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Shape Memory Polyurethane with Polydopamine-Coated Nanosheets: Simultaneous Enhancement of Recovery Stress and Strain Recovery Ratio and the Underlying Mechanisms

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ABSTRACT

Two different sizes of polydopamine-coated layered double hydroxides (D-LDHs) are incorporated into polycaprolactone-based polyurethane (PU) to enhance the mechanical and

shape memory properties of the PU. The results show that D-LDH interacts strongly with hard segments and hence enhancing phase separation between hard and soft segments. It is found that the tensile moduli of the PU/D-LDH nanocomposites are much higher than that of neat PU at 60 °C. In comparison with neat PU, the nanocomposite with 2 wt% of small D-LDH exhibits a 60% increase in recovery stress while shape fixity and strain recovery ratio are also improved simultaneously. This is because at low filler loading, most small D-LDH nanosheets interact with hard domains and they are not large enough to connect neighbor hard domains. They can hence reinforce the hard domains without sacrificing the elasticity of the system. Two-dimensional X-ray diffraction studies indicate that most small D-LDH nanosheets are able to rotate back from aligned state to original random state in shape recovery process, justifying the improved strain recovery ratio.

INTRODUCTION

Shape memory polymers (SMPs) are light-weight smart materials that are able to maintain temporary shapes after deformation and restore the original (permanent) shape upon exposure to a stimulus such as heat¹⁻³, light^{4, 5} and water.⁶⁻⁸ Compared with shape memory alloys, SMPs, however, exhibit poorer dimensional stability, lower recovery stress and longer response time.⁹ Although substantial research work, including modification of polymer chain structures,¹⁰ copolymerization^{11, 12} and blending,¹³⁻¹⁶ has been conducted to enhance the shape memory performance of SMPs, the inferior mechanical properties of SMPs still remain an issue for many applications owing to their intrinsic viscoelastic behaviors. To address this issue, stiff nanofillers such as clay,^{2, 17, 18} nanorods,¹⁹ carbon nanotubes²⁰ and silica²¹ have been incorporated into SMPs in order to enhance their stiffness, recovery stress and dimensional stability. Nevertheless, previous reports showed that there was usually a trade-off between recovery stress and strain recovery ratio for the nanofiller-reinforced SMPs, i.e., the enhancement in recovery stress was usually accompanied by a reduction in recoverable strain.^{2, 22} For example, although the incorporation of 1 wt% organoclay into a polyurethane (PU)-based SMP could increase the recovery stress by 20%, it reduced the recovery strain of the SMP by 9%.²

PU-based block copolymers are one of the most popular classes of SMPs owing to their ability to recover large deformation, lower cost, ease in processing and biocompatibility.²³ The shape memory performance of PU-based SMPs is greatly correlated to their soft-segment crystallinity.²² A higher soft-segment crystallinity is beneficial in enhancing stiffness and shape fixing of the SMPs when the externally applied stress is removed.²⁴ However, although the incorporation of stiff nanofillers into PU would usually improve recovery stress, it may have

negative effect on soft-segment crystallization. As mentioned earlier, the addition of a small amount of organoclay into PU could significantly improve the recovery stress of PU-based SMPs. However, since the large and stiff organoclay are likely to interact with both hard and soft segments, an increase in organoclay loading caused a reduction in soft-segment crystallinity. The incorporation of organoclay also led to faster stress relaxation of the nanocomposites, leading to lower recovery ratio as well as shape fixity.² In fact, shape memory properties of PU nanocomposites are delicately influenced by many factors including the loading, size, shape, aspect ratio and surface chemistry of the nanofillers.^{19, 22} For example, Koerner *et al.* reported that the incorporation of surface functionalized carbon nanofiber (CNF) could promote strain-induced crystallization of a PU-based SMP owing to the formation of hydrogen bonds between the surface functional groups and the urethane linkages of PU. Therefore, the PU/CNF nanocomposites exhibited significant improvement in shape memory performances at low filler loadings.¹⁹ On the contrary, low loadings of alkylated ZnO nanorods, no matter large or small in size, could not give rise to enhanced shape memory properties due to inefficient strain-induced crystallization as a result of poor interfacial interaction.¹⁹ Other than surface chemistry, the size and location of nanofillers will also affect the mechanical properties of PU nanocomposites. Liff *et al.* showed that simultaneous enhancements of stiffness and toughness of PU can be achieved by adding hydrophilic Laponite (diameter of Laponite is around 25 nm and its thickness is 1nm) that has stronger affinity with hard segments of the PU. In this case, the soft segments of the PU remained mobile under deformation while hard microdomains were strongly reinforced by Laponite.²⁵ The aforementioned studies suggest that it may be possible to improve the recovery stress of PU-based SMPs substantially without sacrificing their strain recovery ratio by incorporating small stiff fillers that could selectively interact with hard segments strongly.

Inspired by the versatile adhesion capability of marine adhesive proteins,^{26, 27} polydopamine (PDA) coating has been widely researched in the past few years owing to its ease of preparation and attractive multi-functionalities.²⁸⁻³⁴ Our recent studies indicate that PDA-coated clay could interact strongly with hard segments of polyether-based PU owing to the abundant hydrogen bonding sites and stacking of aromatic rings. This strong interfacial interaction could give rise to higher hard-segment crystallinity and more distinct phase separation.³⁵ To verify that the recovery stress and strain recovery ratio of PU-based SMPs could indeed be improved simultaneously by manipulating filler size and surface chemistry, polydopamine-modified layered double hydroxide (D-LDH) of different sizes were incorporated into polycaprolactone (PCL)-based PU in this work. MgAl-LDH was selected as the fillers because its size can be easily controlled by altering hydrothermal conditions or time,^{36, 37} as well as its good mechanical and flame retardant properties.³⁸ PCL-based PU was chosen as the matrix since it has been widely researched as SMPs and can be facilely synthesized.^{2, 3} Herein we report drastic changes in crystallization behaviors of the shape memory nanocomposites induced by varying LDH size and surface chemistry. The effect of incorporation of D-LDH on phase morphology as well as the resultant mechanical and shape memory properties are investigated to establish structure-property relationships. Simultaneous enhancements of recovery stress and strain recovery ratio of the nanocomposites are demonstrated.

EXPERIMENTAL

Materials. Tris(hydroxymethyl)aminomethane (TRIS, 99%), dopamine hydrochloride (DOPA-HCl, 98%), sodium hydroxide (NaOH), magnesium chloride hexahydrate (MgCl_2), aluminium chloride hexahydrate (AlCl_3), sodium carbonate (Na_2CO_3), dibutyltin dilaurate

(DBTDL), 4,4'-methylenebis(phenyl isocyanate) (MDI) and 1,4-butanediol (BD) were purchased from Sigma-Aldrich and used as received. PCL diol (CAPA 2402, $M_w = 4000$) was kindly sponsored by Fu Yuan Enterprise (Singapore). *N,N*-Dimethylformamide (DMF, anhydrous grade) were obtained from Tedia. Acetone and methanol (technical grade) were obtained from Aik Moh and used without further purification.

Preparation of PCL-based PU. PCL diol and BD were dried overnight in vacuum oven at 45 °C. The prepolymer was synthesized at 90 °C by reacting MDI and PCL diol for 3 hours under nitrogen with mechanical stirring. It was then chain extended by adding BD in the presence of 0.05 wt% of DBTDL as catalyst and reacted at 90 °C for another 3 hours. Anhydrous DMF was added into the reactor occasionally when necessary to reduce the viscosity of reactant mixture. The final polymer concentration in DMF was about 25 wt%. The viscous solution was precipitated in methanol and dried in vacuum oven at 60 °C for 2 days. The feed molar ratio of MDI/PCL diol/BD was 6/1/5, corresponding to estimated hard-segment content of about 33 wt%. The weight-average molecular weight of the synthesized PCL-based PU is 6×10^4 g/mol (polydispersity index = 1.28) as determined by size exclusion chromatography (SEC, Waters 2690, using PMMA as standard) in THF solution at 25 °C.

Preparation of LDH. Mg_2Al-CO_3 -LDH was prepared according to the report by Xu, *et al.*³⁶ $MgCl_2$ (2.0 mmol) and $AlCl_3$ (1.0 mmol) were mixed in 20 mL of deionized (DI) water and the mixed salt solution was then quickly added (within 5s) into 80 mL of mixed base solution containing 0.15 M NaOH and 0.013 M Na_2CO_3 under vigorous stirring for 20 min. The LDH slurry was obtained by high-speed (10000 rpm) centrifugation and washed twice with DI water. The washed slurry was re-dispersed in 80 mL of DI water and the aqueous suspension was transferred into a stainless steel autoclave with a Teflon lining, followed by hydrothermal

treatment in preheated oven at 100 °C for a period of time. Two types of LDH with different sizes were prepared. The small filler was obtained by 4 h of hydrothermal treatment and designated as S-LDH, while the large filler was prepared by 62 h of hydrothermal treatment and named as L-LDH. Both fillers were surface-modified by PDA coating using the method reported in our previous work.^{28, 32, 35, 39} The stable LDH suspension (0.32 g of LDH) was dispersed in 320 mL of DI water containing 0.39 g of TRIS and stirred for 15 min. 0.48 g of DOPA-HCl was added into the LDH suspension and reacted for 2 h, followed by washing with acetone for 4 times. The PDA-coated LDH was then dispersed in DMF for further use. The small and large PDA-coated LDH were named as D-SLDH and D-LLDH, respectively.

Preparation of PU nanocomposites. PU nanocomposites were prepared via solution mixing. The synthesized PCL-based PU was first re-dissolved in anhydrous DMF at the concentration of 3 g/mL. A certain amount of D-SLDH or D-LLDH was added into the PU solution, respectively, and the mixture was stirred continuously for 24 h. To verify the vital role played by PDA modification, a certain amount of unmodified S-LDH was also added into the PU solution to make a reference sample. All nanocomposite films were obtained by solution casting on glass petri dish and subsequently removing the solvent at 60 °C in vacuum for 24 h. Neat PCL-based PU film was obtained using the same method without adding fillers. All casted films (~ 0.2 mm in thickness) were kept at ambient temperature for at least 5 days before characterization.

Characterization. Atomic force microscopic (AFM) images of LDH were obtained in tapping mode using Nanoscope IV from Digital Instruments. The particle sizes of LDH and morphologies of the nanocomposites were characterized using transmission electron microscopy (TEM). TEM was performed using a JOEL 2100 TEM at 200 kV. The nanocomposites were embedded in cured epoxy and microtomed using Leica Ultracut UCT into about 50-100 nm

thickness at $-100\text{ }^{\circ}\text{C}$. To observe the nanophase morphology, the grids were exposed to RuO_4 vapor (0.1 g ruthenium trichloride hydrate mixed with 5 ml of 14.5 % active chlorine aqueous sodium hypochlorite) for 2 h. The staining step provides contrast between the hard and soft segments where hard segments appeared as dark particles in bright soft segments matrix. Fourier transform infrared spectroscopic (FTIR) measurements were performed using a Shimadzu FTIR IR Prestige-21 using KBr pellets. Each sample was scanned 16 times at a resolution of 4 cm^{-1} . LDH contents in the nanocomposites were determined by thermo-gravimetric analysis (TGA) using TA Instrument TGA Q500. The specimens were heated from $25\text{ }^{\circ}\text{C}$ to $800\text{ }^{\circ}\text{C}$ at $20\text{ }^{\circ}\text{C}/\text{min}$ in air (purge rate = $60\text{ mL}/\text{min}$). Based on the TGA results (cf. Figure S1), the nanocomposite samples are designated as PU/D-SLDH-2, PU/D-SLDH-4, PU/D-LLDH-2, PU/D-LLDH-4 and PU/SLDH-2, respectively, where D- indicates PDA modification while the numbers show the weight percentages of LDH. The amount of PDA coating on LDH was about 14 wt% as determined by TGA result (cf. Figure S2). Thermal behaviors of the PCL-based PU and its nanocomposites were characterized using TA Instrument DSC Q10 at a ramp rate of $20\text{ }^{\circ}\text{C}/\text{min}$ in temperature range from $-90\text{ }^{\circ}\text{C}$ to $220\text{ }^{\circ}\text{C}$. The first melting and cooling curves were taken for analysis. For each sample, the heat of crystallization and fusion were calculated based on the mass of PU in the sample. The percentage of soft-segment crystallinity was determined as the ratio of the heat of fusion ($\Delta H_{m,s}$) obtained from DSC to the heat of fusion of 100% crystalline PCL diol, 136 J/g .⁴⁰ To study the orientation of D-LDH in the nanocomposites, X-ray diffraction (XRD) patterns of the strained and recovered shape memory samples were recorded using a Bruker GADDS diffractometer equipped with a two-dimensional (2D) area detector with $\text{CuK}\alpha$ radiation. The azimuthal average of the 2D XRD patterns was determined using the GADDS software package to obtain intensity versus 2θ plot. To obtain the extent of D-LDH orientation,

the radial average intensity of the 2D XRD patterns in the 2θ range of $11-12^\circ$ was determined using the same software to obtain intensity versus azimuthal angle plot.

Measurements of tensile and shape memory properties. The tensile properties were tested at room temperature and 60°C using Instron Micro Tester 5848 which equipped with a temperature chamber. The tests were conducted according to ASTM D882 at a crosshead speed of 20 mm/min with a 2 kN load cell. Samples were cut into rectangular shape (5 mm x 40 mm) and three replicates of each material were tested. Limited by the temperature chamber, the maximum elongation in the tensile test was 780 %. Shape memory properties were evaluated using a TA Instrument DMA 2980 using the tensile mode. The specimens (typically 5 mm x 20 mm x 0.2 mm) were stretched at 60°C at a strain rate of 20 mm/min to 200 %, followed by cooling quickly down to room temperature with the aid of a fan for 15 min. The stress was then released, part of the strain was immediately recovered and the shape fixity was measured. The recovery stress was measured using isostrain mode (preload = 0.002N, displacement = 0.001%) by reheating the specimens at $3^\circ\text{C}/\text{min}$ from ambient temperature to 90°C . The recovery ratio was evaluated by placing the pre-strained specimens in preheated oven at 60°C for 5 min, the recovered length was taken after cooling down the specimens. Shape fixity and recovery ratio are defined as:

$$\text{Shape fixity \%} = \frac{l_d - l_0}{l_{200\%} - l_0} \times 100\%$$

$$\text{Recovery ratio \%} = \frac{l_d - l_f}{l_d - l_0} \times 100\%$$

Where l_d is the sample length after removal of the tensile load during shape fixing, l_0 the original length of the sample at room temperature, $l_{200\%}$ the length after stretching at 60°C with tensile load in place, and l_f the final recovered length of the stretched specimen.

RESULTS AND DISCUSSION

Synthesis of D-LDH

To study synergistic effects of nanofiller size and surface chemistry, LDH nanosheets of different sizes were prepared in the first place. The lateral sizes of S-LDH and L-LDH are 38 ± 9 nm and 126 ± 40 nm, respectively, based on TEM analysis for 100 samples (typical images and size distribution are given in Supporting Information Figures S3a-d). AFM analysis shows that the aspect ratios of both S-LDH and L-LDH are in the range of 10-13 (Figures. 1a and 1b). To enhance the interactions between the nanosheets and the PU, both types of LDHs were coated with PDA. The successful surface modification was verified by FTIR spectra. In Figure 1c, the infrared bands at 787 and 1360 cm^{-1} for S-LDH and D-SLDH are due to the vibrations of metal oxide and CO_3^{2-} in LDH, respectively.³⁶ For PDA and D-SLDH, the strong band at 1610 cm^{-1} can be attributed to O-H bonds in PDA. Meanwhile, the broad peak above 3000 cm^{-1} (O-H stretching) of S-LDH is shifted towards lower wavenumber after PDA coating owing to enhanced hydrogen bonding. This suggests that PDA has been successfully coated on the nanosheets. The successful coating of PDA on S-LDH surface is also verified by TEM image (Figure S3c), the PDA coating is about 2 nm in thickness.

Figure 1. AFM images of (a) S-LDH and (b) L-LDH; the insets show the aspect ratios of typical S-LDH and L-LDH. (c) FTIR spectra of S-LDH, D-SLDH and PDA.

Dispersion states of D-LDH in PU

Upon the surface modification, both types of D-LDH fillers can be dispersed well in DMF, making solution blending with the PU possible (Scheme 1). From TEM images shown in Figure 2, it can be seen that both D-SLDH and D-LLDH are mainly in the form of individual nanosheet

without severe stacking, indicating good compatibility between the D-LDHs and PU matrix. The nanosheets, however, tend to form small and disordered clusters, especially at higher filler content. At the same filler content, the dispersion of D-SLDH in the matrix was in general better than that of D-LLDH, presumably because greater energy is required to overcome the attraction force between larger platelets. By contrast, without PDA coating, the dispersion of S-LDH in the PU was obviously poorer than that of D-SLDH (Figure 2e), which is probably due to the poorer dissolution of S-LDH in DMF.

Scheme 1. Preparation of PU/D-LDH nanocomposites.

Figure 2. TEM images of (a) PU/D-SLDH-2, (b) PU/D-SLDH-4, (c) PU/D-LLDH-2, (d) PU/D-LLDH-4 and (e) PU/SLDH-2, showing dispersion states of the nanosheets.

Effects of incorporation of D-LDH on phase morphology

To enhance recovery stress of the PU while retaining or even improving its reversibility at the same time, it is desirable to have phase separated morphology and selectively incorporate functionalized nanofillers into hard domains. In this case, the deformation of the soft segments could be easily fixed/recovered upon thermal stimuli. To investigate the effects of the incorporation of D-LDH nanosheets on PU phase morphology, the microtomed TEM nanocomposite thin films were stained with RuO₄ for determination of domain sizes. The results show that the hard domains (dark region) in neat PU are spherical in shape and smaller than the ones in the nanocomposites (Figure 3 and Table 1). It suggests that D-LDHs can act as nucleating agents for hard domain, on account of the **strong interactions** between the hard segments and PDA coating on LDH.^{19, 35} **The catechol groups on the PDA coating can form hydrogen bonds with both urethane and ester linkages of the hard segments. In addition, the π - π stacking between the aromatic rings of PDA and MDI units of the hard segments also contribute to the strong interfacial interactions between D-LDHs and hard segments.** It is interesting to note that some hard domains in PU/D-LLDH-2 are connected to each other probably by interacting with the same D-LLDH nanosheet or nearby nanosheets in the same cluster, forming elongated or irregular shaped large hard domains (marked by circles). Still, most hard domains in PU/D-LLDH-2 are much smaller than the size of D-LLDH and hence some D-LLDH nanosheets cross soft domains (marked by arrows). This may hinder the motion of soft segments during deformation and affect strain recovery. Differently, for PU/D-SLDH-2, although some large dark regions can be observed but the distribution of hard-domain size is apparently less heterogeneous than that of PU/D-LLDH-2. In addition, it seems that D-SLDH platelets are mainly found in dark regions. Since the average size of the hard domains in PU/D-SLDH-2 (16 nm) is about 40% of

that of SLDH (38 nm), it is reasonable to assume that most D-SLDH platelets are not large enough to cross two hard domains that are separated by soft-segment region (the distance between two hard domain is about 15 nm). Instead, due to the favorable interactions of PDA with hard segments, a typical D-SLDH platelet may preferably pass through a hard domain with its edge embedded in soft-segment region. This will be beneficial to strain recovery, as will be demonstrated later. Indeed previous research has shown that similar nucleating effect on PU hard domains induced by the incorporation of chitin nanocrystals into the PU results in significant enhancement in shape memory properties of the nanocomposites.⁴¹

Figure 3. TEM images of stained (a) PU (the region in blue box is enlarged), (b) PU/D-SLDH-2 and (c) PU/D-LLDH-2, where the dark regions are hard domains.

Table 1. Hard domain sizes of neat PU and its nanocomposites based on TEM observations. 50 measurements were taken for each sample. **The size distributions are presented in Supporting Information Figures S4.**

	PU	PU/D-SLDH-2	PU/D-SLDH-4	PU/D-LLDH-2	PU/D-LLDH-4
Hard domain size (nm)	11 ± 2	16 ± 4	15 ± 3	22 ± 6	20 ± 5

Thermal behaviors of the nanocomposites

In PCL-based PU, PCL soft domains are the reversible phase, i.e., their crystallization and melting behaviors govern the reversibility. For the nanocomposites, the crystallization and melting behaviors of the soft segments are critically influenced by phase morphology and location of the fillers. From Table 2, it is noticeable that with the D-LDH, the glass transition temperatures (T_g) of the as-casted thin films are all slightly higher than that of neat PU, and the T_g increased with increasing filler content, implying that some PDA-coated nanosheets interacted with the soft segments, restricting the motion of the soft segments to some extent. In contrast to the nanocomposites with D-LDHs, the nanocomposite with unmodified S-LDH (PU/SLDH-2) exhibits significantly lower T_g . This can be attributed to the poor dispersion of S-LDH and the poor interactions between S-LDH and the soft segments, which is probably due to the lack of hydrogen donor on LDH surface. It is also important to note that the T_g of PU/D-SLDH-2 is very close to that of neat PU, implying that the amount of D-SLDH in soft domains is limited when the filler size is small and filler content is low. It is worth noting that here T_g is not determined by crystallinity as all the as-casted nanocomposite samples have roughly the same heat of fusion for soft domains ($\Delta H_{m,s}$), implying that they have almost the same soft-segment crystallinity.

The DSC data obtained from the first heating curves reflect the initial properties of the SMPs used in shape memory tests.⁴⁰ As mentioned in the introduction, shape memory properties of PU-based SMPs are closely related to their soft-segment crystallinity. Previous reports show that the incorporation of organoclay, silicon carbide (SiC) nanoparticles, CNF and carbon black all reduce the soft-segment crystallinity of the PU-based SMP nanocomposites.²² By contrast, the PU nanocomposites studied in this work exhibit no reduction in initial soft-segment crystallinity

regardless of whether the LDH is modified with PDA probably because the flat, relatively rigid LDH and D-LDH would not hinder the crystallization of the soft segments in the casting process. More importantly, the D-LDH surface promotes the crystallization of the soft segments in thermal events, as shown by the DSC data obtained from the first cooling curves.

Table 2. Thermal behaviors of the neat PCL-based PU and its nanocomposties. $T_{g,s}$, $T_{m,s}$, $T_{m,h}$, $\Delta H_{m,s}$ and $\Delta H_{m,h}$ were obtained from the 1st heating DSC traces, while T_c , $\Delta H_{c,s}$ and $\Delta H_{c,h}$ were obtained from the subsequent cooling traces. The heating and cooling were all conducted at 20 °C/min (cf. [Figure S5](#)).

	Soft segment					Hard segment			
	$T_{g,s}$ (°C)	$T_{m,s}$ (°C)	$\Delta H_{m,s}$ (J/g)	$T_{c,s}$ (°C)	$\Delta H_{c,s}$ (J/g)	$T_{m,h}$ (°C)	$\Delta H_{m,h}$ (J/g)	$T_{c,h}$ (°C)	$\Delta H_{c,h}$ (J/g)
PU	-51.3	51.0	21.2	-26.9	4.4	192.1	9.1	161.6	9.5
PU/ SLDH-2	-56.1	46.6	23.4	-18.8	7.7	186.5	7.9	151.4	7.4
PU/D-SLDH-2	-51.1	49.8	22.3	-8.8	14.7	188.5	9.9	169.8	13.0
PU/D-SLDH-4	-47.5	50.0	23.3	-1.0	17.9	189.5	9.6	169.2	12.0
PU/D-LLDH-2	-50.7	50.4	23.6	-18.9	10.8	190.2	10.9	164.1	11.0
PU/D-LLDH-4	-48.9	52.2	22.3	-11.1	11.3	191.0	7.8	168.1	10.2

To verify that D-LDHs could indeed promote phase separation strongly, crystallization behaviors of the nanocomposites upon fast cooling were investigated. It is striking to see that for all the nanocomposites, both hard and soft domains crystallized at much higher temperatures and

achieved much higher crystallinity (as reflected by heat of crystallization) than those of neat PU upon fast cooling (Figure 4 and Table 2). This is because that the strong interactions between the PDA coating and hard segments could act as nucleation sites for crystal growth.^{19, 35} The enhanced crystallization of hard segments promotes phase separation, facilitating subsequent crystallization of soft segments. Consequently, the nanocomposites also exhibit much higher soft-segment crystallization temperature ($T_{c,s}$) and heat of crystallization ($\Delta H_{c,s}$) than neat PU (Figure 4a). At higher filler content, the increase in $T_{c,s}$ and $\Delta H_{c,s}$ may also be related to the nucleating effect of D-LDHs to some extent as some D-LDHs are also in contact with soft domains. It is worth noting that D-SLDH promotes crystallization more effectively than D-LLDH at same filler loading as the former has larger surface area. However, without the PDA-coating, S-LDH does not show any nucleating effect for the hard segments under fast cooling ($T_{c,h}$ and $\Delta H_{c,h}$ are lower than that of neat PU). As a result, soft-segment crystallization is not significantly promoted. This indicates that PDA coating on the LDHs plays a critical role in promoting crystallization. The enhancement in soft-segment crystallization is beneficial for shape fixing process.

Figure 4. (a) Soft-segment crystallinity of neat PU and its nanocomposites determined from 1st heating cycle. Crystallization temperatures and heat of crystallization of (b) soft segment and (c) hard segment of neat PU and its nanocomposites upon fast cooling.

Mechanical properties

Tensile properties of neat PU and its nanocomposites at room temperature and 60 $^{\circ}\text{C}$ are summarized in Figure 5. Typical tensile curves are given in Supporting Information (cf. [Figure S6](#)). Below the soft-segment melting temperature, both the nanocomposites and neat PU show plastic yielding behavior (cf. [Figure S6](#)). The moduli of the nanocomposites at room temperature are only marginally higher than that of neat PU since all the as-casted thin films exhibit similar

crystallinity (Table 2). The reinforcement brought by D-SLDH is slightly more significant than D-LLDH at the same filler content owing to the more effective stress transfer from PU matrix to D-SLDH as a result of the larger surface area of D-SLDH. Without PDA modification, the modulus of PU/SLDH-2 is similar to that of neat PU due to poor dispersion of SLDH and ineffective stress transfer between polymer chains and SLDH. Above soft-segment melting point, the reinforcement effect of nanosheets becomes more dominant in determining the modulus.² Since D-LDHs have preferred interactions with hard segments, more impressive reinforcement effect is observed at 60 °C in comparison with that of neat PU. Notably, the modulus enhancement brought by D-SLDH is significantly higher than that brought by D-LLDH at same filler content. This is due to the larger surface area of the small size filler, which gives rise to more extensive interactions between D-SLDH and hard segments. Furthermore, ultimate elongation of PU/D-SLDH-2 at 60 °C is significantly higher than those of the other three PU/D-LDH nanocomposites as well as neat PU probably because PU/D-SLDH-2 undergoes the most prominent hard-segment crystallization; with larger D-LDH or higher content of D-LDH, significant amounts of D-LDH nanosheets may interact with soft segments that would disturb phase separation and hinder hard-segment crystallization. The presence of D-LDH in soft domains would also retard soft-segment mobility, reducing ductility of the material. Without the surface modification, the poor dispersion of the unmodified S-LDH leads to poor mechanical properties of PU/SLDH-2 at 60 °C.

Figure 5. Tensile properties of PU/D-LDH nanocomposites at (a) room temperature and (b) 60 °C. Strain at break at room temperature is not shown as all the samples did not break within the elongation limit of the tensile test machine.

Shape memory properties

Shape memory properties of the nanocomposites and neat PU are presented in Figure 6. Obviously, the nanocomposites exhibit better shape memory properties, including shape fixity,

recovery stress and recovery ratio, than neat PU. Among the five nanocomposite samples, PU/D-SLDH-2 shows the most prominent enhancement in shape memory performance; the recovery stress is 64 % higher than neat PU while both shape fixity and recovery ratio are also improved simultaneously. The improved shape fixity of the nanocomposites can be attributed to enhanced soft-segment crystallization, which hinders the relaxation of the stretched soft segments so that most deformation can be retained effectively after the shape fixing step. The great enhancement in recovery stress can be attributed to the mechanical reinforcement provided by the D-LDHs and the improvement in hard-segment crystallization. Without PDA surface modification, PU/SLDH-2 exhibits better shape memory properties than neat PU, whereas its recovery stress is much lower than that of PU/D-SLDH-2 because the poorer mechanical properties of PU/SLDH-

2.

Figure 6. Shape memory properties of PU and its nanocomposites.

A great challenge faced by shape memory polymer nanocomposites with stiff fillers is that they usually lead to a reduction in recovery ratio.^{2, 22} By contrast, in this work a substantial increase in recovery stress and moderate enhancements in shape fixity and recovery strain ratio are achieved simultaneously by the incorporation of only 2 wt% D-SLDH. The enhancement in recovery ratio is mainly due to the small size of D-SLDH and the strong interactions between the PDA coating and hard segments, which make D-SLDH preferably interacting with hard segments. In particular, the small size of the nanosheets ensures that most D-SLDH nanosheets would not cross soft-segment region to connect hard domains. Thus, above the soft domain melting temperature, both the hard and soft domains are able to relax freely and hence the recovery capability of the nanocomposite is enhanced significantly. To verify this claim, 2D-XRD was performed to probe the orientation states of the nanosheets after shape fixing and shape recovery steps, respectively. Since all samples were obtained by solvent casting, there is no filler orientation in the as-casted samples, as shown in Figure 2. Figure 7 shows that both D-SLDH and D-LLDH have preferred orientation along the direction of the stress applied after the shape fixing process. The degree of orientation of the nanosheets in PU/D-LLDH-2 is higher than that in PU/D-SLDH-2. After the shape recovery process, some D-LLDH nanosheets remained in the aligned orientation, leading to lower shape recovery ratio as shown in Figure 6. By contrast, there is almost no preferred orientation for the nanosheets in PU/D-SLDH-2 after the shape recovery step, *i.e.*, they are able to rotate back to the original random state.

Figure 7. Azimuthal profiles of 2D XRD patterns in the 2θ ranges of $11-12^\circ$ of pre-strained and recovered nanocomposite samples, showing the different orientational states of the LDH nanosheets. Solid lines are Lorentzian fitting curves.

CONCLUSIONS

In summary, prominent enhancement in shape memory properties is achieved by incorporating D-SLDH at low content. The incorporation of both D-SLDH and D-LLDH promotes phase separation and crystallization of hard and soft domains significantly, on account of the nucleating effects induced by strong interfacial interactions between D-LDHs and hard segments; the enhanced hard-segment crystallization promotes phase separation and the subsequent soft-segment crystallization. The introduction of D-SLDH at low loading gives rise to appreciable enhancements in tensile modulus while preserving the chain mobility of soft segments. On the

contrary, large and rigid nanosheets (D-LLDH) would hamper the chain mobility of soft segments, leading to lower strain recovery ratio. Thus, simultaneous enhancement in shape fixity, recovery stress and strain recovery ratio are achieved by incorporating 2 wt% D-SLDH. The mechanism proposed is verified by the study of orientation states of the D-LDH nanosheets in shape fixing recovery processes. Without PDA surface modification, poor filler dispersion is observed. The incorporation of S-LDH without PDA modification could not boost recovery stress substantially due to the poor interfacial interactions between fillers and the polymer chains.

ASSOCIATED CONTENT

Supporting Information

TGA curves of PU, PU/D-LDH nanocomposites, S-LDH and D-SLDH; TEM images of S-LDH, L-LDH and D-SLDH; DSC curves; Tensile curves of PU and PU/D-LDH nanocomposites. This material is available free of charge via the Internet at <http://www.elsevier.com/>

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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