Shape memory polymer hybrids of SBS/dl-PLA and their shape memory effects

Heng Zhang\textsuperscript{a,b}, Zhi Chen\textsuperscript{a}, Zheng Zheng\textsuperscript{a}, Xiaomin Zhu\textsuperscript{a,b,**}, Haitao Wang\textsuperscript{a,*}

\textsuperscript{a} State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200433, China
\textsuperscript{b} DWI an der RWTH Aachen e.V. and Institute of Technical and Macromolecular Chemistry at RWTH Aachen, Forckenbeckstraße 50, D-52056 Aachen, Germany

**Corresponding author. State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200433, China. Tel.: +86 21 65642392.**

\textsuperscript{*}Corresponding author. Tel.: +86 21 65642392.

E-mail addresses: zhu@dwi.rwth-aachen.de (X. Zhu), wanght@fudan.edu.cn (H. Wang).

HIGHLIGHTS

- The composite materials of SBS and amorphous dl-PLA were prepared by blending.
- A continuous domain was observed with the increasing content of dl-PLA.
- The composites exhibited shape memory effects.

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ABSTRACT

The hybrids of styrene-butadiene-styrene tri-block copolymer (SBS) and amorphous poly(dl-lactic acid) (dl-PLA) are found to exhibit shape memory effects, which gives an example of a dual-domain shape memory system consisting of an elastic domain and a thermo-switch domain. The dual-domain manner in this hybrid is studied by means of differential scanning calorimetry (DSC) and scanning electron microscope (SEM). Subsequently, the tensile test clarifies the interactions of the two domains on shape memory effects. As an elastic domain, SBS offers good shape recovery when its content exceeds 50 wt%. As a thermo-switch domain, dl-PLA triggers the shape memory effect at ca. 55 °C and offers good shape fixing when the content exceeds 30 wt%. An easy-to-do and easy-to-know feature of the hybrid is that the optimization of shape memory effect can be achieved by generating bicontinuous phases of SBS and dl-PLA, in which the dl-PLA content ranges from 30 to 70 wt%.

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1. Introduction

The research of the thermo-responsive shape memory polymers (thermo-SMPs) is attracting great attention of scientists and engineers due to their novel capacities to be manipulated into one desired shape and then change to another desired shape upon heating from a temperature below transition temperature to above it [1–3]. With this feature, thermo-SMPs have great potential applications for sensors, actuators, packaging, medical materials, etc [4–6].

Most thermo-SMPs can be categorized into polymer networks [1–3] and polymer hybrids [7,8]. The polymer networks are based on a hard-soft-domain system, which can be generated by a large number of block polymers [4,9–13]. Generally, hard domains are isolated cross-linkings and the soft domains are connecting each cross-linking to form a network. The shape of the network can be deformed to a temporary shape and this temporary shape is able to be fixed by crystallization or glass transition of the soft domains. The shape recovery can then be triggered by a thermo-stimulus reducing the stiffness of the soft domains. In this dual-domain system, it is a must to keep the cross-linkings an isolated phase and the soft domain a continuous phase to achieve shape memory effects. However, it is a hard-to-know and hard-to-do property for most block polymers; hence it is hardly accessible for conventional industries.

Recently, a new-comer to the field of thermo-SMPs is approaching. Polymer hybridization is a more accessible method to achieve required shape memory functions in applications [7,8,14]. It is made by blending two or more immiscible polymers together to form a dual-domain system (elastic-switch-domain system), in which the elastic domain is an elastomer to offer shape deformation properties, and the switch is able to change the stiffness upon a thermo-stimulus to maintain the temporary shape and to trigger the shape recovery. In our previous article we investigated SBS/PCL polymer hybrids [15], where SBS is the elastomer and melting and...
crystallization of PCL is the thermo-switch. The shape recovery of this hybrid can take place when applying heat above 60 °C, which is the melting temperature of PCL.

Other than semi-crystalline polymers like PCL, the amorphous polymers are still capable of being a thermo-switch using their glass transitions. The advantage is that the glass transition temperature can be adjusted more easily by various means, such as co-/graft-polymerization, blending of two miscible amorphous polymers [16–18] and adding plasticizers, surfactants or nanoparticles [19,20], etc. In the shape memory study, a required transition temperature in a particular application can be achieved in this way [21].

In order to investigate the behavior of the glass-transition type, the hybrid of a thermoplastic elastomer styrene-butadiene-styrene tri-block copolymer (SBS) and an amorphous polymer poly(δ-lactic acid) (δ-PLA) was prepared in this work. Both the materials are non-toxic and biocompatible, which makes these materials superior in the potential medical use. The miscibility, thermal and mechanical properties, phase structure and shape memory properties are studied in this paper.

## 2. Experimental

### 2.1. Materials

Styrene-butadiene-styrene tri-block copolymer (SBS, YH-791, \( M_n = 1.46 \times 10^5, M_w/M_n = 1.09 \)) was purchased from Balin Petroleum Chemical Corporation, Sinopec Group, China. The weight proportion of polystyrene/polybutadiene is 30/70. Poly (δ-lactic acid) (δ-PLA, \( M_n = 1.74 \times 10^5, M_w/M_n = 1.52 \)) was purchased from Senda Biochemicals Corporation, Jiangsu, China. These materials were used without further purification. The molecular weights of the polymers were determined by gel permeation chromatography (GPC, Agilent1100, USA).

### 2.2. Preparation of SBS and δ-PLA hybrids

SBS and δ-PLA were blended in a Banbury mixer (PLE 651, Brabender, Germany) at 180 °C, 60 rad min\(^{-1}\) for 5 min. After cooling down to room temperature, each sample was re-blended in the same condition for a second time. The δ-PLA contents varied from 0 to 100 wt%. The details are listed in Table 1. After blending, the samples were compressed into plates in a hot press at 180 °C with the pressure of 5 kN m\(^{-2}\).

### 2.3. Characterization

The phase morphology of the samples was observed by a scanning electron microscope (SEM, TESCAN, 5136 MM, Czechoslovakia).

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**Table 1** Details of each sample of different δ-PLA contents.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PLA0</th>
<th>PLA10</th>
<th>PLA30</th>
<th>PLA50</th>
<th>PLA70</th>
<th>PLA90</th>
<th>PLA100</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ-PLA content (wt%)</td>
<td>0</td>
<td>10</td>
<td>30</td>
<td>50</td>
<td>70</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td>SBS content (wt%)</td>
<td>100</td>
<td>90</td>
<td>70</td>
<td>50</td>
<td>30</td>
<td>10</td>
<td>0</td>
</tr>
</tbody>
</table>

**Table 2** \( T_g \) s of each component in each sample derived from DSC thermograms on the second heating run.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_g ) (°C)</th>
<th>PB</th>
<th>PS</th>
<th>δ-PLA</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA0</td>
<td>(-86.2)</td>
<td>84.5</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>PLA10</td>
<td>(-86.0)</td>
<td>84.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLA30</td>
<td>(-85.8)</td>
<td>84.1</td>
<td>54.5</td>
<td></td>
</tr>
<tr>
<td>PLA50</td>
<td>(-85.1)</td>
<td>83.9</td>
<td>55.5</td>
<td></td>
</tr>
<tr>
<td>PLA70</td>
<td>(-80.5)</td>
<td>82.0</td>
<td>57.1</td>
<td></td>
</tr>
<tr>
<td>PLA90</td>
<td>(-98.9)</td>
<td>58.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLA100</td>
<td>N/A</td>
<td>N/A</td>
<td>59.0</td>
<td></td>
</tr>
</tbody>
</table>

\( a \) \( T_g \) s were determined by the corresponding peaks of first derivatives.

\( b \) The contents of the component may be too low to determine the \( T_g \).

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**Fig. 1.** DSC thermograms of each sample. (a) \( T_g \) of PB on the second heating run. (b) \( T_g \) s of δ-PLA and PS on the second heating run.

**Fig. 2.** XRD diagrams of each sample, which is prepared according to Experimental part 2.2.
Fig. 3. SEM images of the cross sections of each sample. (a) PLA10, (b) PLA30, (c) PLA50, (d) PLA70 and (e) PLA90.
Before the observation, the samples were quenched and fractured in liquid nitrogen and their cross sections were coated with gold. The glass transition temperatures ($T_g$) of the samples were determined by differential scanning calorimetry (DSC, Pyris 1, Perkin Elmer, USA). To release the thermo-history and to arrest obvious glass transitions, two heating runs were performed. (1) The samples were heated from 0°C to 120°C at a constant rate of 10°C min\(^{-1}\). The samples were held at 120°C for 5 min (2) The samples were cooled down to 20°C in the extended state and were kept for 5 min (3) The samples were heated to 80°C again and were kept for 5 min and then the strain ($\varepsilon_m$) was recorded. (5) The samples were heated to 80°C again and were kept for 5 min and then the strain ($\varepsilon_p$) was recorded. Shape recovery ratio ($R_r$) and shape fixing ratio ($R_f$) were calculated by the following equations, respectively. Five samples of each dl-PLA content were measured to achieve the average $R_r$ and $R_f$.

$$R_r = \frac{\varepsilon_m - \varepsilon_p}{\varepsilon_m} \quad (1)$$

$$R_f = \frac{\varepsilon_u}{\varepsilon_m} \quad (2)$$

### 3. Results and discussion

#### 3.1. Miscibility of SBS and dl-PLA

The thermal properties of SBS/dl-PLA hybrid were determined by differential scanning calorimetry (DSC). Table 2 summarizes the $T_g$ s of the three components, polystyrene (PS), polybutadiene (PB) and poly (dl-lactic acid) (dl-PLA). From thermograms, the presence of the $T_g$ so of dl-PLA, PB and PS in sample PLA30 and PLA50 indicates the immiscibility of the three components. In PLA10 and PLA20, the $T_g$ s of dl-PLA cannot be unambiguously determined, but the almost unchanged $T_g$ s of PB and PS can account for their immiscibility with dl-PLA in these samples. The same conclusion can be made in PLA70, which shows the almost invariable $T_g$ s of PB and dl-PLA.

#### 3.2. Crystalline properties of SBS/dl-PLA hybrid

XRD measurements are applied to determine the crystalline properties of the samples with the results presented in Fig. 2. For a dual-domain polymer hybrid system, either crystalline or amorphous polymers are capable of the switch domain. An example of the semi-crystalline switch type was provided in our previous paper [15]. However in this paper, all samples from PLA0 to PLA90 show an amorphous peak near $2\theta = 20^\circ$ in the XRD diffractograms.
It proves the amorphous manner in SBS/dl-PLA hybrids, which can be an example containing an amorphous thermo-switch.

3.3. Microstructures

The SBS/dl-PLA hybrids generate a variety of microstructures, which are uncovered by SEM images in Fig. 3. According to the dl-PLA contents in these samples, the SBS domains are convex-like and the dl-PLA domains are concave-like.

In the increase direction of dl-PLA content, dl-PLA changes from a droplet domain in PLA10 to a continuous domain in PLA30. Meanwhile, SBS changes from a continuous domain in PLA10 to a droplet domain in PLA90. Bicontinuous structures are observed from PLA30 to PLA70. These phase-separated structures in SEM images are in good accordance with the T_g analysis in DSC results.

In order to make a clear distinguishing of the dual domains in bicontinuous structures, we define the major continuous domain as the one of the larger content, and the minor continuous domain as the one of the smaller. According to this, SBS is the major continuous domain and dl-PLA is the minor continuous domain in PLA30. While in PLA70, the opposite structure is seen.

3.4. Mechanical properties

Having obtained the microstructures, we continue to determine the mechanical properties of the hybrids by tensile tests. The stress–strain (σ–ε) plots are illustrated in Fig. 4a. The dependences of elongation at break (ε_break) and stress at break (σ_break) on dl-PLA content are shown in Fig. 4b.

In the σ–ε plot, the yield points identify the over-all elastic/plastic manners. From Fig. 4a, no yield points are observed before PLAS0, which is due to the presence of the elastic SBS major continuous domains. While from PLA70, yield points emerge from the dl-PLA major continuous domains. These over-all elastic/plastic behaviors have their origins in the microstructures of the hybrids, which has been discussed above.

In Fig. 4b, neat SBS (PLA0) and neat PLA (PLA100) show their typical elastic/plastic manners in σ_break and ε_break, respectively. Moreover, it is indicated that the addition of dl-PLA into SBS reduces σ_break but increases ε_break. Especially for PLA70, σ_break reduces remarkably.

3.5. Shape memory properties

Fig. 5 shows an example of the recovery process when the PLAS0 sample is put in water of 80 °C. The sample automatically knots within 3 s. The fast recovery process could find some applications, for instance in thermo-responsive sutures.

The shape memory properties are represented by shape recovery ratio (R_s) and shape fixing ratio (R_f) according to the literature [1–4]. R_s and R_f of each SBS/dl-PLA hybrid is calculated and illustrated in Table 3 and Fig. 6, respectively.

In the heat-cooling run of the test, all samples were fully relaxed at 80 °C and then cooled to 25 °C. The upper temperature of 80 °C is above the T_g of the dl-PLA (around 55 °C), and at this temperature the materials are allowed to deform very fast to a temporary shape because of the elastic state of dl-PLA. Accordingly, the lower temperature of 25 °C is below the T_g of dl-PLA, and the glass transitions enable the shape fixing of the temporary shape. When the temperature rises up to 80 °C again, the elastomeric transitions of the dl-PLA will trigger the shape recovery from the temporary shape back to the permanent shape. According to Fig. 5, the recovery process is very fast.

While increasing PLA content, R_s drops at PLA70 from 93.7% to 88.5%. Meanwhile, R_f shifts from 38.9% to 94.3% at PLA30. According to the conclusion in our previous paper [15], 4 regions can be considered for a detail discussion.

As shown in Fig. 6, regions 1 and 4 have either an isolated domain in the dual-domain system. Region 1 presents relative bad shape fixing, which is due to the fact that the isolated dl-PLA domains are not capable of maintaining the temporary shape. In a similar way, the hybrids in region 4 shows no elastic behavior with isolated SBS domains, which accounts for the reduced shape recovery.

Both regions 2 and 3 present bicontinuous domains in the dual-domain system. Thus, the hybrids in these regions show both good shape recovery and fixing. A slight difference is the reduced R_s in region 3 from almost 100–93.7%. The origin is the lower content of the elastic SBS domain, which is only the minor continuous domain in the hybrids.

A comparison between SBS/dl-PLA hybrid in this paper and SBS/PCL hybrid in our previous paper [15] can be addressed. They are both dual-domain systems but different in the switch-polymer. PCL is a semi-crystalline polymer and the switch is applying with crystallization and melting. Since the PCL melts into liquid, the hybrids from PCL70 are too viscous to perform the shape memory effects and the R_s is brought down directly to zero [15]. Distinctly, dl-PLA is amorphous applying the switch with glass transition. In this case, hybrids from PLA70 are still in an elastomeric state above the transition temperature to apply shape recovery, not as well as SBS but still notable.

4. Conclusion

SBS and dl-PLA hybrid is proven to be an example of a dual-domain shape memory system which consists of an elastomer
and an amorphous polymer as the switch-polymer. XRD diffractograms prove the amorphous dl-PLA in the hybrids and DSC thermograms demonstrate the shape memory transition temperatures are all around 55 °C. Under our experimental conditions, the addition of dl-PLA generates the hybrid structure from an isolated dl-PLA domain before PLA30 to a continuous domain from PLA30. It is revealed by both SEM images and tensile tests. The shape memory effect is dominated by the formation of bicontinuous structures, where the samples from PLA30 to PLA70 form bicontinuous structures and show much higher shape recovery and fixing ratios than those of the samples beyond the bicontinuous range. Regarding an amorphous switch-polymer of dl-PLA, it differs from a semi-crystalline switch-polymer like PCL that the shape recovery is still notable even if the elastic SBS becomes an isolated domain.

References