



Enhanced shape memory property of polylactide/thermoplastic poly(ether)urethane composites via carbon black self-networking induced co-continuous structure



Xiaodong Qi¹, Hao Xiu¹, Yuan Wei, Yan Zhou, Yilan Guo, Rui Huang, Hongwei Bai^{**}, Qiang Fu^{*}

College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China

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ABSTRACT

The preparation of elastomer/plastic blends with co-continuous structure is beneficial to achieve good shape recovery and fixing performances. In this work, carbon black (CB) nanoparticles with self-networking capability were introduced to tailor the phase morphology and shape memory properties of polylactide (PLA)/thermoplastic poly(ether) urethane (TPU) blend (70/30 by weight). A morphological change from sea-island structure to co-continuous structure was observed with increasing CB content. The strong affinities between CB nanoparticles and TPU as well as the self-networking capability of CB nanoparticles led to the formation of this co-continuous structure. With such novel structure, the PLA70/TPU30/CB ternary composites owned an outstanding shape memory property because the continuous TPU phase provided stronger recovery driving force. Moreover, the selective localization of CB nanoparticles in the continuous TPU phase imparted the composites with enhanced mechanical properties and excellent electrical conductivities with low filler content. The composites then showed a good electroactive shape memory behavior, which could recover to their original shape within 80 s at 30 V. Our work provides a universal strategy via CB self-networking to prepare double percolated conductive polymer composites with optimal shape memory properties and excellent electrical conductivities, which may promote specific applications in intelligent devices.

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1. Introduction

Shape-memory polymers (SMPs) represent a class of smart response materials that are capable to fix the temporary deformed shape and recover to their permanent shape upon external stimulus, including heat, light, electricity, magnetic field or moisture [1–5]. Such a ‘memorize’ property gives SMPs great opportunities to be applied in various fields, such as the packaging, textile, medical and aerospace industries [6,7]. On the basis of structure, SMPs usually contain two components: net-points and switching phases [8]. Net-points are the chemically or physically cross-linked points for preventing chain relaxation during deformation, which determine the permanent shape. Switching phases are responsible

for the fixation of the temporary shape, which are polymer chains with defined glass transition (T_g) or melting temperature (T_m). The ratio between net-points and switching phases has reached to a balance, which is considered to be necessary in producing SMPs with good shape recovery and shape fixation.

Among various strategies developed to prepare SMPs, polymer blending provides a more accessible route because of its good processability [9–16]. SMP blends typically consist of an elastomer serving as permanent phase and an amorphous or a crystalline plastic playing the role of switching phase [14,17,18]. For example, Kurahashi et al. prepared the polyurethane (PU)/poly(oxyethylene) (POE) binary blends via controlling the composition ratio, and the results demonstrated that the co-continuous structure could show optimal recovery and fixing performances [10]. It can be explained from the perspective of mechanical knowledge that in a SMP blend both the shape recovery determined by net-point and the shape fixation determined by switching phase are in connection with the efficiency of stress transfer, in which the continuous degree of each

* Corresponding author.

** Corresponding author.

E-mail addresses: bhw_168@163.com (H. Bai), qiangfu@scu.edu.cn (Q. Fu).

¹ These authors contributed equally to this work.

component plays a key role [19]. Therefore, co-continuous morphology in a blend system is believed to be helpful in balancing shape recovery and fixing performances [20–23]. However, the relative high content of elastomer is needed to obtain co-continuous structure, resulting in the decrease of the modulus and strength. Besides, the co-continuous morphology is usually obtained within a narrow range of compositions, which limits the developments of SMPs based on elastomer/plastic blends.

In recent years, some nanoparticles with self-networking capability have been found effective in expanding the composition range for co-continuity of binary immiscible polymer blends [24–27]. Through adding a small amount of nanoparticles, such as silica dioxide (SiO₂) and carbon black (CB) into binary immiscible polymer blends, a morphological transition from initial sea-island structure to a unique co-continuous structure was observed [28]. Wu et al. pointed out that the nanoparticles had a self-networking capability to form a continuous network structure and the adjacent droplets of the dispersed phase were drove to approach together to form continuous phase during melt blending [29]. Inspired from these interesting results, it's natural to think that the co-continuous structure, which is beneficial for realizing both good fixing and recovery performances, can be obtained by introducing the nanoparticles with the self-networking capability into the elastomer/plastic blends. More importantly, if the nanoparticles used are conductive [30–32], such as CB and carbon nanotubes, SMP composites with electrical conductivity can be achieved. However, high content of conductive fillers is often needed to attain good electrical conductivity that triggers the electroactive shape recovery of SMPs, giving rise to the large agglomerates in polymer matrix and is unfavorable for practical processing.

Forming the double percolated structure, that is to make conductive fillers selectively localize in one phase of polymer blend with the co-continuous structure, is a well-established way to obtain conductive composites with low filler content [33–36]. The term “double percolation” has been demonstrated to explain the reduction of the percolation threshold, which represents the percolation of the conductive filler distributed in one phase and the continuity of the filler-rich phase in the polymer blend occur simultaneously. Our previous study reported that a double percolated conductive composite was prepared through carbon black (CB) self-networking induced co-continuous-like morphology in polylactide (PLA)/thermoplastic poly(ether) urethane (TPU) blends [26].

In this work, we extend our interest in the electroactive shape memory properties of PLA/TPU/CB blends. Carbon black (CB) nanoparticles with the self-networking capability and electrical conductivity were introduced into PLA/TPU blends (70/30 by weight). In contrast to previous SMP blends in which elastomers occupy large proportion, the content of TPU in our study is only 30 wt%. It is expected that the addition of CB nanoparticles extends the composition range for co-continuity of PLA/TPU blends at relative low TPU content. The influence of phase morphology tailored by CB nanoparticles on shape recovery performances was investigated. Besides, the conductive CB nanoparticles could impart composites with electrical conductivities; thus the electroactive shape memory effect was studied as well. We aim to obtain a new type of double percolated conductive polymer composites with optimal shape memory properties, mechanical properties and excellent electrical conductivities.

2. Materials and methods

2.1. Materials

PLA (4032D) with a density of 1.25 g/cm³ was purchased from

Nature Works Co. Ltd., USA. TPU (WHT-1570) with a density of 1.21 g/cm³ was purchased from Yantai Wanhua Co. Ltd., China. CB nanoparticles (Printex-XE2B, Degussa Co. Ltd, Germany) had a primary diameter of 30 nm and were used as received.

2.2. Sample preparation

PLA/TPU/CB ternary composites were firstly mixed through melt blending of PLA, TPU and CB in a Haake mixer at 190 °C and 60 rpm for 6 min. The composition ratio of PLA/TPU was fixed at 70/30 and the loading amount of CB was changed from 0 to 8 phr. After that, the ternary PLA/TPU/CB mixtures were compressed into plates at 190 °C for 6 min under 10 MPa. For convenience, PLA/TPU/CB ternary composites are termed as PLA70/TPU30/CB_x, where x represents the weight percent of CB.

2.3. Characterization

The phase morphology of cryogenically fractured PLA/TPU/CB ternary composites were inspected by using an FEI Inspect F scanning electron microscope (SEM, USA). The morphological structure and the localization of CB in the PLA/TPU blends were observed through transmission electron microscope (TEM, JEM-2010) under an acceleration voltage of 200 KV. The ultra-thin samples with a thickness of 100 nm were prepared via a Leica UCT microtome at –100 °C. Dynamic mechanical analyzer (DMA Q800, TA Company) was employed to evaluate the dynamic mechanical behavior of PLA/TPU/CB ternary composites. The temperature were increased from 0 °C to 120 °C with a heating rate of 3 °C min⁻¹.

The shape memory properties of PLA/TPU/CB ternary composites were measured by using DMA. A four-step procedure was designed as follows. (1) First, the sample was heated to 85 °C and stretched to a certain strain (ϵ) under a constant force. (2) Then, the deformed sample was quenched to room temperature (25 °C) with keeping the force. (3) After the force was removed, the temporary strain (ϵ_{load}) was measured. (4) Lastly, the sample was reheated to 85 °C, maintained at 85 °C for 15 min and the recovery strain (ϵ_{rec}) was recorded. The samples were heated or cooled with a rate of 5 °C min⁻¹. The shape fixing ratio (R_f) and shape recovery ratio (R_r) of PLA/TPU/CB ternary composites could be calculated according to the following Equations (1) and (2):

$$R_f = \frac{\epsilon_{load}}{\epsilon} \quad (1)$$

$$R_r = \frac{\epsilon - \epsilon_{rec}}{\epsilon} \quad (2)$$

The tensile tests at a high temperature of 85 °C were carried out on DMA (Q800, TA Company, USA). The samples were kept at 85 °C for 5 min and then stretched at 3 N min⁻¹ until fracture. The tensile tests at room temperature (25 °C) were measured using an Instron 4302 universal tensile tester (SANSI, China) with a crosshead speed of 5 mm min⁻¹. The notched Izod impact toughness of PLA/TPU/CB ternary composites was evaluated on an impact testing machine (XJU-5.5, China).

The electrical conductivities of PLA/TPU/CB ternary composites were measured using a Keithley 6487 picoammeter. The sides of rectangular samples were coated with silver paint to eliminate contact resistance before testing. The ITECH IT6700 was conducted to yield constant voltage/current on samples to achieve electroactive shape memory behavior. The surface temperature of PLA/TPU/CB ternary composites was recorded in the middle of the rectangular samples by using a digital thermocouple.

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