds which can recover their shape after significant deformations. We report a new type of shape-recovery polymer consisting of polylactic acid (PLA) derived from glucose compounded with a cinnamic acid ester derived from lignin. Unlike existing shape-memory polymers, this shape-recovery polymer exhibits a spontaneous but gradual recovery of its original dimensions, following elongation and release of stress, over a period ranging from several hours to days, without the requirement for external stimulus. In the case of a typical rubber or elastomer, shape-recovery takes place almost instantaneously after deformation due to the energy stored by the material. Although the slow shape-recovery polymer reported herein appears to exhibit plastic deformation as if the energy of elongation is lost, it eventually recovers from the deformation in the same manner as an elastic material. This material may have applicability to the energy-absorbing and shape restoration automotive parts. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41004.

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INTRODUCTION

Polylactic acid (PLA) is a hard, brittle bio-based polymer derived from glucose. There have been numerous reports concerning the addition of plasticizers to PLA in order to improve its ductile properties.^{1–3} Our research group has focused its attention on new plasticizers based on lignin derivatives, such as esters of cinnamic acid, and has evaluated injection molded samples of PLA melt-compounded with benzyl cinnamate (BC). While measuring the mechanical properties of such specimens, we observed a new phenomenon in which samples which had been elongated under external stress at room temperature very slowly returned to their original dimensions in a spontaneous manner, thus releasing the applied stress. We termed this material a “slow shape-recovery polymer.”

Shape-memory polymers are materials which, once deformed, rapidly return to their original dimensions in response to stimuli such as heat, electricity, or magnetism. Many thermal stimuli-responsive shape-memory polymers, such as polyurethane,^{4–6} polynorbornene,⁷ and poly(styrene-*block*-butadiene)⁸ have already been used for practical applications. There has also been a report of a biodegradable poly(caprolactone)-based shape-memory polymer which has potential applications in biomedical devices.⁹ Stimuli-responsive shape-memory polymers which respond to non-thermal stimuli, such as electro-active, magnetic-active, and photoactive materials have also been described,¹⁰ as have self-healing polymers using microencapsula-

tion technology.¹¹ In such systems, chemical reactions between a thermoset polymer and a hardening catalyst are typically applied.

To the best of our knowledge, however, there has never been a report of materials which, once significantly deformed, will spontaneously return to their perfect original dimensions. Plasticized poly(vinyl chloride) is known to have the similar shape recovery phenomenon for some time.¹² However this phenomenon does not completely recover to original form. Our serendipitous discovery of a slow shape-recovery polymer in which recovery takes place over several hours or days thus represents a novel type of polymer.

EXPERIMENTAL

Materials

The PLA resin used in the experimental work was LACEA H-400, produced by Nature Works and sold by Mitsui Chemicals. Its melt flow rate and melting point were 2.7 g/10 min and 166°C, respectively. BC plasticizer was purchased from the Tokyo Kasei Co.

Compounding of PLA and BC

The melt compounding of PLA and BC was carried out using a twin screw extruder (TEX30 α 45.5BW, Japan Steel Works, Ltd.). The screw rotation speed was set at 250 rpm and PLA pellets were added at a feed rate of 20 kg/h. The cylinder preset temperature was 180°C and the actual compounding temperature

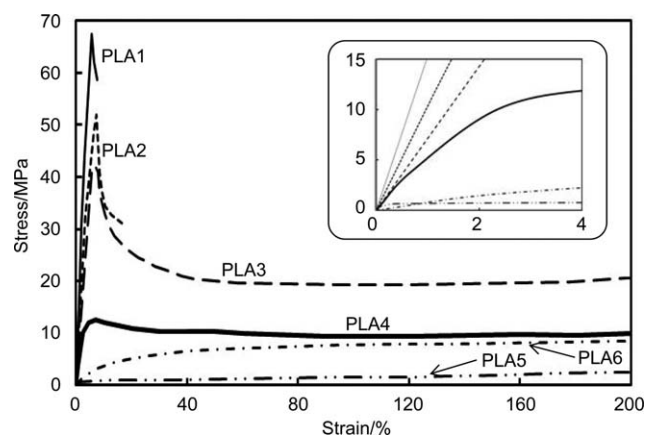


Figure 1. Stress–strain curves for test samples. PLA1 through 6 contain 0, 10, 15, 16.7, 20, and 30% BC by weight. Strain was calculated based on the distance between two marks at an initial distance of 50 mm from one another. The inset shows an enlarged display of the early stages of the curves.

was in the range of 185–200°C. The BC plasticizer was added to the PLA in the central portion of the extruder, which contained molten PLA resin, and sufficient quantities of BC were added to generate samples with 10, 15, 16.7, 20, or 30% BC by weight. The resulting PLA/BC mixtures were extruded and pelletized.

For comparison purposes, similar samples using poly(ethylene terephthalate) (PET, processed at 260°C), polycarbonate (PC, 260°C), poly(methyl methacrylate) (PMMA, 200°C), and polystyrene (PS, 180°C) with BC were made and the same experiments were conducted. PET resin used in the experimental work was DIAPET MA-521H produced by Mitsubishi Rayon Co., PC used was Iupilon ML-300 produced by Mitsubishi Engineering-Plastics Co., PMMA used was PARAPET G1000 produced by Kuraray, and PS used was HF-77 produced by PS Japan Co.

Injection Molding of Test Pieces

The samples generated by compounding and extrusion were vacuum dried at 50°C for 12 h to remove any residual moisture and then introduced into an injection molding machine (PS40E2ASE, Nissei Plastic Industrial Co., Ltd.) which produced dumbbell-shaped tensile test specimens. The cylinder temperature of the molding machine was 180°C, the mold temperature was 35°C, the injection time was 18 s, and the cooling time was 40 s. PLA is an inherently crystalline polymer but almost completely amorphous specimens were obtained using these conditions.

Tensile Testing and Characterization

In accordance with JIS K7113, the tensile testing of the dumbbell-shaped specimens was performed using an Instron universal tester (model 5566). The initial distance between the chucks of the test device and the distance between the gauge lines drawn on the specimens were 115 mm and 50 mm, respectively. The chuck movement speed was 5 mm/min. Five replicate tests were performed for each sample type and their average was calculated.

In the event that a sample could be elongated up to 100 mm without fracture, the specimen was immediately removed from

the chuck after the end of the test and placed on a horizontal surface to observe its contraction behavior. The overall lengths of such specimens and the lengths between gauge lines were measured and photographs of the specimen were taken with a digital camera at appropriate intervals. Such trials were performed twice for each sample. Room temperature during testing was 23°C and ambient humidity was 50% RH.

For the purpose of determining the glass transition temperature of samples, all samples were measured temperature dependence of dynamic viscoelasticity at a frequency 10 Hz by using Dynamic Viscoelastic Analyzer DVA-220 (ITK, Ltd).

RESULTS AND DISCUSSION

In this study, samples of PLA compounded with BC were produced by means of a twin-screw extruder, with BC proportions of 10, 15, 16.7, 20, or 30% by weight. Remarkable improvements in ductility were not obtained until at least 10% BC had been added, and this effect became pronounced at levels of 15% or higher. Stress–strain plots and a plot of the tensile moduli of each sample as a function of BC content are presented in Figures 1 and 2, respectively. The sample code, the properties, and glass transition temperature are summarized in Table I. In Figure 1, PLA1 refers to a sample which does not contain BC, while PLA2, 3, 4, 5, and 6 include 10, 15, 16.7, 20, and 30% by weight BC, respectively. Mechanical properties testing demonstrated that the PLA1 specimen could be elongated by only approximately 4 mm before rupturing, whereas the PLA3, 4, 5, and 6 specimens underwent plastic deformation of up to 100 mm without fracturing. Interestingly, this remarkable improvement in ductility was not observed when BC was added to other common polymers, such as PET, PC, PMMA, and PS.

The recovery behaviors of the PLA3, 4, 5, and 6 specimens were observed following 100 mm elongation. Recovery measurements were performed in duplicate for each level of BC and almost the same results were obtained each time. The recovery process is illustrated in Figure 3, which shows the PLA5 specimen is detached from the tensile test equipment immediately after elongation to 100 mm. It is noteworthy that the PLA5 specimen was approximately 100 mm longer than its original dimension immediately following detachment, demonstrating that the elongational strain imparted to the specimen is not rapidly

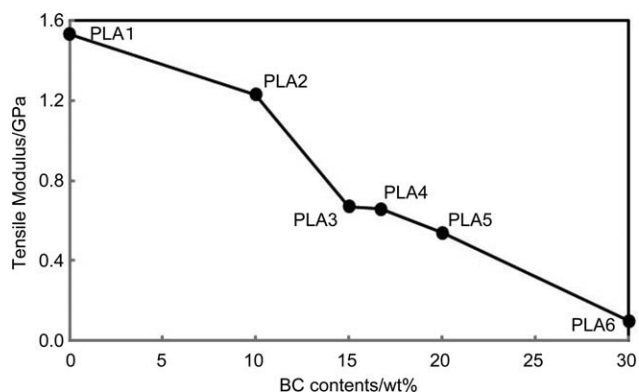


Figure 2. Variations in tensile modulus with the BC content of PLA/BC compounded samples.

Table I. Sample Code and Their Properties

Sample code	PLA/BC content (wt %)	Tensile modulus (GPa)	Tensile strength (MPa)	Glass transition temperature (T_g , °C) ^a
PLA1	100/0	1.53	67.5	68.1
PLA2	90/10	1.23	51.9	56.6
PLA3	85/15	0.67	42.2	48.2
PLA4	83.3/16.7	0.66	12.5	44.2
PLA5	80/20	0.54	2.5	39.0
PLA6	70/30	0.1	8.4	20.8

^a T_g were measured the maximum peak of $\tan \delta(E''/E')$ as a ratio of the loss modulus (E'') to the storage modulus (E') in the dynamic viscoelasticity.

recovered even when the stress is removed. Rather, the deformation of the specimen is gradually reduced and it returns to its original length over 4–8 h. Both the tensile testing and recovery of specimens took place at room temperature and no external stimulus was applied, thus this represents true slow shape-recovery behavior. Figure 4 plots the variations in specimen lengths as a function of time following elongation.

In contrast to the samples above, necking was observed to occur during elongation of the PLA3 specimens and the recovery rate of the elongated PLA3 sample was very slow, such that full recovery to the original length was not achieved even after ten days. Only about one-third of the strain was recovered.

The deformation of the PLA-4 specimen was also gradually reduced over a period of approximately 10 days. The elongated specimen length decreased to around 60 mm after this time span, equivalent to a decrease of the original strain of approximately 60%. This behavior is somewhat similar to that reported for stress-recovery polymeric composites consisting of 1–5 vol % carbon nanotubes in polyurethane. These thermoplastic elastomers have been found to store stress and subsequently show recovery up to 50% more of their original dimensions as compared to the unmodified polymer.¹³

In the case of PLA6, the initial slope of the stress–strain curve is low, meaning that the tensile modulus was small, although the stress value increases above that of the PLA5 specimen at elongations over approximately 10 mm. Because the PLA6 specimen was partially crystallized while awaiting testing, its amorphous regions were in a rubbery state due to its reduced glass transition temperature and so it exhibited rubber-like flexibility in the initial deformation stage. At greater deformations, however, the influence of crystalline regions predominates such that the stress values are higher than that for the PLA5 sample. Despite gradual shape recovery over ten days, the PLA6 specimen did not fully return to its original length. This sample did not undergo full shape recovery because, like an unvulcanized rubber, it underwent both elastic and plastic deformation during the extension process. Extension of the crystallized regions of this material is thought to contribute to its plastic deformation and subsequent incomplete shape recovery.

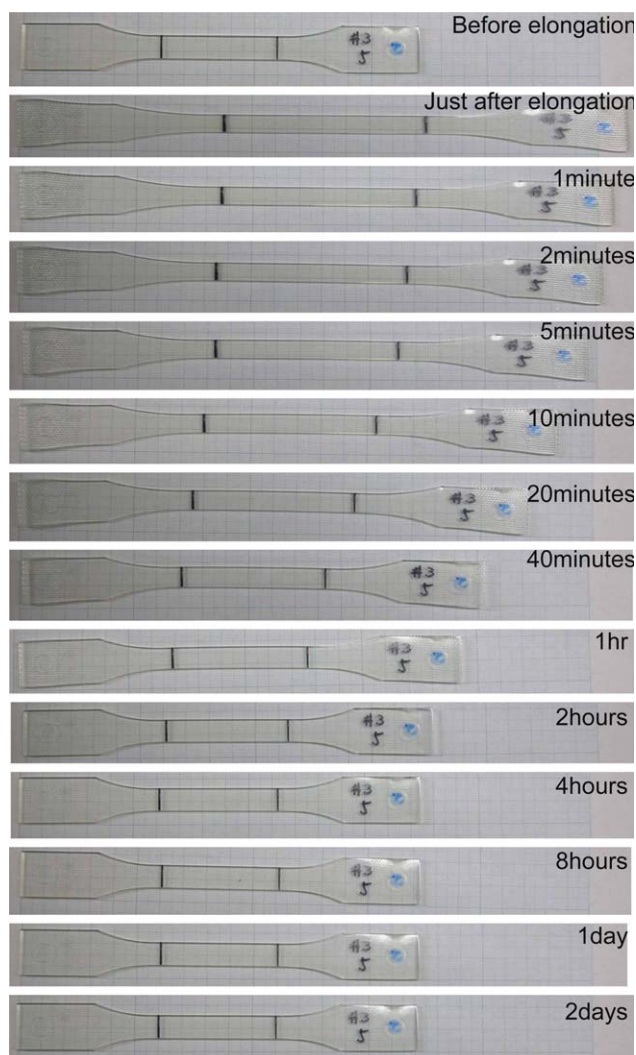


Figure 3. Photographic images of a PLA5 sample over time subsequent to elongation. The sample was elongated to 100 mm and then detached from the tensile test fixture and immediately examined. Environmental factors such as temperature and humidity were constant over the time span recorded. The original dimensions are recovered in 4–8 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Had these samples exhibited the same rubbery elasticity typical of a rubber or an elastomer, stretched samples would have rapidly contracted to their original lengths immediately after being removed from the tensile test equipment. However, this phenomenon was not observed in the experimental trials. Conversely, if these samples had undergone plastic deformation in the manner of typical plastics, significant strain would have remained in the samples following extension and the dimensions of elongated specimens would not have been reduced by 60% or more.

These materials therefore behave as if they undergo plastic deformation in the time period immediately after extension, but actually exhibit elastic recovery over longer time spans. This phenomenon is known as retarded elastic recovery or creep recovery, and is often seen with molten polymers and polymer solutions. However, PLA3, 4, and 5 all show high elastic modulus values above 500 MPa, confirming that they are solid polymers which are harder

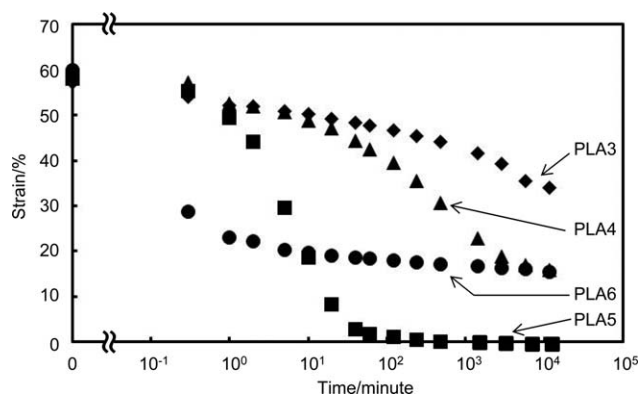


Figure 4. Temporal changes in the strain values of specimens after stress release. The strain, ε , is calculated as $\varepsilon = (L_x - L_i)/L_i \times 100$, in which L_i is the original length of a test specimen prior to elongation (about 172 mm) and L_x is the length of a test specimen at a given time after release of the stress.

than typical rubbers, even though they also exhibit both plastic deformation and retarded elastic recovery. In addition, even when they are deformed so greatly that the stress no longer increases linearly with the strain, they continue to show 60% or more recovery. To the best of our knowledge, there have been no reports of solid polymeric materials which show such remarkable retarded elastic recovery after large deformations. Based on these results, PLA including 20% BC is the first reported material to exhibit perfect shape-recovery following significant extensional deformation. In addition, PLA/BC compounds which include more or less than 20% by weight of BC show imperfect shape-recovery action.

Although the mechanism of the shape-recovery phenomenon have yet to be revealed, it is presumed that the elongation and recovery of PLA polymer chain are controlled by the increment viscous damping of BC in a balanced manner. It is assumed that PLA and BC molecules are good compatible blend because the solubility parameters of PLA and BC are very similar to each other.¹⁴ This compatibility are thought to be an important contributor to the phenomenon.

The solid polymer materials described in this study show retarded elastic recovery and are thought to have a variety of practical applications. As an example, automobile bumpers are subjected to external impact forces and are thus deformed, so the ability to gradually recover from such deformation could be used to recover the original appearance of the bumper. It is true that rubbery polymers also show shape-recovery behavior, but in such cases the energy of deformation is stored and recovery takes place instantaneously when the external force is removed. Returning to the example of a bumper, rubber elasticity may be desirable in terms of shape-recovery, but may also produce an undesirable rebound effect. In the case of slow shape-recovery materials, a deformation can be eliminated over time as the energy of deformation is dissipated. A slow shape-recovery action also differs from the typical shape-memory behaviors. Shape-memory materials return to their original form after the application of an external stimulus such as heat or light while, during slow shape-

recovery, deformation is recovered spontaneously without the use of an external stimulus. If structural components are made from materials which exhibit retarded elastic recovery, they may readily recover their appearance subsequent to a collision without the requirement for any additional treatment.

CONCLUSIONS

We created a new slow shape-recovery polymer melt-compounded PLA and BC. This serendipitous polymer composite material is epoch-making material. This material recovers to the original form slowly without an apparent stimulus at room temperature after release from the stress caused large deformation. If this material is used for the automotive parts, the crash energy is absorbed, protects a living body, and recovers to the original form autonomously. It seems that a principle completely differs from the shape memory materials which have already been reported.

The solubility parameter (δ) of BC was calculated using the following equation from above-mentioned literature, $\delta = (\Sigma E_{\text{cohi}}/\Sigma V_{\text{mi}})^{1/2}$. E_{cohi} is the cohesive energy for the i functional group on the molecules; V_{mi} is its molar volume. ΣE_{cohi} of BC is 95,396 (J/mol, Phenyl; 31,924 \times 2, $-\text{CH}=\text{}$; 4310 \times 2, $-\text{COO}-$; 17,991, $-\text{CH}_2-$; 4937) and ΣV_{mi} of BC is 203.9 (cm^3/mol , Phenyl; 71.4 \times 2, $-\text{CH}=\text{}$; 13.5 \times 2, $-\text{COO}-$; 18.0, $-\text{CH}_2-$; 16.1). δ of BC is calculated with 21.6 (J/cm^3)^{0.5}. The solubility parameter of PLA is 20.2 (J/cm^3)^{0.5} listed in above-mentioned literature.

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