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Biocompatible shape memory polymer actuators with high force capabilities

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ABSTRACT

Shape memory polymers (SMP) are a class of stimuli-responsive materials which can change shape upon activation. The objective of this study is to optimize the actuation (or shape recovery) properties of the biocompatible thermoplastic polyurethane (TPU)/polylactic acid (PLA) shape memory polymer (SMP) blend by altering the blend composition and programming temperature. A comprehensive characterization of the shape memory, morphological, and actuation properties of TPU/PLA blends was carried out on 80/20, 65/35, and 50/50 TPU/PLA blends and neat TPU. Three programming temperatures were utilized: 25 °C (room temperature), 37 °C (body temperature), and 70 °C (above the glass transition temperature). The transition temperature (T_{trans}) range was characterized by recovering the samples between 30 °C and 100 °C, at 10 °C intervals. The results showed that the shape fixity ratio (R_f) increased significantly with increasing PLA composition and programming temperature, and the shape recovery ratio (R_r) was not dependent on the programming temperature. The T_{trans} increased with increasing programming temperature, and its range decreased with increasing PLA composition. The highest shape recovery force was observed in the 80/20 and 65/35 TPU/PLA blends programmed at 70 °C, reaching up to 0.6 N/cm. These samples were able to lift a 50 g weight during the shape recovery process. The actuation forces of the TPU/PLA blends in this study is an order of magnitude higher compared to the currently available biocompatible SMPs. Therefore, these SMP blends can be further developed into actuators for biomedical applications such as artificial muscles.

1. Introduction

Shape memory polymers (SMP) are a class of smart materials with shape changing capabilities. They can be programmed to remember a temporary shape and revert back to the permanent shape upon the application of a specific stimulus, such as heat or light [1–3]. The most common type of SMPs are thermally responsive, they are able to recovery to their permanent shape when heated to above the transition temperature (T_{trans}). The ability of a SMP to recovery to its permanent shape is known as the shape memory effect (SME) [1–3]. The T_{trans} of a SMP is a temperature range which coincides with the polymer's glass transition temperature (T_g) or melting temperature (T_m). It is an important parameters in SMP design, and can be tuned by altering the polymer chemistry and structure, as well as changing the processing and programming parameters [1–3].

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The advantages of SMPs over other classes of shape memory materials (such as shape memory alloys (SMA) and shape memory ceramics) include high elastic deformation, low density, low cost, ease of manufacturing, tunable transition temperature, and potential biocompatible properties [2]. The main area of SMP development has been targeted towards biomedical applications due to their excellent biocompatible and biodegradable properties [3,4]. Some of the novel solutions and designs that have been achieved with SMPs include biodegradable self-tightening sutures, expandable catheters, blood clot removal devices, biodegradable surgical staples, and self-expanding foams in cardiovascular stents [5–10].

Polyurethane (PU) or thermoplastic polyurethane (TPU) is the most common type of SMP developed for biomedical applications [6,7]. A number of research groups have developed PUs with improved shape memory and mechanical properties by altering the chemistry of the polymer. For example, the utilization of ionomers and ethylene diamine chain extenders in polyurethanes results in enhanced mechanical properties such as higher strength and modulus [11,12]. Other chemical alterations of polyurethanes include the utilization of SBS, PCL, PLA and PLLA components, modification of the hard and soft domains, and the introduction of crosslinks [13–18]. However, despite the efforts made in PU development, its low mechanical strength is one major shortcoming that cannot be overcome with altering the polyurethane chemistry alone [6,7].

Polymer blending with polylactic acid (PLA) is an effective technique utilized for improving the mechanical properties of TPU without altering its chemical structure or introducing second phase particle, which could be potentially toxic to biological organisms [19]. The tensile strength of TPU improves with the addition of PLA, and the toughness of TPU increases significantly with the addition of PLA [20,21]. In addition, TPU endows PLA with excellent shape memory properties in the TPU/PLA blend [22]. We have reported in previous studies that TPU and PLA form immiscible and compatible polymer blends in the TPU/PLA compositions of 50/50, 65/35, and 80/20; these polymer blends also exhibited uniform mechanical properties [20,23].

Although SMPs have been utilized for a number of biomedical applications, they have not been successfully utilized as actuators due to the low force generated during the recovery process [2]. In one study, PU was developed for pressure bandage applications and the recorded recovery stresses were in the range of 20–45 mmH (0.0026–0.006 MPa); this is very low for actuation purposes, but suitable for the application that it was developed for [24]. Other studies have characterized the recovery force of SMPs for non-biomedical applications. One study developed robotic grippers utilizing an epoxy based SMP, which was able to yield a maximum recovery force of 3.5 g in bending recovery [25]. Another study which presented a thorough characterization of the relationship between programming temperature and shape recovery properties of SMPs found the maximum recovery stress of PMMA to be 3.5 MPa at the recovery temperature of 101 °C [26]. The highest recovery force exerted by SMPs during the shape recovery process was obtained by a study that utilized thermoplastic perfluorosulphonic acid ionomer (PFSA); a maximum stress of 4–5 MPa was obtained during the iso-strain shape recovery tests [27].

In order to achieve high actuation forces in SMPs, they have been fabricated with nano-particle and shape memory alloy (SMA) reinforcements [2]. One study found that reinforcing the PU matrix with 5% carbon nanotube (CNT) fibers achieved a maximum recovery stress of 1.5 MPa, doubling that found in neat PU [28]. Gall et al. found that epoxy-based SMP reinforced with SiC nano particles was able to achieve a maximum compressive recovery stress of 30 MPa [29]. Another study created a SMP composite actuator with polypyroll and PEE-borate complex that was able to exert a maximum contractile force of 14 N, and maximum stress of 27 MPa [30]. The highest actuation force of SMP composite was achieved with a polyvinyl alcohol (PVA) based SMP containing 20% CNT composite; it was able to exert a maximum recovery stress of 130 MPa [31]. SMP reinforced with one or two SMA NiTi wires or tape were found to produce maximum force in the range of 3.5–16 N [32–35].

Although a number of SMP and SMP-based composite actuators have been developed, there does not exist any biocompatible SMP actuators capable of exerting relatively high recovery forces. Most of the SMP composite actuators with high force actuation properties are made from non-biocompatible SMPs and contain nano-particles which are harmful to biological organisms. On the other hand, most of the biocompatible SMPs exhibit very low actuation forces during the recovery process. In addition, some of the SMPs presented in the literature involve very complicated fabrication processes and are difficult to scale up industrially. Therefore, the goal of this study is to develop biocompatible SMP actuators which are able to exert relatively high actuation forces, and can be fabricated with a relatively simple process that can be scaled up industrially.

In this study, we optimize the recovery force of TPU/PLA SMP blends by alerting the blend composition and the programming temperature. We first conduct a comprehensive study to characterize the morphological, shape memory, and force actuation (shape recovery) properties of 80/20, 65/35, and 50/50 TPU/PLA blends and neat TPU. The shape fixity ratios (R_f) were analyzed at three different programming temperatures: RT (room temperature), 37 °C (body temperature), and 70 °C (just above the T_g of the SMP), in order to better understand the effect of programming temperature on recovery force. The shape recovery ratios (R_r) were then computed over a range of recovery temperatures from 30 °C to 100 °C at 10 °C increments. The microscopic morphologies of the programmed and recovered TPU/PLA blends and neat TPU were analyzed with a scanning electron microscope (SEM). The shape recovery force of all the TPU/PLA blends and neat TPU at the three programming temperatures was measured with a custom-built force sensor, and the shape recovery time of each sample was obtained. The 80/20 and 65/35 TPU/PLA blends programmed at 70 °C yielded the highest recovery force, and we demonstrate their ability to lift a 50 g weight. Finally, we compare the findings of this study with the literature and discuss the potential biomedical applications of the TPU/PLA blends developed in this study.