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Flexible shape memory structures with low activation temperatures through investigation of the plasticizing effect

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Abstract

Shape memory polymer (SMP) systems exhibiting semicrystalline- elastomer blends, such as thermoplastic polyurethane and polylactic acid have been well studied, but their use in biomedical shape memory applications has been limited by their high activation temperature. SMPs are capable of deformation and recovery through the activation of an external stimuli, such as temperature. Critical criteria for SMPs used in biomedical applications is achieving a stimulus temperature close to 37 °C while still experiencing sufficient shape recovery. A polymer's glass transition temperature has been well defined as the SMP system's activation temperature and therefore should be decreased to achieve a decreased activation temperature. In this work, a well-known, biocompatible plasticizer, polyethylene oxide (PEO), was added to thermoplastic polyurethane (TPU)—polylactic acid (PLA) SMP blends to observe the plasticizing effect on the structural, thermal, mechanical, and shape memory properties of the polymer blends. Additionally, the geometry of the fabricated SMP samples was tailored to further enhance the shape memory effect through a bowtie honeycomb structure. Our results suggest that the addition of PEO into the SMP system may be an effective method for decreasing the polymer's glass transition temperature through the alteration of the polymer chain structure. With the addition of 30% PEO, the glass transition temperature of the TPU/PLA blend was successfully decreased from 62.4 °C to 34.6 °C while achieving 86.5% shape recovery when activated at 37 °C, which is only a 5% decrease in shape recovery when activated at 50 °C. These results suggest that the addition of a biocompatible plasticizer may overcome the limitation of employing temperature activated SMP systems in biomedical applications, and enhances the potential of these materials for reconfigurable structures, energy dissipation systems, and structural health monitoring (SHM) in civil engineering applications.

Introduction

Temperature-activated shape memory polymers (SMPs) have been widely studied for biomedical and structural engineering applications [1], including stents, scaffolds, deployable structures, sensors, smart coatings [2], and bone implants [3–5], to name a few. A limitation of current polymer blended temperature activated SMPs is that the applied recovery temperature exceeds that of which is safe for the human body. A critical criterion for SMPs used in biomedical applications is achieving a recovery temperature close to 37 °C while still experiencing sufficient shape recovery.

While there are extensive studies that have investigated the shape recovery of polymer blends, few studies have successfully optimized activation temperature while maintaining high shape retention and an activation temperature close to 37 °C with sufficient shape recovery. Lai *et al* and Song *et al* investigated the recovery of thermoplastic polyurethane (TPU) and polylactic acid (PLA) SMPs when thermally activated at 60 °C and 50 °C but could only achieve 60% and 50% shape recovery, respectively [6]. In adaptive structural components and self-sensing materials, achieving a lower activation temperature without loss of function is crucial for real-time monitoring and damage detection in civil infrastructure and biomedical implants [1, 7]. To decrease the activation temperature of polymeric blend SMPs, the glass transition temperature of the polymer must be decreased.

Plasticizers are known to reduce the glass transition temperature (Tg) of polymers by increasing the plasticity of a polymer matrix and the free volume of the polymer chain [8]. Polyethylene oxide (PEO) is a commonly used plasticizer and has been shown to act as a crystallizable switching segment in the fabrication of SMPs [9]. Antony *et al* characterized poly(ethyleneglycol) dimethacrylated based SMP networks in which the concentration of plasticizer inversely affected the polymer's activation temperature [10]. Therefore, by modulating the polymer network using PEO, this study aims to develop SMPs that operate at biorelevant temperatures, while also exploring their potential as self-sensing materials in structural health monitoring (SHM) applications.

SMPs are a class of materials that experience a shape memory effect, that is they transition back to a pre-programmed shape following a deformation when actuated by an external stimulus. To initialize the shape recovery an external stimulus in the form of heat, light, or an electric or magnetic field must be present. Heat actuated SMPs have gained attention due to their ease of fabrication and low processing temperatures. The polymer's glass transition temperature plays an important role in temperature activated SMPs. A temporary shape deformation of the polymer is achieved when, upon cooling from a higher temperature, the polymer reaches a temperature just below its glass transition temperature, which results in limited rotation of the polymer chain causing the polymer to take on a higher order and internal energy than the original shape [11]. When the temperature is increased above the polymer's glass transition temperature, the polymer chain segments gain mobility which causes changes to the polymer's internal energy and entropy allowing shape recovery to occur [12]. Recently SMPs have been categorized in two ways 1) cross-linked polymer networks, which utilize the reversible phase as the triggering switch during activation and the pre-programmed phase acts as the cross-linking nodes, 2) polymer blends, which are composed of two distinct polymers: a crystalline and an amorphous polymer, where the crystalline phase maintains the overall structure of the polymer while the amorphous phase allows for a shape memory effect [8]. An advantage of polymer blend SMPs as compared to cross linked networks, is that the shape recovery behavior can be controlled by tuning the ratio of crystalline and amorphous polymers [13]. In this work polymer blended SMPs are investigated.

PLA is a well-known thermoplastic for biomedical shape memory applications due to its biocompatibility, enhanced mechanical properties, nontoxic degradation, and relatively low glass transition temperature (55 °C–60 °C). TPU, a flexible, biocompatible, and biodegradable polymer has also been investigated for the fabrication of SMP blends. TPU is composed of hard and soft segments giving the polymer elastic characteristics [14]. Due to the rigid mechanical properties of PLA, the addition of TPU enhances the mechanical properties of the SMP for biomedical applications, specifically for strain sensors [15]. Although the application of PLA/TPU SMPs has been investigated for biomedical applications, the polymers activation temperatures exceed temperatures which are safe for *in vivo* monitoring. This work investigates the addition of PEO to the TPU/PLA composition to decrease the necessary activation temperature while still achieving significant shape recovery.

Recent advances in hyperelastic materials and nanomaterials have empowered the development of flexible sensors and actuators. With innovations in manufacturing, various flexible, stretchable, and wearable strain sensors have been proposed and applied in biomedical applications, including real-time healthcare monitoring, smart prosthetic devices and electronic skins, wound healing monitoring, and mechanical assessment of soft biological tissues [16–19]. Of interest to this study is to investigate the material properties of a shape memory polymer towards creating devices capable of strain tuning and eventually sensing, targeting usages in the biomedical field. In addition to decreasing the shape memory activation temperature of the polymers for the applications of interest, the geometry of the fabricated samples was explored, specifically a bowtie honeycomb geometry, was devised and tailored to enhance the shape memory effect by mechanically amplifying the strain for a given amount of shape memory. This bowtie honeycomb geometry was selected because it has been widely studied in architected materials and energy dissipation systems, where they amplify strain response and improve mechanical resilience [20, 21]. It also demonstrated success in prior work to enhance sensing performance of a soft sensor when used to corrugate the surface of the polymer [16]. Therefore, TPU/PLA/PEO samples were fabricated in a bowtie honeycomb geometry. This work aims at investigating the material and shape memory properties of polymeric blends, specifically investigating if the addition of PEO, a biocompatible plasticizer, to TPU and PLA will decrease the activation temperature of the SMP while maintaining sufficient shape recovery. Achieving a decreased activation temperature will allow for the use of the polymeric blends in biomedical shape memory applications.

While previous studies have broadly investigated polymer blends such as TPU/PLA for shape-memory applications, this study uniquely addresses a critical barrier—achieving substantial shape recovery at activation temperatures specifically targeted for biomedical applications (close to physiological temperature, 37 °C). Our work provides an original approach by systematically examining the incorporation of polyethylene oxide (PEO), a biocompatible plasticizer, to precisely lower the glass transition temperature without substantially compromising mechanical and shape memory performance. This represents a significant step forward in extending the application scope of shape memory polymers, not only in biomedical fields but also for practical civil engineering applications where low activation temperatures are advantageous.

Materials and methods

Fabrication and characterization of thermoplastic polyurethane-polylactic acid-polyethylene oxide powder

Cryogenic milling was utilized to create powder composites containing 80% TPU (75A, NinjaTek), 20% PLA (200000 $g.mol^{-1}$, Prusa3D), and varying percentages of a PEO (1000000 $g.mol^{-1}$, Polysciences Inc.) plasticizer,0 wt%, 10 wt%, 20 wt%, or 30 wt%. The abbreviations 80TPU and 20PLA represent a polymer blend composition consisting of 80 wt% thermoplastic polyurethane (TPU) and 20 wt% polylactic acid (PLA), respectively. The chosen 80:20 TPU-to-PLA ratio is based on previous research [12, 14] demonstrating that this particular blend ratio provides an optimal balance between toughness, elasticity (provided by TPU), and stiffness (provided by PLA). Higher PLA ratios increase brittleness, negatively impacting shape memory behavior and flexibility, while lower PLA ratios result in insufficient structural rigidity. The maximum polyethylene oxide (PEO) content used in this study was set at 30 wt% based on prior literature and preliminary experimental trials [8, 10, 12], which indicated diminishing returns in lowering the glass transition temperature (Tg) beyond this concentration. Additionally, PEO concentrations exceeding 30% substantially compromised mechanical strength and handling properties of the polymer blend, rendering the material unsuitable for practical fabrication or structural applications. Thus, a maximum limit of 30 wt% PEO was determined to optimally balance lowered activation temperatures and adequate mechanical integrity. Received materials were weighed and transferred into vials containing cylindrical stainless-steel impactors. The vials were placed into a freezer mill (6875D, SPEX Sample Prep, USA) maintained at −196 °C. After precooling the samples for 15 min in a liquid nitrogen environment, the materials were milled for five cycles lasting 10 min each. The milled powders containing 0% PEO (80TPU/20PLA), 10% PEO (80TPU/20PLA/10PEO), 20% PEO (80TPU/20PLA/20PEO), and 30% PEO (80TPU/20PLA/30PEO) were stored in a sealed container until further use.

A scanning electron microscope (SEM) (TESCAN Vega 3, TESCAN, US) was used to observe the morphology of the cryomilled composite powders and fabricated samples and to qualitatively confirm the achievement of a homogeneous polymer blend. The samples were sputter coated (Q150T plus, Quorum Technologies Ltd, UK) with gold platinum for 2 min to achieve a uniform coating of 20 nm. Micrographs of the samples were obtained by operating the microscope with a working distance of 10 mm and an accelerating voltage of 10 kV.

Fourier transform infrared spectroscopy (FTIR)(Pike Technologies, GladiATR^{TM}) with a scanning ranged from 400–4000 cm^{-1}, a scanning resolution of 4 cm^{-1} and an average of 42 scans was performed to analyze the chemical structures of the cryomilled powders and fabricated samples.

Melting temperature, glass transition temperature, and crystallinity of the cryomilled powders were measured using a differential scanning calorimeter (DSC) (Polyma 214, NETZSCH Instruments, USA). 8–10 mg of the sample was heated from 25 °C to 200 °C followed by cooling to 25 °C and heating to 200 °C at a constant rate of 10 °C min^{-1}. Empty aluminum pans were used as references and analyses were performed using Proteus® Thermal Analysis version 7.

Rheological measurements of the four cryomilled composites were performed using a rotational rheometer (DHR-2, TA Instruments, USA) equipped with a 20 mm Smart SwapTM parallel-plate geometry and a Peltier system to control the temperature during measurements to study the viscosity and plasticizing effect with the increasing addition of PEO. All the trials were conducted with a measurement gap of 950 μm. First, an amplitude sweep (0.01%–100% strain, 1 Hz) was performed at 190 °C to identify the linear viscoelastic region of the powder material. Once the linear viscoelastic region was identified, oscillatory tests were performed using a strain lower than the detected critical strain (0.5% for 80TPU20PLA, 80TPU20PLA10PEO, 80TPU20PLA20PEO, and 80TPU20PLA30PEO). Frequency sweeps (0.01–10 rad s^{-1}) were performed for all the samples at 190 °C. Cox-Merz transformation was applied to obtain values and generate a log–log plot of shear viscosity as a function of shear rate.

Design and fabrication of shape memory polymer geometry

The re-entrant hexagonal honeycomb structure [22], also known as bowtie honeycomb, is characterized by the angle θ and cell strip length ratio ($\beta = h/l$), shown in figure 1. The effective Poisson's ratio ν_{xy} remains negative and decreases with decreasing θ for $30^\circ \leqslant \theta \leqslant 80^\circ$ and increasing length ratio β between 1 and 2 [23]. In this study, a three-dimensional bowtie shape structure formed using $\theta = 60^\circ$, $l = 8.7$ mm and $\beta = 1.55$ and was

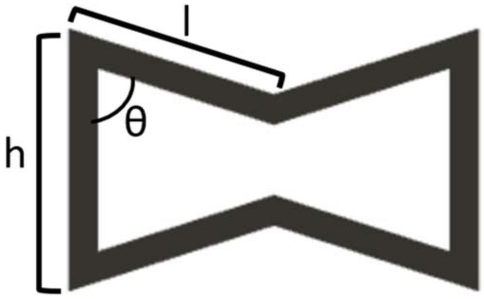

Figure 1. Schematic of the designed bowtie honeycomb structure, which is characterized by the angle θ and cell strip length ratio ($\beta = \mathrm{h/l}$).

designed using Autodesk Fusion360. A stainless-steel mold of the bowtie honeycomb geometry was fabricated using a CNC mill. 15 grams of cryomilled powder was packed into the mold and melted in a hot oven at 180 °C for 20 min. After cooling to room temperature, the samples were removed from the mold and stored in a sealed container until further use.

Characterization of shape memory polymer geometry

Tensile properties of the TPU/PLA/PEO compositions were analyzed using a CellScale mechanical tester (UniVert, CellScale, CA) at room temperature according to standard ASTM D638. Dumbbell shape specimens were fabricated with an average thickness of 2.64 ± 0.30 mm. The tensile modulus of the dumbbell samples was identified by performing tensile tests with a 200N load cell (CellScale, CA) at a stretching speed of 5 mm min^{-1} with a preload magnitude of 0.1 N. The slope of the linear region of the stress–strain curve was taken as the tensile modulus. For each material composition, three independent samples were tested, and the results are reported as mean ± SD.

The shape memory effect of the fabricated samples was investigated for each material composition through a macroscopy scale shape recovery test. Bowtie samples were heated from room temperature to a temperature of 48 °C for 2 min then deformed to a hexagon geometry until an average strain deformation of 45% was achieved. The hexagon geometry samples were held at a constant strain for 10 min. The samples were heated, either at 55 °C or 37 °C, for 2 min to allow the shape memory effect to take place. The shape memory behavior was characterized by percentage of shape recovery which is defined as

$$R = [(d - r)/(d - l)]^{*}\ 100 \tag{1}$$

where R is the percent shape recovery, l is the original sample length, d is the deformed sample length, and r is the sample length after recovery.

Results and discussion

Chemical, thermal, and mechanical analysis of thermoplastic polyurethane-polylactic acid-polyethylene oxide powder

The FTIR absorbance spectra of TPU/PLA/PEO cryomilled powders and of TPU/PLA/PEO melted samples are shown in figures 2(a) and (b), respectively. The characteristic peaks of TPU, the N–H bonds within urethane (-NHCO-) and the broad peak representing C-H stretching, can be identified at 3335 cm^{-1} and 2858 cm^{-1}, respectively. PLA can be identified by its characteristic peak which represents the C=O group, at 1732 cm^{-1}. The presence of PEO can be identified by the single sharp characteristic peak, C-O-C group, at 1103 cm^{-1}. Upon further inspection, subtle spectral changes were observed after melt blending (figure 2(b)). Specifically, the double peak near 1103 cm^{-1} observed in the cryomilled samples became less prominent, suggesting increased polymer compatibility and intermolecular interactions after thermal processing. Additionally, the peak intensity near 700 cm^{-1} decreased, and the double peak around 2858 cm^{-1} merged into a broader, single peak, accompanied by diminished intensity at 3335 cm^{-1}. These spectral changes indicate slight molecular rearrangements and enhanced miscibility among TPU, PLA, and PEO chains. However, no entirely new chemical bonds were formed, as confirmed by the absence of additional peaks. The increase in peak height at 1103 cm^{-1} from the 80TPU20PLA10PEO to the 80TPU20PLA20PEO to the 80TPU20PLA30PEO samples can be attributed to the increase in absorption intensity. This was expected due to the increasing PEO content.

To investigate the plasticizing effect of PEO on the TPU/PLA samples, DSC experiments were performed, and the curves can be seen in figure 3. The glass transition temperature, melting temperature, and crystallization

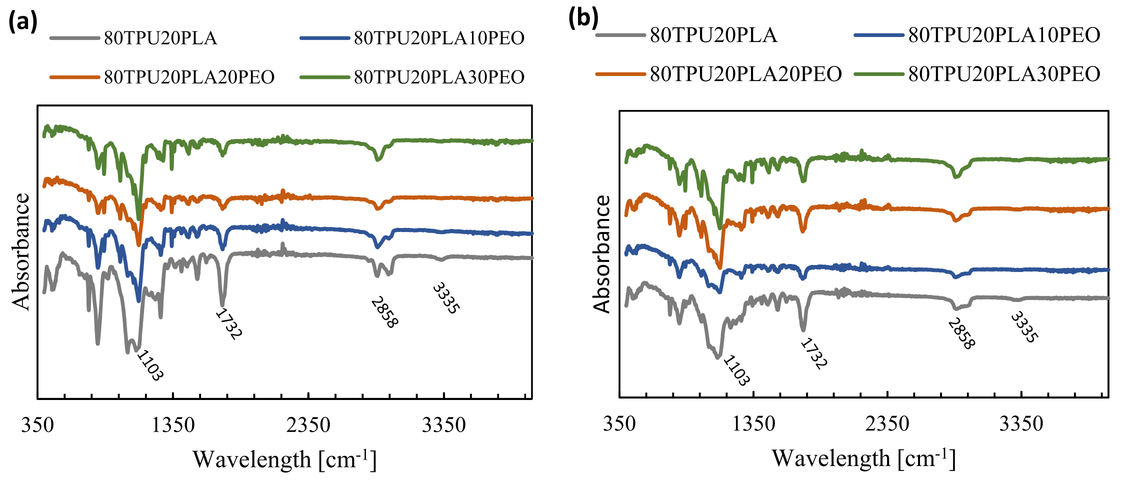

Figure 2. (a) Cryomilled Powders- Fourier transform infrared spectroscopy absorption spectra of cryomilled thermoplastic polyurethane, polylactic acid, and polyethylene oxide composites. (b) Melted Samples- Fourier transform infrared spectroscopy absorption spectra of melted thermoplastic polyurethane, polylactic acid, and polyethylene oxide composite samples.

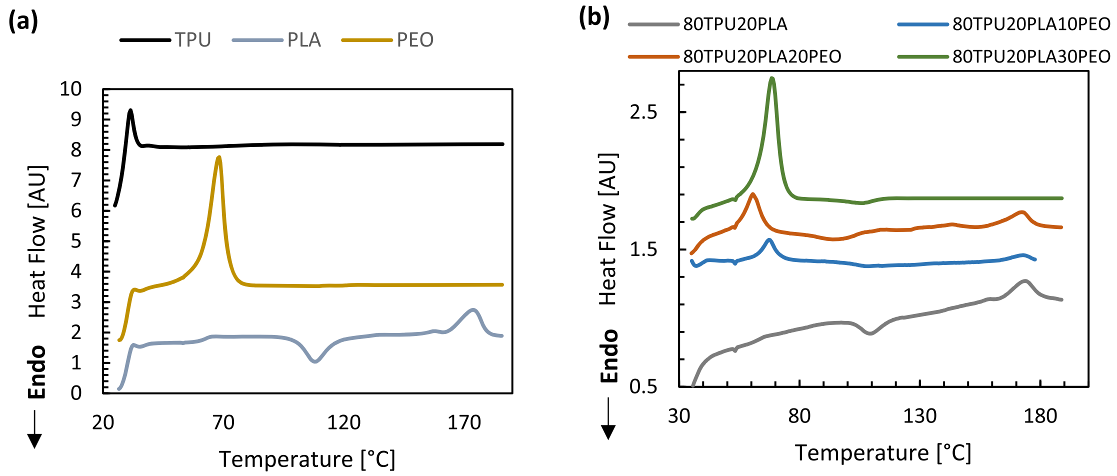

Figure 3. (a) Second heating thermograms from differential scanning calorimetric analysis of pristine thermoplastic polyurethane, polylactic acid, and polyethylene oxide. (b) Second heating thermograms from differential scanning calorimetric analysis of cryomilled thermoplastic polyurethane, polylactic acid, and polyethylene oxide composites. The peaks seen in the thermograms represent crystallization temperature (convex curve) and the melting temperature (concave curve) of the analyzed composites.

temperature were evaluated for neat TPU, PLA, and PEO (figure 3(a)) as well as for the four TPU/PLA/PEO cryomilled powders (figure 3(b)). Neat PLA shows an exemplary semi-crystalline curve with an endothermic and exothermic peak around 115 °C and 175 °C, respectively while neat PEO exhibits a highly crystalline behavior. Neat TPU displays a relatively plain curve. The glass transition temperature and melting temperature of neat PLA are 64.1 °C and 173.8 °C. The addition of TPU to PLA did not alter the melting temperature or crystallization temperature of the polymer as compared to pristine PLA but the addition slightly decreased the glass transition temperature to 62.4 °C. This decrease can be attributed to the shift in glass transition temperature towards the soft segmented polymer, TPU [14]. However, the addition of PEO to the TPU/PLA significantly changed the thermal profile of the polymer blends. With the addition of 10% PEO, the glass transition temperature decreased from 62.4 °C to 54.5 °C and further decreased to 34.6 °C with the addition of 30% PEO. DSC analysis (figure 3 and table 1) shows distinct thermal transitions. Consistent with literature standards, DSC curves were plotted with endothermic processes downward, highlighting melting transitions clearly. Important thermal characteristics—glass transition temperature (Tg), melting temperature (Tm), and crystallization temperature (Tc) - are summarized comprehensively in table 1 for ease of comparison. This clear presentation confirms significant plasticization effects with increasing PEO content, particularly evidenced by the pronounced decrease in glass transition temperature. Previous studies have reported that glass transition temperature is not strongly affected by the blending of TPU to PLA [14] hence the decrease in glass transition

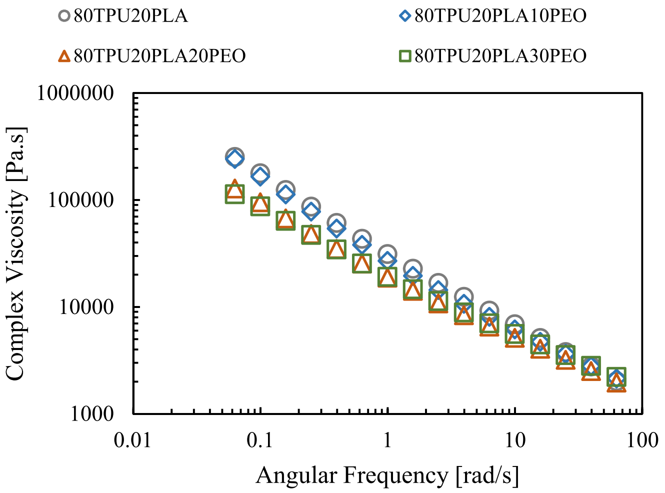

Figure 4. Rheological characterization of cryomilled thermoplastic polyurethane, polylactic acid, and polyethylene oxide powders (n = 3). Frequency sweeps (0.1–100 rad s^{-1}; 0.5% strain) of cryomilled composites performed at 190 °C.

Table 1. Summary of the glass transition temperature, melting temperature, and crystallinity from the second heating thermograms of the analyzed composites.

	Glass transition temperature [°C]	Melting temperature [°C]	Crystallization temperature [°C]
PLA	64.1	173.8	108.0
PEO	45.6	68.1	NA
80TPU20PLA	62.4	173.6	109.5
80TPU20PLA10PEO	54.5	172.9	96.5
80TPU20PLA20PEO	44.2	172.6	94.9
80TPU20PLA30PEO	34.6	172.2	105.3

temperature can be attributed to the addition of PEO. The presence of the plasticizer decreases the intermolecular interactions of the PLA chains, thus decreasing the polymer's glass transition temperature [14]. This inherent decrease in glass transition temperature allows for a decreased shape memory response activation temperature, thus PEO may positively impact the shape memory performance of polymers specifically for biomedical applications.

In addition to analyzing the plasticizing of PEO through DSC, the rheological properties of the TPU/PLA/PEO polymer blends were studied to investigate the plasticizing effect of the addition of PEO to TPU and PLA, which can be seen in figure 4. A decrease in the complex viscosity can be seen with an increase from 10% PEO to 20% PEO, which was expected and has been seen in previous research. No significant decrease in complex viscosity was observed with the addition of 10% PEO from 0% PEO nor with an increase from 20% PEO to 30% PEO. Additionally, a Newtonian plateau, typically seen when investigating the rheological properties of PLA cannot be observed. This may be due to the higher percentage of TPU in the polymer blends. Similar results have been observed in previous studies [8, 24].

DSC results confirmed that increasing PEO content significantly decreased the glass transition temperature (Tg), allowing for activation at lower temperatures. This plasticizing effect enhances the usability of SMPs in biomedical implants and low-energy activation systems in structural engineering applications. The rheological analysis showed a reduction in complex viscosity with increasing PEO content, consistent with the literature on plasticized SMPs for tunable material properties. Lower viscosity facilitates fabrication of intricate geometries, an advantage in adaptive SHM sensors and deployable structures.

To investigate the plasticizing effect on the morphology of the TPU/PLA bowtie geometry samples, SEM was performed. Figures 5(a)–(d) shows the SEM images of the TPU/PLA/PEO samples with increasing PEO content. With 0% and 10% PEO, TPU islands, denoted by the red circles, can be seen in the PLA matrix but as the PEO content increases to 30%, the TPU becomes integrated within the PLA matrix, as reported previously [8]. Additionally, the increase in PEO allows for smoother boundaries between the TPU and PLA suggesting increased compatibility between the two polymers, which is confirmed by increased shape recovery in samples with 30% PEO content.

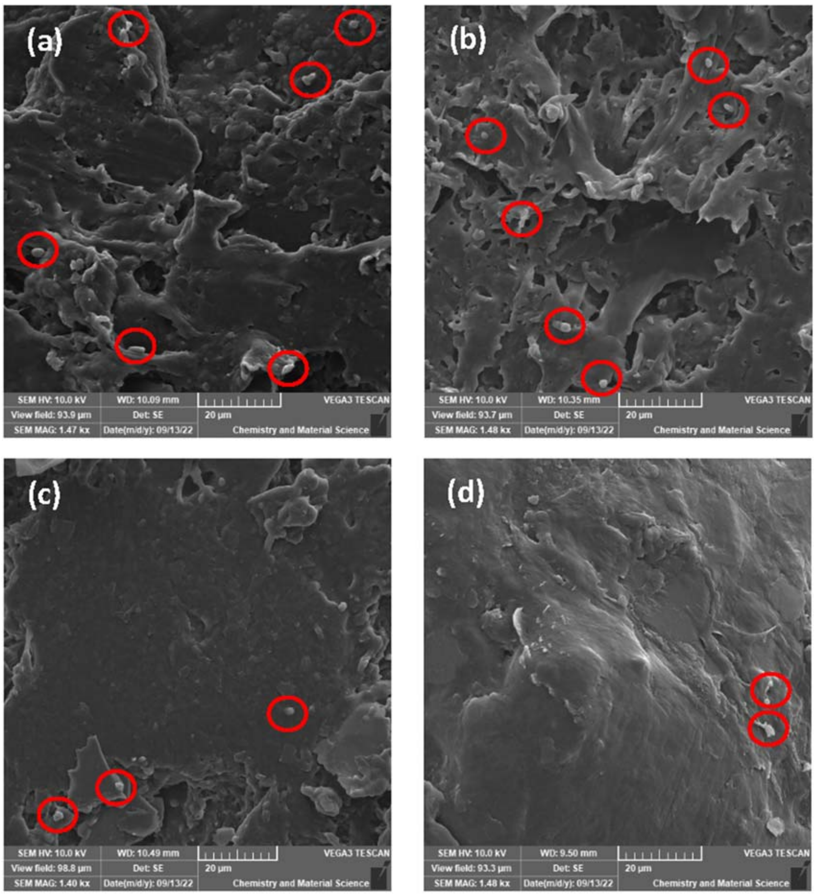

Figure 5. SEM images of melted samples (a) 80TPE20PLA (b) 80TPE20PLA10PEO (c) 80TPE20PLA20PEO (d) 80TPE20PLA30PEO. Scale bar is 20 nm. Red circles denote TPU islands in the sample.

In addition to thermal and morphologic properties, mechanical properties of the TPU/PLA/PEO composites were assessed through the investigation of tensile strength according to standard ASTM D638, to understand the effect of the addition of PEO to TPU and PLA. Samples with increasing PEO content experienced an overall decrease in tensile strength, which was expected (figure 6). The average tensile strength for the 80TPU20PLA, 80TPU20PLA10PEO, 80TPU20PLA20PEO, 80TPU20PLA30PEO samples is 193.91 ± 22.23 MPa, 209.03 ± 15.88 MPa, 116.26 ± 36.88 MPa, and 36.77 ± 3.88 MPa, respectively. PLA has poor toughness limiting its use in biomedical applications. To enhance these properties TPU, a block copolymer consisting of soft and hard segments, was mixed with PLA to improve material ductility, and overcome the brittle characteristics of PLA. The soft segments of TPU are composed of polyol and isocyanate, giving the material flexibility and elastomeric properties [14]. The addition of the plasticizer, PEO, leads to an overall decrease in tensile strength which is due to the plasticizing effect. It was expected for samples fabricated with 80TPU20PLA to have the highest tensile strength, however 80TPU20PLA10PEO had a greater tensile strength at 209.03 ± 15.88 MPa, although not significant. The plasticizing effect cannot be seen with only a 10% increase in PEO content, which aligns with the rheological results. A decrease in tensile strength can be seen with the addition of 20% PEO to the TPU/PLA samples, which also algins with the rheological results where a decrease in complex viscosity was seen with an increase in PEO content from 10% to 20% PEO. This initial increase then decrease in tensile strength with the addition of 10% PEO and 20% PEO in a PLA-based polymer has been reported previously [25, 26]. A 17.7% decrease in tensile strength can be seen with an increase in PEO from 20% to 30% PEO content. The mechanical results suggest that the plasticizing effect can be seen with a 30% addition of a plasticizer to the polymer blend.

Shape memory effect of bowtie honeycomb geometry

Percent shape recovery of TPU/PLA/PEO bowtie honeycomb geometry samples with increasing PEO content was analyzed to determine the plasticizing effect on the polymer's shape memory. Shape recovery was performed at 50 °C and 37 °C to investigate if the presence of PEO could decrease the polymer's activation temperature while still achieving significant shape recovery. All samples were strained to a strain fixity ratio of 92%, which

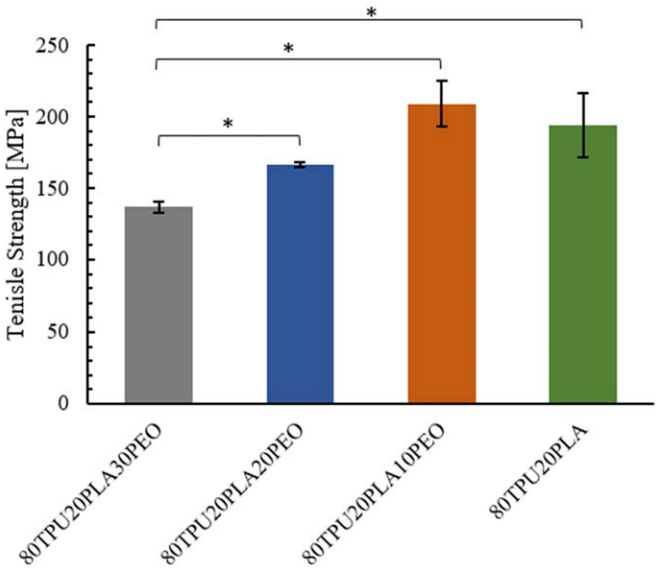

Figure 6. Mean tensile strength of thermoplastic polyurethane, polylactic acid, and polyethylene oxide dumbbell specimens (n = 3). Experiments were performed at room temperature with a 200 N load cell at a stretching speed of 5 mm min^{-1} with a preload magnitude of 0.1 N. Error bars represent standard deviation. Statistical analyses were performed using a one way ANOVA with a Tukey Post Hoc test, $^{*}P > 0.05$.

was calculated as the ratio of the fixed strain and initial strain. As seen in figure 7, the percent shape recovery generally increased with increasing PEO content for both 50 °C and 37 °C, although a significant increase was seen in samples with 20% and 30% PEO content as compared to 0% PEO samples. The addition of a plasticizer into a SMP, which is composed of both soft and hard segments, increases the number of soft segments of the polymer resulting in increased shape recovery. The melting and recrystallization of these segments also increases the polymer's memory effects [27]. Aside from the percentage of plasticizer, activation temperature also was seen to influence shape recovery. Overall, samples activated at 50 °C showed increased shape recovery over samples activated at 37 °C for samples containing the same percentage of PEO. Shape recovery tests indicated an average shape-fixing ratio of 92% ± 2%, highlighting the excellent ability of the polymer blend to maintain its temporary deformed shape. The reported deformation strain (45%) represented the linear extension of the bowtie sides from their initial position. Deformation strain was calculated based on the change in distance of the central points of the bowtie. While this deformation primarily involved bending and flexural changes in the geometry, future investigations employing purely tensile-based deformation will provide more comprehensive insights into the material's shape memory behavior. Although the geometry of the specimens provides a limitation of the shape recovery, traditional linear tensile testing would provide a standardized approach to determining the shape memory behavior of the studied polymers blends. Although a greater shape recovery occurred for samples stimulated at 50 °C, samples containing 30% PEO recovered to over 85% of their original shape when activated at 37 °C and samples containing 20% PEO recovered to over 80% of their original shape. These results suggest that the addition of at least 20% of a plasticizer to a shape memory polymer blend may allow for over 80% shape recovery for SMPs activated at 37 °C. Achieving a low activation temperature, without compromising mechanical or material properties of the polymer, is critical to allow for increased use of temperature activated SMPs in biomedical applications.

The shape recovery experiments demonstrated that TPU/PLA/PEO blends with 30% PEO content achieved 86.5% shape recovery at 37 °C, which is a substantial improvement over conventional SMPs activated at 50 °C or higher. This finding is crucial for self-sensing elements in civil engineering, where materials must respond to temperature changes while maintaining mechanical performance. Potential applications include self-repairing polymer-based structures that recover from deformation due to environmental stresses [28], strain sensors and soft actuator integrated into composite for real-time monitoring of structural integrity [29], and deployable and reconfigurable building components, such as smart windows [30], flexible joints [31], and actuators in adaptive architecture [32].

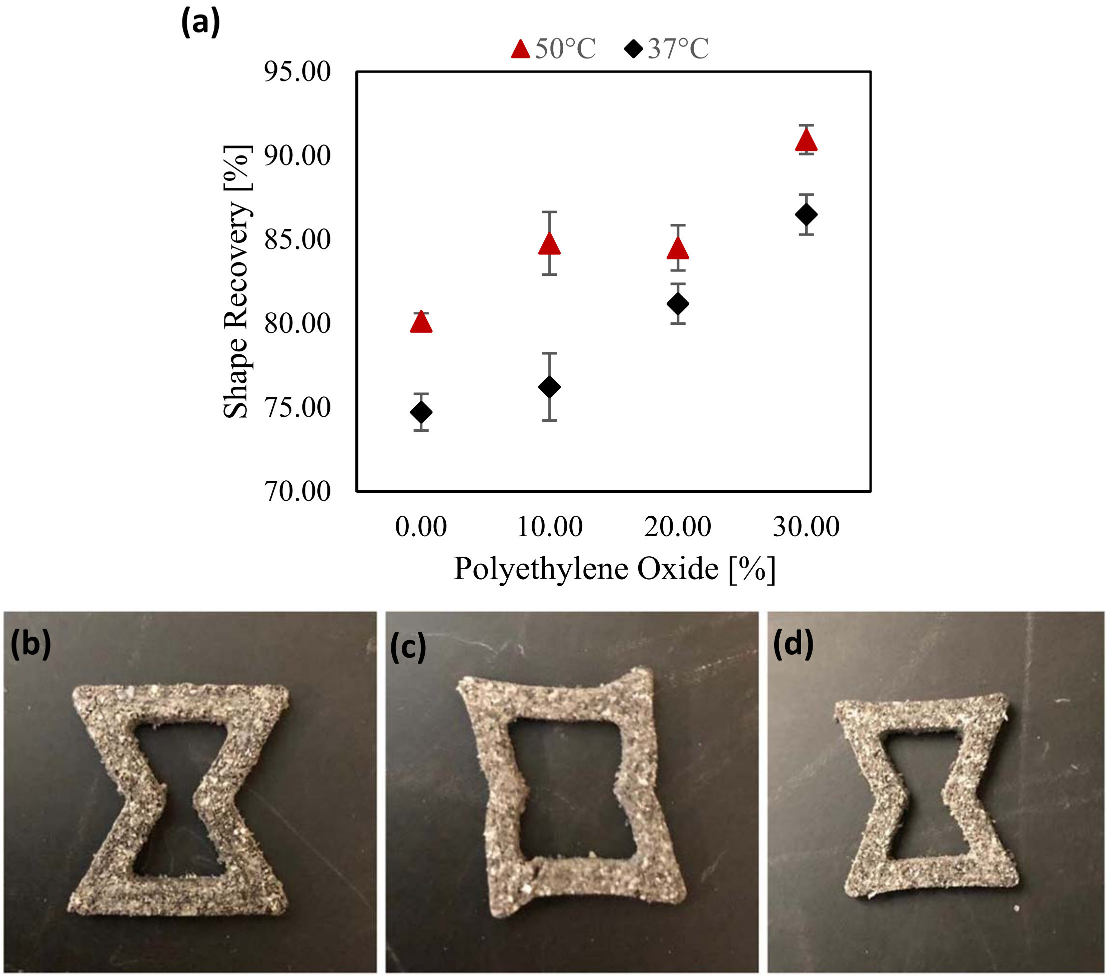

Figure 7. (a) Shape recovery of bowtie honeycomb geometry samples with increasing polyethylene oxide content (0%, 10%, 20% and 30%) under two shape memory conditions (50 °C and 37 °C) (n = 3 for each condition). Error bars represent standard deviation. (b) bowtie honeycomb geometry prior to deformation (c) strained bowtie honeycomb geometry (d) bowtie honeycomb geometry recovery length after experiencing a temperature stimulus.

Conclusion

Shape memory polymers have been well studied but their use in biomedical shape memory applications has been limited due to the high temperatures required to stimulate a shape recovery response. This work investigated the plasticizing effect of PEO on a well-studied TPU/PLA shape memory polymer system to achieve decreased activation temperatures for the use of SMPs in biomedical applications, here targeting the creation of devices capable of strain tuning and eventually sensing. TPU/PLA/PEO bowtie honeycomb geometry samples were fabricated with increasing PEO content to study the thermal, mechanical, and shape memory changes with the addition of the plasticizer. This work resulted in the following advancements:

- DSC results showed a decrease in glass transition temperature with increasing PEO content and therefore allowed for a decrease in the stimulus temperature.
- Thermal results were confirmed through a macroscopic scale shape recovery test where bowtie honeycomb geometry samples were deformed and activated in either a 50 °C or 37 °C environment. Samples with 30% PEO content showed over 85% shape recovery when activated in the 37 °C environment.
- The shape recovery findings indicate that PEO integration effectively lowers activation temperature while maintaining shape recovery, expanding the applicability of SMPs beyond biomedical uses to civil infrastructure and SHM applications.
- Adversely, increasing PEO content decreased the tensile strength of the SMPs due to the plasticizing effect.

Future work should be conducted to optimize the percent plasticizer to achieve both mechanical relevance and significant shape recovery based on the shape memory polymer's application. Additionally, conducting tensile deformation-based shape memory tests to systematically characterize the SMP's recovery performance under uniform tensile strains should be considered. This will provide a more comprehensive evaluation of shape memory behavior across different deformation modes. Overall, the results of this work suggest that thermoresponsive SMP polymers are capable of significant shape recovery in biorelevant environments, overcoming the critical temperature barrier, and therefore can be used in biomedical applications.

Acknowledgments

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Data availability statement

The data cannot be made publicly available upon publication because the cost of preparing, depositing and hosting the data would be prohibitive within the terms of this research project. The data that support the findings of this study are available upon reasonable request from the authors.

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