Thermoplastic polymer nanocomposites based on polydopamine-coated clay : preparation, structures and properties

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NANYANG
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THERMOPLASTIC POLYMER NANOCOMPOSITES
BASED ON POLYDOPAMINE-COATED CLAY:
PREPARATION, STRUCTURES AND PROPERTIES

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Abstract

Polymer/clay nanocomposites have been widely investigated over past three decades due to the dramatic boost in properties at low filler content. Although organoclay (clay modified with organic surfactants) is commonly used to reinforce the polymer, yet the reinforcing extent has yet reached the optimum performance. Besides, both organic surfactants (organic compounds with long hydrophobic tails and hydrophilic heads) and polymers are susceptible to photo-induced degradation especially in outdoor environments, making polymer/clay nanocomposites vulnerable in practical applications. In order to overcome the aforementioned problems, in this research, D-clay (polydopamine-coated clay) was studied as multifunctional filler to improve not only interfacial interactions with a wide range of polymer matrices but also stabilities of the nanocomposites. D-clay was incorporated into both elastomer (polyurethane) and semi-crystalline thermoplastic (polypropylene) systems. The structure-property relationships of the resultant nanocomposites were investigated using TEM, XRD, DMA, tensile testing, FTIR, TGA and DSC. In particular, the reinforcing mechanism of D-clay in polyurethane (PU) nanocomposites was studied with respect to surface chemistry, filler loading and filler size. On the other hand, the stabilizing function of D-clay was verified using polypropylene (PP) as the polymer matrix since PP is well-known for its poor UV stability.

Firstly, D-clay was incorporated into polyether-based PU via solvent mixing and good filler dispersion was obtained. The results showed pronounced improvement in mechanical properties, such as stiffness, tensile strength and strain at break, at 3wt% clay loading. The remarkable improvement can be attributed to the excessive hydrogen bonds between D-clay and the hard segments (hard segments are made of diisocyanate and the short-chain diol) of PU. This strong interfacial interaction between D-clay and

hard segments not only facilitates the stress transfer across the filler and polymer matrix, but also acts as nucleating agent for hard segment crystallization, leading to higher hard segment crystallinity.

Furthermore, the impact of high D-clay loading on mechanical properties and hard segment crystallization was investigated using polyester-based PU as matrix since severe phase separation was observed in the polyether-based PU. The results showed polyester-based PU nanocomposites with D-clay concentration above 5 wt% formed percolated clay network structure, this hindered the movement of both hard and soft segments to a certain extent. Consequently, polyester-based PU/D-clay nanocomposites showed drastic enhancement in tensile modulus.

On the other hand, the effect of particle size was studied using polycaprolactone (PCL)-based PU as matrix. In this case, polydopamine-modified layered double hydroxides (D-LDHs) of different sizes were used as the fillers and the shape memory performance of the nanocomposites was evaluated. It was found that D-LDH interacted strongly with hard segments, enhancing phase separation and promoting crystallization of both hard and soft segments profoundly. The nanocomposite with 2 wt% of small D-LDH exhibited good shape memory properties since most small D-LDH interacted with hard domains at low filler loading. Hence, the incorporation of small D-LDH can reinforce hard domains without sacrificing the elasticity of the system.

In order to verify the stabilizing capability of D-clay, D-clay was also introduced into the PP system. This is because PP is vulnerable to degradation owing to the presence of volatile tertiary hydrogens in the polymer backbone. The results showed drastic improvement in UV resistance and thermal stability of PP/D-clay owing to the effective radical scavenging ability of melanin-like PDA layer on clays. Meanwhile, the excellent UV resistance of PP/D-clay nanocomposites can be attributed to the

masking effect imposed by PDA coating. Besides, the mechanical properties of PP/D-clay were better than organoclay at similar clay loading on account of the stronger interfacial interactions.

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List of Abbreviations

1,4-BD	1,4-butanediol
2D XRD	Two-dimensional wide-angle x-ray diffraction
30B-clay	Cloisite 30B (organoclay)
AFM	Atomic force microscopic
ASTM	American society for testing and materials
ATR	Attenuated total reflection
DBTDL	Dibutyltin dilaurate
DI water	Deionized water
DMA	Dynamic mechanical analysis
DMF	N,N-dimethylformamide
DSC	Differential scanning calorimetry
DOPA	3,4-dihydroxy-L-phenylalanine
DOPA-HCl	Dopamine hydrochloride
D-clay	Polydopamine-coated clay
D-LDH	Polydopamine-coated layered double hydroxide
DPPH	2,2-diphenyl-1-picrylhydrazyl
EDA	Ethylenediamine
FTIR	Fourier transform infrared spectroscopy
IM-clay	Clay modified by 1-hexadecyl-2,3-dimethylimidazolium chloride
LDH	Layered double hydroxide
L-LDH	Large layered double hydroxide
MAP	Mussel adhesive protein
MAPP	Maleic anhydride-grafted-polypropylene
MDI	4,4'-methylenebis(phenyl isocyanate)
MDSC	Modulated differential scanning calorimetry
MMT	Montmorillonite
Na-MMT	Sodium montmorillonite
OOT	Oxidative onset temperature

PCL	Polycaprolactone
PDA	Polydopamine
PP	Polypropylene
PPMA	Maleic anhydride-terminated-polypropylene
PPNH ₂	Amine-terminated-polypropylene
PU	Polyurethane
SMP	Shape memory polymer
SPU	Polyester-based polyurethane
S-LDH	Small layered double hydroxide
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
T _c	Crystallization temperature
T _d	Decomposition temperature
T _{HD}	Melting temperature of hard domain crystallites of variable sizes
T _m	Melting temperature
T _g	Glass transition temperature
TPU	Thermoplastic polyurethane
TRIS	Tris(hydroxymethyl)aminomethane
UV	Ultraviolet
UV-vis	Ultraviolet-visible spectrophotometry
XPS	X-ray photoelectron spectroscopy
WAXD	Wide angle X-ray diffraction
ΔH _c	Enthalpy of crystallization
ΔH _m	Enthalpy of melting

Chapter 1 Introduction

1.1 Background

Polymer nanocomposites have attracted enormous attention in the last three decades ever since Toyota group first discovered that impressive mechanical reinforcement could be achieved by incorporating less than 5 wt% nanoclay in polymer nanocomposites.¹ Layered aluminasilicates, such as montmorillonite (MMT), are potential reinforcement fillers owing to their copiousness, cheap price and high stiffness.² Other than mechanical improvements, homogeneous dispersion of nanoclay in polymer can also lead to superior thermo-oxidative stability, barrier properties, solvent stability, reduced flammability and etc.²⁻⁵ In general, excellent dispersion of nanoclay is the prerequisite in order to achieve optimum stiffness for nanocomposites. Yet, the bonus in stiffness enhancement changes from system to system as a result of the difference in interfacial interactions between the fillers and polymer matrices.

The practical applications of these polymer/clay nanocomposites also depend on their effective lifetime in service environments, particularly in outdoor environments where polymers are prone to photo-degradation due to excessive ultraviolet (UV). Besides, polymers are also susceptible to thermo-oxidative degradation at high temperature under prolonged processing time.⁶ Conventionally, hydrophilic clay surfaces are modified by organic surfactants with long hydrophobic alkyl tails so as to improve their compatibility with polymer matrices and ultimately facilitate their exfoliation. However, these small organic molecules are prone to degrade into free radicals when exposed to the elevated temperature⁷ or in outdoor environments,

expediting the degradation of the polymer matrices.^{8, 9} In addition, such organic modifiers can only interact weakly with the polymer matrices via van der Waals interactions in most cases. This results in a relatively poor interfacial stress transfer.¹⁰

In recent years, mussel adhesive proteins (MAPs) have attracted strong interest owing to their versatile and strong adhesions onto various surfaces in marine environment. It was claimed that the remarkable adhesive capability of MAPs is related to high concentration of 3,4-dihydroxy-L-phenylalanine (DOPA) units near the interface between the adhesive footprint of mussel byssal and the substrate.¹¹⁻¹³ In an attempt to simulate the superior adhesive capability of MAP, polydopamine (PDA) has been successfully synthesized via self-polymerization of synthetic dopamine under basic conditions. Such PDA coating has then been widely used as a versatile surface modification agent for various applications owing to the ease of preparation and its attractive multifunctionalities.¹⁴⁻²⁰ It was found that the PDA coatings form coordination chelate bonds with inorganic surfaces (e.g. metal oxide and silica surfaces) and the bonding strength of three to four such bonds can be as large as a covalent bond.²¹ The chemical reactions of PDA with various kinds of clay minerals were also investigated in previous work.²²⁻²⁴ Moreover, the catechol groups of PDA can form hydrogen bonds with the electronegative functional groups of organic polymers.²¹ It is postulated that the PDA coating can improve the stress transfer across the organic-inorganic interfaces.

Besides, melanin-like PDA can serve as free-radical scavenger.²⁵⁻²⁷ In fact, melanin is commonly known as natural pigments to protect human body from excessive UV exposure by extinguishing reactive radicals generated under UV irradiation.²⁵ For instance, thermal stability of poly(methyl methacrylate) and polypropylene (PP) was found to be impressively enhanced by adding 0.5-5 wt% melanin-like nanoparticles.²⁶

In the presence of reactive radicals, it was shown that melanin oxidized to the related quinone. Consequently, it was able to extinguish the reactive radicals by hydrogen atom transfer.²⁸ Previous research claimed that the efficiency of the radical scavenging activity can be further accelerated by the adding metal ions, such as Mg^{2+} .²⁸ Other than superior free radical scavenging capability, the stabilizing function of melanin-like macromolecule against UV irradiation can be attributed to its ability to absorb deleterious radiation and efficiently scatter the energy via non-radiative paths.^{25, 29, 30}

Inspired by the work mentioned, PDA-coated clay (D-clay) was first introduced into epoxy and it was found that the modulus was impressively enhanced by adding low clay loadings.¹⁰ The drastic improvement in stiffness could be attributed to the formation of both covalent and hydrogen bonds between epoxy and PDA coating.¹⁰ It is postulated that D-clay fits better to those polymer matrices bearing electronegative functional groups.

1.2 Research motivation and hypothesis

Although numerous research has been done to synthesize polymer/clay nanocomposites with a wide range of polymers, the reinforcing extent has yet reached the optimum performance. This is probably due to the inefficient interfacial interactions between organoclay and polymer.³¹ Additionally, the organic modifiers and polymers are commonly susceptible to photo-induced and processing-induced degradations,^{6, 7, 9} leading to shorter service life and even malfunction of the system. To overcome the problems stated, D-clay was incorporated into two model systems in this work and the underlying mechanisms were studied.

It is believed that without the contribution of covalent bonding, the excessive hydrogen bonding sites provided by catechol groups of D-clay can also give rise to impressive improvement in mechanical properties at low filler concentration. In this context, PU was selected as the system to study since the performance of PU is greatly related to the hydrogen bonding between polymer chains and fillers. To avoid the complexity in analysis due to formation of covalent bonding, PU was mixed with D-clay using solvent blending method. It is proposed that the strong interfacial interactions may improve the phase separation of PU system, and eventually translate into the properties, such as mechanical properties, shape memory performance and gas barrier properties, of the resultant nanocomposites. Insights gained from exploring the physical interfacial interaction in PU/D-clay system may help to develop other polymer nanocomposites with significant property enhancements.

In addition to the reinforcement effect, it is also anticipated that D-clay possesses high radical scavenging efficiency owing to the high surface area of thin PDA coating on exfoliated clay layers. In this case, PP was selected as the polymer system to verify the radical scavenging capability of D-clay since PP is well-known to degrade via radical-initiated chain scission due to the presence of tertiary hydrogen with low dissociation energy.²⁶ Knowledge obtained from investigating the stabilizing mechanism of D-clay in PP system may promote the development of reliable polymer nanocomposites, especially for outdoor applications.

1.3 Objectives and scope of the study

The first objective of my PhD work is to verify that the strong physical interfacial interactions between PU polymer chains and D-clay can lead to an impressive boost in

mechanical properties at low filler concentration. To get rid of any possibility of forming covalent bonds, PU/D-clay nanocomposites were synthesized via simple solvent mixing followed by casting at low temperature. The reinforcement mechanism of D-clay in PU was investigated from the aspect of interfacial interaction, filler loading and filler size. The phase morphology and crystallization behaviour of the resultant PU nanocomposites were studied in detail to gain a fundamental understanding on the structure-property relationship.

The second objective of my PhD work is to examine the efficiency of the radical scavenging capability of D-clay in PP system. To facilitate the dispersion of D-clay in PP matrix, amine-functionalized PP oligomer was chosen as the compatibilizer since amine group may form covalent bonds with D-clay. The thermal stability and UV resistance of the resultant nanocomposites were explored and evaluated. In addition, the reinforcement effect of D-clay in semi-crystalline PP was investigated to verify the simultaneous stabilizing and reinforcing functions of D-clay in the polymer system.

1.4 Organization of the thesis

The thesis begins with the background of polymer/clay nanocomposites and highlights the motivation of this research work on the preparation of PU/D-clay and PP/D-clay nanocomposites. In Chapter 2, the structures, preparation and properties of polymer/clay nanocomposites and the characteristic properties of polydopamine are reviewed. Chapter 3 describes the materials and methodology for all the work done in the thesis. The reinforcing effects of PDA-coated filler in PU system in terms of interfacial interaction, filler loading and filler size are discussed in detail in Chapter 4, 5 and 6, respectively. Chapter 4 presents the mechanical properties and crystallization

behaviours of polyether-based PU/D-clay nanocomposites at low D-clay loading. The study is further explored by incorporating high D-clay loading into polyester-based PU in Chapter 5. Chapter 6 examines the impacts of particle size of PCL-based PU/D-LDH nanocomposites on mechanical and shape memory properties. Subsequently, Chapter 7 presents the simultaneous stabilization and reinforcement effects of D-clay in PP system. Finally, Chapter 8 summarizes the important findings that have been done in this thesis and proposes recommendations for future research.

Chapter 2 Literature Review

2.1 Structure and properties of clay

Since 1980s, layered silicates such as montmorillonite (MMT) have been widely researched as reinforcement fillers for polymer nanocomposites owing to their abundance, low price, good chemical stability, good barrier property, good heat resistance, high aspect ratio, high surface area and good stiffness.^{5, 32} Layered silicates are crystalline minerals which consist of very thin and stiff layers that are built up by layers of octahedral sites of either magnesium oxide or alumina fused to two tetrahedral layers of silica. These thin layers are stacked together in parallel arrangement by the strong electrostatic forces between the counter ions and van der Waals forces with a regular gap called interlayer spacing. The thickness of each layer is about 1 nm while the lateral diameters are in the range of 30 nm to several microns.⁵ Therefore, the aspect ratio of each clay layer can be as high as few thousands which is beneficial for polymer reinforcement. The most attractive point of layered silicates is the ease of surface modification since the charge deficiency generated by isomorphic substitution (*i.e.* Fe^{2+} or Mg^{2+} replacing Al^{3+} within the octahedral layer of MMT) within the clay minerals can be easily counterbalanced by organic cations adsorbed between the clay layers.^{1, 33, 34} The ability of clay minerals to adsorb and exchange cations is defined as cation exchange capacity (CEC). In the primary form, the charge deficiency on the clay surfaces is counterbalanced by exchangeable metal ions, such as Na^+ , Li^+ or Ca^{2+} that are located within the interlayer spacing. To optimize the performance of polymer/clay nanocomposites, it is desirable to disperse clay particles

into individual layers and ensure the surface chemistry of the clay mineral is compatible to the respective polymer matrix. Yet, it is challenging to obtain good clay dispersion due to incompatibility and strong electrostatic attraction between clay layers, especially for non-polar polymer matrices.

Although MMT is abundant and relatively cheap, its major disadvantage is the variability in composition and contaminants that are difficult to be removed.³⁵ In recent years, there has been considerable interest in synthetic layered double hydroxides (LDHs) as prominent reinforcement fillers in polymer nanocomposites owing to their tuneable structures and chemical compositions, good mechanical properties, transparency as well as flame retardant properties.³⁶⁻⁴⁰ The generic formula of LDHs can be represented as $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}]_{x/n} \cdot zH_2O$, where M^{2+} and M^{3+} can be common divalent and trivalent metal ions, respectively, while A^{n-} can be any type of anions.^{38, 40} Different with MMT, the surfaces of LDH are usually positively charged and the anionic surface modification is more straightforward than MMT.³⁵ Other than the attractive advantages of other inorganic layered materials, the size of LDHs can be easily controlled by alternating the hydrothermal period and stable suspension of LDH suspensions can be obtained.^{38, 39} Similar with clay, LDHs were usually modified with organic surfactants to enhance their dispersities in polymer nanocomposites and in most cases, significant improvements in mechanical properties and thermal stabilities could be achieved by adding less than 5 wt% LDHs.^{36, 41} Therefore, polymer nanocomposites remained light and stiff with addition of low amount of LDHs. However, the main drawbacks of LDHs are the low dehydroxylation temperature that disrupts of the crystalline structure. In addition, the relatively fragile platelets make the processing of nanocomposites become harder.³⁵

Figure 2-1. Chemical general structure of (a) montmorillonite clay (MMT)³² and (b) layered double hydroxide (LDH). (Reprinted with permission from Leroux, F.; Besse, J. Chem. Mater. **2001**, 13, 3507-3515. Copyright 2001 American Chemical Society.)

2.2 Organic modification of clay

Generally speaking, clay modification is a crucial step to improve its compatibility with a wide range of polymers as well as reduce the unfavorable stacking attraction between the clay layers. Conventionally, organic surfactants with long hydrophobic

tails are used to modify the clay surfaces. The long alkyl chains not only make the clay surfaces become more hydrophobic, but also enlarge the interlayer spacing between the clay layers. The enlarged interlayer spacing could disrupt the strong interlayer electrostatic interactions between the clay layers and enable polymer molecules diffuse into the clay layers. The surface chemistry of clay must be carefully designed for various types of polymer matrices due to compatibility issues. For examples, non-polar polyolefin favours full coverage of aliphatic modifiers on the clay surfaces while polar polyamide demands a balance between the interlayer spacing and the organic modifier loading.⁴²⁻⁴⁶

However, most organic surfactants suffer from poor thermal and environmental stabilities. In fact, the alkyl ammonium surfactants are susceptible to thermo-oxidative and photo degradation especially during melt compounding process and in outdoor environment.³⁴ To tackle the low thermal stability of alkyl ammonium-modified clay, imidazolium and phosphonium salts have been introduced to modify clay via ion exchange procedures. Fox *et al.* claimed that the imidazolium modified clay has much higher decomposition temperature compared to ammonium-treated clays and the corresponding imidazolium salt.⁶ In addition, the thermal degradation temperature of phosphonium modified clay was about 50 °C higher than ammonium modified clay.³³ Recently, Toh *et al.* has successfully synthesized a rigid POSS-imidazolium-modified montmorillonite which exhibited superior high thermal stability and large interlayer spacing.⁴⁷ On the other hand, Naveau *et al.* has invented a greener clay modification process in which clay was modified in supercritical carbon dioxide (scCO₂) environment without using any solvents.⁴⁸

2.3 Polymer/clay nanocomposites

2.3.1 Morphology of polymer/clay nanocomposites

The mixing of polymer and clay may not form a nanocomposite due to thermodynamically immiscible. Commonly, three types of morphology structures can be obtained by adding clay into polymer: phase immiscible microcomposite, intercalated nanocomposites and exfoliated nanocomposites.³²

Figure 2-2. Schematic illustration of three different kinds of morphology obtained in polymer/clay composites: (a) phase immiscible microcomposites, (b) intercalated nanocomposites and (c) exfoliated nanocomposites.

When the two components are totally immiscible, the polymer chains are unable to diffuse into the interlayer spacing between clays and hence large clay tactoids are observed in micron size, a conventional phase-separated microcomposite forms. The microcomposites are usually obtained by direct mixing the unmodified clay with the polymer. The poor interfacial interaction between polymer and clay will result in poor or even deleterious properties. Consequently, it is imperative to modify clay surfaces

so that the mixing process is thermodynamically favourable. In the intercalated nanocomposites, the interlayer spacing between clay platelets is enlarged by the insertion of polymer chains yet clay layers still assembly themselves in ordered multilayer structure with alternating polymer and clay layers. Ideally, an exfoliated nanocomposite is expected to achieve impressive improvement in properties. In exfoliated state, clay platelets are separated into individual layers and dispersed homogeneously throughout the polymer matrix. The exfoliated clay is believed to possess large interfacial area and high aspect ratio, forming a close network with the polymer matrix.⁴⁹ However, exfoliated state still remains a challenge for polymer/clay nanocomposites, a mixture of exfoliated and intercalated dispersion state was obtained in most cases. There are few points to take note to achieve optimum exfoliated dispersion: (a) the interlayer spacing between clay layers must be large enough to allow the polymers enter, (b) the organic surfactants used must be compatible with the polymer matrix, (c) the organic surfactants can sustain to high processing temperature.

The dispersion state of clay in polymer can be evaluated using polarizing optical microscopy (POM), X-ray diffraction (XRD), and transmission electron microscopy (TEM). POM provides an overall illustration of clay dispersion at the micron or sub-micron level. XRD indicates the presence of intercalated structures. In intercalated nanocomposites, the interlayer spacing between clay layers can be determined using Bragg's Law, $\lambda = 2d\sin\theta$, where λ is the wavelength of the X-ray radiation, d corresponds the average spacing between diffraction lattice planes and θ is the diffraction angle. With enlarged interlayer spacing, the diffraction peak shifts to lower angle values. With more disordered clay dispersion, the diffraction peak becomes broaden and lower in intensity. On the other hand, an exfoliated structure results in disappearance of diffraction peak. In this case, TEM is used to examine the dispersion

state of clay in nanocomposite. TEM enables the direct visual observation of dispersed clay layers in the nanometer level, yet the area of TEM observation is too small to represent overall dispersion state of clay. Therefore, TEM is always complemented with XRD analysis to identify the structure of the nanocomposite.

2.3.2 Properties of polymer/clay nanocomposites

Polymer/clay nanocomposites have been widely explored since the Toyota research team published nylon 6 nanocomposites in late 1980s owing to their light-weight and impressive boost in performances, such as improved strength, modulus, thermal stability and barrier property. Generally speaking, the optimum properties of nanocomposites can only be obtained if the layered silicates were exfoliated into individual layers such that the size of the fillers was in atomic or molecular levels.⁵⁰ It is believed that the impressive reinforcements brought by nanoclay can be attributed to the interfacial interactions between the clay and polymer. Besides, the constrained region around the dispersed clay restricts of the mobility of polymer chains, leading to increment of stiffness. In brief, good exfoliated structure and intimate contact between clay and the polymer are the prerequisites for outstanding reinforcement effect.⁴⁴

Nylon is the most popular and successful system in the field of polymer/clay nanocomposites owing to the significant improvement in properties and the ease of processing. Paul group has already published a large deal of detailed scientific works on the organoclay-based nanocomposites. According to composites theories of Halpin-Tsai and Mori-Tanaka, nylon/clay nanocomposites outperformed the conventional

glass fiber reinforced composites in mechanical reinforcement since clay can reinforce in two directions.⁴²⁻⁴⁶

Besides, the surface of dispersed clay can also act as heterogeneous nucleating sites for polymer crystallization, leading to the formation of transcrystalline region at the interface. The formation of this transcrystalline region can serve as reinforcement in semi-crystalline polymer.^{51, 52} In most cases, the incorporation of clay give rise to higher crystallinity owing to the nucleating effects of nanoclay, provided that the polymer has strong interfacial interaction with the organocaly.³²

At the same time, polymer/clay nanocomposites always show enhanced thermal stability at low clay loading due to labyrinth effect imposed by the dispersed clay in the nanocomposites.^{1, 32, 33} The non-volatile inorganic filler can serve as the barrier to delay the evaporation of the degraded products and the diffusion of gas molecules.⁵³ It was reported that the onset degradation temperature of PS/clay nanocomposites is about 50 °C higher than that of neat PS on account of the formation of carbonaceous char layer on the surface of the nanocomposites. The thermal stability of PS/phosphonium-clay nanocomposites was better than that of other counterparts (e.g. ammonium clays) owing to the higher decomposition temperature of the phosphonium-clay. Hence, the char barrier layer formed by phosphonium-clay can sustain to higher temperature to delay the polymer degradation.⁵⁴

Regardless the general enhancement in thermal stability of nanocomposites, the incorporation of clay can also accelerate the thermal degradation.^{9, 55} It was found that the hydroxyl groups on clay's surface can act as active acidic sites to catalyst the initial degradation of the nanocomposites.⁵⁵ The improved thermal stability tested by TGA does not warranty that the nanocomposites show good stability under processing

environments. Previous work claimed that both the organoclay and PP compatibilizer promote the degradation of the nanocomposites during processing.⁹ Besides, the presence of Fe ions in clay intensifies the decomposition of hydroperoxides, promoting the subsequent polymer degradation.⁵⁶ Although the incorporation of clay has two contradictable effects on the thermal stability of the nanocomposites, it is still possible to achieve impressive improvement in thermal stability by modifying the clay modification which will be discussed later in this work.

2.3.3 Typical methods to achieve effective exfoliation

There are three common strategies to fabricate polymer/clay nanocomposites: in-situ polymerization, melt intercalation and solution mixing. Good exfoliation of clay could be obtained using in situ polymerization, however, this method requires extremely stringent synthesis conditions where the layered silicates are first intercalated with monomers and the corresponding catalysts followed by polymerization. In this case, polymerization occurs within the interlayer spacing between clays. As the polymer chain grows, the interlayer spacing between clays becomes larger and eventually the clay layers can be delaminated. Particularly, in-situ polymerization is useful to prepare nanocomposites at high clay loading, such as polypropylene, polyurethane, nylon, epoxy and etc.^{57, 58} Different with in-situ polymerization and solution casting process, melt intercalation does not require any organic solvents and hence it is widely used in industry. Melt compounding method is useful to prepare thermoplastic polymer/clay nanocomposites. During melt compounding, the high shear force facilitates clay exfoliation and enables polymer chains to diffuse into the clay layers at high temperature. The ideal exfoliated dispersion can be easily achieved using twin-screw

extrusion, provided that the clay surfaces have been sufficiently modified to become compatible with the respective polymers.⁵⁰ Yet, the research found that high shear intensity is not the best solution for high levels of exfoliation as the clay particles might fracture and the short processing time is inefficient for polymer diffusion.⁵⁹ For solution mixing method, a common solvent was used to disperse or dissolve clays and polymers. This technique is useful for water soluble polymers, such as PAA, PVP, PEO, PLA.⁵⁰ The layered silicates are first swollen by solvent molecules, followed by intercalation of the polymer chains by substituting the previously intercalated solvent. The effect of different solvents on the clay dispersion and the morphology of the PU/organoclay nanocomposites have been studied. The results showed that the chemical affinity between clays and solvents plays a crucial role in solvent mixing, especially when the interaction between clay and the polymer is rather weak.⁶⁰

2.3.4 Effects of interfacial interactions on properties

According to previous research, the attractive interaction between the polymer and organic modifier is the lowest among all interactions in polymer/clay nanocomposites.⁶¹ In brief, the interaction between the polymer and the clays are mainly attributed to weak intermolecular forces, such as hydrogen bonding, van der Waals forces, phi-phi interactions and etc; covalent bond is hardly involved.⁵⁸ There are some composite theories and equations to monitor and predict the reinforcement degree of polymer/clay composites, including Halpin-Tsai model, Mooney's equation, Einstein equation, Mori-Tanaka theory and so on.^{31, 44, 62} To date, the highest Young's modulus of the polymer/clay nanocomposites is only about 10 GPa although the estimated stiffness of layered silicates is about 250 to 260 GPa. Thus, the interfacial

stress transfer parameter values of polymer/clay nanocomposites are at least one order of magnitude smaller than the composites which form covalent bonds between fillers and matrix.³¹ Therefore, there are still plenty of room to improve the reinforcing extent of nanoclays by further improving the interfacial interactions between polymer and layered silicates.

Other than mechanical properties, the interfacial interactions between clays and polymer will also affect the gas permeability of the nanocomposites. For instance, there is an increase in oxygen transmission rate of polyurethane/clay nanocomposites with poor interfacial interactions, i.e. the clay surfaces are modified by hydrophobic organic surfactants. In contrast, a 30 % reduction in oxygen transmission rate was achieved at 3 vol% when the clay was modified with hydrophilic organic surfactants.⁶³

2.4 Characteristic properties of polydopamine

2.4.1 Strong adhesion capability

In recent years, mussel adhesive protein (MAP) has attracted increasing attention owing to the ease of preparation and impressive adhesion capability towards various materials. Waite group reported that the top of the mussel adhesive protein, which is in contact with the substrates, consists of high loading of DOPA and lysine (Lys) units compared to other parts of the byssal thread.⁶⁴ Previous work claimed that the superior adhesion capability of adhesive pads can be attributed to the chemical interactions between the unoxidized catechol groups of DOPA and the functional groups on the surface of the solid substrate.¹¹

Inspired by the versatile adhesive capability of MAPs, Messersmith group has successfully synthesized several novel DOPA-containing polymers which can be used in biomedical applications and functional polymer composites.⁶⁵⁻⁶⁷ The versatile adhesive capability of DOPA-containing polymers has been demonstrated by Messersmith et al.; they functionalized polyethyleneimine (PEI) with DOPA units and used this modified PEI as a powerful surface primer to facilitate the layer-by-layer assembly on virtually all substrates.⁶⁷ A copolymer glue based on methyl methacrylate and mussel-inspired dopamine methacrylamide has been produced and the results showed impressive improvement in bonding strength between metal substrate and polymeric cement.⁶⁸ The superior stress transfer ability of DOPA was proven by using modified PEG which contains large amount of DOPA units. The results showed that catechols can serve as effective load transfer agents within LbL composite films, leading to impressive improvement in both stiffness and toughness.⁶⁵

Scheme 2-1. Schematic illustration of mussel adhesive protein and the possible chemical structures of polydopamine.

Other than the impressive adhesion strength of DOPA, Lee et al. found that the PDA coating is capable to carry out secondary reactions with organic materials, such as Michael addition or Schiff base reactions, showing its promising potential in organic chemistry.¹⁵ In 2006, Phillip Messersmith and his colleagues have first quantified the remarkable attraction force of DOPA onto both organic and inorganic surfaces using single-molecule force experiments. The results showed that three to four coordination bonds between DOPA and inorganic surface are as strong as a covalent bond.^{12, 21} It is also believed that the formation of DOPA-metal coordination interactions is reversible and self-healable under water.^{11, 12, 69} Furthermore, large amount of work have been done to functionalize the material surfaces with DOPA building blocks using a simple dipping method to obtain material-independent and multifunctional reagents for further applications.^{64, 66} On the other hand, the PDA exhibited different reactivity with various types of clay minerals.²²⁻²⁴

Inspired by the versatile strong adhesion of DOPA to both organic and inorganic materials, it is hypothesized that DOPA can serve as a bridging as well as load transfer agent between clay and polymer. In this work, clay surfaces are modified with adhesive polydopamine to render catechol-rich coating on the clay surfaces. This catechol-rich coating may interact stronger with the polymer matrices compared to the conventional organic surfactants via the extensive hydrogen bonding. As a result, the properties of the polymer/clay systems can be significantly enhanced at relatively low clay concentration.

2.4.2 Photo-protective capability

Other than superior adhesion capability, PDA can also serve as free-radical scavenger since its chemical structure is analogous to that of melanins.²⁵⁻²⁷ Melanins are also well-known as anti-oxidants as well as natural sunscreens against broad range UV and visible radiations.²⁵ Recent research claimed that the thermal stabilities of poly(methyl methacrylate) and polypropylene (PP) have been significantly enhanced by adding 0.5-5 wt% melanin-like synthetic particles.²⁶ It has been postulated that melanin can be easily transformed to the corresponding quinone in the presence of reactive oxygen radicals and radicals, extinguishing the reactive radicals by hydrogen atom transfer. In addition, the efficiency of the radical scavenging activity can be augmented in the presence of metal ions, such as Mg^{2+} .²⁸ Despite the excellent radical scavenging ability, recent studies also showed that the UV-protective function of melanin-like macromolecule can be attributed to its ability to absorb harmful radiation and scatter the excited energy effectively via non-radiative relaxations.^{25, 29, 30} Previous research claimed that melanin is able to quench the excited states of positively charged porphyrin pigments by ionic bonding the molecules in femto or pico second, and hence the excited energy can be transfer from porphyrin to melanin molecule effectively.²⁵

2.4.3 Polydopamine as multifunctional interface agent

Other than attractive adhesion capability and radical scavenging ability of PDA, polydopamine can also be used as multi-functional interface agent to improve the performance of the materials. Recently, Lee and his co-workers have successfully

modified graphene oxide via one step method in which the polymerization of poly(norepinephrine) will simultaneously reduce and surface functionalize the graphene oxide.⁷⁰ Furthermore, PDA-coated graphene nanocomposites showed significant enhancements in mechanical, thermal, anti-UV and electrical properties owing to the multifunctional interfacial PDA coating.²⁰ PDA-modified clay hydrogel also exhibited excellent performance in water treatment and self-healing capability upon removal of applied force.¹⁸ Moreover, PDA can be utilized as the carbon source for energy storage applications and SnO₂ nanoparticles coated with thin carbonized PDA coatings showed pronounced improvement in cycling capability and coulombic efficiency. This can be attributed to the buffering effect and good electrical conductivity of the carbonized PDA layers.¹⁷ PDA coating can also be used to fabricate advanced mineralized biomaterials since the PDA layers assist the nucleating of hydroxyapatite by concentrating calcium ions at the interfaces.⁷¹

2.5 Polyurethane/clay nanocomposites

In this work, PU was selected as the model matrix to investigate the reinforcement effect of PDA-coated filler. Herein, a brief background about PU is reviewed. Thermoplastic polyurethanes (TPUs) are composed of alternating hard and soft segments. Due to the difference in polarities of hard and soft segments, TPU usually exhibits two-phase morphologies. In general, the stiffness of TPU is governed by the hard segments, whereas their elasticity is governed by the soft segments. Typically, TPUs usually exhibit low stiffness and stresses at low to intermediate strains,^{72, 73} and it is challenging to improve the tensile modulus of a TPU while retaining its high elongation and *vice versa*.

In 1998, PU/clay nanocomposites have been first introduced by Pinnavaia and his colleagues and the resulting nanocomposites showed impressive improvement in mechanical properties; the stiffness, tensile stress, and tensile strain are enhanced simultaneously by more than 100% by adding only 10 wt% organoclay.⁷⁴ The dramatic enhancement in tensile properties can be attributed to the exfoliated clay dispersion and the hydrogen bonding formed between the clay surfactants and the polymer chains. The strong hydrogen bond between surfactants and hard segments can be evidenced from the FTIR spectra at 1709 cm^{-1} owing to hydrogen-bonded carbonyl groups, this hydrogen bond enhances the stiffness of the polymer significantly. Moreover, the organic surfactants located on clay surfaces may also act as plasticizers during stretching, leading to chain conformation at the filler-polymer interface during deformation and hence lead to higher elongation.⁷⁵⁻⁸⁰

Other than the impressive mechanical performance, PU/clay nanocomposites also exhibit enhanced barrier properties. It is well-accepted that the impermeable clay layers will form a tortuous pathway on gas and molecular diffusion and hence good permeation-barrier properties can be easily obtained by adding low volume concentration of clay. In spite of the impermeability of the fillers, the interface between the fillers and the polymer chains also plays a crucial part in permeation performance. The organoclay modified by two long alkyl chains without hydroxyl groups will eventually lead to incompatibility between the surfactants and PU chains, thus small gas molecules are able to diffuse through the loosely-packed interface. Conversely, modifiers with hydroxyl groups which form strong hydrogen bonds with the polymer chains will give rise to significant decrease in transmission rate for both water and gases owing to the densely-packed interface.⁶³

Numerous researches have been focused on the synthesis of PU/clay nanocomposites by using solution and melt compounding methods. Among the synthesis methods, melt compounding is less effective to disperse clay throughout the matrix. For solution based processes, in-situ polymerization enables close interactions between the fillers and polymer as cross-linking structures can be obtained during the synthesis, yet this strong interactions may reduce the molecular weight of the polymer chains and eventually result in poorer elongation.⁸¹ Mishra et al. claimed that the properties of TPU/clay can be further fine-tuned by adding organoclays at different stages during polymerization.⁸² To further optimize the mechanical properties, unmodified laponite was successfully incorporated into TPU system via solvent-exchange method. AFM results showed that clay particles were mainly located in hard microdomains, hence the toughness of TPU/laponite can be preserved. This can be attributed to the greater affinity of laponite to hard domains due to hydrogen bonding. In other words, the soft segments remain mobile under deformation.⁸³

In general, the performance of TPU is mainly contributed by hydrogen bonding between the polymer chains and the fillers. It is believed that the PDA-coated fillers could stiffen and toughen TPU more effectively compared to organoclay owing to the extensive hydrogen bonding provided by catechol groups.

Scheme 2-2. General chemical structure of polyurethane.

2.6 Polypropylene/clay nanocomposites

Since one of the objectives of this work is to explore the radical scavenging capability of PDA-coated filler, PP was selected as the polymer matrix as it is susceptible to thermal and photo-degradations.²⁶ Polypropylene is the most widely used commodity thermoplastics owing to its low price, light weight, ease of preparation and recyclability. However, its mechanical properties and environmental stabilities are inferior to most engineering plastics such as nylons. As a consequence, clay was incorporated into PP to make it become more competitive. Nevertheless, the incompatibility of the non-polar PP and polar clay surfaces is the main challenge to delaminate the clay layers in PP matrix. In order to conquer this issue, compatibilizer with polar functional group and polyolefin unit was added to promote the clay dispersion. The most popular compatibilizer is maleic anhydride-grafted-PP (MAPP) in which maleic anhydride unit can form hydrogen bond with the silica unit of the clay.⁸⁴⁻⁸⁶ In addition, Szazdi et al. claimed that MA groups can also form strong chemical bonds with organic modifiers which contain active hydrogen groups.⁸⁷ The loading of MA group and the molecular weight of the MAPP used in nanocomposites system must be carefully designed to avoid the immiscibility of the compatibilizer in the PP matrix. Although higher amount of MA units can assist the diffusion of MAPP oligomers into the clay galleries, it may lead to phase separation and heterogeneous structure in the matrix, resulting in poor mechanical performance.⁸⁸⁻⁹¹ To obtain the best dispersion state, the hydrophobic clay was first melt compounded with MAPP to attain the intercalated MAPP/clay master batch and this master batch was subsequently compounded with PP resins to further disperse clay in the matrix.

Since PP is non-polar polymer, it is necessary to alter the polarity of clay surfaces with organic modifiers so that the mixing process is thermodynamically favourable. Reichert and his co-workers found that the length of the alkyl chain surfactants must be larger than 12 carbon atoms in order to achieve good dispersion state and improved mechanical properties.⁹² However, most of the organic small molecules suffer from poor thermal and environmental stabilities; they are susceptible to degrade during the melt compounding process. In addition, the unmodified clay surfaces may catalyst the initial thermal decomposition of PP due to the active hydroxyl groups at the edge of the clay layers and the metal cations between the silicate galleries.⁵⁵ In order to further improve the clay dispersion, organic swelling agent has been introduced into clay layers. The swelling agent evaporated during compounding process, facilitating the diffusion of polymer chains into clay layers.⁹³

Despite the interfacial interactions between PP and fillers, PP is also inclined to processing-induced and UV-induced degradation⁹⁴ due to the existence of volatile tertiary hydrogen.²⁶ Therefore, it is imperative to improve the UV resistance of PP since it is widely utilized in outdoor environments. However, the organic modifiers with long alkyl tails are prone to degrade into reactive free radicals at high temperature⁷ as well as under UV exposure through oxidative reactions. This resulted in adverse degradation of the polymer and eventually shorten the service life of the resulting products.^{8,9}

Plenty of work has been done to improve the adhesion interaction between the polyolefin and the layered silicates. Yet, the breakthrough is sparsely achieved due to the poor chemical compatibility. In this case, PDA-coated filler can serve as a solution for better interfacial interaction due to the superior adhesive capability of the catechol

groups. At the same time, the radical-initiated degradation of polypropylene can be drastically reduced by incorporating low amount of D-clay on account of the effective radical scavenging capability of PDA coating.

2.7 Summary

A brief review of the literature regarding the preparation and properties of polymer/clay nanocomposites has been introduced in this chapter. Generally speaking, the extent of enhancement brought by the incorporation of clay is greatly influenced by the dispersion state of clay in the nanocomposite and the interfacial interaction between clay and the corresponding polymer. However, obtaining optimum clay exfoliation still remains a challenge and the reinforcement extent achieved to date still far from the expected optimum performance. In addition, organic surfactants used to modify the clay surfaces are prone to degrade when exposed to high temperature and outdoor environment. As a result, it is necessary to optimize the clay modification such that the clay surfaces can provide strong interfacial interaction with a wide range of polymers. At the same time, the modifier used can stabilize the polymer under harsh environmental conditions. In this case, polydopamine (PDA) coating is introduced to serve as a universal surface modifier since PDA exhibits strong adhesive capability towards a wide range of materials. In addition, melanin-like PDA particle can act as free-radical scavenger to protect the underlying polymer from degradation. In this work, the fillers were modified with PDA coating and subsequently incorporated into PU and PP systems. PU serves as a platform to verify the important role played by hydrogen bonding of PDA-coated fillers in reinforcing the polymer. Meanwhile, the radical scavenging capability of D-clay is examined using PP as the polymer matrix.

Chapter 3 Materials and Methods

3.1 Materials

Polyether-based PU (Skythane R185A) and polyester-based PU (Skythane S180A) were obtained from SK Chemicals (Suwon, Korea). The chemical structure of polyether-based PU is made of 4,4'-methylenebis(phenyl isocyanate), 1,4-butanediol and poly(tetramethylene oxide) glycol ($M_w = 1000$) as shown in Scheme 4-1. The soft segment of ester-based type is poly(butylene adipate) glycol ($M_w = 1000$) while the hard segment of ester-based polyurethane is same with polyether-based type (4,4'-methylenebis(phenyl isocyanate) and 1,4-butanediol). Unmodified PGW grade Na-MMT (specific gravity = 2.6 g/cm³) with cationic exchange capacity (CEC) of 145 mmol/100 g was purchased from Nanocor, Inc (Arlington Heights, USA). Tris(hydroxymethyl)aminomethane (TRIS, 99%) and dopamine hydrochloride (DOPA-HCl, 98%) were obtained from Sigma-Aldrich (Singapore). Acetone (Technical grade, Aik Moh) and dimethylformamide (DMF, HPLC grade, Tedia) were used without further purification. Cloisite 30B (30B-clay, Southern Clay Products, specific gravity of Cloisite Na⁺ = 2.86 g/cm³, CEC of Cloisite Na⁺ = 92 mmol/100g) was selected as reference material for PU system since it is the most commonly used organoclay for TPU system.¹⁹ All organoclays were dried in vacuum oven at 80 °C for 24 h before use.

For PCL-based PU synthesis, PCL diol (CAPA 2402, $M_w = 4000$) was kindly supplied by Fu Yuan Enterprise (Singapore), whereas dibutyltin dilaurate (DBTDL), 4,4'-methylenebis(phenyl isocyanate) (MDI) and 1,4-butanediol (BD) were obtained from Sigma-Aldrich. For LDH synthesis, sodium hydroxide (NaOH), magnesium

chloride hexahydrate (MgCl_2), aluminium chloride hexahydrate (AlCl_3) and sodium carbonate (Na_2CO_3) were purchased from Sigma-Aldrich and used as received. *N,N*-Dimethylformamide (DMF, anhydrous grade) was obtained from Tedia for PU synthesis.

PP (Cosmoplene ® H101E, melt flow index = 3.5 g/10min, density = 0.9g/cm^3) was obtained from Polyolefin Company (Singapore) Pte. Ltd. 2,2-diphenyl-1-picrylhydrazyl (DPPH) was obtained from Sigma-Aldrich and used without purification. Maleic anhydride-terminated PP (PPMA, $M_n = 8000$, melting point = 140°C , acid number = 15) was kindly sponsored by Baker Hughes (Houston, TX). Ethylenediamine (EDA, purum grade) was obtained from Fluka. For clay modification of non-polar system, 1-Hexadecyl-2,3-dimethylimidazolium chloride (IM) was purchased from Merck, Germany. Toluene (ACS grade) was obtained from Tedia while acetone and methanol (technical grade) were obtained from Aik Moh and used as received.

3.2 Preparation of D-clay

Na-MMT (1g) was first dispersed in 100 ml DI-water via magnetic stirring for one day to exfoliate clay layers. The clay suspension was then kept at room temperature for two days and the large clay stacks at the bottom of the flask was removed. The remaining suspension was then mixed with 250 ml of 10 mM of TRIS buffer solution ($\text{pH} = 8.5$) for 20 minutes to ensure homogeneous clay dispersion in the solution before adding 0.53 g of DOPA-HCl into the clay suspension. DOPA coating reaction was carried out under open air condition for another two hours at room temperature. The D-clay suspension was then centrifuged and washed with acetone for four times. The resulting D-clay was then dispersed in DMF (PU system) or toluene (PP system) via stirring and ultrasonication in preparation for the synthesis of the nanocomposites. TGA

was performed using dried D-clay powder, the result showed that about 16 wt% of polydopamine was coated on clay (Figure 3-1).

Figure 3-1. Thermogravimetric curve (TGA) of clay and D-clay (10 °C/min in air).

3.3 Preparation of polymer/clay nanocomposites

3.3.1 Preparation of polyether-based and polyester-based PU/D-clay nanocomposites

PU/D-clay nanocomposites were synthesized by first dissolving PU in DMF (in PU concentration of 1g/10 mL) by magnetic stirring overnight. Measured amount of D-clay in DMF was then added into the PU solution and the mixture was stirred for another 24 h. Finally, the viscous solution was casted on glass slides followed by drying the solvent at 60 °C in vacuum for 24 h. To confirm the reinforcement brought by D-clay is indeed stronger than organoclay, PU/30B-clay nanocomposite films were synthesized through similar process to serve as the reference material. Neat PU films were prepared by direct solution casting without adding clay. All thin films were kept in ambient environment for at least 5 days before characterization to make sure they had reached a near-equilibrium state. The thicknesses of the thin films were in a range of 0.1 mm to 0.2 mm.

3.3.2 Preparation of PCL-based PU/D-LDH nanocomposites

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 molar ratio of MDI/PCL diol/BD was 6/1/5, corresponding to hard-segment content of about 33 wt%. The molecular weight of the synthesized PCL-based PU is 6×10^4 g/mol as determined by size exclusion chromatography (SEC, Waters 2690, using PMMA as standard) in THF solution at 25 °C.

Preparation of LDH.

Mg₂Al-CO₃-LDH was prepared according to the report by Xu, *et al.*³⁸ MgCl₂ (2.0 mmol) and AlCl₃ (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 Na₂CO₃ 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.^{10, 18, 95, 96} 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 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. The mass density of the synthesized LDH is about 2.0-2.2 g/cm³.

Preparation of PCL-based 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 followed by drying 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.

3.3.3 Preparation of PP/D-clay nanocomposites

The synthesis of PP/D-clay consists of three steps: (I) synthesis of PPNH₂, (II) solution blending of PPNH₂ and D-clay and (III) melt extrusion of PPNH₂/D-clay with PP. In step I, 30 g PPMA was dissolved in 350 ml toluene at 120 °C and refluxed overnight. Subsequently, 1.35 g ethylenediamine (PPMA/EDA molar ratio = 1/6) was added into the solution and the mixture was stirred for another 24 h. The resultant PPNH₂ was then precipitated in methanol and dried in vacuum oven at 70 °C for one day. In step II, PPNH₂ was intercalated into D-clay layers in toluene. Both D-clay and PPNH₂ were dispersed in toluene separately prior to mixing. Then, both suspensions were mixed at PPNH₂/clay weight ratio of 3/1 and reacted for three days at 120 °C in N₂ environment. The product was then precipitated in methanol and dried under vacuum at 70 °C for one day. In step III, measured amounts of PPNH₂/D-clay powders were compounded with PP pellets by melt extrusion using PRISM twin screw extruder at 190 °C. For fair comparison, trialkylimidazolium-modified clay (IM-clay) was prepared using the method reported in our previous publication.⁹⁷ Firstly, 3 g of Na-MMT was dispersed in 300 L of distilled water at 80 °C. Separately, 1.2 equivalent of 1-hexadecyl-2,3-dimethylimidazolium chloride, with respect to the clay CEC value, was dissolved in 60 ml of ethanol and added dropwise into the clay suspension. The suspension was further reacted at 80 °C for 7 hours. The ion-exchanged clay (IM-clay) was then washed with ethanol for several times before use. Both IM-clay and pristine clay were dried overnight at 80 °C prior to melt compounding with PPMA and then with PP. They serve as the reference materials, PP/IM-clay and PP/clay. Same with PPNH₂/D-clay, the weight ratio of PPMA/clay was fixed at 3/1. Pure PP was also prepared under the same condition as a reference. For free radical scavenging capability study, PDA particle was

synthesized as a reference material by self-polymerization of DOPA without clay for 24 h in Tris buffer solution. Washing was repeated at least four times in acetone. The dark brown sediments were subsequently dried in vacuum oven at 50 °C for 48 h.

3.4 Characterizations

3.4.1 Clay and LDH contents in nanocomposites

The clay and LDH contents of the nanocomposites were determined using TA Instrument TGA Q500. The figures (numbers) in all the denoted samples represent the filler loadings by weight percentage. The D-clay nanocomposites were heated from 25 to 850 °C at 10 °C/min in air with a purge rate of 60 mL/min. D-LDH nanocomposites were heated from 25 to 850 °C at 20 °C/min in air with a purge rate of 60 mL/min. Decomposition temperature (T_d) is determined as the temperature at 5 % weight loss.

3.4.2 Polyether and polyester-based PU nanocomposites

The structures and morphologies of the nanocomposites were characterized using wide angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM). The films were scanned at room temperature from $2\theta = 2^\circ$ to 40° at a scanning rate of 1 °/min using a PANalytical X'Pert PRO diffractometer with Cu K α radiation. *In situ* high-temperature XRD data was collected on a Siemens D5005 diffractometer equipped with a hot stage. TEM was conducted using a JOEL 2100 TEM. The PU samples were embedded in cured epoxy and microtomed using Leica Ultracut UCT into about 50-100 nm thickness at -100 °C.

The tensile properties were measured using an Instron 5567 machine according to ASTM D638 type V at a crosshead speed of 50 mm/min with a 500 N load cell. Five specimens of each material were tested.

Tensile-mode DMA measurements were conducted using a TA Instrument DMA 2980 at a frequency of 1 Hz and a ramp rate of 4 °C/min from -100 °C to 100 °C. The glass transition temperatures were determined by the maximum $\tan \delta$ values.

The thermal behaviours of the PU/D-clay nanocomposites were characterized using differential scanning calorimetry (DSC) performed on a TA Instrument DSC Q10 at a heating rate of 10 °C/min, and modulated DSC (MDSC) carried out on a TA Instrument DSC 2920 at a heating rate of 5 °C/min with a modulating amplitude of 0.796 °C over a period of 60 s.

FTIR measurements were carried out using a Shimadzu FTIR IR Prestige-21 equipped with Golden Gate ATR accessory. Each sample was scanned 32 times at a resolution of 4 cm^{-1} and all the spectra were normalized according to CH_2 stretching near 2856 cm^{-1} . To estimate the concentration of the hydrogen bonding between polyurethane and D-clay, deconvolution of the superposed hydrogen-bonded and free carbonyl infrared absorption bands was carried out using the profile fitting program where individual band was modeled by a Lorentzian-Gaussian profile function. The areas corresponding to the hydrogen-bonded carbonyl groups were divided by 1.71 to compensate for the differences in absorptivity between the free and hydrogen-bonded carbonyl groups.⁹⁸

3.4.3 PCL-based PU/D-LDH nanocomposites

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 °C.

To observe the nanophase morphology, the grids were exposed to RuO₄ 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 °C to 800 °C at 20 °C/min in air (purge rate = 60 ml/min). Based on the TGA results (cf. Figure S2), 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.

Thermal behaviors of the PCL-based PU and its nanocomposites were characterized using TA Instrument DSC Q10 at a ramp rate of 20 °C/min in temperature range from -90 °C to 220 °C. The first melting and cooling curves were taken for analysis. To study 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 CuK α 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.

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_o 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.

3.4.4 PP/D-clay nanocomposites

The tensile properties of PP nanocomposites were determined using an Instron 5567 machine according to ASTM D638 type V at a crosshead speed of 25 mm/min using injection-molded dog-bone specimens (ASTM Type V in 1 mm thickness, 500 N load cell).

To examine the percent crystallinity (X_c) of the molded PP tensile specimen, MDSC was done on DSC 2920 at a heating rate of 5 °C/min and a modulating amplitude of 0.796 °C over a period of 60 s. X_c was estimated by subtracting the reversing heat flow from the non-reversing heat flow as detected by MDSC, and dividing by the heat of fusion for 100% crystalline PP (209 J/g).⁹⁴

To explore the oxidative stability of PP/D-clay nanocomposites, the onset oxidation temperature (OOT) was examined according to ASTM E2009 using TA Instrument DSC 2010 at 10 °C/min heating rate (sample size= 3.0 to 3.3 mg). OOT was determined in oxygen environment (flow rate= 50 mL/min) from the baseline to the extrapolated onset temperature of the exothermic process. To further explore the photo-stability of the samples, PP thin films of 0.3-0.33 mm thickness were irradiated with UV light for 3 weeks using RPR-200 (Rayonet) with light intensity of 92 W/m² at the center of the reactor. The surface topography of UV-exposed samples was examined with an Olympus BX53 optical microscope at a magnification of 4x. Thermal degradation

temperatures of the degraded samples were characterized by heating the samples from 25 °C to 850 °C at 10 °C/min in nitrogen (sample purge rate = 60 ml/min) using TGA Q500. The thermal crystallization behaviours of the unexposed and UV-exposed nanocomposites were determined using TA Instrument DSC Q10 at a heating rate of 10 °C/min and the second melting was recorded for analysis.

FTIR measurements were carried out using a Shimadzu FTIR IR Prestige-21 equipped with Golden Gate ATR accessory. Each sample was scanned 32 times at a resolution of 4 cm⁻¹ and all the spectra were normalized according to CH₃ stretching and CH bending near 2722 cm⁻¹.⁹⁹

The radical scavenging activity of D-clay was analyzed using DPPH assay according to the method stated in literature²⁷ with slight modifications. 0.01 mM of DPPH solution in DMF was freshly made prior to usage. 150 µL of D-clay suspension (1mg/ml in DMF) was added into 3 ml of DPPH solution. The scavenging activity was evaluated with a UV-2501PC spectrophotometer (Shimadzu) by monitoring in the dark the absorbance change at 516 nm at different time durations. DPPH radical scavenging activity is defined as $I = [1 - (A_i - A_s)/A_{\text{dpph}}] \times 100\%$, where A_{dpph} represents the absorbance of the DPPH without D-clay, A_i represents the absorbance of the DPPH with D-clay taken at different time, and A_s represents the absorbance of D-clay itself without the DPPH solution. In order to investigate the scavenging efficiency of D-clay compared to that of PDA, 0.2 mg/ml of PDA in DMF and 0.8 mg/ml of clay in DI water were also prepared, and 150 µL of each suspension was added into DPPH solution for analysis (the PDA content in D-clay is about 20 wt%¹⁰).

Chapter 4 Polyether-based PU/D-clay Nanocomposites

4.1 Introduction

Previous work on Epoxy/D-clay nanocomposites has confirmed that the incorporation of low D-clay concentration will lead to significant improvement in mechanical properties owing to strong interfacial interaction. Yet, the impressive reinforcement could be due to the formation of covalent bond and hydrogen bond between D-clay and epoxy. To verify that the reinforcement is indeed brought by extensive hydrogen bond, it is desirable to eliminate the contribution of covalent bond. As a result, polyurethane was selected as the polymer matrix since the impressive improvements on mechanical properties of polyurethane nanocomposites is mainly attributed to the hydrogen bonding between polymer chains and reinforcing fillers. At the same time, the PU/D-clay nanocomposites in this work were obtained via solvent blending and solvent casting at low temperature to avoid the chances to form any covalent bonds between polymers and fillers. This chapter aims to investigate the underlying reinforcement mechanisms. For comparison, commercial Cloisite 30B organoclay was used as reference material to confirm that the impressive reinforcement is due to the strong and extensive hydrogen bonds provided by the catechol groups of PDA coating on clay.

4.2 Morphology of the nanocomposites

Scheme 4-1 illustrates the preparation of polyether-based PU in this chapter. As indicated, both 30B-clay and D-clay can form hydrogen bonds with PU. However, the flexible long alkyl tails of the former would reduce the degree of hydrogen bonding between 30B-clay and the polymer. In contrast, the latter contains rigid aromatic rings. Hence, compared to 30B-clay, it is proposed that the hydrogen bonds between the catechol groups of PDA and PU are stronger. As a result, the incorporation of 30B-clay and D-clay would lead to different morphologies due to the difference in chemical structures and degree of hydrogen bonding.

*Scheme 4-1. Schematic illustration of the preparation of PU/clay nanocomposites. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Huang, S.; Tsakadze, Z.; Lau, S. K.; Mai, Y.-W.; Lu, X., ACS Appl. Mater. Interfaces **2012**, 4 (9), 4571–4578. Copyright 2012 American Chemical Society.)*

Figure 4-1a presents the X-ray diffraction patterns of unmodified clay, D-clay and 30B-clay. A peak at $2\theta = 5.77^\circ$, corresponding to d -spacing of 1.53 nm was observed from D-clay, whereas the d -spacing of the unmodified clay is about 1.23 nm. From the variance in d -spacing, it is concluded that the thickness of the PDA coating is about 0.15 nm on each side. Since PU chains can form hydrogen bonds with the catechol groups of D-clay and the hydroxyl groups of 30B-clay, PU chains are able to diffuse into the clay's interlayer spacing during solution mixing process. As shown in Figure 4-1b, the peak in the region $2\theta < 10^\circ$ is contributed by the intercalated morphologies while the high-angle peaks are related to the crystallization of the PU matrix, which will be covered later. A broad peak appears at $2\theta = 5.46^\circ$ for all PU/D-clay nanocomposites, inferring the presence of intercalated D-clay stacks and maybe a small fraction of un-intercalated D-clay stacks. Apparently, the clay peak becomes more obvious with increasing D-clay loading. On the contrary, the dispersion of 30B-clay in PU is better than that of D-clay as no obvious peak can be observed in small angle region for PU/30B-clay-3.0%. The results are consistent with TEM observations. From Figure 4-2, the dark riotous areas are due to the exfoliated clays, yet thick clay stacks can still be seen. Since the samples were prepared via casting, both D-clay and 30B-clay were dispersed without preferred orientation. At similar clay concentrations, 30B-clay dispersed more homogeneously and exfoliated to a greater extent in the polymer matrix compared to D-clay. This is probably owing to the wider interlayer spacing and weak van der Waals interactions between the 30B-clay layers, which made them easier to be separated. On the contrary, the stronger hydrogen bondings between the D-clay layers made them difficult to be exfoliated as expected.

Figure 4-1. X-ray diffraction patterns of (a) unmodified clay, D-clay and 30B-clay, and (b) PU/D-clay and PU/30B-clay nanocomposites. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Huang, S.; Tsakadze, Z.; Lau, S. K.; Mai, Y.-W.; Lu, X., *ACS Appl. Mater. Interfaces* **2012**, 4 (9), 4571–4578. Copyright 2012 American Chemical Society.)

Figure 4-2. TEM micrographs of (a,b) PU/D-clay-2.8% and (c,d) PU/30B-clay-3.0%. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Huang, S.; Tsakadze, Z.; Lau, S. K.; Mai, Y.-W.; Lu, X., *ACS Appl. Mater. Interfaces* **2012**, 4 (9), 4571–4578. Copyright 2012 American Chemical Society.)

4.3 Mechanical properties

According to literature, the tensile curves of neat PU and its nanocomposites can be separated into three regions which are indicated in Figure 4-4a. Region I is a quasi-

linear region where the initial modulus is greatly related to the tilting of the hard micro-domains in the strain direction and the crystallinity of PU.¹⁰² With increasing tensile load, hard domains will eventually break down into small pieces. At larger elongation after destruction of hard domains, two distinct regions of plastic deformation will usually be observed.¹⁰² In this work, 5% strain is presumed as the point where the destruction of hard domains occur (i.e. the starting point of Region II). In Region II, the gradients of the tensile curves initially decrease with larger elongation and finally balance at a fixed value (Figure 4-4b). The modulus estimated in this region can be related to the disentanglement of soft segments and tilting of small hard domains.^{83, 102} Region III is defined as strain larger than 200% up to fracture point, which is represented by a steep upturn in the tensile curve owing to the strain-induced crystallization of the soft segments.¹⁰³

Table 4-1 tabulated the mechanical properties of neat PU and its nanocomposites. Despite the poorer D-clay dispersion, it is surprising to notice that PU/D-clay-2.8% showed not only much higher initial modulus in Region I, but also much higher stress in Region II, and even larger strain-at-break than PU/30B-3.0%. The initial modulus of PU/D-clay improved by more than 250% over that of neat PU with addition of 2.8wt% of D-clay, whereas PU/30B-clay-3.0% showed about only 7% increment.

Figure 4-3. (a) Typical tensile plots of polyether-based PU and its nanocomposites. (b) Typical tensile plots of PU and PU/D-clay nanocomposites in Region I and II. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Huang, S.; Tsakadze, Z.; Lau, S. K.; Mai, Y.-W.; Lu, X., *ACS Appl. Mater. Interfaces* **2012**, 4 (9), 4571–4578. Copyright 2012 American Chemical Society.)

Figure 4-4. Typical tensile graphs of PU/D-clay nanocomposites. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Huang, S.; Tsakadze, Z.; Lau, S. K.; Mai, Y.-W.; Lu, X., *ACS Appl. Mater. Interfaces* **2012**, 4 (9), 4571–4578. Copyright 2012 American Chemical Society.)

Table 4-1. Tensile properties of the neat PU and nanocomposites. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Huang, S.; Tsakadze, Z.; Lau, S. K.; Mai, Y.-W.; Lu, X., *ACS Appl. Mater. Interfaces* **2012**, 4 (9), 4571–4578. Copyright 2012 American Chemical Society.)

Sample	Initial Young's Modulus, E^a (MPa)	E/E_n^b (%)	Stress at 100% Strain (MPa)	Tensile Strength (MPa)	Ultimate Elongation (%)
PU	5.6 ± 0.4	-	2.3 ± 0.1	24.6 ± 8.3	712 ± 148
PU/D-clay-0.5%	9.6 ± 0.5	171	2.9 ± 0.1	27.7 ± 1.3	709 ± 45
PU/D-clay-2.8%	19.7 ± 0.7	352	4.0 ± 0.1	35.0 ± 1.9	1020 ± 128
PU/D-clay-7.7%	42.1 ± 2.3	752	5.9 ± 0.2	25.3 ± 3.1	610 ± 96
PU/30B-clay-3.0%	6.0 ± 0.3	107	2.1 ± 0.1	33.3 ± 3.1	804 ± 78

E^a is defined as the stress at 5% strain divided by the strain.

E_n^b is the initial modulus of the neat PU.

The significant enhancement in the initial modulus (E) of the nanocomposite with D-clay can be attributed mainly to the efficient stress transfer through the PDA interface. As proven in earlier section, the catechol groups on the surfaces of D-clay can form strong hydrogen bonds with the hard segments. Hence, the load transfer during deformation of the D-clay nanocomposite is more impressive compared to that with 30B-clay. In general, the typical sizes of the hard micro-domains are in a range of 3 to 11 nm,¹⁸ while the diameters of D-clay stacks are about 200 to 400 nm. The reorientation of hard domains during deformation also accompanies the tilting of large D-clay stacks, hence much larger force was needed for deformation and this led to higher modulus. In Region II, the tensile stress values of the PU/D-clay nanocomposites are much higher than the other counterparts and the values become higher with increasing clay content. The results indicate that the strong hydrogen bondings between the D-clays and hard segments make the hard domains larger and/or stronger. As a result, larger force is required to fracture the hard domains. Even though 30B-clays are able to form hydrogen bonds with hard segments, the available bonding sites are presumably lesser than D-clay due to the presence of long alkyl tails. As a result, 30B-clay nanocomposites showed lower values for initial modulus and stress in Region II. In Region III, an upturn in stress is observed owing to soft segment crystallization. Note that all PU/D-clay nanocomposites display a saturation point where the slopes of the stress-strain curves start to decrease (Figure 4-5). At this point, the oxygen atoms of the disentangled polyol soft segments would form hydrogen bonds with PDA coating on D-clay and become immobilized, hindering the strain-induced crystallization of the soft segments. Thus, the higher ultimate elongation of PU/D-clay-2.8% composite can be attributed to the reduced strain-induced crystallization, which in turn leads to enhanced ductility.

Typical DMA curves of neat PU and its nanocomposites are shown in Figure 4-6 and the corresponding thermo-mechanical property data are tabulated in Table 4-2. All samples exhibit glass transition below $-40\text{ }^{\circ}\text{C}$ and the T_g values are almost independent of clay content. There is a broad peak on the storage modulus curves between -30 and $10\text{ }^{\circ}\text{C}$ for all specimens owing to the crystallization and subsequent melting of the soft domains. Above the melting point of soft segments, the storage modulus is mainly governed by hard domains and clays. Apparently, the storage modulus increases with increasing D-clay loading and the enhancement brought by D-clay is more prominent than 30B-clay at similar clay content. With $\sim 3\text{ wt\%}$ clay, the increments in storage moduli offered by D-clay are three and twelve times higher than that of 30B-clay at 25 and $100\text{ }^{\circ}\text{C}$, respectively. The storage moduli of all samples display more intense reduction above $60\text{ }^{\circ}\text{C}$ (Figure 4-6a) owing to the melting of hard domains, which is consistent with the DSC results. It is noticeable that all the PU/D-clay nanocomposite films also show substantial E' values up to $100\text{ }^{\circ}\text{C}$ as a result of their stable hard domains. This was verified by the WAXD results which will be discussed in the following section. Therefore, D-clay benefits the stiffness at high temperatures.

Figure 4-5. (a) Storage modulus (E') and (b) $\tan \delta$ as a function of temperature for neat PU and its nanocomposites. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Huang, S.; Tsakadze, Z.; Lau, S. K.; Mai, Y.-W.; Lu, X., *ACS Appl. Mater. Interfaces* 2012, 4 (9), 4571–4578. Copyright 2012 American Chemical Society.)

Table 4-2. Dynamic thermo-mechanical properties of the neat PU and nanocomposites. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Huang, S.; Tsakadze, Z.; Lau, S. K.; Mai, Y.-W.; Lu, X., ACS Appl. Mater. Interfaces 2012, 4 (9), 4571–4578. Copyright 2012 American Chemical Society.)

Sample	Peak of Tan δ ($^{\circ}\text{C}$)	E' @ -80 $^{\circ}\text{C}$ (MPa)	E' @ 25 $^{\circ}\text{C}$ (MPa)	E' @ 50 $^{\circ}\text{C}$ (MPa)	E' @ 100 $^{\circ}\text{C}$ (MPa)
PU	-46.7	2375	9.5	6.4	1.4
PU/D-clay-0.5%	-45.8	2465	17.5	12.7	7.0
PU/D-clay-2.8%	-46.5	2951	34.7	27.8	19.2
PU/D-clay-7.7%	-46.9	3617	113.4	91.6	62.7
PU/30B-clay-3.0%	-43.9	2562	13.0	7.6	1.6

4.4 Hard segment crystallinity

In order to prove that the hard domains in the PU/D-clay nanocomposites were indeed stronger, the thermal transition behaviours of the as-cast films were examined using DSC and MDSC. Thermal transitions of PUs are intricate as they involve several processes, including glass transition (T_g), crystallization/recrystallization (T_c) and the subsequent melting (T_m) of the soft segments, and melting of hard domain crystallites of variable sizes (T_{HD}).¹⁰⁴ Figure 4-6 shows the first heating curves of the samples. Above T_g , all samples exhibit an exothermic peak followed by an endothermic peak owing to the crystallization and subsequent melting of soft segment crystallites, respectively. The heat of soft segment crystallization (ΔH_c) and the heat of soft segment melting (ΔH_m) were tabulated in Table 4-3. The enhancement in tensile properties is clearly not due to the soft segment crystallization since the melting point of the soft segment is far below the testing temperature (Table 4-3). Yet, it is

noticeable that the melting temperature of soft segment increased with increasing D-clay loading, implying that soft segment did interact with D-clay.

Figure 4-6. First heating profiles of neat PU and its nanocomposites obtained from DSC. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Huang, S.; Tsakadze, Z.; Lau, S. K.; Mai, Y.-W.; Lu, X., *ACS Appl. Mater. Interfaces* **2012**, 4 (9), 4571–4578. Copyright 2012 American Chemical Society.)

There is no sharp melting endotherm of hard domains obtained from the DSC curves, hence, it is reasonable to conclude that the hard segment concentration is fairly low and they are poorly organized. It is noticeable that there are some broad endotherms above 25 °C for all samples and these endotherms do not look like typical melting peaks. Thus, MDSC was performed to study the nature of these broad endotherms. The reversing heat flow of all samples exhibits a straight line between 25 to 225 °C, whereas the non-reversing curve exhibits a broad endothermic dip between 25 and 180 °C (Figure 4-7). This implies that the formation of the hard micro-domains with random dimensions is a kinetics-controlled process.¹⁰⁴ The non-reversing heats of hard segments melting (ΔH_{HD}^{NR}) estimated from the integral of the amplitudes of the

quasi-isothermal experiment with a normal baseline extrapolated from outside the melting region (25 to 225 °C) are indicated in Table 4-3. Undoubtedly, such endotherms can be obtained on the second heating curves if the samples are given sufficient period to recover at room temperature (Figure 4-8). It is striking to observe that the hard domain crystallinity obtained from the area of this broad endotherm increases with increasing D-clay loading, indicating that the strong interfacial interactions between the hard segments and the D-clay induce the time-dependent densification of para-crystalline hard domains.

*Table 4-3. Crystallization and melting properties of neat PU and its nanocomposites measured from their first heating DSC curves. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Huang, S.; Tsakadze, Z.; Lau, S. K.; Mai, Y.-W.; Lu, X., ACS Appl. Mater. Interfaces **2012**, 4 (9), 4571–4578. Copyright 2012 American Chemical Society.)*

Sample	T _g (°C)	T _c (°C)	ΔH _c (J/g)	T _m (°C)	ΔH _m (J/g)	ΔH _{HD} ^{NR} (J/g)
PU	-72.4	-27.2	11.6	6.4	15.2	14.9
PU/D-clay-0.5%	-72.1	-29.5	13.1	6.7	17.2	18.7
PU/D-clay-2.8%	-72.2	-28.8	11.3	6.6	15.2	21.8
PU/D-clay-7.7%	-72.4	-29.0	10.8	7.6	16.2	26.0
PU/30B-clay-3.0%	-71.9	-30.4	13.1	6.2	17.1	16.3

Figure 4-7. MDSC data of PU and PU/clay nanocomposites. The curves have been shifted vertically for clarify.

Figure 4-8. DSC thermograms of the neat PU at different time after quenching from 200 °C. T_{HD} appears 4 days after the quenching, indicating that the densification of the para-crystalline hard micro-domains is a kinetically controlled process. The curves have been shifted vertically for clarify. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Huang, S.; Tsakadze, Z.; Lau, S. K.; Mai, Y.-W.; Lu, X., *ACS Appl. Mater. Interfaces* **2012**, 4 (9), 4571–4578. Copyright 2012 American Chemical Society.)

The presence of para-crystalline hard domains is also verified by the WAXD data. As discussed earlier in Figure 4-1b, the high angle peaks, including the amorphous halo at around $2\theta = 20^\circ$, are attributed to PU matrix. As the temperature increases, the amorphous halo becomes broader and shifts towards the low angle as a result of the increased average inter-chain distance (Figure 4-9). The shoulder peak at $2\theta = 22.5^\circ$ can be attributed to the crystallization of the hard domains of PU.¹⁰⁵ It is intriguing that the shoulder peak intensity becomes higher with increasing D-clay loading (Figure 4-1b). This again suggests that the D-clay induces the ordered packing of the para-crystalline hard domains. Moreover, the shoulder peak of PU/D-clay-2.8% at about $2\theta = 22.5^\circ$ remains visible up to 115 °C, while the shoulder peak of PU/30B-clay-3.0%

almost disappears at 115 °C. Thus, the strong hydrogen bonding between D-clay and hard segments enables the hard segment crystallites to sustain a higher temperature compared to other counterparts.

Figure 4-9. X-ray diffraction patterns of (a) PU/Dclay-2.8% and (b) PU/30B-3.0% at 30 °C and 115 °C. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Huang, S.; Tsakadze, Z.; Lau, S. K.; Mai, Y.-W.; Lu, X., *ACS Appl. Mater. Interfaces* **2012**, 4 (9), 4571–4578. Copyright 2012 American Chemical Society.)

4.5 Hydrogen bond with hard segment

To further confirm the hydrogen bonding strength between fillers and polymer chains, FTIR spectra of polymer thin films were examined at different temperatures and the results of PU/D-clay-2.8% are shown in Figure 4-10a. Profile fitting for the carbonyl groups ($1650 - 1780\text{ cm}^{-1}$) was conducted according to the methods done by Runt's group.^{100, 101} The three absorption peaks at ~ 1704 , ~ 1715 and $\sim 1734\text{ cm}^{-1}$ are corresponded to the stretching of strongly hydrogen-bonded, loosely hydrogen-bonded and free carbonyl groups, respectively. The fraction of each type of carbonyl groups is calculated by dividing the area of each peak by the total area. As shown in Figure 4-10b, the fraction of strongly hydrogen-bonded carbonyl groups of PU/D-clay-2.8% is slightly more than neat PU and PU/30B-clay-3.0%. Apparently, PU and PU/30B-clay exhibit a sharp drop in the fractions of strongly hydrogen-bonded carbonyl groups above $150\text{ }^{\circ}\text{C}$ decrease owing to the melting of the PU hard domains. Yet, there is larger amount of "strongly hydrogen-bonded carbonyl groups" in PU/D-clay-2.8% in all testing temperatures compared to the other counterparts. It is believed that the hydrogen bonds between catechol groups of D-clay and hard segments are stronger than that of organic surfactants. As a result, the hydrogen bonds between D-clay and PU chains can sustain to higher temperature although D-clay has lesser surface area to interact with PU chains than 30B-clay due to the poorer dispersion of D-clay.

Figure 4-10. (a) FTIR profiles of PU/D-clay-2.8% at various temperatures; the inset shows the typical profile fitting result. (b) Fractions of strongly hydrogen-bonded carbonyl groups of neat PU, PU/30B-clay-3.0% and PU/D-clay-2.8% (estimated from profile fitting) as a function of temperature. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Huang, S.; Tsakadze, Z.; Lau, S. K.; Mai, Y.-W.; Lu, X., *ACS Appl. Mater. Interfaces* **2012**, 4 (9), 4571–4578. Copyright 2012 American Chemical Society.)

Scheme 4-2 proposes the mechanisms for the different reinforcement effects brought by D-clay and 30B-clay. Without clay, phase separation in the PU is minimal since the hard segment content is quite low. With the incorporation of 30B-clay, the hydroxyl groups on the surfaces of some 30B-clay layers may interact with the hard segments to augment the initial modulus. However, the flexible long alkyl chains of 30B-clay also improve the dissolution of the hard segments into the soft domains. As a result, some hard segments and 30B-clays are dispersed in the soft segment matrix. On the contrary, D-clay is more compatible and interacts strongly with the hard segments; this not only results in more hydrogen bonds between hard segments and D-clay stacks, but also promotes further phase separation and densification of the poorly-organized hard domains. Therefore, the hard domains are harder to be strained, tilted and broken down, consequently much higher initial modulus and Region II stress could be obtained without sacrificing the elasticity.

*Scheme 4-2. Schematic diagrams of phase morphology in (a) neat PU, (b) PU/30B-clay and (c) PU/D-clay nanocomposites, in which $\sim$ represents soft segment, — hard segment, — 30B-clay and — D-clay. The plots are not drawn to scale. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Huang, S.; Tsakadze, Z.; Lau, S. K.; Mai, Y.-W.; Lu, X., ACS Appl. Mater. Interfaces **2012**, 4 (9), 4571–4578. Copyright 2012 American Chemical Society.)*

4.6 Summary

In this chapter, we successfully incorporated D-clay into polyurethane system via a facile method and the reinforcing mechanism was investigated. D-clay containing nearly a monolayer of PDA coating was easily dispersed in PU matrices via solvent mixing method. The results showed impressive improvements in mechanical properties, including initial modulus, tensile strength and elongation at break, at a very low clay concentration owing to the strong interfacial interactions between D-clay and PU matrices. Apparently, the enhancement brought by D-clay is much more impressive than commercial organoclay (30B-clay) at similar clay loading. This can be attributed to the excessive hydrogen bonding sites provided by D-clay surfaces. The strong hydrogen bonding interaction between the hard segments of PU and D-clay stimulates more ordered packing of the hard segments, leading to more favorable phase separation. The stable hard micro-domains in the vicinity of D-clay can hinder the mobility of polymer chains upon imposed deformation and results in significant improvement in tensile modulus. On the other hand, these strong hydrogen bonds between D-clays and hard segments can sustain up to 115 °C, giving rise to high stiffness in the PU at high temperatures.

Chapter 5 Polyester-based PU/D-clay Nanocomposites

5.1 Introduction

Having probed the strong interfacial interactions between D-clay and PU, it is intriguing to further explore the content dependence of the reinforcement extent of D-clay in thermoplastic elastomer system. However, high D-clay content (>8 wt%) in polyether-based PU will eventually lead to severe phase separation and poor clay dispersion. In this case, polyester-based PU (SPU) was used as the polymer matrix since there is less phase segregation between polyester soft segment and hard segment, this allows the incorporation of high D-clay content without morphology defects. To minimize the difference, the polyester-based PU (SPU) used in this work has same molecular weight ($M_w = 250\,000$) and similar Shore Hardness of 87A with polyether-based PU. Besides, the hard segments of both PUs are made of MDI and 1,4-BD. In this chapter, the effects of high D-clay loading will be discussed in the aspect of the morphology, tensile properties and crystallization behaviors.

5.2 Dispersion of D-clay in the nanocomposites

Similar with polyether-based PU, the dispersion of D-clay in SPU is a mixture of intercalated and exfoliated structures as shown in Figure 5-1. Even at low D-clay

content such as 1 wt%, thin D-clay stacks which consist of unintercalated and intercalated D-clays are observed owing to the strong interfacial interaction between D-clay themselves, hence it is difficult to exfoliate D-clay into individual single layer. It is striking to notice that the thickness of the D-clay stacks does not increase even at high D-clay loading. However, long and thin D-clay stacks are observed for nanocomposites with D-clay content larger than 5 wt%, especially for SPU/D-clay-15 and SPU/D-clay-20. And some of the edges of these long clay stacks connected to other clay stacks (jammed structure), this would restrict the movement of the polymer chains during deformation. The jammed structure will give rise to significant improvement in mechanical properties which will be discussed in the following section.

Figure 5-1. TEM micrographs of (a) SPU/D-clay-1, (b) SPU/D-clay-3, (c) SPU/D-clay-5, (d) SPU/D-clay-7, (e) SPU/D-clay-10, (f) SPU/D-clay-15, (g) SPU/D-clay-20. The numbers in sample names represent the clay loadings by weight percentage.

5.3 Mechanical properties

The typical tensile curves and the corresponding tensile properties are shown in Figure 5-2 and Table 5-1, respectively. The initial Young's modulus of the nanocomposites increases close to exponentially with increasing clay content at clay loading larger than 5 wt%. Above 5 wt%, D-clay may form a jammed structure as shown in TEM images that drastically immobilize the movement of hard and soft polymer chains during stretching. At D-clay loading lower than this percolated concentration, most of the soft segments still free to move and response to the deformations. It is interesting to note that the nanocomposites containing 20 wt% D-clay exhibit a sudden decrease in tensile stress after yield point, a typical behaviour of glassy thermoplastic polymers, owing to the sudden break down of the jammed structure and soft segments will reorientate and align with further deformations. Besides, no strain-induced crystallization was observed for the nanocomposites containing 15 wt% and 20 wt% D-clay, probably due to the hindering effects of the jammed structure, obstructing the chain disentanglements of soft segments which attached onto the D-clays. Yet, the soft segments which do not in touch with D-clay surfaces are still remained mobile, hence the ultimate elongation does not decrease much.

Figure 5-2. (a) Typical tensile graphs of SPU and its nanocomposites. (b) Initial modulus increases exponentially with increasing D-clay content. The number in sample names represents the weight percentage of clay.

Table 5-1. Tensile properties of the polyester-based PU and its nanocomposites. Initial Young's modulus is defined as the stress at 5% strain divided by the strain.

Sample	Initial Young's modulus (MPa)	Tensile strength (MPa)	Ultimate elongation (%)
SPU	13 ± 2	45 ± 6	499 ± 65
SPU/D-clay-1	17 ± 1	38 ± 4	566 ± 110
SPU/D-clay-3	32 ± 3	46 ± 10	521 ± 63
SPU/D-clay-5	46 ± 6	41 ± 3	498 ± 53
SPU/D-clay-7	116 ± 9	49 ± 9	448 ± 33
SPU/D-clay-10	210 ± 23	54 ± 7	414 ± 57
SPU/D-clay-15	251 ± 44	32 ± 3	594 ± 66
SPU/D-clay-20	654 ± 116	34 ± 3	401 ± 5

5.3 Crystallization behaviors

Similar with polyether PU, D-clay interacts stronger with hard segments than polyester soft segments. The surface of D-clay could act as heterogeneous nucleating agent for hard segment crystallization. Thus, the crystallization peak of hard segments ($20 \sim 22.5^\circ$) becomes more obvious with D-clay content above 5 wt% as indicated in Figure 4-8. Note that percolated structure may form at D-clay loading above 5 wt% and the consequent immobilization effects may promote the crystallization of hard segments during solvent casting process. As a result, apparent leap in tensile modulus was obtained above this percolated concentration.

Figure 5-3. WAXD patterns of polyester-based polyurethane and its nanocomposites. The hard segment crystallization peak becomes more obvious with high clay loading.

5.4 Conclusion

The impacts of high D-clay loading on mechanical properties and hard segment crystallization of PU nanocomposites were examined in this chapter. It was observed that D-clay concentration above 5 wt% will result in jammed structure which in turn immobilizes the movement of both hard and soft segments to certain extent, leading to drastic enhancement in tensile modulus. Beyond the percolated concentration, the initial modulus increases exponentially with increasing clay content. In addition, the jammed morphology also promotes hard segment crystallization as observed in WAXD curves.

Chapter 6 PCL-based PU/D-LDH

Nanocomposites as Light-Weight Shape Memory

Materials

6.1 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 heat¹⁰⁶⁻¹⁰⁸, light^{109, 110} and water.¹¹¹⁻¹¹³ Compared with shape memory alloys, SMPs, however, exhibit poorer dimensional stability, lower recovery stress and longer response time.¹¹⁴ Although substantial research work, including modification of polymer chain structures,¹¹⁵ copolymerization¹¹⁶ and blending,¹¹⁷⁻¹¹⁹ 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,^{107, 120} nanorods,¹²¹ carbon nanotubes¹²² and silica¹²³ 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,¹⁰⁷ i.e., the enhancement in recovery stress was usually accompanied by a reduction in recoverable strain.^{107, 124}

Among different types of SMPs, polyurethane (PU)-based block copolymers have been widely explored owing to their ability to recover large deformation, lower cost, ease in processing and biocompatibility.^{114, 122, 124-126} The shape memory performance of PU-based SMPs is greatly correlated to their soft-segment crystallinity.¹²⁴ A higher soft-segment crystallinity is beneficial in enhancing stiffness and shape fixing of the SMPs when the externally applied stress is removed.¹²⁷ It was reported that the incorporation of 1 wt% organoclay into PU-based SMPs could increase the recovery stress up to 20%. However, since the large and stiff organoclay are likely to interact with both hard and soft segments, lower soft segment crystallinity was obtained at higher organoclay loading, leading to lower shape fixity as well as recovery ratio.¹⁰⁷ 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.^{121, 124} 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.¹²¹ 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.¹²¹ Other than surface chemistry, the size and location of nanofillers will also affect the mechanical properties of PU nanocomposites. Liff *et al.* showed that by adding hydrophilic Laponite that has stronger affinity with hard segments of a PU, the soft segments of the PU remained mobile under deformation while hard microdomains were strongly reinforced by Laponite, leading to simultaneous enhancements of

stiffness and toughness of the PU.¹²⁸ The aforementioned studies suggest that it may be possible to improve the recovery stress of PU-based SMPs without sacrificing their strain recovery ratio by incorporating small stiff fillers that could selectively interact with hard segments strongly.

In Chapter 4, the results revealed that the impressive enhancement in tensile properties of PU/D-clay nanocomposites is mainly associated with the strong hydrogen bonding between D-clays and hard segments. For optimum performance of PU nanocomposites, it is desirable to reinforce merely the hard segments whereas the soft segments still remain mobile. As a result, high stiffness and high toughness can be achieved concurrently. However, D-clay used in Chapter 4 is much larger than the hard domain of PU, consequently there is appreciable amount of soft segments attached to D-clay surfaces. Hence, the particle size of PDA-coated filler was optimized in this chapter. MgAl-LDH was selected as the fillers because its size can be easily controlled by altering hydrothermal conditions or time.^{38, 39} Besides, the shape memory performance of the nanocomposites was evaluated since the shape memory properties of PU are greatly related to the degree of phase separation.¹²⁶ In this case, PCL-based PU was chosen as the polymer matrix. In this chapter, the variations in thermal behavior and phase morphology of the PCL-based PU induced by varying LDH size and surface chemistry were investigated. 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.

6.2 Synthesis of PDA-coated 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 are given in Figure 6-1). AFM analysis shows that the aspect ratios of both S-LDH and L-LDH are in the range of 10-13. 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 6-2c, 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.³⁸ For PDA and D-SLDH, the strong band at 1610 cm^{-1} can be attributed to O-H bonds in PDA. It suggests that PDA has been successfully coated on the nanosheets.

Figure 6-1. TEM micrographs of (a) S-LDH and (b) L-LDH.

Figure 6-2. 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.

6.3 Dispersion states of PDA-coated LDHs in PU

Upon the surface modification, both types of PDA-coated LDH fillers can be dispersed well in DMF, making solution blending with the PU possible (Scheme 6-1). From TEM images shown in Figure 6-3, 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 PDA-coated 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 6-3e), which is probably due to the poorer dissolution of S-LDH in DMF.

Scheme 6-1. Preparation of PU/D-LDH nanocomposites.

Figure 6-3. TEM micrographs 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.

6.4 Effects of incorporation of PDA-coated LDHs on phase morphology

To enhance recovery stress of the PU by reinforcing the PU with nanofillers while retaining or even improving its reversibility at the same time, it is desirable to have a more 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 RuO_4 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 6-4 and Table 6-1). It suggests that the incorporation of D-LDHs promotes hard-segment aggregation, which is due to the strong tendency of formation of hydrogen bonds between the hard segments and PDA coating on LDH and the nucleating effect induced by the interactions.^{96, 121} 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 most D-SLDH platelets were located mainly in dark regions.

Figure 6-4. TEM image 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 6-1. Hard domain sizes of PCL-based PU and the corresponding nanocomposites based on TEM observations. 50 measurements were taken for each sample.

	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

6.5 Thermal behaviours 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 6-2, it is noticeable that with the PDA-coated 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 PDA-coated LDHs, the nanocomposite with unmodified S-LDH (PU/SLDH-2) exhibits significantly lower T_g , implying poor interactions between S-LDH and the soft segments, which is probably due to the lack of hydrogen donor on LDH surface. Crystallinity should not be a significant factor here as all the as-casted nanocomposite samples have roughly the same heat of fusion for soft domains ($\Delta H_{m,s}$). 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 very limited when the filler size is small and filler content is low.

Table 6-2. Thermal behaviors of the neat PCL-based PU and its nanocomposites based on 1st cycle at 20 °C/min ramp rate.

	Soft segment					Hard segment			
	T _{g,s} (°C)	T _{m,s} (°C)	ΔH _{m,s} (J/g)	T _{c,s} (°C)	ΔH _{c,s} (J/g)	T _{m,h} (°C)	ΔH _{m,h} (J/g)	T _{c,h} (°C)	ΔH _{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 further verify that PDA-coated 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 achieve much higher crystallinity (as reflected by heat of crystallization) than those of neat PU upon fast cooling (Figure 6-5 and Table 6-2). This is because that the strong interactions between the PDA coating and hard segments could act as nucleation sites for crystal growth.^{96, 121} 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 (ΔH_{c,s}) than neat PU (Figure 6-5a). At higher filler

content, the increase in $T_{c,s}$ and $\Delta H_{c,s}$ may also be related to the nucleating effect of PDA-coated LDHs to some extent as some PDA-coated 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 6-5. Crystallization behaviors of (a) soft segment and (b) hard segment of neat PU and its nanocomposites upon fast cooling.

6.6 Mechanical properties

Tensile properties of neat PU and its nanocomposites at room temperature and 60 °C are summarized in Figure 6-6. Typical tensile curves are illustrated in Figure 6-7.

Below the soft-segment melting temperature, both the nanocomposites and neat PU show plastic yielding behavior (Figure 6-7). The moduli of the nanocomposites at room temperature are only 4-23% higher than that of neat PU since all the as-casted thin films exhibit similar crystallinity as shown in Table 6-2. 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. Above soft-segment melting point, the reinforcement effect of nanosheets becomes more dominant in determining the modulus.¹⁰⁷ Since PDA-coated 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.

Figure 6-6. Tensile test results of PCL-based PU/D-LDH nanocomposites at (a) room temperature and (b) 60 °C.

Figure 6-7. Typical tensile plots of PCL-based PU and its nanocomposites up to 200 % elongation tested at (a) room temperature and (b) 60 °C.

6.7 Shape memory properties

Shape memory properties of the nanocomposites and neat PU are presented in Table 6-3. Obviously, the nanocomposites exhibit better shape memory properties, including shape fixity, recovery stress and recovery ratio, than neat PU except PU/D-LLDH-4; PU/D-LLDH4 shows slightly lower recovery ratio than neat PU, which will be discussed later. Among the four nanocomposite samples, PU/D-SLDH-2 shows the most prominent enhancement in shape memory performance; the recovery stress is 94 % 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 PDA-coated LDHs and the improvement in hard-segment crystallization.

Table 6-3. Shape memory properties of PU and its nanocomposites.

	Shape fixity (%)	Recovery stress (MPa)	Recovery ratio (%)
PU	93.2	3.2	80.6
PU/D-SLDH-2	94.5	6.2	86.2
PU/D-SLDH-4	94.2	5.5	83.5
PU/D-LLDH-2	94.7	5.3	81.3
PU/D-LLDH-4	93.9	5.6	79.5

A great challenge faced by shape memory polymer nanocomposites with stiff fillers is that they usually lead to a reduction in recovery ratio.^{107, 124} By contrast, in this work simultaneous enhancement in all the shape memory properties is achieved by incorporation of PDA-coated small LDH nanosheets. 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 mainly interacting with hard segments. In particular, with 2 wt% D-SLDH, while phase separation is improved, very limited amount of D-SLDH nanosheets were located in soft domains. Thus, 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 6-3. Figure 6-8 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 Table 6-3. It is not surprising that PU/D-LLDH-4 shows an even lower recovery ratio because at higher filler loading, more D-LLDH would be in soft domains and hence retain the aligned orientation. 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 6-8. 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.

6.8 Summary

In summary, prominent enhancement in shape memory properties is achieved by incorporating PDA-coated small LDHs at low content. Without PDA surface modification, poor filler dispersion is observed and soft-segment crystallization under fast cooling is not significantly promoted by the incorporation of filler due to the lack of strong interfacial interaction between PU and S-LDH. On the contrary, the incorporation of both D-SLDH and D-LLDH promotes phase separation and crystallization. The pronounced enhancement in both hard-segment and soft-segment crystallization upon fast cooling can be attributed to the nucleating effects induced by

strong interfacial interactions between PDA-coated LDHs and hard segments; the enhanced hard-segment crystallization promotes phase separation and the subsequent soft-segment crystallization. Moreover, it is favorable to incorporate D-SLDH into the PU at a low loading as small fillers would mostly stay in hard domains, leading to appreciable enhancements in tensile modulus while preserving the chain mobility of soft segments. Thus, simultaneous enhancement in shape fixity, recovery stress and strain recovery ratio are achieved by incorporating 2 wt% D-SLDH. On the other hand, large and rigid nanosheets (D-LLDH) would hamper the chain mobility of soft segments, leading to lower strain recovery ratio.

Chapter 7 Polypropylene/D-clay Nanocomposites

7.1 Introduction

In previous chapters, it is demonstrated that the significant improvement in mechanical properties of thermoplastic elastomer (*i.e.* PU) could be attributed to the strong interfacial interaction between D-clay and the polymer. However, other than the superior adhesion capability of PDA, PDA also possesses radical scavenging capability. Hence, the stabilizing effect of D-clay in polymer system was investigated as well. In this case, PP was chosen as the polymer matrix since the polymer chain contains tertiary hydrogens which are prone to radical-induced degradation.²⁶ Different with previous chapters, special emphasis has been placed in studying the stabilizing mechanism and free radical scavenging efficiency of D-clay. On the other hand, the reinforcing effect of D-clay in thermoplastic PP system was also investigated and compared with that of organoclay.

7.2 Dispersion of D-clay in nanocomposites

In order to overcome the compatibility issues, terminal-functionalized PP oligomer was chosen as the compatibilizer so that the terminal functional groups can facilely interact with clay platelets without much steric hindrance.¹²⁹ Additionally, the long PP tails ($M_n = 8000$) may entangle with the PP matrix, promoting clay exfoliation. To

achieve a stronger interface, maleic anhydride-terminated PP (PPMA) was modified into amine-terminated PP (PPNH₂) since the two hydrogen donors of the primary amine group can form stronger hydrogen bonds, and probably also form covalent bonds through Michael addition¹⁵ with the PDA coating on clay (Scheme 7-1).

Scheme 7-1. Preparation route of PP/D-clay nanocomposites. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Guoqiang, D.; Lau, S. K.; Dasari, A.; Lu, X., *ACS Appl. Mater. Interfaces* **2013**, 5 (4), 1302-1309. Copyright 2013 American Chemical Society.)

In step I, the successful modification of PPNH₂ is confirmed by the FTIR spectra as shown in Figure 7-1a. The maleic anhydride (MA) group in PPMA transformed into an amide linkage after the reaction with the diamine.¹³⁰ This is verified by the disappearance of the absorption peaks at 1794 and 1717 cm⁻¹ corresponding to the MA group, and the appearances of a new peak and hump at 1707 and 1574 cm⁻¹ owing respectively to the carbonyl group and N-H bending of the amide linkage.⁸⁷ In step II, the splitting of Si-O band into two peaks at 1091 and 1037 cm⁻¹ for PPNH₂/D-clay (Figure 7-1b) implies the increased separation between clay layers due to PPNH₂ intercalation.¹³¹ The disappearance of the N-H bending band at 1574 cm⁻¹ in PPNH₂/D-clay spectrum implies that a considerable amount of amine groups in PPNH₂ may have reacted with the PDA coating. The intercalation is further evidenced by WAXD results (Figure 7-2a). Apparently, there is a slight increment of the interlayer *d*-spacing from 1.53 nm ($2\theta = 5.77^\circ$) for D-clay to 1.64 nm ($2\theta = 5.38^\circ$) for PPNH₂/D-clay, suggesting that PPNH₂ chains have diffused into the D-clay interlayer spaces owing to the favorable interactions between the PDA coating and PPNH₂. The TEM images of PPNH₂/D-clay also confirmed the presence of intercalated clay stacks that are well dispersed in the matrix, as shown in Figure 7-3. After compounding step (step III), the interlayer spacing of PP/D-clay nanocomposites remains similar with that of D-clay/PPNH₂, indicating the compounding process does not further exfoliate D-clays in PP matrix. For a fair comparison, PP/pristine clay (PP/clay) and PP/trialkylimidazolium-modified clay (PP/IM-clay) were also synthesized using similar method and used as references. As expected, PP/clay exhibits almost the same interlayer spacing with that of the pristine clay due to the poor compatibility between PP and the pristine clay. In contrast, the *d*-spacing of IM-clay increases from 2.2 nm⁹⁷ to 2.74 nm ($2\theta = 3.22^\circ$) after compounding, implying a better intercalation of IM-clay

by PP than D-clay. Similar to the WAXD data, TEM images in Figure 7-4 also reveal that at similar clay content, IM-clay dispersed slightly better in PP than D-clay. Here, some very thin clay stacks and even single layers are seen in the PP/IM-clay nanocomposites, while exfoliated clay layers are almost absent in the corresponding PP/D-clay nanocomposite. This could be attributed to the relatively weak interactions between IM-clay layers, such that they are easier to be separated and exfoliated by shearing during the compounding process. On the contrary, the strong interactions between D-clay layers make the D-clay stacks much harder to be further exfoliated.⁹⁶

Figure 7-1. Representative FTIR profiles of (a) PPMA and PPNH₂ and (b) PPNH₂, D-clay and PPNH₂/D-clay. (c) TGA curves of the PPMA, PPNH₂ and PPNH₂/D-clay nanocomposites (10 °C/min in air). (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Guoqiang, D.; Lau, S. K.; Dasari, A.; Lu, X., *ACS Appl. Mater. Interfaces* **2013**, 5 (4), 1302-1309. Copyright 2013 American Chemical Society.)

Figure 7-2. X-ray diffraction profiles of (a) clay, D-clay and PPNH₂/D-clay and (b) PP/clay nanocomposites. The figures in the sample nomenclatures represent the weight percentages of clay. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Guoqiang, D.; Lau, S. K.; Dasari, A.; Lu, X., *ACS Appl. Mater. Interfaces* **2013**, 5 (4), 1302-1309. Copyright 2013 American Chemical Society.)

Figure 7-3. TEM micrographs of PPNH₂/D-clay. There are some intercalated D-clay stacks dispersed in the matrix and the d-spacing was measured. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Guoqiang, D.; Lau, S. K.; Dasari, A.; Lu, X., *ACS Appl. Mater. Interfaces* **2013**, 5 (4), 1302-1309. Copyright 2013 American Chemical Society.)

Figure 7-4. TEM micrographs of (a1, a2) PP/D-clay-2.3, (b1, b2) PP/IM-clay-2.6 nanocomposites. The inset in (b1) shows the chemical structural of organic surfactant used to synthesise IM-clay. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Guoqiang, D.; Lau, S. K.; Dasari, A.; Lu, X., ACS Appl. Mater. Interfaces **2013**, 5 (4), 1302-1309. Copyright 2013 American Chemical Society.)

7.3 Thermo-oxidative stability

Generally speaking, the addition of clay minerals into polymers usually leads to better thermo-oxidative stability of the nanocomposites on account of Labyrinth barrier effect, which is highly related to clay dispersion. From Figure 7-5a, T_d of PP/clay is apparently lower than that of neat PP due to the catalytic effect of the unmodified layered silicates⁸ and its poor clay dispersion. On the contrary, the T_d of both PP/IM-clay and PP/D-clay nanocomposites increases with clay content owing to the formation of a silicate barrier layer during thermal decomposition, hence blocking the diffusion of oxygen into, and the diffusion of the volatile decomposition products out of the nanocomposites.⁹ Good clay dispersion in nanocomposites will give rise to good barrier properties, and thicker barrier layer can be formed with increasing clay content inhibiting the thermal decomposition. Regardless of the good clay dispersion in PP/IM-clay, the increment in T_d brought by D-clay is much more impressive than its counterparts. In fact, PP polymer chains consist of unstable tertiary hydrogens that are vulnerable to degradation via radical attack upon elevated temperature.²⁶ The significant enhancement in T_d of PP/D-clay nanocomposites implies that the PDA coating on clay can scavenge the chain end radicals by hydrogen atom transfer²⁸ and as a result hinder the chain scission. Even though trialkylimidazolium-modified clay (IM-clay) is more thermally stable than quaternary alkylammonium-modified clay,¹³² IM-clay is unable to impede the chain scission degradation of PP. It is the synergistic effect of the radical scavenging and the formation of the protective barrier by silicate layers that gave rise to the more impressive increase in T_d at higher D-clay contents.

The stabilizing effect of D-clay is further supported by onset oxidation temperature (OOT) characterizations. Different from T_d that relies on the evaporation of the

decomposed products and hence the barrier properties of the layered silicates, OOT characterizes the thermo-oxidative stability of the materials more accurately, and it is a more practical parameter for processing and applications.⁹ As observed in Figure 7-5b, the OOT of the PP/D-clay nanocomposites is 10 °C higher than that of neat PP. It is highlighted that the OOT of PP/IM-clay is lower than that of neat PP despite having a higher T_d as obtained from TGA results. The results suggest that while organoclay accelerates thermo-oxidative degradation, D-clay can retard thermo-oxidative degradation owing to the free-radical scavenger capability of the PDA coating. Distinct from the trend observed in T_d , PP/D-clay and PP/IM-clay does not increase with higher clay content. This may be due to the greater amount of PPNH₂ and PPMA with increasing clay content, which deteriorates the stabilizing effect imposed by D-clay.

Figure 7-5. (a) Thermal decomposition temperatures (T_d) in air and (b) oxidative onset temperature (OOT) of PP and the corresponding nanocomposites. T_d is defined as the temperature at 5 wt% of weight loss. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Guoqiang, D.; Lau, S. K.; Dasari, A.; Lu, X., *ACS Appl. Mater. Interfaces* **2013**, 5 (4), 1302-1309. Copyright 2013 American Chemical Society.)

7.4 Stability under UV irradiation

Other than thermal degradation, PP is also susceptible to sunlight-induced radical degradation, hence it is imperative to improve its UV resistance for practical usages.⁹⁴ Even though good dispersion state of clay minerals may also enhance photo stability owing to barrier effect,¹³³ previous works revealed that both organoclay and PPMA compatibilizer expedites the photo-degradation of PP due to the existence of active species in clay minerals and unstable anhydride units.^{8, 134} To verify if D-clay can indeed improve the photo stability of PP, all PP samples were exposed to intense UV irradiation. After adverse UV exposure for three weeks, an intense yet broad infrared absorption band corresponding to the presence of carbonyl species from photo-degradation was detected in the range of 1700-1800 cm^{-1} for UV-treated PP, PP/IM-clay and PP/clay (Figure 7-6b). According to literature, at the initial state of the photo-degradation, the absorption peak of carboxylic acid start to appear near 1712 cm^{-1} . This was followed by the appearance of the bands at 1720 and 1780 cm^{-1} owing to the formation of ketones and lactones with exposure periods longer than 60 h.^{8, 94} The broad band in the range of 1700-1800 cm^{-1} can be due to the overlapping of the different carbonyl peaks. However, it is striking to notice that the carbonyl absorption bands for the UV-treated PP/D-clay nanocomposites were very weak (Figure 7-6b), implying that D-clay can serve as an effective free radical scavenger and photon absorber to stabilize the PP matrices and lessen the photo-induced degradation. It is noted that the UV-exposed PP/D-clay-1.0, which contains only about 0.2 wt% PDA, showed almost no carbonyl absorption band, indicating the high effectiveness of D-clay as photoprotectant.

Figure 7-6. FTIR profiles of PP and the corresponding nanocomposites (a) before and (b) after UV treatment for three weeks. All the curves are normalized at 2722 cm^{-1} which is associated with CH_3 stretching and CH bending. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Guoqiang, D.; Lau, S. K.; Dasari, A.; Lu, X., *ACS Appl. Mater. Interfaces* **2013**, 5 (4), 1302-1309. Copyright 2013 American Chemical Society.)

The degree of photo-degradation was further examined by measuring the T_d s of the samples before and after the UV treatment. After the intensive UV exposure, the T_d s of neat PP, PP/clay and PP/IM-clay reduced significantly (Figure 7-7a) due to the radical-initialized chain scission. Outstandingly, the T_d s of PP/D-clay-1.0 and PP/D-clay-2.3 are 100 °C higher than that of neat PP and PP/clay, and 85 °C higher than that of PP/IM-clay after the UV exposure. Corroborating with the TGA data, melting points (T_m) of UV-exposed PP/D-clay are higher than the other counterparts owing to lower degree of photo-degradation (Figure 7-7b). In addition, Figure 7-8 illustrates that PP/D-clay-2.3 still possesses some flexibility after two months of hostile UV exposure. On the contrary, the neat PP sample becomes too brittle to be held due to the formation of large surface cracks, as shown in Figure 7-9. Commonly, photo-degradation will result in contraction of the surface layer on polymer materials. Consequently, surface cracks are formed, which in turn leads to appreciable reduction in mechanical properties of the photo-degraded products.⁹⁴ It is noticeable that the cracks on the surface of UV-PP/D-clay-2.3 are much finer and smaller than that on neat PP, PP/clay-2.5 and PP/IM-clay-2.6 surfaces. Hence, PP/D-clay nanocomposites remained fairly tough even after adverse UV exposure. All the results stated above are consistent and they indicate that the photo-stability of PP/D-clay is outstanding compared to unfilled PP and the other PP/clay nanocomposites. The impressive leap in photo-stability can be attributed to the concurrent stabilizing functions of D-clay as radical scavenger and sunscreen, which protects the underlying polymer matrix from severe degradation.

Figure 7-7. (a) T_d tested in nitrogen, (b) T_m of PP and the corresponding nanocomposites before and after UV treatment for three weeks. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Guoqiang, D.; Lau, S. K.; Dasari, A.; Lu, X., *ACS Appl. Mater. Interfaces* **2013**, 5 (4), 1302-1309. Copyright 2013 American Chemical Society.)

Figure 7-8. Thin films of PP and PP/D-clay-2.3 before and after two months of UV treatment. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Guoqiang, D.; Lau, S. K.; Dasari, A.; Lu, X., *ACS Appl. Mater. Interfaces* **2013**, 5 (4), 1302-1309. Copyright 2013 American Chemical Society.)

Figure 7-9. Optical images indicate the surface cracks (dark) observed from the UV-degraded samples after UV treatment for two months. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Guoqiang, D.; Lau, S. K.; Dasari, A.; Lu, X., *ACS Appl. Mater. Interfaces* **2013**, 5 (4), 1302-1309. Copyright 2013 American Chemical Society.)

7.5 Radical scavenging capability of D-clay

The radical scavenging activity of D-clay was investigated using the DPPH assay. Figure 7-10a indicates that the absorbance at 516 nm, which represents the characteristic absorption band of DPPH radicals, decreases with prolonged period upon the addition of D-clay to the DPPH solution. As shown in Figure 7-10b, the radical scavenging efficiency of D-clay is apparently higher than PDA particles. This can be attributed to the larger surface area of the PDA coating on clay. According to

literature, the radical scavenging mechanism of melanin-like PDA is dominated by hydrogen atom transfer from catechol groups.²⁸ In addition, the magnesium cations on clay surface may also serve as an effective catalyst for metal ion-coupled electron-transfer reactions, facilitating the radical scavenging activity of PDA coating.²⁸ As a result, the superior thermo-oxidative and UV stabilities of PP/D-clay nanocomposites can be related to (1) excessive catecholamine moieties in PDA coating on clay surface that serve as efficient free-radical acceptors,^{27, 28} (2) the relatively large surface area of the thin PDA coating that enables PDA to capture PP radicals and (3) presumably also the existence of magnesium cations in vicinity of PDA that facilitate the radical scavenging activity.

Figure 7-10. (a) UV-vis profiles obtained at different times upon addition of D-clay to DPPH solution at 298 K. (b) DPPH radical scavenging activity of D-clay, PDA and clay at different time. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Guoqiang, D.; Lau, S. K.; Dasari, A.; Lu, X., *ACS Appl. Mater. Interfaces* **2013**, 5 (4), 1302-1309. Copyright 2013 American Chemical Society.)

7.6 Mechanical properties

This work does not merely target to improve the stabilities, but also aim to simultaneously achieve reinforcement in PP with a very low content of D-clay. To determine the reinforcement effect of D-clay, the tensile properties of PP and PP/clay nanocomposites are indicated in Table 7-1. The typical tensile curves are given in Figure 7-11. Generally, the stiffness and yield stress of nanocomposites are improved by incorporating small amount of clay. A moderate reduction in elongation at break was observed for all nanocomposites. The Young's modulus of PP/D-clay increases with increasing clay content while the yield stress and elongation at break are independent of the clay content. Despite the slightly poorer clay dispersion state in PP/D-clay-2.3, its tensile properties are comparable with or slightly better than that of PP/IM-clay with a similar clay loading. Although the crystallinity of PP/D-clay-1.0 is similar to that of neat PP as measured using MDSC, PP/D-clay-1.0 exhibited a 30 % increase in modulus accompanied by a 20 % increase in yield stress compared to neat PP. The results indicate that the interactions between the amine groups of PPNH₂ and D-clay as well as that between PP tails of PPNH₂ and the PP matrix may be fairly strong, hence leading to significant reinforcement effect at very low clay loadings. The PP oligomer used in this study has a fairly high molecular weight ($M_n = 8000$). This may enable the PP oligomer that is adhered onto the clay surfaces to entangle with the long PP chains in the matrix or they may even co-crystallize and enhance interfacial stress transfer. Since this work aim to explore the simultaneous reinforcing and stabilizing effects of D-clay as well as its corresponding stabilizing mechanisms, the interfacial structure of D-clay may be a subject for future study. (refer to proposed future work)

Figure 7-11. Typical tensile plots of PP and its nanocomposites. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Guoqiang, D.; Lau, S. K.; Dasari, A.; Lu, X., *ACS Appl. Mater. Interfaces* **2013**, 5 (4), 1302-1309. Copyright 2013 American Chemical Society.)

Table 7-1. Tensile results of the PP and PP/clay nanocomposites. (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Guoqiang, D.; Lau, S. K.; Dasari, A.; Lu, X., *ACS Appl. Mater. Interfaces* **2013**, 5 (4), 1302-1309. Copyright 2013 American Chemical Society.)

	Young's Modulus (MPa)	Yield Stress (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
PP	1730 $\pm$ 68	36.5 $\pm$ 0.7	47.9 $\pm$ 0.6	812 $\pm$ 31
PP/D-clay-1.0	2253 $\pm$ 142	43.9 $\pm$ 1.1	48.5 $\pm$ 0.5	573 $\pm$ 24
PP/D-clay-2.3	2342 $\pm$ 135	43.7 $\pm$ 0.7	46.1 $\pm$ 0.5	561 $\pm$ 48
PP/D-clay-4.1	2536 $\pm$ 148	43.2 $\pm$ 0.5	43.4 $\pm$ 0.3	524 $\pm$ 56
PP/IM-clay-2.6	2309 $\pm$ 158	40.1 $\pm$ 0.8	40.1 $\pm$ 0.8	466 $\pm$ 116
PP/clay-2.5	1936 $\pm$ 117	39.3 $\pm$ 0.9	44.2 $\pm$ 1.9	655 $\pm$ 98

*Table 7-2. Crystallinity (X_c) of molded samples of PP and its nanocomposites estimated based on MDSC results. The percent crystallinity (X_c) was calculated by subtracting the reversing heat flow from the non-reversing heat flow, and dividing by the heat of fusion for 100% crystalline PP (209 J/g). (Reprinted with permission from Phua, S. L.; Yang, L.; Toh, C. L.; Guoqiang, D.; Lau, S. K.; Dasari, A.; Lu, X., ACS Appl. Mater. Interfaces **2013**, 5 (4), 1302-1309. Copyright 2013 American Chemical Society.)*

Sample	X_c (%)
PP	46
PP/D-clay-1.0	46
PP/D-clay-2.3	51
PP/D-clay-4.1	52

7.7 Summary

In this chapter, D-clay was readily incorporated into a semi-crystalline thermoplastic system and the simultaneous stabilizing and reinforcing effects of D-clay have been studied. In order to further improve the compatibility issues and stress transfer capability, PPNH₂ was used as the compatibilizer. The results showed impressive enhancement in both thermo-oxidative stability and UV resistance of PP with the addition of low amount of D-clay owing to the radical scavenging capability of the PDA coating on clay. The strong radical scavenging capability of D-clay was further proven using DPPH test and the radical scavenging effectiveness of D-clay is apparently higher than that of PDA particles on account of the larger surface area of the PDA coating on clay. On the other hand, the impressive boost in photo-stability of

PP/D-clay can be attributed to the screening effect of melanin-like PDA coating, which is able to absorb the hazardous irradiation and dissipates the excess energy via harmless paths.

Although the dispersion of D-clay is not as good as organoclay and that of in polar systems, but the mechanical properties of PP/D-clay nanocomposites are superior to that of neat PP; they are also better than that of the corresponding PP/organoclay nanocomposite owing to the stronger interfacial interactions between D-clay and PP matrix. The simultaneous enhancements in stiffness and stabilities make D-clay potential reinforcing fillers in practical applications, especially for outdoor environments, so as to prolong the service life of the materials.

Chapter 8 Conclusion and Recommendations

8.1 Conclusion

The structure-property relationships of the nanocomposites have been discussed in detail in previous chapters. On the basis of the investigation, a fundamental understanding of the reinforcing and stabilizing mechanisms of PDA-coated fillers in PU and PP systems, has been established, respectively. In fact, the incorporation of PDA-coated filler does not improve the exfoliation of clay to a greater extent compared to commercial organoclay (for both PU and PP systems). This is due to the strong attractive force between D-clay layers. However, the reinforcement effect brought by PDA-coated filler is more significant than that of organic modified filler for both PU and PP systems owing to the stronger interfacial interactions between PDA-coated filler and polymer matrices. The dispersion of D-clay in PU system is better than that of PP system since PU can form strong hydrogen bonding with D-clay. Hence, PU/D-clay showed impressive improvement in mechanical properties. Unlike PU, polymer chains of PP cannot form hydrogen bonding with D-clay and hence compatibilizer (amine-functionalized PP oligomer) was added to promote clay dispersion. It was found that the mechanical properties of PP/D-clay nanocomposites are better than that of the corresponding PP/organoclay nanocomposites despite of their poorer clay dispersion.

In this work, the reinforcement brought by PDA-coated fillers in PU system was studied with respect to filler surface modification, content and size. To circumvent

complexity in analysis, reactions that could lead to covalent bonding were avoided by adopting solution blending method and hence the reinforcement in PU nanocomposites could be attributed to the physical interfacial interactions between the filler and polymer. For polyether-based PU, the results showed that the reinforcement brought by D-clay is much more impressive than organoclay at similar clay loading. This is due to the extensive hydrogen bonding sites provided by the catechol groups of D-clay. Other than efficient stress transfer across the filler and polymer interfaces, the strong interfacial interactions between D-clay and hard segments also promoted more regular packing of the hard segments in the vicinity of D-clay, leading to more defined phase separation.

Furthermore, the effects of high D-clay loading on morphology, tensile properties and crystallization behaviors of PU were examined using polyester-based PU as the polymer matrix. It was found that a percolated D-clay network structure was obtained at above 5 wt% D-clay. The jammed D-clay structure hindered the movement of both hard and soft segments to certain extent, resulting in drastic enhancement in stiffness of the nanocomposites. On the other hand, the percolated morphology also facilitated hard segment crystallization as observed in WAXD patterns.

The reinforcement extent of PDA-coated filler in PU system was further explored by optimizing the filler size. In this case, Mg-Al LDH was chosen as the filler while PCL-based PU was used as the polymer matrix. The impacts of different filler size on phase morphology, crystallization behavior, shape memory performance of PCL-based PU were examined. Similar with previous work, the PDA-coated fillers interacted strongly with hard segments, promoted phase separation and improved the subsequent soft-segment crystallization. It was found that small fillers were mainly distributed in hard

domains at low loading. Hence, PU with low content of small filler (PU/D-SLDH-2) displayed excellent shape memory performance and significant improvement in mechanical properties without sacrificing the elasticity of the polymer matrix. By contrast, the large PDA-coated fillers were dispersed in both hard and soft domains. Consequently, the mobility of soft segment was restrained, leading to reduction recovery ratio.

Other than superior reinforcement brought by PDA-coated filler, the free radical scavenging capability of D-clay was evaluated using PP as the polymer matrix. The results revealed that the impressive improvement in both thermo-oxidative stability and UV resistance of PP with incorporation of a low amount of D-clay can be attributed to the efficient radical scavenging capability of PDA and large surface area of D-clay. Besides, the screening effect of PDA coating on clay also contributed to the superior UV resistance of the nanocomposites. It was found that simultaneous enhancements in stability and mechanical properties can be achieved by adding a very low amount of D-clay in PP.

8.2 Recommendations

Below are some recommendations for future work that can be performed.

8.2.1 Study the reinforcement mechanism of PP/D-clay nanocomposites

As reported in Chapter 7, for PP, the reinforcement brought by D-clay is indeed better than organoclay although the dispersion of D-clay is slightly poorer than that of organoclay. Therefore, the interfacial structure of D-clay could be a subject of future

study so as to understand the reinforcement mechanism of D-clay in PP. In fact, different surface modification will give rise to various interfacial interactions and hence can affect the crystallization of the corresponding polymer at the interface.^{52, 135} The filler surface with strong interfacial interaction could serve as heterogeneous nucleating agent for polymer crystallization, leading to the growth of transcrystalline layer along the interface of semicrystalline thermoplastics if sufficient annealing time is given.⁵² It has been shown that the transcrystalline region of reactive surface is thicker and larger than poorly interacted surface.¹³⁶ In this work, since an amine-terminated PP oligomer is used as the compatibilizer, it is possible that the PP oligomer chains may be attached onto D-clay through both covalent bonds and physical interactions. It is hypothesized that these PP oligomer chains may co-crystallize with PP chains in matrix and hence the interfacial interaction of PP/D-clay may be stronger than that in PP/organoclay. Further studies may be carried out to verify if transcrystalline region is thicker. In addition, the impact of deformation rate on the reinforcement can be a subject to study in the future.

8.2.2 Study the radical scavenging activity of D-clay using ESR spectroscopy

In chapter 7, the radical scavenging capability of D-clay was only evaluated using DPPH assay without the support of EPR (electron paramagnetic resonance) spectrum due to the limitation of instrument access. To further confirm the radical scavenging activity of D-clay, EPR spectroscopy will be performed in the future to semi-quantify the radical reactions between DPPH and D-clay.

8.2.3 Investigate the alignment of the hard segments of polyurethane on D-clay

In Scheme 4.2, it is proposed that hard segments tend to align on D-clay surfaces. Yet, this claim is not supported by any experiment. Thus, future work can be

performed to investigate the alignment of the hard segments on D-clay using solid state NMR (nuclear magnetic resonance) via properly designed testing methods.

8.2.4 Study the fracture toughness of polyester-based PU/D-clay at high loading concentration

As shown in Chapter 5, polyester-based PU/D-clay at high clay loading behaved more like thermoplastic than typical elastomer in tensile properties, yet ultimate elongation did not decrease too much extent. Therefore, it is interesting to study the fracture behaviour of the nanocomposites especially at high clay loading to verify the impact of strong interfacial interactions between the fillers and polymer matrices. Future work can be carried out to investigate the fracture toughness of PU thin films using essential work of fracture (EWF) test method.^{137, 138} It is expected that the hydrogen bonding can be created between D-clay and PU chain once the corresponding bonding sites meet each other during imposed deformation, hence great enhancement in resistance to cracking could be achieved.

8.2.5 Incorporate DOPA molecules into polymers for coating applications

Inspired by the versatile adhesive capability and impressive stability of PDA coating, it is desirable to incorporate DOPA molecules into polymer chains for anti-corrosion and self-healing coating. Indeed, numerous works have been done in synthesis of macromolecules bearing DOPA molecules for the design of adhesive and multifunctional materials.¹³⁹ The anti-corrosion properties of DOPA-containing coating has been successfully proven by Faure *et al.*, the protection provided by the coating is comparable to the banned highly toxic chromic treatments.¹⁴⁰ Yet, it will be more attractive if the coating is transparent in practical viewpoint and hence special

caution need to be taken during synthesis. Ideally, the polymer chain is highly branched by DOPA molecules. On account of the strong adhesion capability of DOPA, the coating can be strongly adhered to the surface of substrate meanwhile some DOPA units still bear the ability to scavenge the free radicals upon degradation, leading to high stability and long service life.

8.2.6 Incorporate PDA-coated fillers as compatibilizers for polymer blends

It has been reported that the domain size of polymer blends can be significantly reduced by incorporating low amount of organoclay.¹⁴¹⁻¹⁴⁴ For instance, the average domain size of incompatible polymer blends of nylon-6/poly(ethylene-ran-propylene) rubber (80/20 w/w) decreased drastically by adding only 0.5 wt% organoclay owing to the pinning effect of the exfoliated clay in nylon matrix.¹⁴³ Yet, the compatibilization efficiency also strongly depends on the filler size and the initial interlayer spacing,^{144, 145} while the extent of reduction in domain size is less related to the surface chemistry of the organoclay.¹⁴⁴ Hence, it is worth to explore the compatibilization efficiency of PDA-coated fillers for various polymer blend systems and investigate the underlying mechanisms. In this case, PDA-coated fillers may act as better stabilizers to prevent coalescence of the dispersed phase owing to the strong interfacial interactions with wide range of polymers. In addition, the particle sizes of PDA-coated fillers also need to be optimized in order to further enhance the compatibilization efficiency.

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APPENDIX A: List of Publications

1. Phua, S. L.; Yang, L.; Toh, C. L.; Huang, S.; Tsakadze, Z.; Lau, S. K.; Mai, Y.-W.; Lu, X., Reinforcement of Polyether Polyurethane with Dopamine-Modified Clay: The Role of Interfacial Hydrogen Bonding. *ACS Appl. Mater. Interfaces* **2012**, 4 (9), 4571–4578.
2. Phua, S. L.; Yang, L.; Toh, C. L.; Guoqiang, D.; Lau, S. K.; Dasari, A.; Lu, X., Simultaneous Enhancements of UV Resistance and Mechanical Properties of Polypropylene by Incorporation of Dopamine-Modified Clay. *ACS Appl. Mater. Interfaces* **2013**, 5 (4), 1302-1309.
3. Phua, S. L.; Yang, L.; Huang, S.; Ding, G.; Zhou, R. ; Lew, J. H.; Lau, S. K.; Lu, X., Shape Memory Polyurethane with Polydopamine-Coated Nanosheets: Simultaneous Enhancement of Recovery Stress and Strain Recovery Ratio and the Underlying Mechanisms. *Eur. Polym. J. (Submitted)*
4. Yang, L.; Phua, S. L.; Teo, J. K. H.; Toh, C. L.; Lau, S. K.; Ma, J.; Lu, X., A Biomimetic Approach to Enhancing Interfacial Interactions: Polydopamine-Coated Clay as Reinforcement for Epoxy Resin. *ACS Appl. Mater. Interfaces* **2011**, 3 (8), 3026-3032.

Note:

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