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Room Temperature Deformable Shape Memory Composite with Fine-tuned Crystallization Induced via Nanoclay Particles

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ABSTRACT: It is known that particular types of semi-crystalline/elastomer polymer blends exhibit shape memory effects (SME) due to the dispersion of two immiscible phases. In this study, the crystal structure of polylactic acid (PLA)/thermoplastic polyurethane (TPU) based shape memory polymer (SMP) is altered by incorporating small amounts of montmorillonite (MMT) nanoclay. The results indicate the incorporation of MMT can improve the compatibility of the two different polymers. Moreover, the presence of MMT affects the total crystallinity of the SMP and improves mechanical properties. Lastly, uniaxial stretching deformation can be applied to the SMP at room temperature conditions while maintaining its shape memory properties. With 1 wt% MMT particles, the recovery ratio (Rr) was nearly 95%, which indicated a strong recovery effect. The shape fixing ratio (Rf) remained above 95% for all composites due to plastic deformation applied at room temperature.

KEYWORDS: Shape Memory Polymer, Crystallization, Nanocomposites, MMT Nanoclay, Annealing

INTRODUCTION

Shape memory polymers (SMPs) are a special class of polymers that have the ability to maintain one or more temporary shapes and revert back to their initial shape once exposed to an external stimulus.1 Such stimuli can be light, heat, or solvent-induced chemical reactions.2-7 The shape memory effect (SME) of different types of SMPs have been well documented over the past few decades, with thermally activated SMPs being studied the most.4 Therapeutically activated SMPs usually consists of two different phases: a soft and thermally reversible phase responsible for maintaining a temporary shape, and a hard phase that has the ability to “memorize” a permanent shape. Furthermore, the shape recovery process of thermally activated SMPs can be characterized by two critical temperatures: the permanent temperature ($T_{perm}$) for programming the permanent shape of the SMP, and the transition temperature ($T_{trans}$) for triggering the recovery from a temporary shape back to its permanent shape. For physically cross-linked thermoplastic polymers or cross-linked block copolymers, $T_{perm}$ is determined by the degree of cross-linking at the molecular level. As a result, the melting temperature ($T_m$) of the polymers can be utilized for programming its permanent shape.4

When a SMP is heated above its $T_{trans}$, a large drop in the elastic modulus of the soft phase can be observed. Under such condition, deformation
can be applied to the SMP to form its temporary shape. This temporary shape can then be fixed by reducing the temperature of the SMP to below its $T_{\text{trans}}$ so that the micro-Brownian movement within the polymer chain can be frozen. By re-heating the SMP in its temporary shape to a temperature above $T_{\text{trans}}$, the SMP would then be able to recover back to its permanent shape. As a result, it is common to select the soft phase based on a polymer with a glass transition temperature ($T_g$) equivalent to the desired $T_{\text{trans}}$.\textsuperscript{8} Due to the special properties of SMPs, it is proposed that they can be used in a wide variety of applications such as actuator textiles,\textsuperscript{9,10} aerospace,\textsuperscript{11} and biomedical devices.\textsuperscript{12,13} Lan et al. demonstrated a prototype solar panel hinge that can be activated by SMP composites.\textsuperscript{14} Bye et al. developed a morphing SMP skin that has to potential to be used in shape shifting unmanned air vehicles.\textsuperscript{15} Xue et al. fabricated a fast self-expandable SMP stents that can be used as biomedical insert.\textsuperscript{16}

SMPs can be further classified into two distinct group: covalently/physically cross-linked polymer network structures and polymer blends.\textsuperscript{4,20} For network based SMPs, the hard phases are usually in droplet form and act as the switching phase. In contrast, polymer blend SMPs consists of two different polymers that are immiscible: a crystalline polymer that acts as the hard phase, and an amorphous polymer that acts as the switching phase. Examples includes poly(ω-pentadecalactone) (PPDL)/poly(ε-caprolactone) (PCL) copolymer,\textsuperscript{21} polyurethanes (PU)/PCL,\textsuperscript{22} styrene–butadiene–styrene tri-block copolymer (SBS)/PCL,\textsuperscript{20} polyvinylidene fluoride (PVDF)/polyvinylacetate (PVA),\textsuperscript{4} and polyactic acid (PLA)/PVA.\textsuperscript{4} Compared to network SMPs, polymer blend based SMPs are easier to fabricate. Furthermore, their activation and shape recovery mechanism can be tailored by carefully designing the ratio of amorphous/crystalline polymer.\textsuperscript{20} Recently, PLA has become one of the most popular polymer choices for the crystalline polymer in SMP composites due to its mechanical properties and biocompatibility.\textsuperscript{23–25}

One of the earliest studies on PLA based SMPs was reported by Zhang et al. in regards to the toughening process of a PLA matrix.\textsuperscript{26} The purpose was to modify the brittleness of PLA by blending it with polyamide elastomer (PAE), which is a polymer that has both polyether and polyamide groups. Previous research have demonstrated that the polyether groups in PAE have good compatibility with PLA, while the polyamide groups form good interfacial polymer-polymer interactions with PLA.\textsuperscript{27} By incorporating 5 and 10 wt% of PAE into the PLA matrix, the elongation at break increased from 5.1% to 161.5% and 194.6% respectively. Moreover, the PLA/PAE blend also exhibited SME properties: 92% recover ratio ($R_r$) was reported for the 10 wt% PAE sample after 100% stretching. Ever since this discovery, intensive studies on PLA based SMP composites have been conducted. For instance, Yuan et al. fabricated a fully bio-based SMP by combining PLA, natural rubber, and thermoplastic vulcanizates together.\textsuperscript{28} Huang et al. verified that SMP behaviour can be observed from polylactide-b-poly(ethylene-co-butylene)-b-polylactide (PLA–PEB–PLA) triblock copolymers and that its performance can be controlled by adjusting the crystallizability of the PLA segments.\textsuperscript{29} Samuel et al. reported a novel SMP composite that has multi-shape memory capability by integrating poly(L-lactide) (PLLA) with poly(methyl methacrylate) (PMMA).\textsuperscript{30}

In order to induce SME in PLA based materials, the incorporation of soft segments is required, which can be done by blending in thermoplastic polyurethane (TPU)\textsuperscript{23,25,31,32} and polyethylene glycol (PEG).\textsuperscript{33,34} TPU is widely selected due to its biocompatibility and the fact that it can be easily blended within the PLA matrix. Since SMP performance and behavior highly depends on its crystalline structure and hard/soft phase interface, therefore it is essential to understand basic polymer properties including crystallinity and the mechanisms within the soft/hard phase interaction region. It is long known that the polymer’s crystalline structure can be altered dramatically through the incorporation of
compatibilizers or coupling agents. Recently, Zare evaluated the SME of several different nanoparticle enhanced SMP composite systems and the work indicated that polymer-particle interfacial regions play an important role in SMP activation performance. Montmorillonite (MMT) is a commonly used filler due to its large surface area and high aspect ratio of its laminar structure. Zou et al. showed that octadecylammonium-treated MMT filler has good compatibility when blend with TPU; an increase in mechanical property was reported with only 3 wt% filler content. Kim et al. intercalated sodium-modified MMT particles with PEG polymer segments and found that the segments behave as physical cross-linkers in the poly(ethyl methacrylate) matrix. More recently, Kelnar et al. investigated the influence of organophilized MMT when blended with PLA/TPU composites. The group reported that the TPU dispersion in the PLA matrix is dramatically improved in addition to enhancements in crystallinity and polymer-polymer compatibility.

Despite the advances in research related to different SMP composite systems and filler-controlled polymer integration, there are only a few studies that focus on adapting nanoparticle induced crystalline/amorphous changes and applying such alteration for fine-tuning SMP behaviour. For instance, Tan et al. reported that MMT can be used to improve the mechanical properties of polyurethane-epoxy composites, but critical SME parameters such as glass transition temperature, storage modulus, and shape recovery ratio remained the same. In this study, we report the effect of sodium-modified MMT on PLA/TPU shape memory composites. To further increase the samples' crystallinity, the composites underwent an annealing process. We have demonstrated that the addition of MMT fillers have a remarkable impact on both the thermal behaviour and the SME properties of the composite. In addition, we showed that the composite can be deformed under room temperature conditions while maintaining its shape memory properties, which leads to the development of a more efficient SMP material)

**EXPERIMENTAL**

**Materials**

Polylactic acid (PLA, 4032D, pellet form) was obtained from NatureWorks Inc. The melting temperature of the polymer is 150°C with a density of 1.24g/cm^3 at 25°C. Prior to any processing, the pellets were dried in an oven at 80°C for at least 8 hours. Thermoplastic polyurethane (TPU, Desmopan 385E, density of 1.20 g/cm^3) was supplied by Bayer Material Science and ammonium salt modified Montmorillonite (MMT, Cloisite 15A, density of 1.66 g/cm^3) was obtained from NeuNano Inc.

**Composite Fabrication**

Both PLA and TPU were weighed according to an 80/20 wt% ratio while MMT content was varied from 0, 1, 2, to 3 wt%. The composites were melt blended by a twin-screw compounder (MiniLab II Microcompounder, HAAKE) at 180°C and screw speed of 200 RPM for a 10-minute cycle time. The compounded samples were then pelletized into smaller pieces.

Two molding techniques, which were injection molding and compression molding, were used. Rectangular samples (50mm in length, 10mm in width, and 3mm in thickness) were prepared using an injection molding machine (Xplore Micro Injection Molding, DSM). The injection barrel was pre-heated to 180°C while the mold was pre-heated to 30°C. The pelletized composite segments were fed into the injection barrel and held for 5 minutes before injection to ensure complete melting of the pellets. The molten matrix was injected into the mold at 100 psi and was extracted from the mold after cooling. To study the effect of annealing and the formation of crystalline phase, the injection
mold was held at 100°C and 100 psi for 10 minutes.

Thin film samples were prepared using a hot compression press (Model 4386, Carver). The hot compression press was pre-heated to 180°C. After reaching desired temperature, the composites pellets were inserted into a circular mold with 0.1 mm in thickness and sandwiched between two steel plates. To prevent the molten matrix from sticking to the steel plates, Teflon sheets were placed between the composite and the plates. The composites were placed in the press at 180°C and heated for 5 minutes, to ensure complete melting of the pellets. A 76 MPa compression pressure was then applied for an additional 5 minutes. After the film was extracted from the mold, the samples were cut into strips (8mm by 3.5 mm) for testing. For the annealed sample, the sample was transferred to a second hot press at 100°C and compressed at 76 MPa for another 10 minutes.

Composites Characterization

SEM

Scanning electronic microscopy (SEM) images of brittle fractured sample were taken for studying the morphologies of the different composite systems. Prior to imaging, samples were subjected to 3 minutes of platinum sputter coating and the images were taken with an environmental SEM (QUANTA FEG 250 ESEM, FEI) at a 3kV voltage setting.

FTIR

Fourier transform infrared spectroscopy (FTIR, Alpha Platinum-ATR, Bruker Inc.) was used for verifying the presence of chemical bonding. During the testing, a scanning resolution of 4 cm⁻¹ was used and an average of 24 scans were taken for each sample.

DSC

Differential scanning calorimetry (DSC, Q2000, TA Instrument) experiments were performed under two different conditions: isothermal and non-isothermal. For the isothermal tests, samples were pre-heated to 220°C, ensuring that the samples’ thermal histories were completely erased. After, the temperature was quickly lowered to the desired testing condition (i.e. 100°C, 110°C, 120°C, and 130°C) and held for 60 minutes to allow crystal growth. For the non-isothermal test, heat-cool-heat experiments were performed. A heating rate of 10°C/min and a cooling rate of 5°C/min were utilized while tests were conducted between 200°C and -50°C.

TGA

The thermal degradation behaviours of the samples were verified by thermogravimetric analyzer (TGA, Q50, TA Instrument). The composite samples were heated from room temperature to 700°C in a nitrogen purged environment with a heating rate of 10°C/min.

DMA

Storage modulus and tan delta results of the composites were obtained from the dynamic mechanical analyzer (DMA, Q800, TA Instrument) by utilizing a dual cantilever setup under a temperature sweep setting. Prior to testing, the samples were first equilibrated at 30°C for 5 minutes, and then a 3°C/min heating rate was applied until the temperature reached 100°C. During the temperature ramping, a 15 µm, 1 Hz frequency oscillation was applied. In addition, the DMA was employed to characterize the shape memory performance of the samples under custom testing procedures by utilizing a tensile testing setup. First, the samples were stretched to 100% strain at 25°C. After stretching, the deformed samples were equilibrated at 75°C and a continuous measurement of recovery strain was recorded. After recovery, the samples were cooled back down to room temperature and prepared for the second SMP cycle.

RESULTS AND DISCUSSIONS

SEM & Morphologies
To study the dispersion of the TPU phase in the PLA matrix and the effect of MMT, SEM images of brittle fractured samples were taken. As shown in FIGURE 1, without the addition of MMT, TPU phases tend to form droplets within the PLA matrix, similar to the result reported in literature.\textsuperscript{42,43} As the sample was subjected to brittle fracture, part of the TPU phase may be knocked off (black spots) during fracture and create similar sized voids with sharp edges, as shown in FIGURE 1a and FIGURE 1b. Such images also imply that the TPU phase is not strongly bonded to the PLA matrix as the secondary phases can be easily removed. On the other hand, the addition of MMT has a significant impact on the morphology, increasing the compatibility of TPU and PLA. With a 1 wt% addition of MMT, the size of TPU particles slightly decreased from 500 nm to between 300 and 400 nm. Similarly, the holes sizes, corresponding to the TPU particles, also decreased. With an addition of 3 wt% MMT, the TPU phase becomes completely surrounded by the PLA matrix, indicating a dramatic improvement in the compatibility of the two polymers.

**FTIR**

The FTIR spectra of PLA, TPU, PLA/TPU blend, and PLA/TPU/1 wt% MMT are shown in FIGURE 2. The band at 1750 cm\textsuperscript{-1} corresponds to the –C=O group, one of the characteristic peaks of PLA.\textsuperscript{42,44} In comparison, the characteristic peak of TPU is found at 3300 cm\textsuperscript{-1}, and corresponds to the N-H bonds in the urethane group (-NHCOO-). The peaks of 2849 cm\textsuperscript{-1} and 2955 cm\textsuperscript{-1} can be identified as the symmetric and asymmetric vibrations of the polymer’s –CH\textsubscript{2} group, respectively.\textsuperscript{42} The presence of MMT can be identified by the peak at 460 cm\textsuperscript{-1}, which represents Si-O stretching.\textsuperscript{44} These results indicate that PLA and TPU were melt blended together successfully. Furthermore, the FTIR shows the absence of chemical reactions during the blending process as there are no newly identifiable chemical bonds.

**DSC**

**Isothermal Crystallization**

To understand the impact of the TPU and MMT blend on crystallization behaviour, isothermal DSC was performed under temperatures ranging from 100°C to 130°C. The isothermal curves are shown in FIGURE 3. Compared to the composite samples, pure PLA has a much broader curve, similar to results reported in literature.\textsuperscript{45} The sharp peaks of the composite samples indicate
fast crystallization rates, occurring much earlier in time than the peak for pure PLA.

**TABLE 1.** Isothermal crystallization half time under different isothermal temperature conditions.

<table>
<thead>
<tr>
<th>Testing condition</th>
<th>100°C</th>
<th>110°C</th>
<th>120°C</th>
<th>130°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PLA (min)</td>
<td>52.35</td>
<td>53.21</td>
<td>49.27</td>
<td>47.10</td>
</tr>
<tr>
<td>PLA/TPU (min)</td>
<td>6.39</td>
<td>6.55</td>
<td>11.46</td>
<td>14.61</td>
</tr>
<tr>
<td>PLA/TPU/1MMT (min)</td>
<td>4.78</td>
<td>4.69</td>
<td>9.75</td>
<td>12.29</td>
</tr>
<tr>
<td>PLA/TPU/2MMT (min)</td>
<td>5.03</td>
<td>5.60</td>
<td>9.40</td>
<td>13.25</td>
</tr>
<tr>
<td>PLA/TPU/3MMT (min)</td>
<td>6.42</td>
<td>8.03</td>
<td>9.03</td>
<td>11.03</td>
</tr>
</tbody>
</table>

**FIGURE 3.** Isothermal DSC curve for (a) 100°C, (b) 110°C, (c) 120°C, and (d) 130°C

The crystallization half time \(t_{1/2}\), when the material contains 50% relative crystallinity, corresponds to the curve peaks as is summarized in Table 1. As indicated in
TABLE 1, the initial addition of TPU significantly decreased the $t_{1/2}$. This is explained by the behaviour of TPU as nucleation sites in the composite, reducing the crystallization energy requirements in the interfacial regions between TPU and PLA and thus allowing faster growth of the PLA crystalline phase. At 100°C and 110°C, the $t_{1/2}$ ranges from 5 to 6 minutes. At isothermal temperature conditions above 120°C, $t_{1/2}$ increased past 10 minutes, indicating slower PLA crystal growth rate in comparison to lower temperature environments. In addition to the temperature effect on the growth rate, the addition of MMT slightly increased the $t_{1/2}$ at 100°C and 110°C. The same addition resulted in a slight decrease in $t_{1/2}$ for temperatures above 120°C. It is possible that MMT particles act as defects within the composite, restricting crystal formation with increases in MMT loading. Conversely, it is possible that higher temperature environments can induce more chain movement, causing the addition of fillers to have less influence on the growth of crystal phases.

**Nonisothermal Crystallization**

To understand the effect of TPU/MMT addition and annealing, DSC experiments were performed and the glass transition temperature ($T_g$), cold-crystallization temperature ($T_{cc}$), melting temperature ($T_m$), enthalpy of cold crystallization ($\Delta H_{cc}$) / melting ($\Delta H_m$), and percent crystallinity ($Xc\%$) are summarized in TABLE 2 and TABLE 3. DSC curves are shown in FIGURE 4. After the incorporation of 20 wt% of TPU, $T_g$ decreases from 62.86°C to 56.31°C, similar to the findings reported in literature. Upon addition of 1% MMT, $T_g$ decreased in comparison to the composite prior to MMT addition. $T_g$ increased for subsequently larger MMT percentages. The initial decrease in $T_g$ is due to presence of MMT particles while the $T_g$ increment in 2 and 3 wt% are due to the fact that more crystals were formed during fabrication. In addition, a small increase in $T_m$ can also be observed, likely due to enhanced crosslinking and the compact structure within the polymer. The addition of TPU is found to lead to a decrease in $T_{cc}$. The addition of MMT led to a further decrease in $T_{cc}$. These decreases are due to enhanced crystallization properties in the PLA/TPU and PLA/TPU/MMT composites. Long chain molecules in the composites are able to arrange themselves into a more structured crystalline phase at a lower temperature. This arrangement also leads to an increase in $\Delta H_{cc}$, as the crystalline structure can be formed easily due to the presence of TPU and MMT. Total crystallinity is calculated by subtracting $\Delta H_{cc}$ from $\Delta H_m$ and dividing this value by the melting enthalpy of a perfect PLA crystal (93.6 J/g). As the presence of TPU and MMT increased both $\Delta H_{cc}$ and $\Delta H_m$, the percent crystallinity only improved slightly. Despite the fact that TPU and MMT can help increase crystal nucleation, the presence of secondary phase, especially at high wt% content, may also prevent the formation of large crystalline structure. This trend aligns itself with the decrease and subsequent increased of $T_g$.

**TABLE 2. Thermal properties of PLA/TPU/MMT composites**

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ (°C)</th>
<th>$T_{cc}$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_{cc}$ (J/g)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$Xc%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PLA</td>
<td>62.86</td>
<td>107.19</td>
<td>159.61</td>
<td>9.924</td>
<td>19.03</td>
<td>9.72%</td>
</tr>
<tr>
<td>PLA/TPU</td>
<td>56.31</td>
<td>86.00</td>
<td>161.39</td>
<td>16.74</td>
<td>28.33</td>
<td>12.37%</td>
</tr>
<tr>
<td>PLA/TPU/1MMT</td>
<td>53.79</td>
<td>80.62</td>
<td>160.50</td>
<td>16.40</td>
<td>29.28</td>
<td>13.74%</td>
</tr>
<tr>
<td>PLA/TPU/2MMT</td>
<td>56.02</td>
<td>82.27</td>
<td>160.73</td>
<td>17.23</td>
<td>26.60</td>
<td>10.00%</td>
</tr>
<tr>
<td>PLA/TPU/3MMT</td>
<td>60.09</td>
<td>81.42</td>
<td>160.52</td>
<td>15.81</td>
<td>27.18</td>
<td>12.13%</td>
</tr>
</tbody>
</table>
In the presence of MMT, annealing has a large effect on the $T_g$ and $T_{cc}$. The annealed composite samples do not exhibit a glass transition phase as shown by the lack of an initial hill peak in FIGURE 4b. Therefore, $T_{cc}$ and $\Delta H_{cc}$ values are not available. The lack of a $T_g$ hill peak indicates that the sample has reached its maximum crystallinity level. Harris et al. indicated that the $T_g$ of annealed pure PLA was completely removed. However, our results indicate that the $T_g$ can only be removed with addition of secondary phase. Such a difference might be due to a pre-longed crystallization time, as the annealing time reported by Harris et al. was at least 15 minutes while the annealing time in our study was significantly longer. The difference in annealing time was also reflected in the percent crystallinity: we reported that in 10 minutes, annealed PLA reached a crystallinity of 26.15%. Harris et al. reported an annealed PLA crystallinity of 43%. On the other hand, we report almost identical crystallinity for samples without annealing. This result indicates that despite the short annealing time, maximum crystallinity was achievable through the blending of PLA with TPU and MMT. With the addition of TPU, a slight improvement can be observed in the percent crystallinity, as more nucleation sites are available for the growth of PLA crystal. With 3 wt% MMT, the MMT particles start to influence the crystalline structure as defects, and a small decrease in percent crystallinity can be observed. Following the overall improvement in crystallinity, a small enhancement of melting temperature can also be observed for samples undergoing annealing. Such a result suggests that better chain and crystalline structure formation can be induced, which also aligns with the results shown in pre-annealed samples.
FIGURE 4. DSC heating curve of (a) PLA/TPU/MMT and (b) annealed PLA/TPU/MMT

TGA

The results of the thermal degradation analysis are shown in FIGURE 5, with initial degradation temperature ($T_i$) and maximum weight loss slope ($T'_{\text{max}}$) data summarized in TABLE 4. Pure PLA exhibited the highest degradation temperature (324°C) while pure TPU exhibited the lowest degradation temperature (281°C). As PLA occupies a large weight percent content in the composites, the degradation curves appear similar to that of pure PLA. The presence of TPU can be seen through the slow-down in degradation rate after 380°C. The PLA was fully degraded at 400°C while the TPU portion within the composites continued degrading till 500°C. With the addition of MMT, the degradation curve shifts slightly to mirror the pure PLA curve, indicating an improvement in compatibility between the two immiscible phases.

FIGURE 5. Thermal degradation of PLA/TPU/MMT composites

TABLE 4. Thermal degradation of different PLA/TPU composites

<table>
<thead>
<tr>
<th></th>
<th>TPU</th>
<th>PLA</th>
<th>PLA/TPU</th>
<th>PLA/TPU/1MMT</th>
<th>PLA/TPU/2MMT</th>
<th>PLA/TPU/3MMT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_i$ (°C)</td>
<td>280.55</td>
<td>323.73</td>
<td>315.16</td>
<td>315.96</td>
<td>305.02</td>
<td>301.11</td>
</tr>
<tr>
<td>$T'_{\text{max}}$ (°C)</td>
<td>420.20</td>
<td>384.61</td>
<td>381.57</td>
<td>382.77</td>
<td>378.95</td>
<td>385.65</td>
</tr>
</tbody>
</table>
**Storage Modulus and Tan Delta**

The storage modulus and tan delta measurements of each composite are shown in FIGURE 6. The initial incorporation of MMT leads to a rise in storage modulus, with additional MMT decreasing the storage modulus from here. This is due to the storage modulus corresponding to the well-packed crystalline structure of the composite, with 1% MMT having higher crystallinity and 2%/3% MMT having a slightly lower crystallinity. With a temperature above 55°C, a significant decrease in the storage modulus is observed. Such behaviour indicates the start of a rubber-like softening in the glass transition phase. The glass transition temperature is indicated in FIGURE 6 by the point on the storage modulus diagram where the slope is a maximum. In the tan delta diagram, the glass transition temperature corresponds to temperature at which the peak occurs. FIGURE 6b shows the same trend in glass transition temperature as shown in Table 3 previously: a slight decrease with 1 wt% MMT and a slight increase with 2 and 3 wt% MMT. When the temperature is increased above 80°C, some fluctuations in tan delta can be observed as in FIGURE 6b. This is likely due to the soft nature of the samples at high temperatures.

Annealing created a significant increase in storage modulus. At 30°C, compared to the base PLA/TPU composite, a 1% addition of MMT led to a 150 MPa increase in modulus and a 2% addition of MMT led to a 650 MPa increase in modulus. This increase is likely due to the large amount of PLA crystalline phase created during the annealing process. The trend is also in conjunction with the results reported in Table 3. After annealing, an overall drop in tan delta from 1.3 to 0.35 can be observed, indicating a decrease in viscoelastic properties due to the crystalline phase. Furthermore, broader tan delta peaks can be observed in the annealed samples. It should be noted that unlike the DSC results in FIGURE 4b, the DMA results in FIGURE 6d show clear identification of annealed sample glass transition temperature. Annealing is shown to increase $T_g$ from 70°C to approximately 80°C, indicating that a larger energy input is required to reach the glass transition phase for annealed samples.
Shape Memory Recovery

To study the shape memory behaviour of the PLA/TPU/MMT composites, thin film samples were tested in a DMA environment for 2 continuous cycles, as shown in FIGURE 7. Each sample was stretched at 25°C to 100% strain and showed typical tensile elongation behaviour (shown by curve 1 in FIGURE 7). After 100% strain, the stress was removed and a small recovery in strain was observed (curve 2). The sample was then heated to 80°C and shape recovery occurred (curve 3). After the completion of shape recovery, the sample was cooled back to 30°C for a second shape memory testing cycle (curve 4).

The composites’ shape memory behaviours were characterized by the parameters of shape recovery ratio ($R_r$) and shape fixing ratio ($R_f$). These parameters are determined using the Equation (1) and Equation (2):

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

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

$\varepsilon_u$ is the strain after the unloading of the testing stress, $\varepsilon_p$ is the strain after shape recovery, and $\varepsilon_m$ is constant representing 100% strain. $R_r$ and $R_f$ results are shown in FIGURE 8. In this study, we only present the result of pre-annealed samples. Annealed composites were extremely brittle due to a large crystalline phase, featuring limited shape memory properties and an inability to stretch at room temperature.
In traditional SMP composites, deformation is usually applied at a temperature above the designed $T_{\text{trans}}$ for softening.\textsuperscript{6} We have demonstrated that PLA/TPU/MMT composites can be directly deformed at room temperature with almost 100% strain recovery, even across repeatable cycles. One of the earliest studies in the field depicts how high internal strain stored energy and low configurational state entropy contribute to the shape recovery process.\textsuperscript{13,25} If deformation is applied at a temperature below $T_g$, the low configuration state energy can be released at a low recovery temperature.\textsuperscript{25} As shown in FIGURE 7, the release of low state energy is less obvious for samples without MMT, while an initial 20% strain recovery can be observed in samples containing MMT at 40°C.

Such results indicate the improvement of PLA/TPU compatibility, as the stored strain energy can only be released when the two immiscible phases are closely connected by the compatibilizer. This result is supported by the SEM images in FIGURE 1. In comparison, the low state strain energy release is less obvious in the second cycle. The recovery curves (curve 2) show that about 10% strain is recovered between 30°C to 50°C. After the transition temperature, it can be observed that a major shape recovery occurred as full shape recovery is achieved before 75°C. The reason behind the less obvious strain energy release is likely due to the chain alignment during the first stretch/recovery cycle. Such alignment may overcome the effect of MMT presented in the matrix, as all curves

FIGURE 7. Shape memory cycle for (a) PLA/TPU, (b) PLA/TPU/1MMT, (c) PLA/TPU/2MMT, and (d) PLA/TPU/3MMT composites
exhibit a similar trend. This chain alignment hypothesis is also supported by the stress/strain curve during the stretching process. It can be observed that the force required to achieve same amount of strain (100%) in the second cycle is much less than in the first cycle as polymer chains are already aligned in favorable locations following the stretching in the first cycle.

FIGURE 8. Shape recovery ratio ($R_r$) and shape fixing ratio ($R_f$) of different wt% MMT in PLA/TPU composites

In addition, the incorporation of MMT significantly decreased the recovery ratio ($R_r$) of the PLA/TPU system, as shown in FIGURE 8. These results are also in good agreement with literature: Lai et al. showed composites with 70/30 wt% ratio of PLA/TPU system to have $R_r$ value of about 80% when stretched at room temperature. Due to the difference in material grade and TPU/PLA amount, this study reports a slightly higher value of 85%. However, with 1 wt% addition MMT, the $R_r$ value increased dramatically to close to 95% for the first cycle and 92% for the second cycle. Such improvement are likely due to the enhanced compatibility between PLA and TPU. With more than 2 wt% addition of MMT, the $R_r$ ratio starts to decrease. It is likely that the excess MMT particles act as defects between polymer chains and prevent shape recovery. On the other hand, the shape fixing ratio ($R_f$) stays close to 97% for all composites. This high $R_f$ is achieved due to the fact that deformation is applied under room temperature, and thus the samples undergo a large amount of plastic deformation. One of the major advantages of applying deformation at room temperature is that the materials do not need to be cooled to “freeze” the elastic phase for shape fixation after a strain is applied. Therefore, ability to deform in a low temperature environment indicates higher SMP efficiency.

CONCLUSIONS

In this paper, we present the effect of varying MMT content on PLA/TPU shape memory polymer composites. The incorporation of MMT altered the glass transition temperature and the crystallinity of the composites. In addition, small amounts of MMT were found to improve the mechanical properties of the composites as reflected by an increase in storage modulus. Due to these changes, the shape memory properties of the composites were also changed. When stretched at room temperature, an increase in recovery ratio from 85% to 95% was observed due to the improved polymer-polymer interactions induced by the MMT fillers. In comparison, the annealing process significantly enhanced the crystallinity of the composites and was followed by a large increase in storage modulus. However, due to the limitations posed on the shape memory effect due to high composite crystallinity, an optimized crystal content is essential for the best shape memory performance.

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GRAPHICAL ABSTRACT

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TITLE: Room Temperature Deformable Shape Memory Composite with Fine-tuned Crystallization Induced via Montmorillonite (MMT) Particles

PLA/TPU/MMT Nanoclay blends demonstrate superior shape memory effect with room temperature deformable capability. By adding 1 wt% MMT nanoclay content into the polymer blend, crystallinity of the composite can be fine tuned and shows 95% recovery ratio when stretched 100% under room temperature condition.