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Surprising shape-memory effect of polylactide resulted from toughening by polyamide elastomer

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ABSTRACT

Melt blending of polylactide (PLA) and biodegradable polyamide elastomer (PAE) has been performed in an effort to toughen the PLA. DMA tests showed good compatibility between PAE and PLA blends, and the PAE were dispersed in PLA matrix uniformly shown in SEM photos. Mechanical properties of blends with different PAE concentrations were observed. With the PAE contents increasing, the elongation at break of blends increased and the brittle break became ductile break. When the PAE content is 10%, the tensile strength of blend is similar to neat PLA, and the elongation increased to 194.6% significantly. Remarkably, the blends showed wonderful shape-memory effect. PAE domains act as stress concentrators in system with the stress release locally and lead to energy-dissipation process. These will prevent PLA matrix from breaking under high deformation, and lead to the PLA molecular orientation. Consequently, the blends occurred to deformation upon tensile load, and heating up the material will reform the shape back to the original shape.

1. Introduction

Polylactide (PLA) is aliphatic polyester derived from corn and sugar beets, and degrades to nontoxic compounds in landfill. It can be synthesized from direct condensation of lactic acid and by ring-opening polymerization of the cyclic lactide dimmer. Of many polymers, PLA has been chosen for its high biocompatibility and biodegradability. It has attracted much attention, especially in environmental and biomedical uses [1,2]. But PLA falls short of the required properties for potential applications because of its inherent brittleness and low toughness. In general, copolymerization and blending are the common methods to modify the brittleness of PLA. Blending usually is a more practical and economic way compared with copolymer synthesis. However, most of these blends have no biocompatibility or biodegradability, which clearly limits the environmental and biomedical applications of the prepared blends. So substantive research has been done on the blends of PLA with various polymers, such as poly(ether)urethane [3], poly(ethylene oxide) [4–6], and other polymers [7–9]. Polyamide elastomer (PAE) may be an alternative with complete biodegradability. It is usually prepared by a two-step polycondensation using poly(ethylene glycol) or poly(tetramethylene glycol) as polyethers. The segment of polyethers can provide good compatibility with PLA, and its segment of polyamide may form interaction with PLA [10,11]. These will provide good interfacial adhesion between PLA and PAE and toughen the PLA matrix.

Shape-memory polymer has attracted much interest in recent years used for biomedical applications. These polymers can be compressed to a smaller and more compact temporary shape, inserted by minimally invasive surgery, and then using heat, it will expand back to the permanent shape. Another possible application is as sutures, whereby the suture knot can be applied loosely in its temporary shape, followed by an increase in the temperature, which would tighten the knot as it goes back to its permanent shape.

In this work, we report a modification method by using PAE to improve the toughness of PLA. We are surprised to find that the blends not only showed a great toughness, but also a wonderful shape-memory effect. To our best knowledge, it is the first time to demonstrate the blends based PLA showed shape-memory behavior in high deformation using melt blending. Miscibility, disperse morphology, mechanical properties and shape-memory behavior are performed, and a proper mechanism is given too.

2. Experimental section

2.1. Materials

PLA was purchased from BrightChina Industrial Co., Ltd. (China). Its average molecular weight was measured by viscosity in

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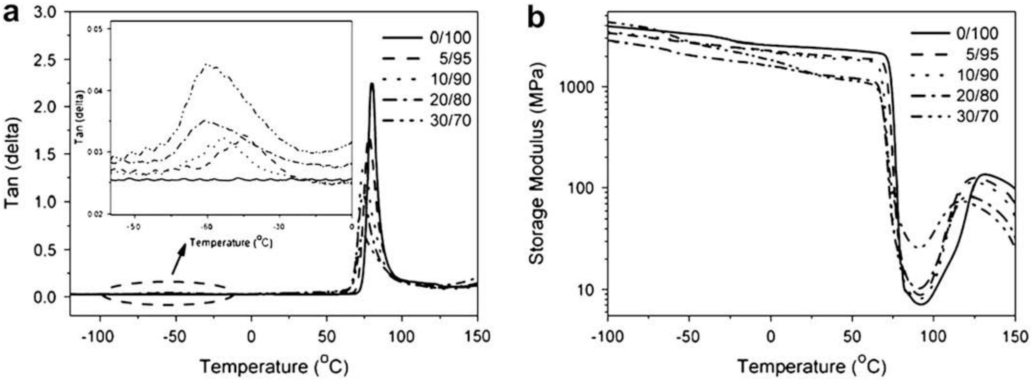

Fig. 1. Dynamic viscoelastic curves for the PAE/PLA blends: (a) tan δ versus temperature; (b) storage modulus versus temperature.

chloroform and yielded $M_\eta = 1.0 \times 10^5$ g/mol. The PAE used in this study was supplied by Atofina Chemicals corporation (France), having the trade name PEBAX 2533 based on polyamide-12 ($M_W = 530$, 22 wt.%) and polytetramethyleneoxide ($M_W = 2000$, 78 wt.%).

2.2. Preparation of PAE/PLA blends

The PLA and PAE were dried at 70 °C for 24 h in vacuum oven before processing, respectively. The blends were prepared by melt mixing in a microcompounder (Haake RC90, Germany). Polymers were mixed at screw speed of 75 rpm for 5 min at 170 °C. PLA was mixed with PAE from 5 to 30% (w/w). Also, the neat PLA was subjected to the same mixing treatment so as to have the same thermal history as the blends.

2.3. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out with a DMA Q800 (TA Corp.) in the tensile mode. The dynamic loss (tan δ) was determined at a frequency of 1 Hz and a heating rate of 3 °C/min as a function of temperature from −120 °C to 170 °C.

2.4. Scanning electron microscope

Scanning electron microscope (SEM) measurements were observed with a JSM-5600 LV scanning electron microscope using a tungsten filament (JEOL, Japan). The samples were broken into pieces in liquid nitrogen and were sputtered with gold and observed under a working voltage of 10 kV with 5000 magnification.

2.5. Measurements of tensile properties

Tension properties were determined using a screw-driven universal testing machine (DXLL-20000). Tensile bars were hot injection-molded at 170 °C, 5 MPa for 3 min by a DACA instrument, and then cooled to room temperature under ambient condition. Test conditions were as follows: temperature, 25 °C; gauge length, 30 mm; and crosshead speed, 5 mm/min. All the data were the mean and standard deviation from five determinations.

3. Results and discussion

3.1. Miscibility and disperse phase morphology

The dynamic viscoelastic curves for PAE/PLA blends with different PAE concentrations were observed, shown in Fig. 1. Glass transition temperatures (T_g) were calculated from the tan δ peak temperature and are summarized in Table 1. The T_g of both PAE and PLA shifted toward each other when the blends' ratios were varied, suggesting that PAE and PLA were partially miscible. In the PAE molecules, the polyether is the soft segment and polyamide acts as the hard segment. The soft segment played an important role of enhancing the compatibility between PLA and PAE molecules. The good compatibility made the hard segment was close to the PLA molecules. The hard segment of PAE can make an interaction with the PLA molecules theoretically. The hard segment containing amide groups can form hydrogen bonds with the PLA molecules. As is well-known, the hydrogen bond can enhance interfacial adhesion and improve compatibility better. Fig. 1b shows that the storage modulus at room temperature for PAE/PLA blends gradually decreased with the PAE contents increasing. The storage modulus of PLA rose at about 125 °C because of the cold crystallization. Compared with neat PLA, the storage modulus of blends exhibited lower temperature of cold crystallization with the PAE contents increasing. These suggested that the addition of PAE lowered the crystallization temperature of PLA.

Fig. 2 represents the SEM photos of the PAE/PLA blends with various PAE contents. As shown in Fig. 2a, the surface of neat PLA was extremely flat, indicating the brittle failure of PLA. The SEM photos of PAE/PLA blends with 5% and 10% PAE contents are shown in Fig. 1b and c, respectively. The PAE was dispersed in PLA matrix uniformly and the size of the PAE domains was of sub-micrometer order. It is easily observed that the interfacial compatibility is good between PAE and PLA.

3.2. Mechanical properties and shape-memory effect

The addition of PAE changed the tensile behavior of the PLA which is shown in Fig. 3, and the detail mechanical properties are summarized in Table 1. Neat PLA was very brittle and displayed no yield point. Its tensile strength was 46.8 MPa, while the elongation at break was only 5.1%. On the contrary, all of the blends showed

Table 1
Glass transition temperatures and mechanical properties of PAE/PLA blends.

PAE content (%)	$T_{g,PAE}$ (°C)	$T_{g,PLA}$ (°C)	Storage modulus[a] (MPa)	Static modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
0		79.48	2462	1814	46.8	5.1
5	−47.31	77.85	2116	1517	48.1	161.5
10	−53.87	75.97	2017	1633	40.9	194.6
20	−57.89	74.47	1442	1240	23.7	184.6
30	−60.26	73.84	1395	1050	24.6	367.2

[a] At 20 °C from DMA measurements.

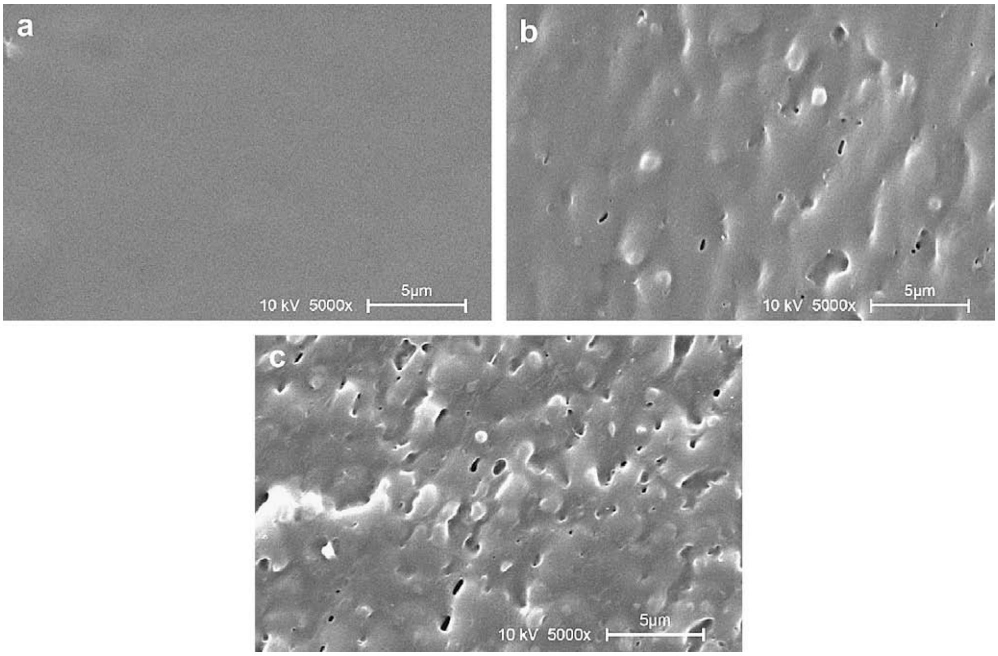

Fig. 2. SEM photos of blends with various PAE/PLA weight compositions of (a) 0/100, (b) 5/95 and (c) 10/90 (magnification ×5000).

typical yielding behavior and stable neck growth upon the tensile load. The tensile strength of composites with 5% and 10% PAE contents is 48.1 MPa and 40.9 MPa, respectively. Meanwhile the elongation at break increased from 161.5% to 194.6%. When the PAE contents were more than 20%, the tensile strength of blends decreased significantly. The tensile strength of composites with 20% and 30% PAE contents was only 23.7 MPa and 24.6 MPa, respectively. But the elongation at break increased enormously from 184.6% to 367.2%. The different mechanical properties depend on the disperse morphology and the phase structure with various PAE concentrations. The detailed effects of the morphology and the phase structure on the mechanical properties will be reported in our future publications. The results revealed that an optimum in mechanical properties of composites can obtained with 10% PAE contents.

PLA has the shape-memory ability theoretically, but its intrinsic brittleness limited the shape-memory effect for wide application. The neat PLA will break up upon tensile load, and then the molecules cannot deform from coil state to extend and orientational state in time. Generally, neat PLA will break up and its shape-memory effect cannot exhibit, when the deformation ratio is more than 5%. There are no reports about the blend of PLA exhibiting shape-memory ability upon high deformation. But the PAE/PLA blends exhibited wonderful shape-memory ability, as shown in Fig. 4. To our knowledge, it is never seen in the past reports. The sample of blends with 10% PAE contents was stretched at 100% strain and kept the temporary shape in room temperature, firstly. Then the sample was put into heating temperature and then exhibited quick shrinkage and recovered to its original shape quickly. Temperature is a vital parameter to the shape-memory effect. In fact, the shape-memory behavior should occur, when the temperature is above the glass transition temperature of PLA at about 60 °C. The shape-memory rate increased with the temperature increasing in a certain temperature range because of the higher molecular activity. The PAE/PLA blends can recover to original state in 8 s and 3 s at 80 °C and 90 °C, shown in Fig. 4a and c respectively. But the recovery ratio of blends was opposite and decreased with the temperature. It suggested that the molecules

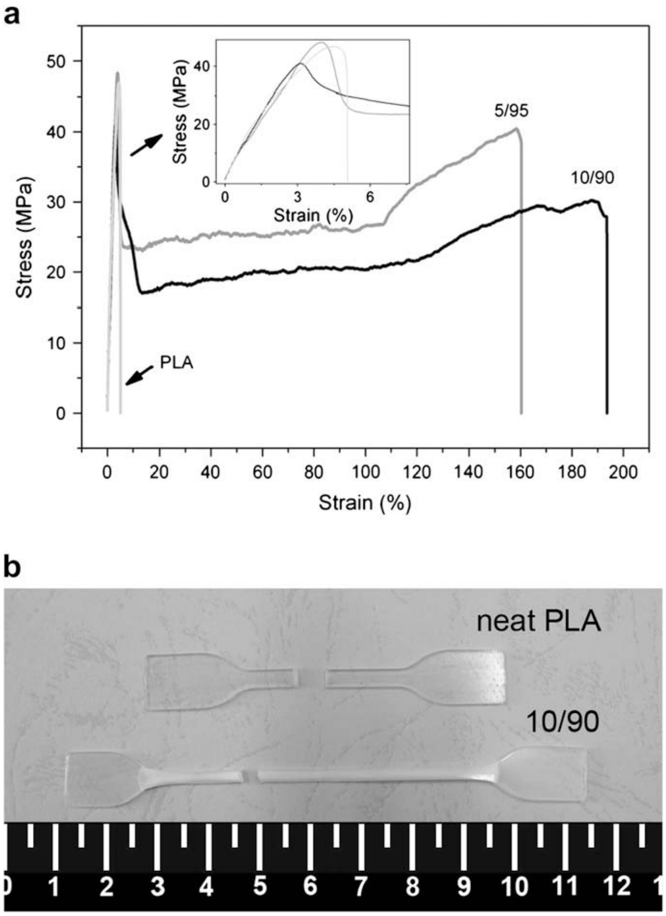

Fig. 3. (a) Tensile stress–strain curves of the blends with various PAE/PLA weight compositions and (b) the photos of tensile failure neat PLA and the blend with 10% PAE contents.

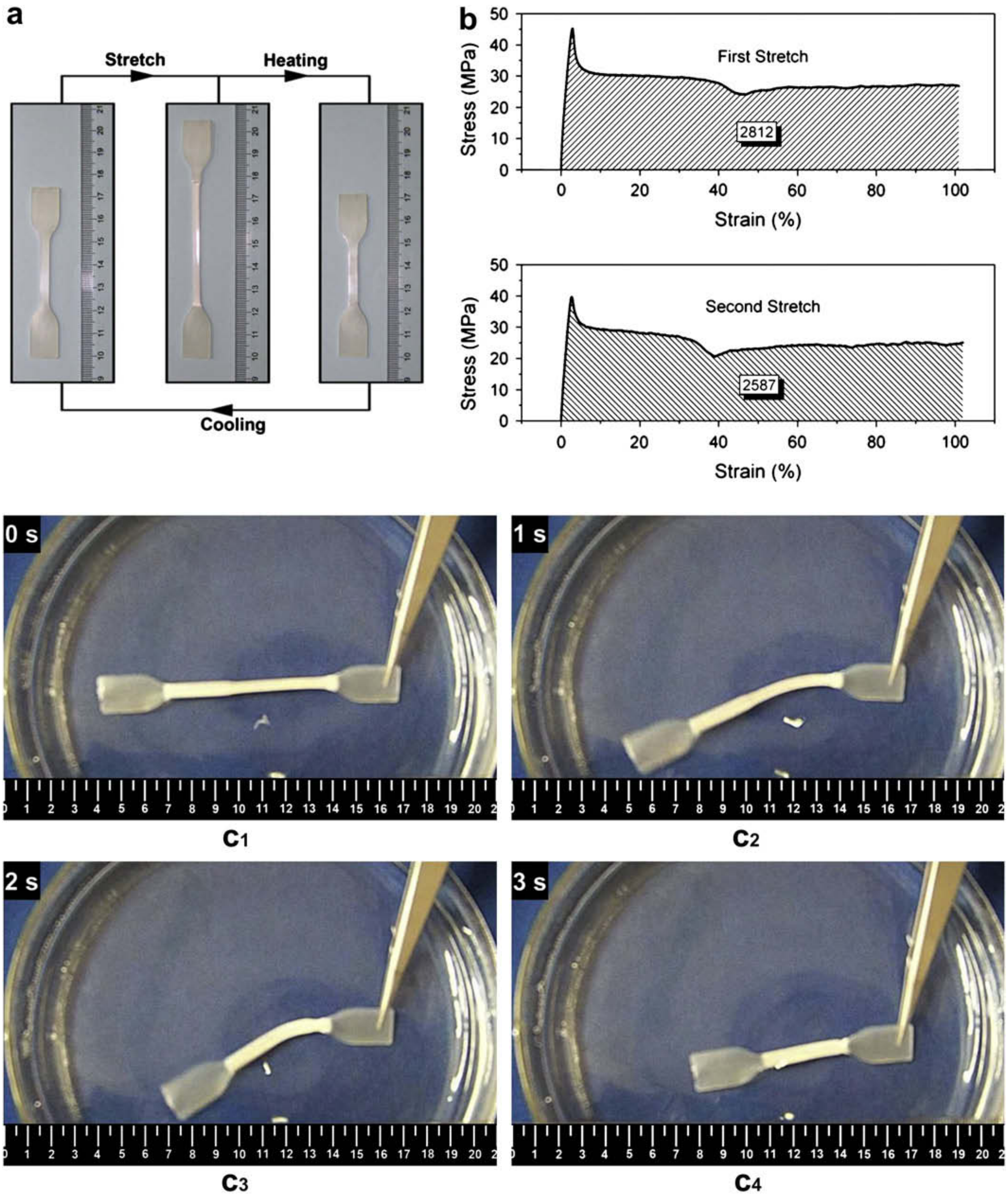

Fig. 4. Shape-memory effect of blends with 10% PAE contents at 100% strain: (a) illustration of cyclic stretch-recovery process, (b) tensile stress–strain curves for two times, and (c) thermal recovery process.

shrank too quickly and had no enough time to reorganize and reconstruct with intermolecular slippage. We also tested the second tensile properties of recovered sample at 80 °C, and found that the strain energy ratio between second stretch and first stretch is 2587/2812. The results revealed that the stretched sample recovered to its original mechanical properties basically and the recover ratio was about 92%.

The toughening and shape-memory effect implied an energy-dissipation process for a rubber-toughened plastic system. The PAE exhibited good compatibility with PLA, and there were some molecular interactions between two components. These would supply good interfacial adhesion between PAE and PLA. As PAE elastomer dispersed in PLA matrix, PAE acted as stress concentrators upon being subjected to the tensile test and led to triaxial stress locally released and energy dissipated. These could explain the blends with 5% and 10% PAE contents showed great tensile properties and ductile behavior. But due to the lower modulus and tensile strength of PAE, the modulus and tensile strength of composites decreased with the PAE contents increasing.

The shape-memory effect of PAE/PLA blends is different from the traditional shape-memory polymers. Remarkably, the temporary shape was formed in room temperature and was different to traditional shape-memory polymers, such as polyurethane [12,13]. PLA is a typical semicrystalline polymer [10]. In the system, crystalline region acted as the crosslink points to keep the original structure. On the other hand, the amorphous region occurred to deformation involving molecular orientation during elongating upon the tensile load. When the tensile load was removed, the elongation shape was kept and the stress was left in the system. So the molecules obtained the activity and recovered to its original shape with the stress releasing instantaneously after the temperature increased. PAE played an important role in the system. The compatibility stated previously between PAE with PLA make PAE worked as plasticizer and decreased the glass transition temperature of PLA. These promoted the orientation and reorganization of PLA molecules in the lower temperature. In a word, the addition of PAE elastomers toughened the PLA and endowed it with surprising shape-memory ability.

4. Conclusions

PAE/PLA blends were prepared by melt blending with improved mechanical properties. DMA tests showed that PAE/PLA blends are partially miscible system, and the PAE were dispersed in PLA matrix uniformly shown in SEM photos. The PAE/PLA showed significantly increased elongation at break compared with neat PLA. Especially, the blends exhibited wonderful shape-memory effect. The mechanism investigation can be explained that the stress release locally and energy-dissipation process by PAE acting as concentrators prevent the PLA from breaking up under high deformation. The molecular orientation occurred during the energy-dissipation process in amorphous region, and the stress was kept in the system. Consequently, heating up the material and releasing the stress will deform the shape back to the original shape.

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