Polyethylene terephthalate/clay nanocomposites with polyhedral oligomeric silsesquioxane as dispersant

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DISPERSANT**

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Abstract

Polyethylene terephthalate (PET)/clay nanocomposite is an attractive high performance material that can be used for demanding applications due to its potential to exhibit superior properties at low clay loadings. However, organoclays do not have the adequate thermal stability to withstand the high temperatures required for processing PET and this limits the complete exfoliation of the organoclays and ultimately the properties and applications of the resultant nanocomposites. In order to overcome the degradation issues of the organic surfactants, the thesis focuses on two approaches, i.e. (1) to incorporate thermal stable polyhedral oligomeric silsesquioxane (POSS) into the PET/clay system to replace conventional organic surfactants, and (2) to completely do away with organic surfactant and prepare PET/clay nanocomposites with surfactant-free clay. In this work, the preparation of PET/clay nanocomposites using POSS compounds either as a surfactant (POSS-imidazolium salt) or a spacer (trisilanolphenyl POSS, Tsp-POSS) was investigated. In particular, the resultant structures and properties of the nanocomposites were evaluated in the areas of the extent of clay dispersion, thermo-mechanical properties and thermo-oxidative properties.

In order to facilitate the understanding of the impact of POSS aggregation on the structure of the nanocomposites, a fundamental study on the packing behaviors of the POSS-imidazolium surfactants with different molecular rigidities and at various surfactant loadings was carried out. Wide angle X-ray scattering (WAXS), transmission electron microscopy (TEM) and molecular modeling studies established a bilayer packing structure of the POSS-imidazolium surfactants within the clay intergalleries. It was found via WAXS and differential scanning calorimetry (DSC) studies that relative flexible POSS-imidazolium surfactants form a two-dimensionally ordered structure in clay, while the more rigid POSS-imidazolium surfactants display a disordered packing structure in clay. The relatively rigid

POSS-imidazolium surfactant-modified clay also exhibits a dramatic enhancement in thermo-oxidative stability as evidenced by thermogravimetric analysis (TGA) and DSC results. This is probably due to the presence of lesser trapped free surfactants amidst the disordered packing structure of the rigid POSS-imidazolium surfactants. In addition, different from what is typically observed in organoclays, the rigid POSS-imidazolium surfactant-modified clay exhibits increased clay interlayer spacings at reduced surfactant loadings.

Although the loose and random packing of the rigid POSS-imidazolium surfactant at reduced surfactant loading is believed to promote the exfoliation of POSS-modified clay in PET, the bilayer packing structure of the POSS-imidazolium surfactants and the poor compatibility between the surfactant and polymer resulted in an extremely poor dispersion of the POSS-modified clay in PET. This is despite that the POSS-imidazolium surfactant-modified clay has a very large interlayer spacing. At the same time, it was discovered that when Tsp-POSS, which comprises of active silanol groups, was introduced as a spacer to the POSS-imidazolium surfactant-modified clay, the level of clay dispersion of the nanocomposites and its properties improved to a limited extent.

Building upon the findings discussed above, surfactant-free PET/clay nanocomposites were successfully prepared using only a very small amount of Tsp-POSS to intercalate the clay and prevent recombination of clay stacks. Tsp-POSS not only acts as spacer to keep clay platelets apart, it also draws monomers and PET chains into the clay intergalleries. The addition of Tsp-POSS hence notably increased the state of clay exfoliation in the surfactant-free PET/clay nanocomposites. The lack of surface treatment of the clay also led to a higher degree of flow-induced clay orientation in the surfactant-free PET/clay nanocomposites. Consequently, dynamic mechanical analysis (DMA), TGA and DSC results revealed that thermo-mechanical and thermo-oxidative properties of the surfactant-free PET/clay nanocomposites were simultaneously enhanced.

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List of Symbols

d	d -spacing
λ	Wavelength of the X-ray radiation
θ	Diffraction angle
wt %	Weight percentage
T_c	Crystallization temperature
$t_{1/2}$	Crystallization half-time
S	Order parameter
n	Direction of preferred orientation
p	Silicate sheet normal
R	Exchange ratio
M_w	Molecular weight
A_r	Atomic weight
T_m	Melting temperature
$T_m - T_c$	Degree of undercooling
T_d	Thermal degradation temperature
L/D	Length to diameter ratio
E'	Storage modulus
T_g	Glass transition temperature
E'_n	Storage modulus of the neat polymer
E'_h	Storage modulus of the hybrid
T_{cc}	Cold crystallization temperature
X_c	Percentage of crystallinity
ΔH_m	Heat of fusion
ΔH_{cc}	Latent heat of cold crystallization
ΔH_m°	Melting enthalpy of 100 % crystalline PET
η_{inh}	Inherent viscosity

List of Abbreviations

2D WAXS	Two-dimensional wide-angle X-ray scattering
BHET	Bis-hydroxyethyl terephthalate
CDCl ₃	Deuterated chloroform
CEC	Cation exchange capacity
DI	Deionized water
DMA	Dynamic mechanical analysis
DMF	Dimethylformamide
DMT	Dimethyl terephthalate
DSC	Differential scanning calorimetric
EG	Ethylene glycol
ESI-MS	Electrospray ionization-mass spectra
EtOH	Ethanol
FD	Injection/flow direction
FWHM	Full width at half maximum
IMC	1-hexadecyl-2,3-dimethylimidazolium chloride
MMT	Montmorillonite
Na-MMT	Sodium montmorillonite
ND	Normal direction
NMR	Nuclear magnetic resonance
OIT	Oxidation induction time
OOT	Oxidation onset temperature
PAN	Polyacrylonitrile
PCL	Poly(ϵ -caprolactone)
PEO	Poly(ethylene oxide)
PET	Polyethylene terephthalate
PMMA	Poly(methyl methacrylate)
POM	Polarizing optical microscopy
POSS	Polyhedral oligomeric silsesquioxane
PP	Polypropylene
PP-g-MA	Maleic anhydride grafted polypropylene
PP-MA	Polypropylene-maleic anhydride
PS	Polystyrene
PVDF	Polyvinylidene fluoride
SAXS	Small angle X-ray scattering
TD	Transverse direction
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TPA	Terephthalic acid
Tsp-POSS	Trisilanolphenyl POSS
WAXS	Wide-angle X-ray scattering
XRD	X-ray diffraction

1 Introduction

1.1 Background

Nanocomposites are multiphase materials where at least one of the distinct constituents has a dimension in the nanometer scale (< 100 nm). Polymer/clay nanocomposites are achieved when clay sheets in the polymer matrices are delaminated into single layers with thicknesses in the nanometer length scale. Compared with conventional polymer composites, polymer/clay nanocomposites have a wide range of potential applications as structural, coating and packaging materials owing mainly to their light weight, ease of processing and dramatic improvements in thermal, flammability, mechanical and barrier properties at fairly low clay loadings (< 10 wt %). The superior properties were brought about by nanoscale dispersion of clay in the polymer matrices, resulting in a large aspect ratio found in individual clay sheet and resultant high surface area for polymer/clay interactions. Polymer/clay nanocomposites garnered tremendous interests amongst researchers in the past decades, because clay not only provides a direct reinforcement effect on the properties of the nanocomposites but its introduction also alters the structures and morphologies of the polymer matrices. This presents opportunities for further improving and tailoring the properties of the nanocomposites due to the synergistic effects of clay.

Among different levels of clay dispersion found in the nanocomposites, exfoliated clay dispersion offers maximum polymer/clay interactions and it is likely to give the most drastic

changes and enhancements in properties. Nevertheless, complete clay exfoliation is still a challenge and remains an issue that researchers actively pursue to solve. Primarily, this is because pristine clays are highly hydrophilic due to their charged nature and thus incompatible with polymers which are mostly hydrophobic. To disperse clay into polymer, it is necessary to convert the hydrophilic surface of the clay to hydrophobic via cation exchange, where compatibilizing organic modifiers/surfactants replace the inherent cations found within the clay galleries. The surface modification of the clay is therefore, a key element in the design and preparation of polymer/clay nanocomposites. It not only influences the extent of clay dispersion and clay orientation, but properties of the surfactants can also affect the structures and morphologies of the polymer, and hence, the final performance of the nanocomposites.

1.2 Motivation

The thesis is focused on the preparation, structures and characterization of polyethylene terephthalate (PET)/clay nanocomposites. PET is a high performance polymer, widely accepted for use in food packaging, automobiles and electronic applications. It is strong, tough, chemical resistant and environmentally friendly with the ease of recyclability. PET/clay nanocomposite provides unique and dramatic improvements in properties at low inorganic loadings, which makes it an attractive material for more demanding applications. Yet, there are several major drawbacks in the PET/clay system which limits their applications in high temperature and outdoor environments. At present, clay surfaces are often treated with organic surfactants containing long alkyl chains, such as quaternary alkylammonium, trialkylimidazolium and tetra-alkyl phosphonium salts [1-5], where the long alkyl chains help to expand the clay's interlayer spacing to facilitate their exfoliation in polymers. Such

organoclays do not, however, have adequate thermal stability to withstand the high temperatures required for processing PET [5]. PET can undergo thermal, hydrolytic, thermo-oxidative degradations due to the decomposition of the compatibilizing surfactant in clay [5-7]. These cause discoloration, poor clay dispersion state and reduced molecular weight, which ultimately result in poorer mechanical and physical properties. In addition, organoclays require high surfactant content, which makes them very expensive. Organic surfactants are also often specific to polymer matrices due to various degrees of compatibilities. Furthermore, the flexible surface of the organoclay can hinder the stable energy condition to form critical nuclei and retard nucleating effects of clay on enhancing crystallization rate of PET; a vital consideration in injection molded products [8-10].

Polyhedral oligomeric silsesquioxane (POSS) is an inorganic-organic hybrid $((R-SiO_{1.5})_8)$ that has higher thermal stability than organic surfactants. Its rigid and bulky structure can help to keep clay platelets apart and prevent clay to collapse into stacks. Another advantage of POSS is its cage has eight Si atoms at the corners, which allows chemical functionalization with attachments to tailor the hydrophobicity of the clay, and complement the organophilic nature of the polymer matrices. The hypothesis is that POSS can potentially help to minimize the degradation issue of conventional organic surfactants. At the same time, POSS can help to improve the dispersion state of clay to ultimately result in enhanced thermo-mechanical and thermo-oxidative properties of the nanocomposites.

To address the degradation issues of organic surfactants in PET/clay hybrids and to verify the hypothesis stated above, two approaches were adopted in this research work:

- One way is to replace the long alkyl chains in organic surfactants with POSS [11-23]. Yet, there is a great concern that the inherent tendency for POSS compounds to aggregate or crystallize may hinder the exfoliation of POSS-modified clay in the polymer matrix [11,14]. Consequently, the packing structure of POSS surfactants within the clay galleries is an

important contributing factor to the extent of clay dispersion achieved, and the thermal properties displayed by the material. In particular, the effect of molecular rigidity of the POSS surfactants on the orderedness of the packing needs to be examined; assuming the more ordered the packing, the more difficult is clay exfoliation. The new insights gained and the underlying principles governing packing structures of the POSS surfactants can serve as a foundation for studies on PET/POSS-modified clay system. As a result, the impact on the state of clay exfoliation in PET and their resultant properties by introducing POSS as surfactant can be better understood and controlled. This area of research is still relatively new and the findings are beneficial and may be applied onto other polymer/POSS-modified clay systems.

- Another method to resolve the degradation issues of organic surfactants is to do away with surfactants and fabricate PET nanocomposites with untreated clay [24-28]. However, when clay is not modified with surfactants, re-agglomeration of delaminated clay during processing is inevitable. Instead of using POSS as a surfactant (i.e. usually in excess of the cation exchange capacity (CEC) value of clay), POSS can be added in a small amount as a spacer to prevent collapse of clay into stacks. Due to the rigid and bulky structure of POSS, the surface of the clay need not be modified entirely to enable a large enough intergallery spacing for the intercalation of polymer chains. This reduces the cost for clay treatment with POSS and the detrimental aggregation issue of POSS surfactants can be minimized or avoided. To date, using POSS as spacer rather than a surface modifier in polymer/clay nanocomposite has not yet been reported. Exploitation of POSS with appropriate functional groups can also be aptly applied to further enhance clay dispersion and hence, properties. Herein, the hypothesis that POSS spacer can help to improve the dispersion state of clay to attain simultaneously good thermo-mechanical and thermo-oxidative properties in PET/clay nanocomposites is verified for the first time. Subsequently, using this new synthesis route to attain comparable clay

dispersion, allows a practical investigation on the polymer/clay interfacial behavior for organoclay and untreated clay. Knowledge gained will help to clarify how a flexible versus rigid surface can influence the interaction and behavior of the polymer and clay at their interface, and their consequential effects on structural and property development.

1.3 Scope and Organization of Thesis

Degradation of conventional organic surfactants cannot be avoided due to high processing temperature of PET. This led to recent efforts to prepare PET/clay nanocomposites using clay modified with POSS surfactants. Yet, reasonable dispersion of the POSS-modified clay in polymer matrices remains elusive. In an attempt to build a fundamental understanding on the influence of the packing structure of POSS surfactants, the first objective is to examine the structures and properties of POSS surfactant with different molecular rigidities. The second objective of the thesis is to evaluate the effects of POSS aggregation on the state of clay exfoliation in PET/POSS-modified clay hybrid and gain an insight into the advantages and limitations of using POSS-modified clay as potential filler for PET. The third objective is to develop and explore PET/clay/POSS nanocomposite using POSS as a spacer instead of surfactant, such that the issue of POSS aggregation can be mitigated and the issue of surfactant degradation can be reduced. Specifically, the impact of introducing a small amount of POSS compound on the degree of clay dispersion and its thermo-mechanical and thermo-oxidative properties are determined. Finally, upon achieving good clay dispersion in PET/clay/POSS nanocomposite, the fourth objective is to examine polymer/clay interfacial behavior, and evaluate the orientation of clay in PET/clay nanocomposites fabricated from organo treated and untreated clay. Such a study is important because the interface between the organic surfactant treated clay and polymer can significantly alter clay's orientation and

PET's crystallization behavior. These structural changes can have an effect on the nanocomposite's properties, such as oxygen barrier property, and subsequently, PET/clay nanocomposite's performance as a packaging material [28-29]. Ultimately, the knowledge gained from this research work is not just limited to PET/clay/POSS nanocomposites and can be extended to other semi-crystalline polymer/clay systems.

The thesis begins with an overview on the interest in PET/clay/POSS nanocomposites and the driving force of this research work. Chapter 2 provides literature review on the structure, preparation and properties of PET/clay nanocomposites. Chapter 3 presents the studies on the thermal properties and structures of the POSS surfactants in clay. In particular, the packing behaviors of the structurally different POSS surfactants in clay are discussed in depth. Chapter 4 describes the melt intercalation of PET with the synthesized POSS-modified clay, and examines the clay dispersion state of the nanocomposites. Possible reasons for poor POSS-modified clay dispersion in PET such as POSS aggregation and poor compatibility between the POSS treated clay and PET were proposed. In a proposition to tackle the aforementioned challenges, clay modified by dual POSS surfactant was prepared and reported. Chapter 5 examines how the utilization of POSS spacer can aid the state of clay exfoliation in in-situ polymerized PET/clay nanocomposites. It also describes the influence of POSS spacer incorporation on the properties of the resultant nanocomposite. Finally, Chapter 6 reviews general thoughts and summarizes important findings and recommendations for future research work.

2 Polymer/Clay Nanocomposites- A Review

This review chapter begins with a general background to clay, the purposes of clay modification, and the types of compatibilizing surfactant used for treating clay surfaces. Next, introductions to polymer/clay nanocomposites, its properties and its preparation are discussed. Critical issues to achieve exfoliated clay nanocomposites and characterization techniques to evaluate the state of clay dispersion are addressed too. Lastly, a brief description on the work that has been done on PET/clay nanocomposites and polymer nanocomposites based on POSS-modified clay will be presented.

2.1 Structure of Clay

In polymer nanocomposites, the most widely used nanofillers are layered silicates, in particular, montmorillonite (MMT). MMT consists of very thin layers, each made up of an octahedral sheet of alumina fused in between two tetrahedral sheets of silica, such that, the oxygen atoms from the alumina octahedral sheet also belong to the silica tetrahedral sheet (Figure 2.1). Although the layer thickness is around 1 nm, its lateral platelet dimensions may vary from 30 nm to several microns [30]. Therefore, the aspect ratio (length/thickness) of clay is very high. The MMT layers organize themselves in a parallel fashion (face-to-face) to form agglomerated tactoids with a regular van der Waals gap between them called interlayer [31]. Isomorphic substitution of Al^{3+} for Mg^{2+} or Fe^{2+} within the octahedral sheet generates a

negative charge defined by the cation exchange capacity (CEC). In the pristine form, the charges on the clay layers are counterbalanced by exchangeable metal ions, such as Na^+ or Li^+ or Ca^{2+} that are situated within the interlayer spacing. Other than the preferred face-to-face coagulation, MMT platelets can also form edge-to-face and edge-to-edge structures. The interactions among the MMT platelets depend on the pH, ionic concentrations as well as the additives, such as surfactants present [32].

Figure 2.1. The structure of montmorillonite (MMT) [33].

2.2 Properties of Clay

Clays are excellent candidates for the preparation of polymer nanocomposites because they are abundant, inexpensive and safe to use in consumer products. Clay has high aspect ratio of as large as 1000 when fully dispersed into single layers. This results in high surface area for polymer/clay interactions. Another important aspect of clay is that the surface chemistry of clay can be easily modified by ion-exchange procedures. It is also attractive due to its chemical stability and toughness, meaning it can withstand solvents, polymerization temperature and compounding shear without fear of degradation. Clay has dimension below

the visible light wavelength and this allows the nanocomposites to remain transparent. In addition, property enhancement in nanocomposites can be observed at low loading levels of clay, thus maintaining light weight and low cost. These properties thus, render clay as suitable and popular nanofiller in nanocomposites.

2.3 Organic Modification of Clay

Nanodispersed clay in most polymers is not easily achieved because of their preferred face-to-face agglomeration. Moreover, due to the charged nature of clays, the alkali counter-ions allow the formation of a water layer to form in the interlayer spacing [34-35]. The hydrate formation of alkali cations within the intergallery causes water swelling of the clay. This characteristic renders the clays to be highly hydrophilic and intrinsically incompatible with the hydrophobic polymer, and as a result further hinders the dispersion of clay. It is hence necessary to convert the hydrophilicity of the clay to suit the hydrophobicity of the polymer by cation exchange procedures where compatibilizing modifiers/surfactants can easily replace the cations that are not strongly bound to the clay surface (Figure 2.2).

Figure 2.2. Schematic picture of an ion-exchange reaction. The inorganic, relatively small sodium ions are exchanged against more voluminous organic onium cations [36].

The two main purposes of clay modification are (1) to expand the intergallery distance between the clay layers such that large polymer chains can enter into this extended spacing and (2) to change the surface chemistries of the clay and improve the compatibility of the hydrophilic clay and hydrophobic polymer [36]. Both objectives aim to ultimately achieve good clay dispersion, which is believed to be vital for the improvement in properties of the nanocomposites to reach maximum potential. The degree of clay dispersion and their correlation to the enhancement in properties will be discussed later.

The compatibilizing surfactant is generally a molecule constituted of both a hydrophilic function and an organophilic function. Occasionally, the surfactant may contain functional groups that can interact with the polymer or induce polymerization. The type of surfactants to be used in clay modification affects suitable compatibilization and can influence the effectiveness of clay delamination. At present, clay surfaces are often treated with organic surfactants containing long alkyl chains, such as quaternary alkylammonium, trialkylimidazolium and tetra-alkyl phosphonium salts such as those shown below in Figure 2.3 [1-5].

Figure 2.3. Some of the conventional organic surfactants used in clay modification.

The interlayer distance of the clay depends on both the length of the surfactant and its packing density (or charge density of the clay). The longer is the surfactant length and the larger is the packing density, the further the clay layers are expanded. The surfactant molecules can either form lateral mono or bilayers within the interlayer spacing. However, as the negative charge generates within the silicate layer, the cationic head group of the surfactant prefers to reside on the clay's surface, while the organic tail radiates away from the surface [30]. This can lead to tilted paraffin-type mono or bilayer arrangements as depicted in Figure 2.4. Moreover, through molecular dynamics simulations, it was verified that the interlayer structure becomes more ordered and then forms bilayer arrangement as the chain length of the surfactant increases [37]. Therefore, the interlayer distance also depends on the organization and orientation of the surfactants in the organoclay.

Figure 2.4. Alkyl chain aggregation in layered silicates: (a) lateral monolayer; (b) lateral bilayer; (c) paraffin-type monolayer and (d) paraffin-type bilayer [38].

2.4 Structure of Polymer/Clay Nanocomposites

Polymer/clay nanocomposite refers to a composite where the major constituent is a polymer and the minor constituent, i.e. clay has at least one dimension below 100 nm. Indeed,

the mixing of polymer and clay does not necessary yield a nanocomposite. When a phase separated composite is formed, i.e. analogous to conventional composite, poor interaction between polymer and clay leads to poorer than expected mechanical properties. In fact, clay agglomeration weakens the material [39]. The properties enhancement in nanocomposites is largely due to the interfacial interaction of the clay and the polymer matrix [40]. Hence, it is no wonder that the key to the improvement of the properties of polymer/clay nanocomposites lies in how the silicates are disperse in the polymer matrix. There are 3 types of polymer/clay nanocomposites depending on the degree of clay dispersion, namely, conventional microcomposite, intercalated nanocomposite and exfoliated nanocomposite as illustrated in Figure 2.5. Conventional microcomposite contains clay that is dispersed in the segregated phase and there is no intercalation of the polymer. The intercalated nanocomposite consists of a regular insertion of the polymer in between the clay layers such that the interlayer spacing is expanded but still bears a well-defined spatial relationship to each other. On the other hand, the exfoliated or delaminated nanocomposite has the clay layers individually dispersed in the polymer matrix.

It is believed that exfoliated clay dispersion maximizes the polymer clay interactions and should lead to the most drastic changes in properties. Therefore, a considerable on-going effort has been done to exfoliate clay in polymer nanocomposites. This is because when clays are exfoliated, the great interfacial area and high aspect ratio created is believed to form a network with the polymer matrix to carry the applied load and deflect cracks [41]. Consequently, this results in remarkable enhancements in the properties of the nanocomposites. However, it remains a challenge as to how polymer with average radius of gyration 10- 20 times higher than the interlayer spacing of clay is able to diffuse into the galleries [42]. There are several factors that are crucial for the formation of exfoliated structures. This includes having (1) an adequately large interlayer spacing for the polymer

chains to enter, (2) sufficient thermal stability of the surfactants to withstand high processing conditions so as to make sure clay remains surface treated, (3) good compatibility between polymer and surfactant and (4) having enough conformational freedom of the polymer chains to intercalate into and within the clay layers.

Figure 2.5. Scheme of different types of composite arising from the interaction of layered silicates and polymers: (a) phase separated microcomposite; (b) intercalated nanocomposite and (c) exfoliated nanocomposite [30].

2.5 Determination of the Degree of Clay Dispersion

As highlighted, a certain extent of clay dispersion must be attained before significant improvements in properties can be observed. The evaluation of clay dispersion state in the polymer/clay nanocomposite is carried out by a combination of techniques, namely, X-ray diffraction (XRD), polarizing optical microscopy (POM) and transmission electron microscopy (TEM). Figure 2.6 summarizes the primary techniques carried out to evaluate the clay dispersion state. The dispersion of the clay is determined by *d*-spacing (or basal spacing),

which is the sum of the thickness of a single layer clay (i.e. typically 1 nm) and the interlayer distance. The average d -spacing (d) can be determined conveniently by XRD and calculated by Bragg's Law, $\lambda = 2d\sin\theta$, where θ is the diffraction angle obtained from the X-ray diffraction pattern and λ is the wavelength of the X-ray radiation. The position, shape and intensity of the basal diffraction of clay are used to identify the structure of the polymer/clay nanocomposites (Figure 2.7). As an example, a disordered system results in broadening of the clay's diffraction peak and reduction in the intensity. The intensity of the diffraction peak gives information on the number of tactoids (stacks of clay) and the full-width-at-half-maximum (FWHM) of the peak assess the degree of the order of clay stacks.

Figure 2.6. Complementary techniques used to determine the degree of clay dispersion.

For an incompatible polymer/clay system, the diffraction peak of clay exhibits no change in position as the structure of clay is unaffected. If the diffraction angle of clay is shifted to lower angles, it indicates the strong intercalation capabilities of polymer in the silicate layers. On the contrary, the basal reflection shifts to higher angles when degradation of the organic

surfactant occurs and clay collapses. In the case when the clay is completely dispersed in the exfoliated nanocomposite, no low angle diffraction peak is displayed. This is either because too large a d -spacing is obtained or because the silicate layers no longer exhibit any ordering. Nonetheless, absence of the low angle clay diffraction peak does not necessary correlate to well dispersed exfoliated clay in the polymer matrix, as it can be the result of insensitive detection of the clay in small amounts or disordered but poorly dispersed clay. Indeed, surface defects in the polymer/clay nanocomposite specimen and a heterogeneous distribution of interlayer periodicity can also result in broadening and shifting of the peaks [43]. This means that relying alone on XRD, makes the evaluation of clay dispersion difficult. Furthermore, XRD do not provide information on the spatial distribution and structural inhomogeneities (i.e. for instance, having both intercalated and exfoliated morphologies) of the clay in the nanocomposites.

Therefore, POM and TEM are strategies often employed to complement the inadequacies of XRD. TEM provides direct observation of the clay layers in the nanometer scale, but as the area of observation is very small, a good representative of the state of clay dispersion in the nanocomposite as a whole cannot be obtained. Hence, in order to define the overall structure of the nanocomposite, POM complements by identifying any clay tactoids in the micron or sub-micron level.

Figure 2.7. Schematic depicting the expected x-ray diffraction patterns for various types of hybrid structures [44].

2.6 Preparation of Polymer/Clay Nanocomposites

The success of polymer/clay nanocomposites preparation lies in suitable organic modification of clay (as discussed in section 2.3) and the effective mixing of the clay and polymer matrix. In order to achieve effective clay dispersion, sometimes, even before organic modification of the clay, the starting size of the clay particles can be reduced. Clay comes in various sizes; primary particles of clay are made of tightly bound tactoids (consist of platelets that are parallel silicate layers), which can align to form even larger ellipsoidal agglomerates as illustrated in Figure 2.8. On the contrary to single clay layers, which has an aspect ratio as high as 1000, poorly dispersed large clay particles only have an aspect ratio of around 10. The large clay particles and clay agglomerates are hence, undesirable as they do not allow any polymer intercalation and they are ineffective at reinforcing the polymer matrix. It is therefore necessary to reduce the starting size of the primary clay particles or remove the large agglomerates of clay. There are several methods to fractionate the clay. This includes

using (1) high speed homogenizer to break down the particle size of the modified clay and (2) centrifugal separation of raw clay particles, where the larger agglomerates of clay are separated from the supernatant [45-46].

Figure 2.8. (a) Schematic of the morphology of clay [45]. (b) The original MMT dispersion in water is centrifuged to separate out the large aggregates and fractionated MMT (FMT) [46].

In general, there are 3 main routes at which the polymer and clay can be incorporated to form nanocomposites and they include, (1) solution intercalation, (2) in-situ polymerization and (3) melt intercalation. Another less popular approach that prepares polymer/clay nanocomposite based on sol-gel technology is also sometimes adopted. The silicates are synthesized and formed in-situ within an aqueous solution (gel) of the polymer matrix and silicate building blocks. The idea is that the polymer gets trapped within the silicate layers as they grow. As this technique is more often used for double-layer hydroxide based nanocomposites and less applicable for layered silicates, it will not be discussed further in the following section.

2.6.1 Solution Intercalation

Solution intercalation is based on a solvent system where the clay is swelled and the polymer is soluble. In the solution, the polymer chains are able to intercalate into the interlayers of the swelled clay and disperse the clay into individual layers. However, when the solvent is removed, the polymer chains are not able to keep the silicate layers apart and the clay tends to collapse and aggregate again. This often leads to an intercalated nanocomposite. The major advantage of this technique is that it can be used to synthesize nanocomposites of polymers with no or low polarity [31]. Nevertheless, very few polymer/clay nanocomposites are prepared using this method due to the copious amount of organic solvents used. This approach is therefore, not environmental friendly and not practical from an industrial point of view.

2.6.2 In-situ Polymerization

Preparation of the nanocomposites by in-situ polymerization involves the polymerization of monomers situated within the interlayer of the clay to consequently result in an expanded interlayer distance. As the monomers are smaller in size, they are believed to be able to diffuse more easily into the clay galleries compared to polymer chains. Ideally, the silicate layers are homogeneously dispersed on a nanometer level at the end of the polymerization, whereby the clay structure will be destroyed by the growing polymer, giving rise to an exfoliated nanocomposite (Figure 2.9). In order to achieve exfoliated clay, polymerization that takes place within the galleries should proceed faster than the polymerization that takes place on the external of the galleries and that there must be effective monomer diffusion into the interlayer spacing for polymerization to proceed [47]. This means that the clay is often intercalated with the catalyst [47-49] or with surfactants that have reactive groups that can interact with the monomer [50-51]. The additional modifier acts as a catalyst that further

increase the polymerization rate within the galleries and facilitates absorption of the monomers between adjacent clay layers during polymerization. Although nanocomposites prepared using this method exhibit enhanced properties, large reactors are required and thus industrial bulk production is unlikely.

Figure 2.9. A schematic representation of polymer/clay nanocomposites obtained by in-situ polymerization [48].

2.6.3 Melt Intercalation

Melt intercalation involves blending a molten thermoplastic polymers typically with an already organically modified clay by a compounding equipment, such as an extruder. The heat and mechanical shear force during extrusion helps to facilitate mixing and optimize the polymer clay interactions. Melt intercalation method is more environmentally benign with respect to solution intercalation due to the absence of solvents. Additionally, in comparison to in-situ polymerization, synthesizing polymer/clay nanocomposites by melt intercalation is industrially more viable and closer to commercialization.

However, there is no straightforward approach to predict whether a nanocomposite will be formed via this technique. Depending on the shear force and the compatibility between polymer and clay, this process generally leads to the formation of intercalated and/or exfoliated nanocomposites. Factors affecting the level of clay dispersion can be summarized below:

Thermodynamic interactions. To generalize factors governing the degree of intercalation/exfoliation in the nanocomposites, Vaia and Giannelis et al. developed a mean-field, lattice based model [52-53]. The model concludes that the outcome of polymer intercalation is determined by a combination of entropic and enthalpic factors. From an entropic standpoint, the entropy loss due to the confinement of the polymer melt within the clay interlayer may be compensated by the entropy gain associated with the separation of the clay (i.e. increased d -spacing) and greater conformational freedom of the surfactant chains. This can result in a thermodynamically stable system, where the net entropy change is near zero. In the case where there is a change in net entropy due to inadequate compensation in entropy loss, even if clay has been delaminated due to large shear forces, the system remains thermodynamically unstable and re-agglomeration of the clay particles can take place. Consequently, the effectiveness of the formation of the nanocomposites by polymer intercalation is greatly affected by the conformational freedom between the polymer and surface of the clay, which in turn is influenced by d -spacing and packing density of the surfactants. This means that the type of surfactant, length of surfactant chain, packing density and packing structures all play important roles.

Polymer/clay interactions. Upon achieving a net entropy change near zero, polymer intercalation now depends on the enthalpic factor, i.e. polymer/clay interactions. High levels of clay exfoliation can be achieved in nylon 6/clay nanocomposites due to good polymer/clay interactions brought about by hydrogen bonding. In this case, surfactant with single alkyl tail

gives the best degree of clay dispersion, while surfactant with more than one alkyl tails diminishes the favorable polymer/clay interaction and decreases the extent of exfoliation [54]. On the other hand, non-polar polymers require surfactant with increasing number of alkyl tails to improve the dispersion of organoclay in the polymer matrix. Sometimes even with organic treatment to the clay, dispersion of the organoclay in non-polar polymers cannot be achieved. These polymers will need to be functionalized with polar groups in order to increase the polymer/clay interaction. An example is found in the preparation of polypropylene (PP)/clay hybrids, where maleic anhydride grafted polypropylene (PP-g-MA) is added as a compatibilizer to enhance interaction between PP and clay [55]. Hence, it is established that the interactions between polymer and clay should be maximized in order to promote polymer intercalation into clay galleries and attain exfoliated clay. It is no wonder that the organic modification of the clay is thus a critical consideration determining the resultant structures of the nanocomposite.

Type of polymer. Fornes et al. also reported that the degree of intercalation or exfoliation of silicate layers is based on a step-wise mechanism (Figure 2.10), i.e. (1) shearing of organoclay particle to stacks of platelets and then to smaller tactoids, and (2) diffusion of the polymer chains into the clay intergalleries [56]. This suggests that the molecular weight of the polymer can influence the level of clay dispersion in the resulting nanocomposites in two ways, depending on the mechanism which dominates. One is that the greater the molecular weight of the polymer matrix, the larger is the melt viscosity and hence the higher the shearing force. On the other hand, the diffusion of the polymer chains decreases when molecular weight increases.

Processing conditions. Based on the above discussed stepwise mechanism, the mixing equipment and conditions can also influence the state of clay exfoliation [57]. For instance, the extruder screw configuration, the residence times and the melt viscosity during the

extrusion (as discussed earlier) impose different stresses on the clay to break up aggregates and to shear the clay stacks into smaller tactoids. However, it is apparent that no matter how well the processing conditions are optimized; there is still a limit to the extent of clay dispersion that can be attained by purely mechanical forces. In fact, the processing conditions have negligible effects on clay dispersion if the polymer/clay affinity is low [58].

Figure 2.10. Stepwise mechanism of clay platelet exfoliation in the melt compounding of nanocomposites: (a) organoclay particle breakup, (b) clay tactoids breakup, and (c) platelet exfoliation [56].

2.7 Properties of Polymer/Clay Nanocomposites

The addition of a small weight percentage of clay, typically 1-10 wt % into polymers often leads to dramatic improvements in the performance of the nanocomposite, such as mechanical, barrier and thermal properties.

2.7.1 Mechanical Properties

The first reported drastic improvements in tensile strength and modulus were achieved in nylon 6/ clay nanocomposites by the Toyota researchers with just only 4 wt % of delaminated clay. Like in conventional composites, one of the explanations put forth for the reinforcing mechanism of clay is that the rigid filler has higher modulus, and load applied can be efficiently shared between the polymer and clay. Many researchers believe that the substantial reinforcements may also be attributed to the interfacial properties between the clay and polymer and the formation of a constrained region in the vicinity of the clay where the stiffened polymer chains have restricted mobility. Regardless, it is obvious that the reinforcement effect requires the polymer and clay to have maximum contact and bonding. This means that adequate exfoliation and strong polymer/clay affinity are needed to accomplish improved mechanical properties. Varlot et al. observed from their experiments that exfoliated nylon 6/clay nanocomposites have better properties than their intercalated counterparts [59]. Indeed, Brune and Bicerano et al. and Fornes and Paul et al. developed theoretical models and proved that the mechanical properties exhibited by the nanocomposites hinges strongly on the degree of clay exfoliation [60-61]. Thus, despite that clay in the nanocomposites is present in very small amounts, the clay's high aspect ratio when exfoliated, ensures large surface area for polymer/clay interactions such that significant improvement in modulus can be observed.

At the same time, some researchers also proposed that the silicate layers could generate some crystallinity at the interface, explaining part of the reinforcement effect. In semi-crystalline polymer, crystalline lamellae that are present can be seen as nanofillers that are reinforcing the polymer matrix [62]. In polymer/clay nanocomposites, the incorporation of just a small amount of clay can alter the structure of the semi-crystalline matrix leading to effects that further strengthen the polymer matrix. In fact, crystallinity, crystallization rate,

crystalline lamellae orientation and crystal perfection can be modified upon the introduction of clay [63-66]. It is well established that clay is a good nucleating agent for crystallization of the polymer in for example, PET/clay [67] and polyamide-6/clay [68] nanocomposites. In these cases, clay fillers act as primary nuclei to promote heterogeneous crystallization. Stronger nucleating effects are typically evidenced by a decrease in the crystallization temperature (T_c) and crystallization half-time ($t_{1/2}$). However, there are contradicting reports on overall crystallization rate, degree of crystallinity and crystal perfection upon clay addition. For instance, in polypropylene- maleic anhydride (PP-MA) polymeric system, Maiti et al. reported that the crystallization rate is not affected by the addition of clay [69]. Also, Di Maio et al. observed in poly(ϵ -caprolactone) (PCL)/clay nanocomposites that in spite clay acted as nucleating agents, reduced crystal perfection and degree of crystallinity were attained [70]. This can be attributed to the confinement of polymer chains and restricted crystal growth in the presence of clay. Lower polymer chain diffusion rate owing to higher viscosity at high clay content can also lead to reduced crystallization kinetics [54]. Thus, it appears that the outcome of the introduction of clay on the structural behaviors of the semi-crystalline matrix is more complex than it seems and perhaps also polymer-specific.

2.7.2 Barrier Properties

The considerable decrease of permeability brought by nanocomposites has a major advantage in applications that include packaging films for moisture and oxygen sensitive foods and electronics. The permeability to liquids and gases had been demonstrated to reduce to half when a low loading of clay was dispersed in polypropylene [71]. A similar reduction in oxygen permeability in nylon 6/clay nanocomposites had also been reported [72]. It is widely accepted that the significant improvement in barrier properties can be explained by

the concept of tortuous path described by Nielsen [73]. That is, the slow down in transmission of gases and moisture in nanocomposites was achieved by creating a tortuous path for the diffusion of gas molecules through the polymer matrix among the clay layers as illustrated in Figure 2.11. Compared to fillers such as spheres and fibers, platelets (or sheets) are able to most effectively maximize the diffusive path length due to their large length-to-width ratio. Clearly, the highest tortuosity is achieved when the sheets normal (**p**) are arranged in the direction of diffusion (or the preferred orientation, **n**) (i.e. when $S = 1$) as demonstrated in Figure 2.12. In this arrangement, the enhancement in barrier properties is believed to be the most pronounced. Therefore, the relative permeability is highly dependent on the sheet length, concentration, orientation and state of clay exfoliation [72].

Figure 2.11. Formation of tortuous path in polymer/clay nanocomposites [33].

Figure 2.12. Schematic illustration showing the orientation order of the clay sheet. The order parameter (S) defines the direction of preferred orientation ($\mathbf{n}$) of the silicate sheet normals ($\mathbf{p}$) with respect to the film plane [72].

2.7.3 Thermal Properties

Polymer/clay nanocomposites are able to show improved thermal stability at lower clay loadings than conventional composites [74-75]. The thermal stability of the nanocomposite is often determined by thermogravimetric analysis (TGA), where the weight loss during degradation due to volatile products is examined as a function of temperature or time under nitrogen or air atmospheres. The nanocomposites usually exhibit more obvious increase in thermal stability under oxidative conditions than in non-oxidative conditions [76-77]. Enhanced thermal stability in nanocomposites is realized due to the development of a carbonaceous char layer on the surface of the clay during oxidative combustion as illustrated in Figure 2.13. The surface char acts as an excellent insulator and a mass transport barrier. This barrier slows down the oxygen supply as well as the escape of the combustion products generated during decomposition [71]. As a result, this degradation mechanism is greatly related to the level of clay dispersion. Furthermore, in order to achieve effective surface char layer, it is necessary to have maximum interaction between the clay and polymer matrix.

Hence, the barrier effect is more likely to be observed in exfoliated nanocomposites than in microcomposites.

Figure 2.13. Schematic representation of the ablative reassembling mechanism of a nanocomposite during combustion [76].

Despite the general improvement of thermal stability observed in nanocomposites, decrease in thermal stability has also been reported [78-79]. In these cases, the accelerated decomposition can be attributed to Hoffmann elimination reaction of the alkylammonium cations [80] and clay-catalyzed degradation [81-83]. It is noted that the catalytic activity of clay give rise to not only char formation resulting in the barrier effect but also polymer degradation. The polymer degradation occur due to the hydroxyl groups on the clay's surface and hydrated water bound to clay that can act as acidic sites [82]. In addition, transition metal ions in clay, such as iron (Fe) can act as catalysts for accelerated decomposition of hydroperoxides, which is a by-product during polymer degradation. The decomposition of hydroperoxides can then produces new free radicals and propagate polymer degradation [83].

This suggests that clay can have two opposing effects on the thermal stability of nanocomposites, i.e. a barrier effect leading to improved thermal stability as well as a catalytic effect on degradation resulting in reduced thermal stability. The clay morphology and barrier effect prevails with low clay loading and the catalytic effect becomes dominant

with increasing clay loading such that the thermal stability of the nanocomposites becomes poorer [78]. Even though the effects of clay on the thermal stability of the nanocomposites is contradictory, the possibility to attain improvement in thermal stability at low clay loading, lower cost, light weight and ease of processing helps to open up opportunities for more applications.

2.7.4 Summary

On the whole, an obvious conclusion is drawn that the extent of property enhancements attained in the polymer/clay nanocomposites is highly dependent on its level of clay dispersion. Other contributing factors include clay orientation, polymer/clay interactions and type of polymer, etc.

2.8 PET/Clay Nanocomposites

2.8.1 Introduction

Polyethylene terephthalate (PET) is a thermoplastic polymer widely used in packaging, automobiles and electronic applications. PET is synthesized by a two-step reaction as shown in Figure 2.14. The first step is the transesterification of ethylene glycol (EG) and dimethyl terephthalate (DMT) with methanol as a byproduct to form bis-hydroxyethyl terephthalate (BHET). Alternatively, BHET can also be prepared via esterification reaction of terephthalic acid (TPA) and EG with water generated as a byproduct. The second step involves the polycondensation reaction of the BHET monomers to form the PET polymer.

Figure 2.14. Synthesis route of PET polymerization.

PET/clay nanocomposites compared to neat PET provide great improvements in thermo-mechanical and barrier properties at low inorganic loadings. Overall, among the preparation routes for polymer/clay nanocomposites (as discussed in section 2.6), in-situ polymerization and melt intercalation/compounding are more popular approaches [84], while solution intercalation is least employed to prepare PET/clay nanocomposites due to the copious amount of toxic solvents used (i.e. solvent mixtures of phenol/chloroform or phenol/tetrachloroethane) [85].

In the beginning, PET/clay nanocomposite was primarily developed to attain improved barrier properties that are essential in packaging materials. However, as the preparation of PET/clay nanocomposite is not as successful compared to other polymers, plus the relative permeability relies heavily on the state of exfoliation of clay in the polymer matrix, there is still a lack of success in the enhancement of the barrier properties displayed by PET/clay nanocomposites.

2.8.2 PET/Organic Surfactant-Modified Clay Nanocomposites

Indeed, current PET/clay systems have a number of drawbacks that limit their applications and recyclability. At present, clay surfaces are often treated with surfactants containing long alkyl chains, such as quaternary alkylammonium, trialkylimidazolium and tetra-alkyl phosphonium salts [1-3]. These organoclays require high surfactant content, which makes them fairly expensive. The coverage of clay surface by organic surfactants also retards nucleating effects of clay [8], which is a vital issue for injection molded products. Most importantly, organoclays do not have the adequate thermal stability to withstand the high temperatures required for processing PET [86-88]. PET can undergo thermal, hydrolytic, thermo-oxidative degradations owing to the decomposition of the surfactants [5, 89]. Although trialkylimidazolium and tetra-alkyl phosphonium are reported to be more thermally stable than their alkylammonium counterparts, significant degradation is still observed with the former two surfactants [5]. It causes poor clay dispersion state and reduced molecular weight, ultimately resulting in poorer mechanical and physical properties. This suggests that the preparation of PET/clay nanocomposites poses a challenge because of its high processing temperature, and that neither melt intercalation, nor in-situ polymerization can be effectively utilized for PET/organoclay systems.

2.8.3 PET/Surfactant-Free Clay Nanocomposites

In spite of the need to treat hydrophilic clay with organic surfactants to facilitate polymer intercalation by increasing interlayer spacing and compatibility, there are continuous attempts to fabricate PET nanocomposites with untreated clays so as to eliminate degradation issue of organic surfactants [90-94]. Yet on the other hand, it is challenging to exfoliate pristine clay in PET, since there is no driving force for the diffusion of polymer chains into the clay intergalleries. Theoretically, in-situ polymerization is the most effectual approach. Chen et al.

reported on an intercalated PET/Na-MMT nanocomposite via in-situ polymerization by replacing conventional organic surfactants with BHET monomers to modify the clay surface [90]. Tsai et al. successfully prepared exfoliated PET/clay nanocomposites with improved properties using organoclay that has been supported with catalyst [48]. The catalyst-supported clay ensures polymerization occurs within the clay intergalleries. However, due to the presence of organic surfactant, degradation of the surfactant is inevitable. Similarly using catalyst-supported clay but without any modification with organic surfactant, Choi et al. managed to only synthesized a partially exfoliated PET/clay nanocomposites by in-situ polymerization [94].

Conversely, PET/Na-MMT nanocomposite prepared by melt compounding was also reported by Wang et al. [93], where solid state shear milling is carried out to mix, and break down PET and pristine clay mixture. The nanocomposite however, yields only partially delaminated and intercalated clay in the PET matrix. Indeed, the dispersion state of clay depends on efficient mixing and optimization of the polymer/clay interactions by mechanical shear force. This means that organically modified clay is often required. Alternatively, both Wang Ke et al.'s "slurry compounding" [95] and Hasegawa et al.'s [96] modified melt compounding processes successfully produced exfoliated epoxy/clay nanocomposite and nylon/clay nanocomposite respectively, on the basis of transferring exfoliated state of clay in water to the polymer matrix. Based on a similar model of transferring nano-dispersed clay to the polymer matrix, Chung et al. prepared exfoliated PET/clay nanocomposite by melt compounding via solution method, and enhanced thermal and mechanical properties were achieved [92]. In their work, a PET/Na-MMT master batch was prepared by selective removal of organic modifiers from the clay silicates using trifluoroacetic acid after solution blending exfoliated clay and PET in chloroform. However, this approach has a shortcoming,

i.e. PET has limited solubility in common solvents; this technique hence, requires the processing of organic solvents which can have adverse health and environmental impacts.

Overall, the success of the fabrication of PET nanocomposites with untreated clays without any organic surfactant modification is still limited, with most of the nanocomposites exhibiting intercalated clay morphologies and sometimes displaying clay tactoids.

2.9 Polymer/Polyhedral Oligomeric Silsesquioxane (POSS) Surfactant-Modified clay Nanocomposites

Polyhedral oligomeric silsesquioxane (POSS) is a class of nanometer-sized organic-inorganic hybrid compounds with excellent thermal stability. A T_8 POSS (Figure 2.15) has an empirical formula of $(\text{RSiO}_{1.5})_8$ and a diameter of around 0.5 nm, making it the smallest possible silica particle. Each silicon atom can be attached to a single R substituent, which can either be organic (reactive or non-reactive) or organic-inorganic hybrids.

Figure 2.15. The structure of T_8 polyhedral oligomeric silsesquioxane (POSS) cage.

Copolymers containing POSS substituents covalently attached to the polymer block had been studied for high temperature and fire resistance applications due to its increased thermal stability, glass transition temperature, modulus and reduced flammability. Both non-reactive

POSS [97-98] and reactive POSS [99-102] have been incorporated into polyesters. When POSS cages are attached onto polyester chains, the aggregation/crystallization of POSS brings about a compact nanostructure, restricting the motion of polymer chains nearby and eventually giving rise to enhanced mechanical and thermal properties [97-102]. However, the improvement in thermo-mechanical property depends greatly on the dispersion/aggregation of POSS in polymer matrices and the extent of POSS reaction with the polymer chains [101-102]. For example, Yoon et al. reported that their melt mixed PET/triepoxy-POSS composite displayed poorer thermo-mechanical property than PET owing to phase separation between POSS compounds and PET. Recently, Ciolacu et al. reported that the active hydroxyl groups on trisilanolisobutyl POSS can undergo a melt reaction with the carboxyl end groups in PET, and lead to extension of PET chains [99]. Although the presence of trisilanolisobutyl POSS in PET lessens the processing-induced degradation, again it leads to very limited improvements in thermo-mechanical properties.

It can be seen that despite the limited improvements in mechanical properties of polymer/POSS nanocomposites, the high thermal stability of POSS compounds can be aptly exploited to improve the thermal stability of the surfactants used to treat clay. Simultaneously, the incorporation of clay can provide mechanical reinforcement in the nanocomposites. Thus, recently, researchers replace the long alkyl chains in conventional surfactants with POSS to synthesize POSS-modified clay [11-23]. POSS-modified clay exhibits significantly enhanced thermal stability so that it can now endure higher processing temperature required for the preparation of the nanocomposites. Other advantages of incorporating the POSS cage includes (1) its bulkiness and rigidity, which aids physical delamination of the clay, and (2) its ability to be chemically functionalized at the arms, which allows better compatibilization with polymers or monomers.

Chang and co-workers had been working on polystyrene (PS) nanocomposites based on POSS-modified clay, where the surfactant is an ammonium salt with isobutyl POSS attached [19, 23]. Using emulsion polymerization to prepare the PS/POSS-modified clay nanocomposites, they had achieved exfoliated dispersion of clay in the polymer and observed enhanced thermal degradation temperature of more than 20 °C as well as increased glass transition temperature of more than 5 °C with the addition of 3 wt % POSS-modified clay. In addition, via in-situ polymerization technique, POSS-modified clay (3 wt %) supported with catalyst was found to exfoliate effectively into the polyethylene matrix, and significant improvement of 100 % in storage modulus and enhancement of 62 °C in thermal stability were observed [21]. On the other hand, Bao and co-workers reported on polyester/POSS-modified clay nanocomposites prepared by ring-opening polymerization [12, 16-17]. They improve the compatibility of the POSS-modified clay and polymer by sequentially treating the clay with aminopropyl-POSS and ditallowdimethylammonium chloride to yield a dual-surfactant organoclay. Although, only clay networks and intercalated clay were achieved in the polyester/POSS-modified clay nanocomposites, dual-surfactant with superior thermal stability of 330 °C (i.e. decomposition peak temperature) was demonstrated. POSS-modified clay was also introduced into poly(ϵ -caprolactone) matrix and improved properties were obtained in spite of the limited extent of clay exfoliation. Specifically, at 1 wt % POSS-modified clay, an improvement of 33 °C in T_d based on 25 % weight loss was attained compared to the neat poly(ϵ -caprolactone) [13]. Other than nanocomposites based on thermoplastics, Liu H. et al. also reported using POSS-modified clay in nanocomposites with epoxy resin [22]. An exfoliated epoxy/clay nanocomposite with improved thermal stability was achieved by mixing POSS-modified clay with epoxy monomer and curing agent.

To summarize, most of the approaches adopted to prepare polymer/POSS-modified clay nanocomposites were by (1) using an additional organic surfactant as the clay modifier to improve the compatibility of the clay and polymer, (2) using in-situ and emulsion polymerization techniques to enhance the mixing of the POSS-modified clay and monomers and (3) utilizing crosslinking reactions in epoxy systems to exfoliate the POSS-modified clay. It is apparent that despite melt compounding is a more straightforward and cost effective method, none of the reported literatures describe successful melt compounded nanocomposites prepared from solely POSS-modified clay. It is only very recently that Fox et al. presents preparation of POSS-modified clay nanocomposites in polystyrene, poly(ethylene-co-vinyl acetate) and polyamide-6 by melt compounding [11]. The nanocomposites revealed that the POSS-modified clay does not completely exfoliate and small clay tactoids were present even in polyamide-6. Primarily, this is because the tendency for POSS to aggregate and crystallize does not allow the POSS-modified clay to fully exfoliate in the polymers. Hence, it is not surprising that melt compounding is not commonly used to prepare POSS-modified clay nanocomposites. This is because the shearing during melt compounding is inadequate to cause delamination of the POSS-modified clay, where the POSS surfactants act as strong “pillars” to hold adjacent clay platelets together. Nonetheless, it is not ruled out that with suitable functionalization of the POSS core, good extent of intercalation of the POSS-modified clay in polymers can be achieved by melt compounding.

2.10 Summary

From literature reviews, it has gathered that obtaining exfoliated nanocomposites has always been actively pursued due to their potential property enhancements. Unfortunately, achieving complete clay exfoliation is an ideal morphology and remains a challenge

regardless of the type of polymer matrices. Specifically for PET matrix, using organic surfactant as the modifier for clay has not been effective in PET/clay systems because of the degradation issues discussed abovementioned. However, PET is extensively used in many applications, and the property improvements that PET/clay nanocomposites stand to offer, elucidate the need for an investigation on how the extent of clay dispersion and thermal stability can be further improved. The lack of success to-date in attaining PET/clay nanocomposites with exfoliated clay dispersion using thermal stable surfactants therefore forms the motivation for this research work. In order to overcome the degradation issues stated above, the thesis focuses on two approaches, i.e. (1) to incorporate polyhedral oligomeric silsesquioxane (POSS) into the PET/clay system to replace conventional organic surfactants, and (2) to completely do away with organic surfactant and prepare PET/clay nanocomposites with surfactant-free clay.

3 POSS Surfactant-Modified Clay: Synthesis, Structures & Properties

This chapter provides an insight into the structure and properties of the POSS-modified clay. It describes the packing behavior of two types of POSS-imidazolium surfactants with different molecular rigidities in the clay's intergalleries and at various surfactant loadings. The thermal and thermo-oxidative stabilities of the POSS-imidazolium surfactants are addressed as well. These results aim to present a prelude to the preparation and evaluation of PET/POSS-modified clay nanocomposites and are useful for the understanding of the structure and properties of the nanocomposites.

3.1 Introduction

As highlighted in the earlier chapters, organoclays do not have adequate thermal stability to withstand the high temperatures required for processing PET. To address the degradation issue, an attractive approach is to replace the long alkyl chains in the surfactants with polyhedral oligomeric silsesquioxane (POSS). Not only is the POSS cage thermally stable, the bulkiness of the cage may aid the expansion of the clay interlayer space so that the amount of such hybrid surfactants required to achieve a large expansion of the interlayer space may be fairly small. Although POSS-based surfactants hold sound promise in lessening the degradation, there is also a great concern that the inherent tendency for POSS compounds to aggregate and crystallize may hinder the exfoliation of POSS-modified clay in polymer

matrices, and consequently limit the properties of the nanocomposite [103-104]. In order to minimize the attraction forces between individual layers of the POSS-modified clay arising from hydrophobic interactions or crystallization of the POSS surfactants, a loose and disordered packing of the surfactant molecules in the clay interlayer is believed to be beneficial. Ordered packing of POSS surfactants in clay may also affect thermal and thermo-oxidative stabilities of the POSS-modified clays as unbonded surfactant molecules may be present in the clay galleries in a significant amount due to the strong interactions among the surfactant molecules.

In addition, it is well known that for the clays modified with organic surfactants containing long alkyl chains, the interlayer spacing generally increases as the surfactant loading increases until a saturation limit, which is equal to or larger than the cation exchange capacity (CEC) of the clay, is reached [18, 105]. For POSS surfactants, some recent studies have shown that the interlayer spacing increases sharply as the surfactant loading increases, but contrary to organic surfactant, the saturation limit is far below CEC [18, 105]. The large *d*-spacings achieved at low surfactant loadings are attributed to the bilayer packing of the POSS surfactant molecules in clay galleries and the bulkiness of the surfactant molecules [17-18]. However, no direct evidence in support of the bilayer packing structure has yet been reported, and it is not clear how the relationship between the interlayer *d*-spacing and POSS surfactant loading would be influenced by the molecular structures of the POSS surfactants and the way they pack.

In this chapter, the packing structures of two types of POSS-imidazolium cations, one being highly rigid while the other relatively flexible, in the intergallery regions of montmorillonite (MMT) clay were studied. In addition to molecular modeling and X-ray scattering, which are common tools for probing surfactant packing structures in clay, transmission electron microscopy (TEM) was also used to directly visualize the packing

structures of the POSS surfactants in clay. The goals are to clarify how the molecular rigidity of the POSS surfactants influences their packing structures, in particular, the orderedness of the packing in clay at different surfactant loadings, and to investigate whether the thermal and thermo-oxidative stabilities of the POSS-modified clays are influenced by the surfactant packing structures.

3.2 Experimental

3.2.1 Materials

Chlorobenzyl-isobutyl-POSS and chlorobenzylethyl-isobutyl-POSS were obtained from Hybrid Plastics Ltd. 1,2-dimethylimidazole and 1-hexadecyl-2,3-dimethylimidazolium chloride (IMC) were obtained from Merck, Germany. All chemicals were used without further purification. The PGW grade sodium montmorillonite (Na-MMT) with CEC of 145 meq/100 g was obtained from Nanocor.

3.2.2 Synthesis of POSS-Imidazolium Surfactants

The synthesis route for the two POSS-imidazolium surfactants is depicted in Scheme 3.1. The relative flexible one (**A**, $n = 2$) was synthesized according to the procedure reported in ref. 20. Yield: 66 %. ^1H NMR (CDCl_3 , 25 °C, δ ppm): 7.55 (s, 1H), 7.33- 7.28 (m, 2H), 7.22- 7.18 (m, 2H), 7.05 (s, 1H), 5.40 (s, 2H), 4.00 (d, 3H, $J = 6.52$ Hz), 2.81 (s, 3H), 2.72- 2.68 (m, 2H), 1.91- 1.81 (m, 7H), 9.96 (d, 44H, $J = 6.52$ Hz), 0.61 (d, 14H, $J = 6.96$ Hz). MS (ESI, m/z): 1029.3 (M^+). Expected is 1030.8. Anal. Cald. for $\text{C}_{42}\text{H}_{81}\text{ClN}_2\text{O}_{12}\text{Si}_8$: C, 47.31; H, 7.66; N, 2.63. Found: C, 45.05; H, 7.46; N, 2.49. The rigid one (**B**, $n = 0$) was synthesized using the procedure described as follows. In a typical reaction, chlorobenzyl-isobutyl-POSS (10.0 g, 10.6 mmol) and 1,2-dimethylimidazole (1.33 g, 13.8 mmol) were added to 25 ml of

tetrahydrofuran (THF). The solution mixture was refluxed at 80 °C for 3 days. Upon the completion of the reaction, the excess THF was removed by rotary evaporation. The purification of the crude product was performed by recrystallization in ethyl acetate. The precipitated white solid was filtered, washed with acetonitrile and dried overnight under vacuum. Yield: 78 %. ^1H NMR (CDCl_3 , 25 °C, δ ppm): 7.68 (d, 2H, J = 7.5 Hz), 7.55 (d, 1H, J = 5.0 Hz), 7.43 (d, 1H, J = 6.3 Hz), 7.27 (d, 2H, J = 7.9 Hz), 5.51 (s, 2H), 3.98 (s, 3H), 2.77 (s, 3H), 1.90- 1.81 (m, 7H), 0.97- 0.92 (m, 42H), 0.64- 0.61 (m, 14H). MS (ESI, m/z): 1001.3 (M^+). Expected is 1002.7. Anal. Cald. for $\text{C}_{40}\text{H}_{77}\text{ClN}_2\text{O}_{12}\text{Si}_8$: C, 46.28; H, 7.48; N, 2.70. Found: C, 43.85; H, 7.43; N, 2.55.

Scheme 3.1. Synthesis route leading to the POSS-imidazolium compounds **A** and **B**.

3.2.3 Clay Modification

The modified clays were prepared via a standard aqueous cation exchange procedure. In a slurry of Na-MMT (3 g) and deionized water (350 ml), solution of the imidazolium salts completely dissolved in ethanol (100 ml) was slowly added. The amounts of the imidazolium salts (**A** or **B** or **IMC**) used were 20, 50 and 120 mol%, respectively, of the CEC value of the Na-MMT. The slurry was stirred for 3 days at 70-80 °C, and subsequently stored at room temperature for another 2 days. The modified clay was then washed with ethanol at least 4

times using centrifugal extraction, followed by washing in a soxhlet extractor with hot THF/water (4:3, v/v) for 24 hours and lastly, washing with ethanol again using centrifugal extraction. Finally, the modified clay was dried under vacuum at 80 °C for 2 days before it was ground into fine powder of size 80 µm. In total, 7 modified clay samples were obtained. For clarification, the types of the POSS-imidazolium salts and their feed loadings are specified in the names of the samples. For example, the modified clay obtained using 120 mol% of **A** is denoted as **A-MMT-120**.

The exchange ratios (R) of the modified clays were calculated according to the cation exchange capacity of the Na-MMT (145 mequiv/100 g) and the weight losses of the modified clays determined by TGA using the following formula:

For organoclay **IMC-MMT**,

$$\text{Organic weight loss, X (\%)} = \left[\frac{R \times 145 \times 10^{-3} \times Mw_{\text{surfactant}}}{100 + R \times 145 \times 10^{-3} (Mw_{\text{surfactant}} - A_r(\text{Na}))} \right] \times 100 \quad (3.1)$$

where the organic weight loss (%) is determined from TGA, taking into account the weight loss of 4.87 wt % due to the hydrolysis of the pristine clay.

For **A-MMT** and **B-MMT**, the calculation for the exchange ratios (R) was also performed using the formula (3.1), but the organic weight loss (%) was replaced by the weight percentages of the POSS surfactants in the modified clays that were determined from the degradation residues of **A**, **B**, the pristine clay and the POSS-modified clays using the formula below:

$$a\left(\frac{X}{100}\right) + b\left(1 - \frac{X}{100}\right) = c$$

$$X = \frac{(c - b)}{(a - b)} \times 100 \quad (3.2)$$

where a (%) is the residue of POSS compound, b (%) is the residue of the raw clay and c (%) is the residue of POSS-modified clay. ($M_{wA} = 1030.8$; $M_{wB} = 1002.7$; $M_{wIMC} = 321.6$).

3.2.4 Characterization & Measurements

The nuclear magnetic resonance (NMR) spectra were acquired on a Bruker DCR 400 MHz spectrometer in deuterated chloroform ($CDCl_3$) and all the NMR spectra were calibrated according to the solvent peak at 7.26 ppm. Elemental analysis was conducted on a Perkin-Elmer 240C elemental analyzer for C, H and N determination. Electrospray ionization-mass spectra (ESI-MS) were recorded on a Micromass 7034 mass spectrometer. Wide angle X-ray scattering (WAXS) patterns were recorded on a Bruker GADDS X-ray diffractometer using $Cu K_{\alpha}$ radiation generated at 40 kV and 40 mA. The specimens for TEM were prepared by dispensing a few drops of the POSS-modified clay/water suspension onto carbon-coated copper grids and examined using a JEOL 2010 microscope with LaB_6 filament at an acceleration voltage of 200 kV. Differential scanning calorimetric (DSC) measurements were carried out using a TA Instrument DSC Q10 at a heating and cooling rate of 5 °C/min in nitrogen. The thermogravimetric analysis (TGA) was performed on a TA Instrument TGA Q500 where the samples were heated at 10 °C/min from room temperature to 140 °C, held isothermal for 60 min and further heated at 10 °C/min to 850 °C in nitrogen and air, respectively.

3.3 Results & Discussion

3.3.1 Structures of the Surfactants and Cation Exchange

The synthetic route leading to the new POSS-imidazolium salt, **B**, is outlined in scheme 3.1. The compound can be obtained with a relatively high yield of 78 %. Its chemical

structure is verified by ^1H NMR, MS and elemental analysis. In the ^1H NMR spectrum of **B** (Figure 3.1), the disappearance of chloromethylene resonance, i.e. $\delta = 4.59$ ppm (s, 2H) and the appearance of new resonances, i.e. $\delta = 7.55$ ppm (d, 1H, $J = 5.0$ Hz), 7.43 ppm (d, 1H, $J = 6.3$ Hz), 5.51 ppm (s, 2H), 3.98 ppm (s, 3H) and 2.77 (s, 3H), which corresponds to the hydrogens from the imidazolium, demonstrate that the imidazolium salt has been successfully attached to the POSS cage and there is no chlorobenzyl-isobutyl POSS impurity in the final product.

Figure 3.1. ^1H NMR spectrum of the compound **B** in CDCl_3 at room temperature. (*) residual water and undeuterated chloroform.

Both POSS-imidazolium surfactants **A** and **B** comprise an isobutyl POSS and a benzyl dimethylimidazolium salt. The difference is that in **A**, the POSS cage is joined to the benzene ring via an ethane spacer while in **B**, the POSS cage is directly attached to the benzene ring, which makes **B** more rigid than **A**. The surfactant **IMC** is an alkylimidazolium salt, which is used as a reference in this study.

The exchange ratios estimated based on the degradation residues of **A**, **B**, the pristine clay and modified clays, that are determined by TGA and the CEC value of the pristine clay (145 meqv/100 g) are listed in Table 3.1. The calculation method is described in the experimental section. From Table 3.1, it is clear that the exchange ratios of **A**-MMT-120 and **B**-MMT-120 are lower than that of **IMC**-MMT-120 (76%). The low exchange ratios of **A**-MMT-120 and **B**-MMT-120 obtained with the feed surfactant loading of 120 mol% (20 mol% in excess of the CEC value of Na-MMT) are caused by the steric hindrance effect of the bulky POSS cage [20, 106]. Additionally, it was observed that **A**-MMT-120 has a lower exchange ratio compared to **B**-MMT-120. As mentioned, modifiers with the smaller size can more easily enter the limited spacing between the clay layers due to lower steric hindrance, subsequently resulting in a higher exchange ratio. However, it is believed that the difference in molecular size between **A** and **B** is too small to greatly affect the exchange ratio. Thus, it is proposed that the lower exchange ratio of **A**-MMT-120 than **B**-MMT-120 may be caused by the formation of orderly packed regions of **A** molecules during the modification process, which hindered the entry of additional **A** molecules into the spacing between the silicate layers. This is supported by the fact that on the contrary to the large difference observed at the high feed surfactant loading of 120 %, there is no significant difference in the exchange ratios of the modified clays at lower feed surfactant loadings. This is probably because at low feed surfactant loading, there is less steric hindrance, and consequently a smaller difference in the exchange ratios of the modified clays. It indirectly supports that the lower exchange ratio of **A**-MMT-120 compared to **B**-MMT-120 at the high feed surfactant loading is related to the steric hindrance caused by ordered packing domains which hindered the entrance of additional **A** molecules. Further evidence to the ordered packing of **A** molecules will be presented in the next section.

Table 3.1. The estimated exchange ratios of the modified clays.

Sample	Residue ^a (%)	Exchange ratio (%)	Sample	Residue ^a (%)	Exchange ratio (%)	Sample	Residue ^a (%)	Exchange ratio (%)
A	38	-	B	46	-	IMC	10	-
A-MMT-120	70	51	B-MMT-120	71	65	IMC-MMT-120	68	76
A-MMT-50	74	39	B-MMT-50	76	43	Na-MMT	95	0
A-MMT-20	80	23	B-MMT-20	84	19			

^a Residue at 850 °C determined by TGA in air.

3.3.2 Packing Structures of the POSS-Imidazolium Surfactants in Clay

WAXS patterns of the modified clays and reference materials (**A**, **B** and Na-MMT) are shown in Figure 3.2. In comparison with the clay treated with the alkylimidazolium salt, both **A**-MMT-120 and **B**-MMT-120 show much larger basal *d*-spacings. Despite the lower exchange ratio of **A**-MMT-120 than **B**-MMT-120, **A**-MMT-120 gives larger (001) *d*-spacing than **B**-MMT-120 due to the additional ethane spacer in **A**. From molecular modeling, it is found that the lengths of **A** and **B** in their minimized conformations are only about 2.0 nm and 1.9 nm, respectively, as illustrated in Figure 3.3. Considering that the thickness of a MMT sheet is about 1 nm, it is impossible to expand the basal *d*-spacing to the measured values if the POSS-imidazolium cations form a single layer in each interlayer spacing of the clay. Hence, it is proposed that the POSS-imidazolium cations have a bilayer packing structure in clay and within each layer, the long axes of the molecules are tilted with respect to the basal plane [107]. Based on the minimized conformations of **A** and **B** and the assumption that the positive charge on the imidazolium cation is delocalized in the ring so that the ring lies parallel to the clay surface, the tilt angles is approximately 111° and 113° for **A**-MMT and **B**-MMT, respectively, as shown in Figure 3.3. These would give rise to the

expansion of 1.7 nm and 1.6 nm for a single layer, 3.4 nm and 3.2 nm for a bilayer, and basal d -spacings of about 4.4 nm and 4.2 nm for **A**-MMT and **B**-MMT, respectively, for a bilayer packing structure. The basal d -spacings are slightly larger than the observed values for **A**-MMT-120 and **B**-MMT-120 probably because there is slight interdigitation between the two layers and that the surfactant molecules are unable to take minimized conformation at high surfactant loadings. The dependence of the d -spacings on the surfactant loading will be discussed further in the next section.

Figure 3.2. WAXS patterns of Na-MMT, **IMC**-MMT-120, **A**, **B**, **A**-MMT-120 and **B**-MMT-120. The intensities of the peaks were normalized according to the characteristic quartz peak at $2\theta = 20^\circ$ found in clay [108].

Figure 3.3. Molecular models of the compounds **A** (left) and **B** (right) generated using CS Chem3D with MM2 energy minimization. Herein, the lengths of the POSS compounds are the distances from the imidazolium nitrogen that is linked to a methyl group to the furthest hydrogen atom, as shown by the vertical arrows in the figure. The tilt angles are defined as the angles between the plane of the imidazolium ring and the long axes of the molecules (i.e. the bond angles of N (imidazolium)-C-C (benzene)). The estimated clay basal *d*-spacings expanded by a single layer of POSS molecules are the lengths of the POSS compounds in the direction perpendicular to the imidazolium ring.

The packing of free octa-alkyl POSS molecules are generally hexagonal-rhombohedral and they are stacked in hexagonal planes in sequence of ABCA [109]. Octa-isobutyl POSS commonly exhibits two distinct sharp X-ray diffraction peaks at $2\theta = 7.9^\circ$ and 8.8° , and some crystalline peaks at higher angles [110]. Slightly different from octa-isobutyl POSS, compound **A** exhibits a broad diffraction peak that can be seen as an overlap of two reflections with 2θ values of 8.1° and 8.5° , respectively (derived from deconvolution and

curve fitting using TOPAS), while compound **B** exhibits a singlet at $2\theta = 8.4^\circ$, as shown in Figure 3.2. The packing structures of the POSS-imidazolium cations in clay intergalleries are expected to be different from those of free **A** and **B** since the POSS-imidazolium cations are ionically bonded to the clay surface. However, some experimental evidence has shown that despite the restricted motion of the cations by the clay surface, the POSS cages still prefer to aggregate [111]. Indeed, a well-defined peak can be observed at $2\theta = 8.5^\circ$ ($d = 1.04$ nm) for **A**-MMT-120, which can be attributed to the intermolecular distance of the POSS-imidazolium cations within a layer. It implies that a two-dimensional ordered structure is established in the interlayer of **A**-MMT-120. It is reasonable to deduce that across the clay's negative charged surface plane, there is possibly only short-range order and no long-range order in the z-direction and thus, the POSS-imidazolium surfactants display only a two-dimensional ordered structure. In contrast, although **B**-MMT-120 has a higher exchange ratio than that of **A**-MMT-120, only a weak shoulder peak can be seen from **B**-MMT-120 in the same 2θ region, which implies that the packing of **B** in the clay interlayer is more disordered.

The significant difference between **A**-MMT and **B**-MMT lies in their different molecular rigidity. Although the motion of the POSS-imidazolium cations are constrained at one end, the flexible ethane spacer of **A** allows the POSS cage to rotate and move relatively freely, which can induce two-dimensionally ordered packing of **A** in the clay intergalleries. On the other hand, the high rigidity of **B** coupled with its ionic bonding with the clay surface makes the ordered arrangement of the molecules difficult. Based on the discussion above, a schematic illustration of the packing structures of the POSS-imidazolium cations is presented in Figure 3.4.

Figure 3.4. A schematic illustration of the packing structures of the POSS-imidazolium cations, (a) **A** (flexible) and (b) **B** (rigid), in the clay intergalleries.

The packing structures of the POSS-imidazolium cations can be clearly observed using TEM when the clay platelets are stacked perpendicular to the carbon-coated copper grids (Figure 3.5). The clay layers are seen as dark solid lines of about 1 nm thick in the TEM images. The POSS-rich regions are expected to appear darker than void or organic regions, due to the presence of Si atoms. Indeed, a well-defined dark line that runs continuously between two clay layers can be observed for **A**-MMT-120, as shown in Figure 3.5a (highlighted by the arrows). This line falls exactly in between two individual clay layers, which provides direct evidence for the bilayer packing structure. The well-defined shape of the line suggests the ordered arrangement of the POSS cages in **A**-MMT. In contrast, diffuse and less well-defined dark lines are observed between the individual clay layers of **B**-MMT-

120 (Figure 3.5b), which may be attributed to the more disordered packing of the more rigid **B** molecules. The TEM micrograph of **B**-MMT-120 looks similar to that of **IMC**-MMT-120 as the contrast provided by loosely packed POSS compounds is too small to be observed.

Figure 3.5. TEM images of (a) **A**-MMT-120, (b) **B**-MMT-120 and (c) **IMC**-MMT-120 prepared from their suspensions.

3.3.3 Effect of POSS-Imidazolium Surfactant Loading

It has been reported that as surfactant loading increases, although the interlayer d -spacings of the corresponding organoclays increase, the dispersion of the clays in polymer matrices becomes unfavorable during composite preparation with too high a surfactant loading [44, 112]. On the other hand, the clay interlayer expansion and the compatibility between the clays and polymer matrices could be very poor with too low a surfactant loading. For POSS-modified clay, a lower surfactant loading may be beneficial in reducing POSS aggregation whereas it may also reduce the chance to form the bilayer packing structure. It is hence imperative to optimize surfactant loading.

Surprisingly, the POSS-modified clays do not exhibit reduced interlayer d -spacings with reduced surfactant loadings; instead, the d -spacings, especially that of **B**-MMT, even increase with decreasing surfactant loading in the studied surfactant loading range, as shown in Figure 3.6. This is because the rigid **B** molecules are unable to “crystallize” in the interlayer spacing. Thus, when the surfactant population is low, the **B** molecules can easily take more extended (minimized) conformation, which leads to the further expansion of the interlayer spacing of the clay. On the other hand, the flexible **A** molecules are able to “crystallize”. Thus, despite reducing the feed surfactant loading to 50 %, they still aggregate to form “crystals” and expand the interlayer to roughly the same extent.

Figure 3.6. WAXS patterns of (a) A-MMT and (b) B-MMT at different feed loadings of surfactants. The intensity of the peaks had been normalized according to the characteristic quartz peak at $2\theta = 20^\circ$ found in clay.

In the WAXS pattern of A-MMT-120, three peaks with d -spacing of 3.68, 1.85 and 1.25 nm can be observed, which corresponds respectively to the (001), (002) and (003) peaks of the basal planes of the expanded clay, and the good periodicity of the reflections indicates that most of the clay had been modified into the bilayer structure. When the feed surfactant loading is decreased to 50 %, all peaks become weaker and broader. The periodicity of the three peaks also reduces, implying that some of the clay had not been modified into the

bilayer structure. Table 3.2 lists the full width at half maximum (FWHM) of the (001) peaks of the modified clays. The FWHM measures the random fluctuation of the basal spacings. As the feed surfactant loading reduces from 120 % to 50 %, FWHM increases from 0.47 to 0.50 for **A**-MMT, indicating a slightly wider distribution in the basal spacings. When the feed loading is further reduced to 20 %, the (001) basal reflection becomes very weak, implying that most of the clay had not been modified into the bilayer structure as the amount of the POSS-imidazolium cations is not enough to sufficiently exchange the clay. In addition, the (001) peak shifts to $2\theta = 2.3^\circ$ (3.92 nm), which is closer to the value predicted based on the bilayer model. This implies that when the population of the POSS-imidazolium cations in the intergellaries becomes very small, they may be able to take the minimized conformation. In addition to (001), a weak second-order peak can be observed for **A**-MMT-20. The peak positions of (001) and (002) are aperiodic as some intergellaries are not expanded or only expanded into single layer structure [43]. The third peak is broader but stronger and shifts to a slightly higher angle due to the overlap with the POSS peak and the Na-MMT peak.

Table 3.2. Full width at half maximum of (001) X-ray diffraction peaks of the modified clays.

	A -MMT-120	A -MMT-50	B -MMT-120	B -MMT-50
FWHM	0.47	0.50	0.66	0.58

As mentioned earlier, the surfactant **B** has disordered packing in clay due to its high molecular rigidity. Indeed, the basal reflections of **B**-MMT-120 show a poorer periodicity than **A**-MMT-120 and **A**-MMT-50. However, it is striking to see that when the clay loading is reduced, the (001) peak of **B**-MMT-50 becomes much sharper and intense than that of **B**-

MMT-120. The (001), (002) and (003) peaks of the basal plane of **B**-MMT-50 also show better periodicity, and the FWHM of the (001) peak is significantly reduced (Table 3.2). These observations support the earlier claim that **B** molecules are able to take more extended conformation at lower feed surfactant loadings. When the loading is further reduced, **B**-MMT-20 exhibits similar behavior as that of **A**-MMT-20, i.e. as the population of the cations in the intergalleries is too low, only some interlayers are expanded even though the cations are able to achieve more extended conformation.

The packing structures proposed above are strongly supported by DSC results. In the thermograms of the compound **A** (Figure 3.7), a sharp endotherm at 215 °C during heating and a sharp exotherm at 163 °C during cooling can be observed, which clearly demonstrates its ability to crystallize. Unlike **A**, **A**-MMT-120 and **A**-MMT-50 display weak, broad melting and “crystallization” peaks, and the melting and “crystallization” temperatures are higher than those of **A**. These confirm the ordered packing of **A** in clay intergalleries. When the feed surfactant loading is decreased from 120 % to 50 %, the melting and “crystallization” temperatures increase, implying that the **A** molecules are able to pack better with less defects at the feed loading of 50 %. When the feed surfactant loading is reduced to 20 %, no DSC peak can be observed, indicating that the surfactant packing becomes disordered at such a low surfactant loading. The DSC data thus compliment the WAXS results that with a flexible spacer, **A** molecules are able to pack orderly at the feed loadings 120% and 50% but have disordered packing at the loading of 20%. It is also interesting to note that the “crystallization” of **A** in **A**-MMT-50 and **A**-MMT-120 possesses almost the same degree of undercooling ($T_m - T_c$) as that of free **A** molecules although the former is carried out in a confined environment. This implies that when **A** molecules are ionically bonded to the clay surface, although their mobility is reduced, the nucleation of the two-dimensionally ordered

structure may be easier than the nucleation of the crystals of free **A** molecules due to the regular head-tail arrangement of **A** in the clay interlayer.

Figure 3.7. The (a) first heating and (b) cooling thermograms of **A**-MMT and (c) first heating and (d) cooling thermograms of **B**-MMT at different surfactant loadings.

In addition to the POSS-imidazolium cations, a monolayer of confined water is also absorbed in clay due to clay's affinity for water. For Na-MMT, the adsorbed water molecules interact with both the sodium cation and the clay surface forming a hydrated layer of Si-O-(H₂O)-Na⁺ [34]. As a result, the first heating cycle of the unmodified clay, Na-MMT exhibits a strong, broad endothermic peak corresponding to the “melting” of this monolayer of confined water, as shown in Figure 3.7a. As the surfactant loading increases, the enthalpy of this broad endothermic peak becomes smaller. This is because as more of the sodium cations

are exchanged by the POSS-imidazolium cations, less water molecules are absorbed to form the hydrated layer. The broad endothermic peak almost disappears when the feed surfactant loading is increased to 120 %.

Except for the broad endotherm due to the absorbed water, **B**-MMTs with different surfactant loadings exhibit no endotherm on first heating, as shown in Figure 3.7c, although a small endotherm at 138 °C can be observed for the compound **B**. In addition, no “crystallization” peak can be observed on cooling (Figure 3.7d). These results confirm that although the compound **B** is able to crystallize slightly, it is unable to pack to form two-dimensionally ordered structure in the clay intergalleries. This is again consistent with the WAXS and TEM results.

3.3.4 Thermal and Thermo-oxidative Stabilities of the POSS Surfactant-Modified Clay

TGA was performed on the three different types of surfactants and their corresponding modified clays in nitrogen and air atmospheres, respectively, to evaluate their thermal and thermo-oxidative stabilities. The degradation temperatures obtained from the TGA tests are summarized in Table 3.3. The surfactant **IMC** and **IMC**-MMT-120 are used here as references to assess the effects of the introduction of the POSS cage on the stabilities of the POSS-imidazolium surfactants and the POSS-modified clays.

Table 3.3. Degradation temperatures (T_d) of the surfactants and the modified clays measured using TGA in nitrogen and air. T_d is defined as the temperature at 5 % weight loss.

Samples	T_d (°C)	
	Nitrogen	Air
A	249	242
B	262	237
IMC	248	249
A-MMT-120	350	270
B-MMT-120	403	389
IMC-MMT-120	353	292
A-MMT-50	351	322
B-MMT-50	398	395

In nitrogen atmosphere, **A** and **IMC** exhibit about the same T_d , while **B** is more thermally stable as it has the lowest aliphatic content among the three. A similar trend is observed for the modified clays in nitrogen atmosphere. In air, **A** and **B** have slightly lower T_d than **IMC** possibly because the oxidation of **A** and **B** can produce some stable aromatic free radicals. Although **B** has a slightly lower T_d in air than **A** (Figure 3.8a), it is striking to see that **B-MMT-120** displays a T_d of more than 100 °C higher than that of **A-MMT-120** in air despite that they exhibit similar total weight loss (Figure 3.8b). In addition, **B-MMT-50** exhibits a large increase in T_d in air as compared with **A-MMT-50** (Figure 3.8c) although their exchange ratios are roughly the same (Table 3.1). A plausible explanation for the above is that free surfactant molecules are easier to be thermo-oxidized than those ionically bonded to clay surface. For **B-MMT** series, the disordered packing structure of the POSS surfactant in the interlayer ensures that most surfactant molecules in the interlayer are ionically bonded to the clay surface since the majority of unbonded ones would have been washed out. While in

the case of **A**-MMT series, a substantial amount of unbonded surfactant molecules may be trapped in the interlayer as they strongly interact with the bonded ones in ordered domains. The presence of unbonded **A** molecules causes the lower thermo-oxidative degradation temperatures of the **A**-MMT series.

Figure 3.8. Typical TGA curves of (a) **A** and **B** in air, (b) **A**-MMT-120 and **B**-MMT-120 in air and (c) **A**-MMT-50 and **B**-MMT-50 in air.

A piece of indirect evidence to support the above claim is that regardless of the surfactant loading, **B**-MMTs exhibit similar thermal stabilities, suggesting that the amount of free surfactant is small at these loadings to affect their T_{ds} . Conversely, as the surfactant loading decreases from 120 % to 50 %, **A**-MMT-50 displayed a 52 °C increase in degradation

temperature. This is probably because at a lower feed surfactant loading, the surfactants are more likely to be ionically bonded to the clay surface than to be unbonded. Therefore, based on logical deductions it is believed that the lower thermo-oxidative degradation in **A**-MMT-120 is likely to be due to the greater amount of non-ionically bonded **A** molecules.

3.4 Conclusions

In summary, WAXS and molecular modeling studies suggest that the POSS-imidazolium cations have a bilayer packing structure in clay with the long axes of the molecules largely tilted with respect to the basal plane. The bilayer packing structure is verified by direct visualization of the POSS-rich regions in between the individual clay layers via TEM. WAXS and DSC results indicate that the rigidity of the POSS-imidazolium cations plays a significant role in influencing their molecular packing order in the clay intergalleries. With a flexible ethane spacer, the relatively flexible **A** molecules are able to form a two-dimensionally ordered structure in clay, while the high rigidity of **B** molecules results in its disordered packing in clay. Furthermore, the POSS-modified clays **A**-MMT and **B**-MMT do not exhibit reduced interlayer d -spacings with reduced surfactant loadings. On the contrary, with a reduced surfactant loading, the POSS-imidazolium cations, especially **B**, are able to further expand the interlayer. Moreover, the results demonstrated that **B**-MMT exhibits better thermal and thermo-oxidative stabilities than **A**-MMT due to its low organic content and disordered surfactant packing structure.

4 PET/POSS-Modified Clay Hybrid: POSS as Surfactants

This chapter gives a discussion on the preparation, structure and properties of PET/POSS-modified clay nanocomposites. The effectiveness of employing the POSS-imidazolium surfactants to obtain nano-dispersed clay in the polymer is evaluated. Factors that may affect clay exfoliation in PET, such as POSS aggregation and incompatibility between PET and POSS-modified clay are considered. Lastly, the preparation of PET/dual POSS-modified clay, where reactive POSS spacer is added to improve clay dispersion is presented.

4.1 Introduction

In the previous chapter, it was demonstrated that POSS-modified clays have higher thermal and thermo-oxidative stabilities compared to organoclays. Theoretically, the POSS-modified clays can be aptly exploited in high processing temperature polymers, such as PET. However, WAXS, TEM and molecular modeling studies also confirmed that the POSS-imidazolium cations have a bilayer packing structure in clay. The inherent tendency for POSS compounds to aggregate and form a defined organization may hinder the exfoliation of the POSS-modified clay in the PET matrix. A clearer understanding of how the bilayer packing is likely to influence exfoliation of clay in PET and how it affects the properties of the resultant nanocomposites is vital when utilizing POSS as a potential surfactant for clay.

In addition, although there are several published articles on polymer/POSS-modified clay

nanocomposites [11-23], no PET/POSS-modified clay systems have been prepared and studied. Furthermore, at the point of study, there are no reports on polymer/POSS-modified composites prepared directly by melt intercalation/compounding, despite melt compounding being the most straightforward and industrially viable polymer/clay preparation technique. It is practical therefore, to prepare and conduct an examination on PET/POSS-modified clay prepared by melt compounding.

In the earlier analysis on POSS surfactant (Chapter 3), it was found that loose and random packing of the rigid POSS-imidazolium surfactant, **B** (Figure 4.1) renders a relatively weaker interaction between the POSS cages. Therefore, the disordered packing structure of the POSS surfactants may be more favorable for the exfoliation of POSS-modified clay in PET. In addition, **B** also exhibited greater thermal and thermo-oxidative stabilities. Thus, the PET/POSS-modified nanocomposites were mainly prepared with clay which is surface treated with **B**.

To further facilitate POSS-modified clay dispersion in PET, a small amount of trisilanol POSS was added as a spacer, where it aims to further weakens the interactions of POSS-imidazolium surfactants. Unlike utilizing dual-surfactant organoclays as reported by Bao and co-workers [12, 18], employing a dual POSS surfactant system reduces the organic content of the surfactant and ensures thermal degradation of the surfactant is minimized. Additionally, Ciolacu et al. reported that the active silanol groups on the partially formed cage of trisilanolisobutyl POSS can also react with PET end groups [99]. It is believed that this characteristic may assist the clay exfoliation in PET, whereby polymer chains may be more effectively drawn into the clay intergalleries. At the same time, it can also increase the molecular weight of PET, such that the adverse effects due to the degradation of the polymer matrix is reduced during melt compounding [99]. As the isobutyl groups in trisilanolisobutyl POSS may limit the thermal stability of the resultant nanocomposites [113], trisilanolphenyl

POSS (Tsp-POSS) (Figure 4.1) was used as the spacer in this work instead. Overall, this chapter seeks to gain an understanding and provide an insight into the advantages and limitations of using POSS-modified clay as filler for high processing temperature polymer, specifically evaluating the degree of clay dispersion in PET, thermo-mechanical properties and thermo-oxidative stability of the resultant PET/POSS-modified clay nanocomposites.

Figure 4.1. The chemical structures of the POSS compounds used in the clay modification.

4.2 Experimental

4.2.1 Materials

The POSS-modified clays (**A**-MMT and **B**-MMT) and alkylimidazolium-modified clay (**IMC**-MMT) were synthesized according to the procedure reported in chapter 3. Trisilanophenyl POSS (Tsp-POSS) was obtained from Hybrid Plastics Ltd. and used without further purification. Commercially available organoclay, Cloisite 30B was obtained from Southern Clay Products. Cloisite 30B is a natural montmorillonite modified with a ternary ammonium salt with methyl, bis-2-hydroxyethyl and tallow (~65% C18; ~30% C16; ~5%

C14) groups. Additive-free PET granules (3 mm) were obtained from Goodfellow Cambridge Ltd.

4.2.2 Dual POSS Clay Modification

Due to the reasons mentioned in the introduction and for fair comparison, dual POSS-modified clays were also synthesized using POSS-imidazolium surfactant, **B**. The preparation procedures of dual POSS-modified clays, (B+Tsp-POSS)-MMTs were adapted with some slight adjustments from the clay modification procedures used by Wang Ke et al. [95], where they replaced water with an organic solvent to assist surface modification. Na-MMT (5 g) was dispersed in deionized water (300 ml) to form a suspension and magnetically stirred vigorously at room temperature for 2 days. The clay suspension was allowed to settle and the clay sedimentation (0.5 g) was removed. The clay suspension then underwent a solvent exchange procedure, where water was replaced by ethanol (EtOH) by a series of filtration and homogenization steps for at least four times. In the last step, the clay was re-dispersed in ethanol (300 ml), homogenized and further sonicated for 10 minutes. Tsp-POSS (3.3 wt % and 10 wt % of the clay) was dissolved in ethanol (60 ml) and added dropwise into the clay/ethanol suspension. The mixture was stirred at 50 °C for overnight. Next, POSS-imidazolium salt, **B** (2.71 g, i.e. 40 mol% CEC value of Na-MMT) dissolved in ethanol (75 ml) was added dropwise to the mixture and stirred at 50 °C for another 2 days. Subsequently, the slurry was stored at room temperature for 2 days. The modified clay was then washed with ethanol at least 4 times using centrifugal extraction. Finally, the modified clay was freeze dried before it was ground into fine powder of size 80 μm .

4.2.3 Melt Compounding of PET/Clay Nanocomposites

Prior to processing, PET granules and the surface modified clays were dried in vacuum at 50 °C for at least 24 hours. The PET/clay nanocomposites were prepared by melt compounding PET and 2 wt % of the modified clay in a PRISM twin-screw extruder with L/D ratio of 25:1 at a temperature of 260 °C and a screw speed of 165 rpm. The nanocomposites were subjected to two extrusion cycles to ensure maximum mixing and shearing possible. In the dual POSS surfactant system, the Tsp-POSS contents in PET/dual POSS-modified clay nanocomposites are respectively about 0.1 and 0.3 wt % after the compounding. PET/IMC-MMT nanocomposite with 2 wt % clay and PET/Tsp-POSS nanocomposite with 0.1 wt % Tsp-POSS were prepared as reference materials via melt compounding using the same conditions. For comparison, a physical melt blend of PET, B-MMT-40 and Tsp-POSS (0.1 wt %) was prepared too. Table 4.1 summarizes the melt compounded composites prepared and discussed in this chapter.

Table 4.1. Abbreviations of the PET/clay hybrids prepared via melt compounding.

	Abbreviation for Clay/POSS	Abbreviation for Hybrid
Without clay	Tsp-POSS-0.1	PET/Tsp-POSS-0.1
POSS-modified clay	A-MMT-50	PET/A-MMT-50
	A-MMT-120	PET/A-MMT-120
	B-MMT-50	PET/B-MMT-50
	B-MMT-120	PET/B-MMT-120
Dual POSS-modified clay	B-MMT-40 and Tsp-POSS-0.1	PET/B-MMT/Tsp-POSS (physical blend)
	(B+Tsp-POSS-0.1)-MMT	PET/(B+Tsp-POSS-0.1)-MMT
	(B+Tsp-POSS-0.3)-MMT	PET/(B+Tsp-POSS-0.3)-MMT
Organoclay	IMC-MMT-120	PET/IMC-MMT
	Cloisite 30B	PET/Cloisite30B-MMT

4.2.4 Solution Intercalation of Polymer/POSS-Modified Clay Hybrids

The solution intercalated hybrids were based on 2 wt % clay. **B**-MMT-50 was dispersed in DMF and magnetically stirred for at least a day. Separately, PVDF, PAN, PEO, PS, PMMA were also dispersed in DMF and magnetically stirred for at least a day. The two mixtures were then added together and further magnetically stirred for at least 36 hours and ultrasonicated for 15 minutes before film casted onto glass sides. The samples were allowed to dry in the fumehood. To ensure complete removal of solvent, the polymer/**B**-MMT-50 hybrids were dried in a vacuum oven for an additional 2 hours before characterization. Solution intercalated PET/**B**-MMT-50 was prepared using the same procedures, except that DMF was replaced by phenol/1,1,2,2-tetrachloroethane (60/40 wt %). All the chemicals were used as purchased. Table 4.2 lists the polymers and solvents used for the preparation of the solution intercalated polymer/**B**-MMT-50 hybrids, including their molecular weights and sources.

Table 4.2. Materials used to prepare polymer/POSS-modified clay hybrids by solution intercalation.

	Name		Supplier
Solvent	All polymers except PET	Dimethylformamide (DMF)	Tedia
	PET	Phenol/1,1,2,2-tetrachloroethane (60/40 wt%)	Merck, Fluka
Polymer	Polyvinylidene fluoride (PVDF) MW: 268 K		Aldrich
	Polyacrylonitrile (PAN) MW: 150 K		Aldrich
	Poly(ethylene oxide) (PEO) MW: 600 K		Aldrich
	Polyethylene terephthalate (PET) MW: Not determined ($T_g = 81\text{ }^{\circ}\text{C}$)		Goodfellow
	Polystyrene (PS) MW: 350 K		Aldrich
	Poly(methyl methacrylate) (PMMA) MW: 120 K		Aldrich

4.2.5 Characterization & Measurements

In order to study the degree of clay dispersion in the nanocomposites, transmission electron microscopy (TEM), wide angle X-ray scattering (WAXS) and polarizing optical microscopy (POM) were performed. For WAXS and TEM, studies, the instruments and measurement conditions were the same as those reported in chapter 3. Ultrathin sections of the PET/clay samples were prepared using a Leica Ultracut UCT Ultramicrotome and collected on 400 mesh carbon-coated copper grids for TEM observation. POM was performed to examine the clay dispersion at a macro scale. POM was performed under crossed polarizers with a Nikon Optiphot-pol Universal Stage polarizing optical microscope. The sample was sandwiched between two glass coverslips, placed onto a Linkam THMS 600 hot stage equipped with a Linkam TMS 92 temperature controller and melted at 300 °C.

Dynamic mechanical analysis (DMA) samples were molded to specimens with a microinjection molding machine, HAAKE MiniJet at a barrel temperature of 290 °C and a mold temperature of 50 °C. The storage modulus (E') and glass transition temperature (T_g) of the as-molded samples were measured on a TA Q800 using a single cantilever mode. A typical sample with 17.5 mm (length), 10 mm (width) and 1 mm (thickness) was used. The samples were heated at 3 °C/min from room temperature to 180 °C at a frequency of 1 Hz. The results reported were based on the average of 2 independent measurements. Crystallinity measurements were carried out using the same DSC instrument and measurement conditions as reported in chapter 3.

The thermo-oxidative resistance of the PET/clay nanocomposites was evaluated using TGA and DSC. TGA was performed on a TA Instrument Q500. The samples were heated at 10 °C/min from room temperature to 850 °C in air and nitrogen atmospheres. Thermal degradation temperature (T_d) is defined as the temperature at 5 % weight loss. Oxidation

onset temperature (OOT) was measured via DSC in accordance with ASTM standards E2009. The measurements were conducted on a TA Instrument DSC 2010 in air with a flow rate of 50 ml/min.

4.3 Results & Discussion

4.3.1 PET/POSS-Modified Clay Composite

4.3.1.1 Clay Dispersion State

To verify the effectiveness of using POSS-modified clay as filler in PET matrix, PET/**B**-MMT-50 was prepared. Rigid POSS-imidazolium surfactant, **B** was exploited due to its loose and random packing and the feed surfactant loading used was 50 mol% CEC value of Na-MMT. In chapter 3, it was demonstrated that even with a reduced surfactant loading, the POSS-imidazolium surfactant, **B** is still able to expand the clay intergalleries and maintain large interlayer d -spacing. This means that the amount of POSS surfactant required to sufficiently expand the clay intergalleries is lesser than that needed for an organic surfactant. Moreover, compared to feed surfactant loading of 120 mol%, the effects of POSS aggregation in 50 mol% feed loading is expected to weaken. A more detailed account on how surfactant loading can have great impact on clay exfoliation will be discussed later in the chapter.

The state of clay exfoliation in PET/**B**-MMT-50 was examined by TEM, WAXS and POM. From the WAXS pattern (Figure 4.2a), it was found that there is no intercalation of the clay as the (001) clay peak of PET/**B**-MMT-50 did not shift to lower angle. In addition, as clay is a birefringent material and will appear as bright regions when polarized light passes through crossed polarizers; this allows the presence of micron-sized clay aggregates in the composites to be identified. As shown in Figure 4.2b, observations of PET/**B**-MMT-50 under

POM indicate that micron-sized clays are present. TEM micrograph of PET/**B**-MMT-50 (Figure 4.2c) also display large compact clay agglomerates. The results suggest that PET/**B**-MMT-50 is a microcomposite rather than a nanocomposite, where most of the POSS-modified clay remained in stacks and were not intercalated.

Figure 4.2. (a) WAXS patterns of PET/**B**-MMT-50 and its corresponding clay, and the state of clay dispersion of PET/**B**-MMT-50 observed in (b) micron and (c) nano scale.

In order to attain good clay dispersion as highlighted in chapter 2, there are some criteria that should be met and they include, (1) large enough intergallery spacing for the polymer chains to enter, (2) sufficient thermal stability of the surfactants to withstand high processing conditions, (3) good compatibility between polymer and surfactant and (4) enough

conformational freedom of the polymer chains to intercalate into and within the clay layers. Herein, the POSS-modified clay did not collapse (i.e. d -spacing of clay did not decrease), suggesting that there was little or no degradation of the POSS-imidazolium surfactants (Figure 4.2a). In addition, the large d -spacing of the clay was maintained by the POSS surfactants, which are rigid and incompressible. These data indicate that criteria (1) and (2) had been fulfilled.

It is proposed that one of the reasons for the poor POSS-modified clay dispersion in PET may be attributed to the strong POSS interaction among the surfactants within the clay intergalleries. POSS aggregation is evident from the bilayer packing of the POSS-imidazolium surfactants, which has been verified by WAXS, TEM and molecular modeling studies discussed in chapter 3. The POSS-imidazolium surfactants can “glue” the clay platelets together, preventing the entrance and diffusion of polymer chains, thus inhibiting the delamination of clay. At the same time, the “gluing” effect of POSS-imidazolium surfactants can lead to poor conformational freedom of the polymer chains within the clay spacing, suggesting that criterion (4) has not been satisfied. In fact, the aggregation of POSS cores is analogous to the “gluing” effect of adjacent clay sheets and edge-blocking effect observed in high concentration of telechelic polymer chains found in end-functionalized polymer/clay nanocomposites [114]. Such nanocomposites normally yield poor clay exfoliation as the gluing and edge-blocking effect ceases the dispersion process by preventing more polymer chains to enter the clay intergalleries. Hence, it is believed that the inherent tendency for POSS compounds to crystallize can have a significant impact on the effectiveness of clay exfoliating in the polymer matrix, which ironically, the large d -spacing it provides does not facilitate the insertion of large polymer chains.

Another reason for the unsatisfactory clay dispersion in the PET/POSS-modified clay composite may be due to the poor interaction between the polymer and the surfactant (i.e.

referring to condition (3)). The POSS-imidazolium surfactant has relatively short isobutyl groups at the corners of the POSS cage, which may render the clay surface inadequately hydrophobic to ensure proper mixing of the POSS-modified clay and PET. In other words, there is no driving force for the diffusion of polymer chains into the clay intergalleries. However, it is noted that the alkyl side groups had been intentionally designed to be shorter than conventional surfactants such that degradation due to organic components is minimized.

In the sections below, critical issues leading to the poor dispersion of POSS-modified clay in PET are explored in more depth and verified with experimental data.

4.3.1.2 Gluing Effect of POSS Surfactant within Clay Intergalleries

It is assumed that a lower feed surfactant loading would mean less forces of aggregation due to POSS surfactants in the bilayer packing and less resultant physical hindrance effect by the POSS cores. A lower feed surfactant loading would be more beneficial for exfoliating clay, as long as adequately large *d*-spacing is present and that the clay surface remains sufficiently organo-treated. Thus, the effects of POSS aggregation on the level of clay dispersion can be examined by varying the feed surfactant loading.

It is noted that in this particular section, the discussion is based on composites prepared using the following experimental procedures: The PET pellets and POSS-modified clay were dried in vacuum at 80 °C overnight and they were dry mixed by shaking in a Ziploc bag prior to melt compounding. Melt blending of the PET pellets and clay was carried out on a counter rotating twin-screw extruder from Thermo Scientific HAAKE MiniLab II Micro Compounder with a barrel temperature of 265 °C and a rotating speed of 58 rpm. A PET/POSS-modified clay masterbatch containing 4 wt % clay was first prepared and diluted with pure PET pellets to obtain 2 wt % clay/polymer composites.

The results revealed that with lower feed surfactant loading, both PET/**A**-MMT-50 and PET/**B**-MMT-50 display a much lower intensity in the (001) clay peak compared to their counterparts at 120 % feed surfactant loading as shown in Figure 4.3. This suggests that with a lower surfactant loading resulting in less POSS aggregation, a reduction in the number of clay tactoids and a greater extent of clay intercalation can be observed in the composites. The WAXS patterns of PET/**A**-MMT-50 also displayed an expansion in the basal spacing of the clay from 3.66 to 4.01 nm. This entails that the polymer chains were able to enter the clay galleries and intercalate the clay. On the contrary, with high feed surfactant loading, expanded clays due to intercalated polymer were absent in PET/**A**-MMT-120 and PET/**B**-MMT-120. Although, PET/**B**-MMT-50 also did not display an expansion in the *d*-spacing like PET/**A**-MMT-50, the former exhibited a broader (001) peak which extends in the direction of the lower diffraction angles, suggesting more disordered clay present.

Figure 4.3. WAXS patterns of the POSS-modified clays and its corresponding composites at various surfactant loadings. The intensities of the peaks are normalized according to the amorphous halo from the polymer.

Overall, the results showed that the reduction in surfactant loading did help to improve clay dispersion as a result of reduced POSS aggregation and lessen physical hindrance effect of the bulky POSS surfactants. However, judging the poor clay morphology of PET/**B**-MMT-50 based on POM and TEM micrographs as demonstrated in the earlier section, the decrease in surfactant loading did not significantly improve the clay dispersion. Indeed, recently Fox et al. also reported that the altering of the POSS surfactant loading did not drastically increase the *d*-spacing and clay dispersion in their polymer/POSS-modified hybrids [11]. Similarly, they explained that it is due to the bulky and rigid structure of POSS, and the bilayer packing structure of the surfactants within the clay intergalleries, which prevented complete exfoliation of POSS-modified clay even in polymer such as polyamide-6. Considering that polyamide-6/clay nanocomposites readily display exfoliated clay morphologies, this means that the POSS aggregation is a critical issue.

4.3.1.3 Effect of Polymer/Surfactant Interaction

Despite that POSS aggregation can potentially restrict clay exfoliation, the lack of interaction between the polymer and clay or the polymer and the surfactant could be another apparent reason. This is because taking into account that not the entire clay surface was covered by the POSS surfactant and that with such a large *d*-spacing, there should be adequate volume for the PET chains to intercalate into the clay galleries. In order to maintain the thermal stability of the POSS surfactant, there are constraints in altering and varying the structures of the POSS-imidazolium cation by modifying the side groups with longer alkyl chains to enhance Van der Waals interactions between the POSS surfactant and PET. Consequently, the effect of polymer/clay and polymer/surfactant interactions on clay dispersion is indirectly established by solution intercalation of **B**-MMT-50 with various polymer matrices. It is noted that unlike in melt compounding where shear forces during

extrusion can help to delaminate the clay, solution intercalation method of preparing polymer/clay nanocomposites relies heavily on the strength of the interactions among polymer, surfactant and clay to facilitate the diffusion of polymer chains into the clay intergalleries.

Figure 4.4. POM images of solution intercalated polymer/**B**-MMT-50 hybrids prepared from (a) PVDF, (b), PAN, (c) PEO, (d) PET, (e) PS and (f) PMMA.

Figure 4.4 presents the POM images of the solution intercalated composites of various polymers with **B**-MMT-50. The states of clay exfoliation in the hybrids were assessed based on the observations of micron and sub-micron sized clay present in their POM images. Nano-dispersed clays were observed in PVDF/**B**-MMT-50, PAN/**B**-MMT-50 and PEO/**B**-MMT-50 hybrids which exhibit stronger polymer/clay and/or polymer/surfactant interactions. On the other hand, micron and sub-micron sized clays were present in PET/**B**-MMT-50, PS/**B**-MMT-50 and PMMA/**B**-MMT-50 hybrids which display weaker polymer interactions with

both clay and surfactant. The reasons for the differences in the state of clay dispersion observed in the polymers will be elaborated later.

To verify the state of clay dispersion in the solution intercalated polymer/**B**-MMT-50 hybrids, TEM was performed on the drop cast film samples of PVDF/**B**-MMT-50 and PMMA/**B**-MMT-50. The samples for TEM characterization were prepared by drop casting the solution of the hybrids directly on the carbon-coated copper grids. As expected, large clay agglomerates were observed in the TEM images of PMMA/**B**-MMT-50, while intercalated clays were found in the TEM image of PVDF/**B**-MMT-50 (Figure 4.5).

Figure 4.5. TEM images of (a) PVDF/**B**-MMT-50 and (b) PMMA/**B**-MMT-50 prepared from drop casting film samples.

In addition, it was found that the WAXS patterns of PVDF/**B**-MMT-50, PAN/**B**-MMT-50 and PEO/**B**-MMT-50 hybrids (Figure 4.6) exhibit broad but obvious (001) clay diffraction peaks that shifted slightly to a lower 2θ regions. This suggests that the POSS-modified clay in these hybrids were intercalated by PVDF, PAN and PEO respectively. On the contrary, the WAXS patterns of PET/**B**-MMT-50, PS/**B**-MMT-50 and PMMA/**B**-MMT-50 hybrids display no obvious low-angle diffraction peaks in the same 2θ region other than a

very broad clay peak that can be observed at around $2\theta = 6.7^\circ$. Here, the disappearance of the low-angle clay peaks do not associate with clay exfoliation, but rather it is due to disordered structure of clay stacks. As DMF and phenol/1,1,2,2-tetrachloroethane are good solvents for POSS-imidazolium surfactants, it is possible for the surfactants in the solution intercalated samples to detach from the surface of the clay and drop out of the clay intergalleries. In fact, this is verified by the presence of POSS aggregates or crystals found on the exterior of the clay intergalleries (highlighted by the arrows) as shown in the TEM image of PEO/**B**-MMT-50 (Figure 4.7). Therefore, a possible reason for the disappearance in the low-angle clay peaks is that the clays in PET/**B**-MMT-50, PS/**B**-MMT-50 and PMMA/**B**-MMT-50 hybrids are not intercalated by the polymer, and when the POSS-imidazolium surfactants in the clay drop out of the clay intergalleries partially, the bilayer packing structure of the POSS-imidazolium surfactants is destroyed. Consequently, a disordered clay structure is obtained due to the absence of polymers to maintain the ordered spacing of the clay platelets.

On the contrary, the dropping out of the POSS-imidazolium surfactants from the clay galleries in PAN/**B**-MMT-50, PVDF/**B**-MMT-50 and PEO/**B**-MMT-50 samples will less likely result in the disordered clay structure because the polymers are intercalated in the clay galleries due to better polymer/clay and/or polymer/surfactant interactions. In these cases, the polymers may block the dropping out of B-MMT and hence preserve the intercalated structure of clay. As a result, their WAXS patterns exhibit broad but obvious low-angle clay peaks.

Figure 4.6. WAXS patterns of **B-MMT-50** and its corresponding hybrids with various polymers. The intensities of the clay peaks were adjusted to scale by using the amorphous halo of the polymer as a reference.

Figure 4.7. TEM image of PEO/B-MMT-50 prepared from drop casting film samples. (Arrow: clusters of POSS aggregates)

Overall, it can be observed that the POSS-modified clay can disperse reasonably well in polymers with highly polar groups, such as PVDF and PAN, and that with high content of polar groups such as PEO, but not in less polar PET and PMMA, and non-polar PS. An explanation is proposed as follow: The good clay dispersions observed in PVDF, PAN and PEO-based nanocomposites may be due to the stronger interactions between polymer and surfactant, and/or hydrogen-bonding interaction between polymer and clay. The POSS-imidazolium surfactant is amphiphilic and possessed both a polar functional group (i.e. imidazolium cation with a positive charge) as well as a hydrophobic group (i.e. isobutyl group). This results in two possible types of interactions with polymers as shown in Figure 4.8. Polymers with electronegative functional groups can form dipole-dipole interaction with the polar imidazolium cation, while polymers with non-polar groups prefer to interact with the isobutyl side groups via London dispersion force, which is much weaker. Consequently, the POSS-imidazolium cation in the clay is able to effectively draw polymers such as PVDF and PAN into the clay intergalleries via dipole-dipole interactions. The hydrogen bonding

interaction between the polymers (i.e. PVDF, PAN and PEO) and hydrophilic clay also enhance the miscibility of the polymers and clay. At the same time, because POSS-imidazolium surfactants may detach itself from the surface of the clay destroying the bilayer packing of the POSS-imidazolium surfactants, this may reduce the physical hindrance effect of POSS-imidazolium surfactants at the edge of the clay and further allow the polymers to enter the clay galleries.

Figure 4.8. A schematic diagram to illustrate the interactions between POSS-imidazolium surfactant and various polymers.

However, it is noted that not all the POSS-imidazolium surfactants are washed out of the clay intergalleries. Some of the POSS-imidazolium surfactants (probably in a small amount and in a disordered manner) remain in the interlayer spacing to keep clay platelets apart and facilitate the insertion of the polymer chains. Indeed, surfactant-free PEO/Na-MMT hybrid yielded significantly poorer clay dispersion compared to PEO/**B**-MMT-50 nanocomposite as demonstrated in Figure 4.9, suggesting that the presence of the POSS-imidazolium surfactant as a spacer is beneficial. Nonetheless, from PET/**B**-MMT-50, PS/**B**-MMT-50 and PMMA/**B**-MMT-50 composites, it is deduced that strong polymer/surfactant and/or polymer/clay

interactions are still necessary to obtain good clay dispersion even though the POSS-modified clay has large d -spacing.

Figure 4.9. POM images of (a) PEO/Na-MMT (surfactant-free clay) and (b) PEO/B-MMT-50.

The results obtained herein substantiate the hypothesis that the strong polymer/surfactant/clay interactions displayed in PVDF, PAN and PEO systems are the key elements to the improved state of clay intercalation. On the other hand, for polymers such as PET, PS and PMMA, the poor polymer interactions with surfactant and clay do not allow the polymer chains to intercalate into the clay intergalleries. The impact of the interactions between polymers and the POSS-imidazolium surfactant-modified clay on the hybrid's clay dispersion state is demonstrated schematically in Figure 4.10. In summary, the findings highlight the importance of polymer/surfactant/clay interactions and indicate that the introduction of compatible functional groups on POSS compound may enhance the extent of intercalation of POSS-modified clay in PET. At the same time, although the preparation of PET/B-MMT-50 nanocomposites may not be successful, the results suggest that POSS-modified clay may be potentially used for polymer matrices such as PVDF, PAN and PEO.

Figure 4.10. A schematic diagram to illustrate the effect of the interactions between polymers and POSS-imidazolium surfactant-modified clay on the hybrid's clay dispersion state.

4.3.2 PET/Dual POSS-Modified Clay Nanocomposite

4.3.2.1 Dual POSS-Modified Clay

In spite of the poor clay dispersion in PET/**B**-MMT-50, the thermo-oxidative stability of the **B**-MMT-50 is significantly better than organoclay by around 100 °C (as discussed in chapter 3). Considering that even a small degree of degradation occurring during the manufacturing process of PET nanocomposites can affect the physical appearance, molecular weight and properties of the product, **B**-MMT-50 makes a valuable candidate as a thermal stable filler for PET. However, the dispersion of POSS-modified clay in PET needs to be significantly improved. From the discussion in the previous sections, it was concluded that

the main challenges in utilizing POSS as a surfactant for clay are POSS aggregation issue and its poor compatibility with polymer.

To tackle the aforementioned challenges, the approach adopted is to modify clay using both the POSS-imidazolium surfactant, **B** and a trisilanolphenyl POSS (Tsp-POSS) spacer. The step by step modification of the dual POSS-modified clay is described in the experimental section and shown schematically in Figure 4.11. Tsp-POSS is introduced as a spacer to the clay suspension initially to keep the clay stacks apart, then to weaken the interactions of POSS-imidazolium surfactants and ultimately to prevent the latter from crystallizing. Subsequently, upon solvent removal, both POSS-imidazolium surfactant and Tsp-POSS are assumed to mostly remain within the clay intergalleries. It is believed that the active silanol groups on Tsp-POSS can promote the diffusion of PET chains into the clay intergalleries and undergo a melt reaction with the carboxyl end groups in PET leading to branching of PET chains [99]. This helps to potentially facilitate the clay exfoliation in PET during compounding. It is emphasized that Tsp-POSS is added in a small amount as a spacer and not as a surfactant because high concentration of Tsp-POSS can lead to POSS networks [99], rendering it an ineffective aid to the dispersion of clay.

Figure 4.11. A schematic diagram on the modification process to yield dual POSS-modified clay.

From WAXS pattern of the dual POSS-modified clay, it is observed that the addition of Tsp-POSS did not result in the expansion of clay intergalleries, except for some changes to the diffraction pattern of quartz (i.e. SiO_2) at higher 2θ angle regions as shown in Figure 4.12. This observation is reasonable as silanol groups on the Tsp-POSS can interact with the hydroxyl groups on both the edges and surfaces of the clay. Since there are more hydroxyl groups on the edges of the clay, it is proposed that Tsp-POSS is more inclined to forming hydrogen-bond on the edges than on the surfaces of the clay. Another possibility is that the content of Tsp-POSS in the clay galleries may be too small and disordered to be detected by WAXS.

Figure 4.12. WAXS patterns of (a) Na-MMT, (b) **Tsp-POSS-0.1-MMT**, (c) **B-MMT-40**, (d) **(B+Tsp-POSS-0.1)-MMT** and (e) **PET/(B+Tsp-POSS-0.1)-MMT**. (Q) Diffraction peaks due to quartz.

Table 4.3. Degradation temperatures (T_d) and the residue content of the dual POSS-modified clays measured using TGA in nitrogen and air.

Samples	T_d (°C)		Residue (%)
	Nitrogen	Air	
B-MMT-40	394	392	79
(B+Tsp-POSS-0.1)-MMT	389	357	77
(B+Tsp-POSS-0.3)-MMT	385	354	74

However from Table 4.3, it is evident that Tsp-POSS has been integrated onto the clay. This is because with the addition of Tsp-POSS spacer, T_d of the dual POSS-modified clay drops drastically by 35 °C in air. It is highlighted that dual POSS-modified clay had been washed at least 4 times with ethanol to remove excess and unattached Tsp-POSS and POSS-imidazolium surfactant. In fact, the higher the content of Tsp-POSS, the lower is the thermo-oxidative stability. In addition, the residue content on degradation decreases when more Tsp-POSS is added, confirming that its inclusion led to more weight loss from its degraded

products. The thermo-oxidative degradation in dual POSS-modified clay may have been accelerated by the hydroxyl groups. It can also be attributed to a decrease in the aggregation of POSS-imidazolium surfactant when Tsp-POSS resides between them. Typically, higher thermo-oxidative stability is obtained by surfactant molecules that are packed into ordered structures rather than disordered structures. The intervention of Tsp-POSS spacers in the bilayer packing of the POSS-imidazolium surfactants may have prevented formation of crystalline domains.

There is no clear comprehension on how Tsp-POSS is incorporated into clay. It is deduced that from the absence of a larger d -spacing and as Tsp-POSS does not extend the length of the existing POSS-imidazolium cations; Tsp-POSS likely resides in between/amidst the cations or is hydrogen-bonded at the edges of clay. In order to establish the hypothesis that Tsp-POSS resides within the clay intergalleries and not outside the clay galleries, a physical blend of **B**-MMT-40, Tsp-POSS and PET granules was melt compounded to yield PET/**B**-MMT/Tsp-POSS. Its clay morphology is compared with PET/(**B**+**Tsp-POSS-0.1**)-MMT and discussed in the next section.

4.3.2.2 Clay Dispersion State

The degree of clay dispersion is investigated by TEM, WAXS and POM. The polarizing optical micrograph of PET/**IMC**-MMT as shown in Figure 4.13a exhibited no or little clay tactoids at the micron scale, suggesting that IMC-MMT-120 is nano-dispersed. In contrast, the POM image of the PET/**B**-MMT/Tsp-POSS physical blend (Figure 4.13d) displayed large particles and agglomerates at the micron and sub-micron level that is similar to PET/**B**-MMT-50 (Figure 4.2b), implying that the clay dispersion in the physical blend is extremely poor. However, the polarizing optical micrographs of the PET/dual POSS-modified clay nanocomposites revealed a significant improvement compared to PET/POSS-modified clay

composites and the physical blend. The differences observed in the polarizing optical micrographs of PET/dual POSS-modified clay nanocomposites and its corresponding physical blend verifies that Tsp-POSS resides within the intergalleries of the dual POSS-modified clay. From the WAXS pattern of PET/(**B+Tsp-POSS-0.1**)-MMT (Figure 4.12), a low intensity (001) clay peak is shifted to lower diffraction angle, signifying an intercalated clay morphology. The clay morphologies observed under TEM (Figure 4.14) complement the POM images of the nanocomposites. The reason for the improvement in clay dispersion of PET(**B+Tsp-POSS**)-MMT compared to PET/**B**-MMT-50 is believed to be due to weakened POSS aggregation and stronger interactions between PET end groups and the active silanol group on Tsp-POSS.

Figure 4.13. POM images of (a) PET/**IMC**-MMT, (b) PET/(**B+Tsp-POSS-0.1**)-MMT, (c) PET/(**B+Tsp-POSS-0.3**)-MMT and (d) PET/**B**-MMT/**Tsp-POSS** (physical blend).

Figure 4.14. TEM images of (A) PET/IMC-MMT, (B) PET/(**B+Tsp-POSS-0.1**)-MMT and (C) PET/(**B+Tsp-POSS-0.3**)-MMT.

As discussed earlier, it is observed that when the amount of Tsp-POSS in the nanocomposites increases from 0.1 wt % to 0.3 wt %, thermo-oxidative properties deteriorate slightly. Moreover, compared to the TEM micrograph of PET/(**B+Tsp-POSS-0.3**)-MMT, the TEM micrograph of PET/(**B+Tsp-POSS-0.1**)-MMT exhibits thinner tactoids. In addition, Ciolacu et al. reported that higher open POSS cage content can retard the mobility of the polymer, reduce processability and lower crystallinity [99]. Indeed, PET/(**B+Tsp-POSS-0.1**)-MMT exhibits superior properties compared to PET/(**B+Tsp-POSS-0.3**)-MMT and implies that a minimal amount of Tsp-POSS is adequate. Thus, discussions that follow will be focused on PET/(**B+Tsp-POSS-0.1**)-MMT.

4.3.2.3 Thermo-mechanical & Crystallization Properties

To evaluate the thermo-mechanical properties displayed by the nanocomposites, storage modulus (E') of the samples were determined and their data summarized in Table 4.4. The storage modulus of PET that had been extruded twice like the nanocomposites (E'_n), and the various hybrids (E'_h) were compared at 40 °C. E'_h/E'_n measures the reinforcement effect of the clay. It was found that PET/dual POSS-modified clay nanocomposites exhibited lower E' than PET/**IMC**-MMT, which is likely due to the former's inferior clay dispersion compared to the latter. A higher E' can be achieved if the level of clay dispersion is improved and the degree of crystallinity is increased. As shown in Table 4.5, there is no major difference in the degree of crystallinity between PET/**IMC**-MMT and PET/(**B+Tsp-POSS-0.1**)-MMT. Hence, the difference in E' is primarily due to the disparity in the state of clay exfoliation.

As the flexible surface of the PET/**IMC**-MMT can hinder the stable energy condition to form critical nuclei, it is believed that POSS-modified clay having a more rigid surface like Na-MMT can display stronger nucleating behavior. However, the cold crystallization temperature (T_{cc}) (Table 4.5) of PET/(**B+Tsp-POSS-0.1**)-MMT is greater than that of PET/**IMC**-MMT, suggesting that (**B+Tsp-POSS-0.1**)-MMT has a poorer nucleating effect compared to **IMC**-MMT-120. On the other hand, the higher T_{cc} exhibited by PET/(**B+Tsp-POSS-0.1**)-MMT compared to PET/**IMC**-MMT may not be due to the poorer nucleating effect of the dual POSS-modified clay but may also be attributed to the unsatisfactory level of clay dispersion or it can be because of the PET chain extension effects of Tsp-POSS, which limit the reorganization of polymer chains.

Table 4.4. Storage moduli (E') and glass transition temperature (T_g) of the as-molded PET and its hybrids.

Sample	E' at 40 °C (MPa)	E'_h/E'_n (40 °C)	T_g (°C)*
PET-extruded	2016 ± 85	-	83
PET/ IMC -MMT	2483 ± 23	1.23	81
PET/Tsp-POSS-0.1	2120 ± 28	1.05	82
PET/(B+Tsp-POSS-0.1)-MMT	2271 ± 7	1.13	82

* Errors of E' given are one standard deviation. T_g of the samples were determined by the peak in the $\tan \delta$ versus temperature curves.

Table 4.5. DSC results of the as-molded PET and its hybrids taken from the first heating curves.

Sample	T_m (°C)	ΔH_m (J/g)	T_{cc} (°C)	ΔH_{cc} (J/g)	X_c (%)*
PET-extruded	257	52	120	22	21
PET/ IMC -MMT	258	57	113	28	21
PET/Tsp-POSS-0.1	257	52	118	23	21
PET/(B+Tsp-POSS-0.1)-MMT	257	51	117	24	20

* The percentage of crystallinity (X_c) was calculated using the equation: $X_c = [(\Delta H_m - \Delta H_{cc}) / (1-x) / \Delta H_m^\circ] \times 100 \%$, where ΔH_m is the heat of fusion, ΔH_{cc} is the latent heat of cold crystallization, ΔH_m° is the melting enthalpy of 100 % crystalline PET (i.e. 140.1 J/g) and x is the weight fraction of clay measured by TGA. T_m : Melting temperature and T_{cc} : Cold crystallization temperature.

4.3.2.4 Thermo-oxidative Stability

The degradation issue of the organic surfactants can induce thermo-oxidative degradation of the polymer matrices resulting in poor mechanical and physical properties. In order to verify the effects of POSS-modified clay on the thermo-oxidative stability of the resultant nanocomposites, TGA and DSC were performed.

Table 4.6. Degradation temperatures (T_d) of the nanocomposites measured in air using TGA.

Sample	T_d (°C) In Air	Corresponding Modified Clay T_d (°C) In Air	Residue (%)
PET-extruded	368	-	-
PET/Tsp-POSS-0.1	379	-	-
PET/IMC-MMT	381	295	1.71
PET/(B+Tsp-POSS-0.1)-MMT	380	357	2.12

From TGA results (Table 4.6), T_d of the dual POSS-modified clay is 62 °C higher compared to the organoclay in the air atmosphere. Nonetheless, the trend in T_d s of the modified clay does not translate into similar increment in the T_d s of its corresponding nanocomposites. In fact, it is observed that both the T_d s of PET/IMC-MMT and PET/(B+Tsp-POSS-0.1)-MMT is around 380 °C. TGA measures the weight loss of volatile decomposition products. The presence of clay enhances the formation of char and prevents the diffusion and escape of these products. Hence, the degradation temperatures measured by TGA depend largely on the state of clay exfoliation. In fact, the barrier effect of clay on T_d is dominant in the air atmosphere [115]. Although the presence of IMC may promote the

degradation reactions in PET/**IMC**-MMT, well dispersed clay may hinder the evaporation of the decomposition products so that its T_d is not significantly lower.

DSC on the other hand, can be used to measure the exothermic event as a result of oxidative degradation reactions. The thermo-oxidative stability measured by DSC is not based upon weight loss and thus less dependent on the degree of clay dispersion. It better reflects the extent of degradation reactions that occurred in the nanocomposites. The assessment of thermal oxidative stability by DSC can be done in dynamic mode to obtain oxidation onset temperature (OOT). The OOT results are presented in Figure 4.15. The OOT thermograms of PET, PET/Tsp-POSS-0.1 and PET/(**B+Tsp-POSS-0.1**)-MMT display relatively flat baselines after the melting peak, allowing the estimation of OOT (marked in the figure). OOT is determined by extrapolating the slope of the oxidation exotherm from the inflection point on the curve to the extended temperature baseline in accordance to ASTM E2009. It is obvious that PET/(**B+Tsp-POSS-0.1**)-MMT exhibits a higher OOT than PET/Tsp-POSS-0.1 and PET and that the flat baseline before inflection shifts towards higher temperature in the following ascending order: PET, PET/Tsp-POSS-0.1 and PET/(**B+Tsp-POSS-0.1**)-MMT (Figure 4.15a). The improvement in OOT is attributed not only to the presence of clay but also that of Tsp-POSS. At the processing temperature, random chain scissions of PET chains lead to reduction in molecular weight as well as generation of carboxyl end groups, which can ultimately promote thermo-oxidative degradation [116]. Although Tsp-POSS in its unreacted state lowers the thermo-oxidative stability of the dual POSS-modified clay (Table 4.3), it can create chain extensions among PET chains and reduce the amount of carboxyl end groups during the melt state.

On the other hand, the OOT thermogram of PET/**IMC**-MMT (Figure 4.15b) displays an obvious exothermic peak (highlighted by an arrow) immediately after the melting endotherm, which resembles the thermogram of PET/commercial alkylammonium-modified clay

nanocomposite. This is because organic surfactant can easily decompose to form macro radicals, which can readily react with oxygen to form peroxy radicals and accelerate degradation of the PET matrix. It implies that oxidative decomposition of the long alkyl chain in the organic surfactants, in fact, occurs at temperatures below the typical processing temperature of PET. It is emphasized that the organic surfactant, IMC used in this work was reported to possess greater thermal stability compared to commonly used quaternary alkylammonium salts [2-3]. Even so, it is demonstrated that the degradation of the alkyl chains remains a real issue.

Figure 4.15. The OOT thermograms of (a) PET-extruded, PET/Tsp-POSS-0.1 and PET/(B+Tsp-POSS-0.1)-MMT and (b) PET/IMC-MMT and PET/Cloisite30B-MMT.

4.4 Conclusions

Table 4.7. A summary of the PET/clay hybrids studied and their state of clay exfoliation.

Composite	Surfactant	Degree of Clay dispersion
PET/IMC-MMT	Organic	Intercalation & Exfoliation
PET/B-MMT-50	POSS	Microcomposite
PET/(B+Tsp-POSS-0.1)-MMT	Dual POSS	Small tactoids

In this chapter, the advantages and limitations of utilizing POSS-imidazolium as a surfactant for clay in PET were studied. Table 4.7 summarizes the state of clay exfoliation exhibited by PET/clay hybrids investigated. WAXS, POM and TEM results suggest that poor degree of clay dispersion is displayed by PET/POSS-modified clay composites. It is proposed that the bilayer packing structure of POSS-imidazolium surfactants and poor compatibility between the surfactant and polymer made exfoliation of POSS-modified clay in PET extremely challenging. In order to address these issues, Tsp-POSS was added as a spacer during clay modification with POSS-imidazolium surfactant to yield PET/dual POSS-modified clay nanocomposites. It was found that the degree of clay dispersion improved with the addition of a very small amount of Tsp-POSS (0.1 wt %). Clay tactoids instead of compact clay agglomerates were observed under TEM. The improvement in clay dispersion also led to a small enhancement in E' . The findings established that although POSS surfactants increase the d -spacing to facilitate intercalation of polymer chains, but a driving force to initiate the intercalation is equally crucial. In fact, it has been demonstrated that the addition of functional groups on POSS surfactant can enhance the effectiveness of using POSS compounds as surfactant for clay. It is also evident from OOT results that the

PET/dual POSS-modified clay nanocomposites displayed higher thermo-oxidative stability compared to the PET/organoclay nanocomposites. Even so, the properties enhancement found in PET/dual POSS-modified clay nanocomposite is clearly limited due to its less than ideal clay dispersion when compared to PET/organoclay nanocomposites.

5 PET/Clay/POSS Nanocomposites: POSS as Spacers

This chapter describes an alternative approach to resolve the degradation issues of organic surfactants found in PET/organoclay nanocomposites, whereby a straightforward method for fabrication of PET/clay nanocomposites using surfactant-free clay (Na-MMT) with trisilanolphenyl POSS (Tsp-POSS) as a spacer to enhance clay dispersion is presented. The influence of Tsp-POSS spacer incorporation on the properties of the resultant nanocomposites is also described.

5.1 Introduction

In chapter 4, it is established that the bilayer packing structure of POSS surfactants and poor compatibility between the surfactant and polymer hinder the exfoliation of POSS-modified clay in PET. Till the issue of POSS aggregation can be resolved, the path to using POSS as surfactants to treat clay will probably be ineffective. Therefore, in an attempt to tackle the degradation issue of organic surfactants in clay, surfactant-free PET/sodium montmorillonite (Na-MMT) nanocomposites have been prepared via in-situ polymerization using bis-hydroxyethyl terephthalate (BHET) monomer to intercalate the clay [90]. BHET may be obtained by depolymerization of waste PET, making this a potential green approach [89]. However, when the clay surface is completely unmodified, clay agglomeration is inevitable and partial re-agglomeration of the clay particles can take place when the

nanocomposite is heated above the melting temperature because of the lack of favorable polymer/clay interactions [36].

An alternative approach is to incorporate stable nanofillers as spacers into clay intergalleries to prevent the recombination of clay into stacks and to increase the interlayer spacing of clay [117-118]. In light of the previous work performed on dual POSS surfactant, the conclusion drawn was that the addition of Tsp-POSS as spacer can help to improve the clay dispersion and thermo-oxidative stability of the nanocomposite. Because of the rigid and bulky structures of the Tsp-POSS compounds, it is hypothesized that even without surfactants to increase interlayer spacing of the clay, they may act as spacers to keep clay platelets apart and prevent clay to form stacks. By combining clay with Tsp-POSS, not only the dispersion of clay may be improved by the POSS spacers, the sandwich of the POSS molecules between clay platelets may also help to prevent the agglomeration of unreacted POSS. Furthermore, the silanol groups may be capable of pulling PET monomers into the clay intergalleries via hydrogen-bonding interactions to enhance the clay dispersion. This would further maximize the reinforcement effect of clay and consequently, significantly enhanced thermo-mechanical properties and thermal stability may be achieved simultaneously.

To verify the effectiveness of the above approach, in this work, PET/Na-MMT/Tsp-POSS nanocomposite was prepared and compared with PET/Na-MMT nanocomposite as well as PET/trialkylimidazolium-modified clay nanocomposite. In this chapter, insights into the effects of incorporating Tsp-POSS spacers on the degree of clay dispersion, thermo-mechanical properties and thermo-oxidative stabilities of the PET/clay nanocomposites are provided. In view of the possible different polymer/clay interfacial behavior between surface organo treated and untreated clay, their effects on the orientation of clay in the PET/clay nanocomposites and PET's crystallization behavior were also examined.

5.2 Experimental

5.2.1 Materials

The monomer, catalyst and stabilizer used in the in-situ polymerization, namely, BHET ($\geq 94\%$), manganese (II) acetate (MnAc, 98%), antimony (III) acetate ($\text{Sb}(\text{OAc})_3$, 99.99%) and triphenyl phosphate (TPP, $>99\%$) were purchased from Sigma-Aldrich. All chemicals were used without further purification.

5.2.2 Preparation of Prepolymer

Firstly, Na-MMT (6 g) was dispersed in deionized (DI) water (1000 ml) via 2 days of magnetic stirring and 15 minutes of homogenization. Large clay agglomerates were allowed to settle for 2 days and the precipitate was removed to obtain a clay suspension. Next, the suspension was added into ethanol (500 ml for Na-MMT system and 250 ml for Na-MMT/Tsp-POSS system) and homogenized for 15 minutes. In the case of Na-MMT/Tsp-POSS system, Tsp-POSS (3.3 wt % of Na-MMT) dissolved in ethanol (250 ml) was then added to the clay/water/ethanol suspension and magnetically stirred overnight to yield mixture **A**. 120 g BHET was dissolved in 500 ml THF and subsequently added into the mixture **A**, while homogenizing at high speed with heat. A viscous slurry was obtained after continuous shearing and vaporization of solvent. Lastly, the slurry was freeze-dried to yield the prepolymer.

5.2.3 Preparation of PET/Clay/POSS Nanocomposites

A master batch containing 4-5 wt % of clay was synthesized by in-situ polymerization of the BHET/Na-MMT/Tsp-POSS prepolymer. 120 g prepolymer and MnAc (0.14 mol %) were mixed in a 500 ml 3-neck round-bottom flask and heated to $200\text{ }^{\circ}\text{C}$ to completely melt the

BHET. Then, TPP (0.09 mol %) and $\text{Sb}(\text{OAc})_3$ (0.075 mol %) were added and the melt was maintained at 200 °C for 15 minutes. Next, the vacuum was applied slowly. In order to maintain high viscosity to prevent the aggregation of the clay (Figure 5.1), at least 5 ml of ethylene glycol was collected before the temperature was slowly raised to 290 °C for the polycondensation of BHET to PET. At the same time, the vacuum was gradually increased to less than 0.5 mbar over a period of 1 hour. The melt was maintained at 290 °C with high vacuum for another 1 hour. After the reaction was completed, it was allowed to cool to room temperature. Neat PET and PET/Na-MMT nanocomposite were also prepared using the similar procedure.

Figure 5.1. POM images of BHET/Na-MMT at the same area held isothermal at (a) 200 °C and (b) 250 °C. At 200 °C, clay is nano-dispersed but as the temperature increases to 250 °C, clay re-agglomerates and bright spots (i.e. clay in large agglomerates) were observed.

In-situ polymerized PET/Na-MMT/Tsp-POSS and PET/Na-MMT nanocomposites were diluted to clay content of 2 wt % by melt compounding with the commercial neat PET using the same extrusion conditions as in chapter 4. The Tsp-POSS content in PET/Na-MMT/Tsp-

POSS is about 0.1 wt % after the melt compounding. PET/IMC-MMT nanocomposite with 2 wt % clay and PET/Tsp-POSS nanocomposite with 0.1 wt % Tsp-POSS were prepared as reference materials via direct melt compounding. To ensure a fair comparison, the neat PET and all nanocomposite samples herein contain about 50 wt % commercial PET and 50 wt % in-situ polymerized PET. For clarity, the PET/IMC-MMT discussed in this chapter contains 50 wt % commercial PET and 50 wt % in-situ polymerized PET and is not the same as the PET/**IMC**-MMT reported in chapter 4.

5.2.4 Characterization & Measurements

For WAXS, TEM, POM, DSC, TGA and DMA studies, the instruments and measurement conditions were the same as those reported in chapter 4. To study the orientation of the clay in the PET matrix, two-dimensional (2D) WAXS patterns of the as-molded and stretched samples were collected on a Bruker GADDS X-ray diffractometer with 2D area detector using Cu K $_{\alpha}$ radiation. Stretching experiment was carried out on an INSTRON 5848 MicroTester equipped with a furnace that has hot air blowing above and below the clamped samples. The as-molded samples were stretched to a stretch ratio of 1.5, resulting in an average thickness of 0.5 mm. The strain rate applied was 1 mm/min and the stretching temperature was 110-115 °C. Oxidation onset temperature (OOT) and oxidation induction time (OIT) were measured via DSC using ASTM standards E2009 and D3895, respectively. The measurements were collected on a TA Instrument DSC 2010 in air. The OIT test was measured isothermally at 280 °C with flow rate of 50 ml/min. The inherent viscosities (η_{inh}) of the nanocomposites before and after compounding were determined by glass capillary viscometer in accordance to ASTM D4603-03. The samples before compounding were

prepared by a solution blend of in-situ polymerized samples and commercial neat PET in the same ratio that was used to prepare the melt compounded samples.

5.3 Results & Discussion

5.3.1 Effect of Solvent on Clay Dispersion

BHET and the POSS compounds were dissolved in organic solvents before they were added to the clay/water suspension. Pristine clay however, can best disperse in water. In an organic/water solvent system, clay flocculation occurs when the percentage of water decreases. Hence, it is imperative to select an optimum solvent system with minimal clay flocculation when preparing the BHET/Na-MMT prepolymer mixture to maximize the dispersion state of the surfactant-free clay.

Typically, ethanol/water solvent system was used for clay modification during ion exchange procedures. However, the solubility of BHET is poor in ethanol and good in tetrahydrofuran (THF) and acetone. Thus, a study on the extent of clay sedimentation/agglomeration in various organic/water systems was carried out to acquire an optimum condition for the preparation of the prepolymer mixture. In all the sedimentation tests, the amount of organic solvent to water is kept at 1:1 ratio. It is observed that after the clay was allowed to settle for 30 days, compact clay residue (highlighted by arrows) was observed in 100 % water, acetone/water and ethanol/water systems as demonstrated in Figure 5.2. However, the top layer solution of 100 % water and acetone/water systems comprising of nano-dispersed clay appears clear. On the contrary, flocculated clay which appears “fluffy” was observed in ethanol/water, THF/water and ethanol/THF/water systems. Both the presence of clay residue settled at the bottom of the centrifuge tube and a lower height of settled flocculated clay implies more compact clay stacks and less nano-dispersed clay.

Overall, judging from the amount of clay residue and height of settled flocculated clay, the best clay dispersion is exhibited by the ethanol/THF/water system.

Figure 5.2. Clay sedimentation in different organic/water solvent systems after 30 days. (Arrow: Compact clay residue.)

In order to verify the phenomenon, PET/Na-MMT nanocomposites were prepared using different solvent systems, namely, (1) ethanol/THF/water, (2) THF/water and (3) acetone/water. These 3 systems allow the comparison between the flocculated clay and the clay mixture that comprises of nano-dispersed and compact clay, to determine what state of clay morphologies in the solvent systems gives the best extent of clay exfoliation in the resultant nanocomposites. The degree of clay dispersion was investigated by TEM, WAXS and POM. As expected, the nanocomposite prepared using the ethanol/THF/water system displays the greatest degree of clay dispersion and the largest d -spacing after melt compounding. It exhibits intercalated clay that shows an expansion of d -spacing from 1.23 nm to 1.82 nm. POM and TEM micrographs of the nanocomposites provided in Figure 5.3 also complement the results.

Figure 5.3. (a) POM and (b) TEM images of PET/Na-MMT nanocomposites prepared using (i) ethanol/THF/water, (ii) THF/water and (iii) acetone/water solvent systems.

5.3.2 Effect of POSS Spacer on Clay Dispersion

As discussed in earlier chapters, POSS surfactants have been exploited to treat clay surfaces to address degradation issues of polymer/clay nanocomposites. However, due to the inherent tendency for POSS compounds to aggregate and crystallize [11], uniform dispersion of the POSS-modified clay in polymer matrices remains elusive. In this chapter, instead of using POSS as a surfactant, only reactive Tsp-POSS was used in a smaller amount as spacers to promote clay exfoliation in PET/Na-MMT nanocomposites. The synthesis routes for the nanocomposites are illustrated in Scheme 5.1. The effects of the incorporation of Tsp-POSS on the degree of clay dispersion and morphologies of the nanocomposites were investigated via WAXS, POM and TEM.

Scheme 5.1. The synthetic routes for the PET/clay nanocomposites.

The WAXS patterns of the prepolymer mixtures are presented in Figure 5.4a. A sharp peak at $2\theta = 7.1^\circ$ and a broad peak at $2\theta = 7.2^\circ$ are observed in the WAXS patterns of BHET and Na-MMT, respectively, which can be attributed to BHET crystallization and the intergallery spacing of Na-MMT, respectively. In the WAXS patterns of BHET/Na-MMT and BHET/Na-MMT/Tsp-POSS, two additional broad and overlapped peaks are observed at around $2\theta = 4.5^\circ$ ($d = 1.97$ nm) and 5.7° ($d = 1.54$ nm), indicating intercalation of Na-MMT by BHET monomers. The key differences between BHET/Na-MMT and BHET/Na-MMT/Tsp-POSS are that for the latter the intensity of the BHET crystal peak at $2\theta = 7.1^\circ$ is reduced dramatically, whereas the peak at $2\theta = 5.7^\circ$ arisen from the expanded clay becomes much stronger. This implies that Tsp-POSS has been placed between clay platelets and hence can draw BHET into the clay intergalleries more effectively owing to the interactions of the hydroxyl groups with BHET. Thus, BHET molecules are less likely to crystallize into large

domains at the exterior of the clay stacks. The result proves that Na-MMT can be better intercalated by BHET with the aid of Tsp-POSS spacers.

Figure 5.4. (a) WAXS patterns of Na-MMT, BHET, the prepolymer mixtures and IMC-MMT. (b) WAXS patterns of the nanocomposites after melt compounding.

WAXS patterns of the resultant nanocomposites after compounding are presented in Figure 5.4b. The results suggest that after in-situ polymerization and compounding, intercalated clay stacks still exist and the d -spacing of the clay is 1.71–1.78 nm. The clay peak of PET/Na-MMT/Tsp-POSS at $2\theta = 5.2^\circ$ is slightly broader than that of PET/Na-MMT, signifying that the former displays slightly more disordered clay morphology. In addition, the crystalline peak of Tsp-POSS is not visible from the WAXS pattern of PET/Na-MMT/Tsp-POSS likely because (1) Tsp-POSS is added in a very small amount (only 0.1 wt %) and this result in a lack of adequate amount for detection, and (2) Tsp-POSS does not form crystalline POSS domains as they can take part in a melt reaction to form cross links between PET chains.

The incorporation of Tsp-POSS aids clay dispersion in PET in two ways. Firstly, Tsp-POSS can form hydrogen bonds with hydroxyl groups on clay surface, as well as with BHET. This allows effective intercalation of BHET into the intergalleries of clay as demonstrated earlier. As a result, PET polymer chains grow within the clay platelets, causing breakdown of some thick clay stacks during the polymerization. This can be seen clearly from the TEM image of the in-situ polymerized PET/Na-MMT/Tsp-POSS (Figure 5.5a) in comparison with that of PET/Na-MMT (Figure 5.5b); the former exhibits a more loose state of clay dispersion with smaller clay tactoids due to polymer diffusion promoted by Tsp-POSS within the clay intergalleries. Secondly, the hydroxyl groups on Tsp-POSS can also undergo a melt reaction with the end groups in PET, further pulling PET chains into the clay intergalleries during melt compounding [99]. The degree of clay dispersion in both PET/Na-MMT/Tsp-POSS and PET/Na-MMT increases drastically after melt compounding, as shown by the reduction in the size of the clay aggregates (Figures 5.5 and 5.6). However, from POM images of the compounded nanocomposites (Figure 5.6a), it is found that PET/Na-MMT/Tsp-POSS has lesser and smaller micron-sized clay aggregates compared to PET/Na-MMT. Indeed, the TEM images shown in Figure 5.6b complement the POM findings. Subtle but visible differences in clay morphologies can be observed in the TEM images, i.e., PET/Na-MMT/Tsp-POSS has more of the thinner tactoids than PET/Na-MMT, signifying the role played by Tsp-POSS during the melt compounding. Evidence of the Tsp-POSS's chain extension/branching function will be presented in the following section.

In fact, the extent of clay intercalation achieved in PET/Na-MMT/Tsp-POSS seems better than that in PET/IMC-MMT based on TEM observations. Nonetheless, it is noted that the amount of clay observed in the TEM images of PET/Na-MMT/Tsp-POSS is less than that in PET/IMC-MMT, despite both should have the same weight percentage of clay. As the dispersion of clay shows a heterogeneous distribution, i.e., co-existence of single layers/thin

sheets of clay with tactoids in micron scale, this implies that there are still slightly more micron-sized clay aggregates in PET/Na-MMT/Tsp-POSS than in PET/IMC-MMT, and this is supported by POM observation.

Figure 5.5. TEM images of in-situ polymerized (a) PET/Na-MMT/Tsp-POSS and (b) PET/Na-MMT nanocomposites.

Figure 5.6. (a) POM and (b) TEM images of (i) PET/Na-MMT, (ii) PET/Na-MMT/Tsp-POSS and (iii) PET/IMC-MMT after melt compounding.

In summary, we have demonstrated that with only a small amount of Tsp-POSS as spacers, clay dispersion can be significantly improved as a result of effective intercalation of the BHET monomers and “reactive” melt compounding.

5.3.3 Thermo-mechanical Properties

To understand the impact of the surfactant-free clay on the thermo-mechanical properties of the nanocomposites, storage moduli (E') of the samples were determined via DMA and the data are listed in Table 5.1. The typical DMA curves are shown in Figure 5.7. The storage modulus of the neat PET (E'_n) and the various hybrids (E'_h) are compared at 40 °C. A reinforcement effect ($E'_h/E'_n > 1$) can be observed for all the nanocomposites. The greatest improvement in E' is observed in PET/Na-MMT/Tsp-POSS and the least improvement in E' observed in PET/IMC-MMT. Without clay, PET/Tsp-POSS shows a slight enhancement in E' ($E'_h/E'_n = 1.01$) as the reactive hydroxyl groups in Tsp-POSS can create “crosslink” between PET chains and increase the molecular weight of PET [99]. It is however no doubt that in PET/Na-MMT/Tsp-POSS, the reinforcement effect is predominantly provided by the clay.

Table 5.1. Storage moduli (E') and glass transition temperatures (T_g) of the as-molded PET and nanocomposites.

Sample	E' at 40 °C (MPa)	E'_h/E'_n (40 °C)	T_g (°C) ^a
PET	1922 ± 6	-	84
PET/Tsp-POSS	1945 ± 3	1.01	84
PET/Na-MMT	2350 ± 35	1.22	83
PET/Na-MMT/Tsp-POSS	2422 ± 13	1.26	84
PET/IMC-MMT	2334 ± 7	1.21	83

^a T_g of the samples were determined by the peak position in the $\tan \delta$ versus temperature curves.

Figure 5.7. (a) Storage modulus (E') and (b) $\tan \delta$ versus temperature curves for the as-molded samples of PET and the nanocomposites.

The extent of stiffness enhancements attained by the nanocomposites may be influenced by their (1) strength of polymer/clay interactions, (2) changes in crystallinity (X_c) and crystallization properties of PET brought about by the clay, (3) level of clay dispersion and (4) extent of clay orientation.

- **Strength of polymer/clay interactions.** The clay platelets present in polymers may inhibit mobility of polymer chains to some extent if interfacial interactions are strong [119-120]. This would result in an increase in T_g or an additional transition peak above the glass transition. In PET/IMC-MMT, the long alkyl chains on IMC may allow some entanglement with the PET chains. However, Na-MMT surface is more polar, which may provide stronger interactions with PET than nonpolar alkyl chains. There is no significant difference in the T_g of the nanocomposites, as shown in Table 5.1, suggesting that there is no large distinction among the interfacial interactions in the nanocomposites. Therefore, the interfacial interactions are unlikely to be the major factor influencing the reinforcement effect.

- **Changes in crystallinity (X_c) and crystallization properties of PET brought about by the clay.** Table 5.2 summarizes the crystallization properties of the as-molded samples of PET and the hybrids. The disparity in surface characteristics of the surfactant-free clay and organoclays can have significant impact on the crystallization properties of the resulting nanocomposites. Na-MMT usually displays stronger nucleating effect than organoclays. However, as previously discussed in chapter 4, the PET chain extender function of Tsp-POSS may be a factor that limits the nucleating effect of dual POSS-modified clay, but this is not the case in PET/Na-MMT/Tsp-POSS as it displays similar T_{cc} as PET/Na-MMT, which are both lower than that of PET/IMC-MMT, signifying the strong nucleating effect of the former. In addition, by comparing the WAXS patterns of the as-molded nanocomposites (Figure 5.8), it is revealed that crystalline peaks are observed in PET/Na-MMT/Tsp-POSS while PET/IMC-MMT exhibits only a broad amorphous halo. This substantiates the results that

even in the presence of Tsp-POSS, the nucleating effect of Na-MMT has not been compromised. The presence of crystalline peaks in the WAXS pattern of PET/Na-MMT/Tsp-POSS suggests that it has either larger crystals or higher crystallinity than PET/IMC-MMT. However, based on DSC studies, it is found that the degree of crystallinity generally has no significant difference among the three nanocomposites containing the same amount of clay. It is believed that although the surfactant-free clay exhibits stronger nucleating effect than organoclay, as evidenced by the lower cold crystallization temperatures (T_{cc}) of the former, the dispersed clay platelets inhibited crystal growth [121-122] and ultimately limit the increment of crystallinity in all the nanocomposites. Therefore, it can be deduced that the changes in E' of the nanocomposites are not related to crystallinity changes.

Generally, the organoclays disperse better in PET so that there are more nucleating centers leading to smaller crystals, while the surfactant-free clays disperse relatively poorer in PET so that there are lesser nucleating centers resulting in larger crystals. However, as crystal growth/size is also anisotropic (as indicated in Figure 5.8a by the disparity in sharpness of the crystalline peaks recorded on various specimen planes), this causes the influence of crystal sizes on mechanical properties to be complex and hence will require further investigation.

Table 5.2. DSC results of the as-molded PET and nanocomposites taken from the first heating curves.

Sample	T _m (°C)	ΔH _m (J/g)	T _{cc} (°C)	ΔH _{cc} (J/g)	X _c (%) ^b
PET	258	54	117	18	26
PET/Na-MMT	258	52	113	19	24
PET/Na-MMT/Tsp-POSS	257	48	114	18	22
PET/IMC-MMT	259	58	116	26	23

^b The percentage of crystallinity (X_c) was calculated using the equation: $X_c = [(\Delta H_m - \Delta H_{cc}) / (1-x) / \Delta H_m^\circ] \times 100 \%$, where ΔH_m is the heat of fusion, ΔH_{cc} is the latent heat of cold crystallization, ΔH_m[°] is the melting enthalpy of 100 % crystalline PET (i.e. 140.1 J/g) and x is the weight fraction of clay measured by TGA. T_m: Melting temperature and T_{cc}: Cold crystallization temperature.

Figure 5.8. WAXS patterns of the as-molded (a) PET/Na-MMT/Tsp-POSS and (b) PET/IMC-MMT when the X-ray beam is incident on FD-TD, ND-FD and ND-TD planes.

- **Level of clay dispersion.** An important factor influencing E' of the nanocomposites is the clay dispersion in the nanocomposites. Generally, enhanced thermo-mechanical properties are observed with greater extent of clay exfoliation. However, although PET/IMC-MMT shows better clay dispersion, it exhibits the lowest E' among the three nanocomposites with clay. Thus, it is believed that the greater reinforcement effect found in PET/Na-MMT/Tsp-POSS compared to PET/IMC-MMT is not attributed to the level of clay dispersion.

- **Extent of clay orientation.** As the reinforcement effect induced by clay also strongly hinges on clay orientation, 2D WAXS patterns were collected to evaluate the orientation of clay in the molded specimens. Figure 5.9 illustrates the 2D WAXS patterns of the as-molded specimens of PET/Na-MMT/Tsp-POSS and PET/IMC-MMT when the X-ray beam is incident on the FD-TD, ND-FD and ND-TD planes, respectively, where FD, TD and ND refer to the injection/flow, transverse and normal directions as marked in the figure. In the case of PET/Na-MMT/Tsp-POSS, a strong diffraction peak is observed on equator at $2\theta = 5.2^\circ$ when the X-ray beam is incident on the FD-TD and ND-FD planes. In contrast, a weak equatorial peak is observed at the same position when the X-ray beam is incident on the ND-TD plane, suggesting that insignificant amount of intercalated clay sheets are aligned normal to the injection direction. This means that the clay platelets in the as-molded PET/Na-MMT/Tsp-POSS specimen prefer to align in such a way that their basal planes are parallel to the injection direction, as illustrated in Scheme 5.2a.

Figure 5.9. 2D WAXS patterns of the as-molded (a) PET/Na-MMT/Tsp-POSS and (b) PET/IMC-MMT specimen when the X-ray beam is incident on the (i) FD-TD, (ii) ND-FD and (iii) ND-TD planes.

Scheme 5.2. Clay orientation states in as-molded (a) PET/Na-MMT/Tsp-POSS and (b) PET/IMC-MMT specimens.

In 2D WAXS patterns of the as-molded PET/IMC-MMT specimen, three diffraction peaks corresponding to (001), (002) and (003) clay reflections can be observed on equator when the X-ray beam is incident on the FD-TD plane. Differently, the equatorial peaks are stronger and spread out to form rings when the beam is incident on the ND-FD and ND-TD planes. The results suggest that the clay platelets in PET/IMC-MMT have a more random arrangement (Scheme 5.2b) with a substantial amount of clay arranged perpendicular to the flow direction. This is likely to be caused by the flow-induced orientation of long alkyl chains that rotate the clay platelets to the position normal to the flow direction [123-124]. It reveals that the more pronounced stiffness enhancement exhibited by PET/Na-MMT/Tsp-POSS is related to its higher degree of flow-induced clay orientation. Indeed, previous studies have shown that unidirectionally aligned clay favors mechanical property enhancement more than that with random orientation [125].

Figure 5.10. 2D WAXS patterns of the stretched (a) PET/Na-MMT/Tsp-POSS and (b) PET/IMC-MMT specimen when the X-ray beam is incident on the (i) FD-TD, (ii) ND-FD and (iii) ND-TD planes.

In order to confirm that the long alkyl chains of the surfactant indeed interfere with the orientation of the clay during processing, the as-molded samples were uniaxially hot stretched to a ratio of 1.5, resulting in a thickness reduction from 1 mm to 0.5 mm and the clay orientation states in the stretched specimens were examined.

Similar to the as-molded specimen, the 2D WAXS pattern (Figure 5.10a) of the stretched PET/Na-MMT/Tsp-POSS specimen exhibits a strong diffraction peak on the equator at $2\theta = 5.2^\circ$ when the X-ray beam is incident on the FD-TD plane. On the other hand, the equatorial peak spread out to form a ring with slightly higher intensity on meridian when the beam is incident on the ND-FD plane and in addition to the weak equatorial peak, weak meridional peaks are also observed when the beam is incident on the ND-TD plane. The results indicate that the clay platelets that are parallel to the FD-TD plane remained aligned in the same

direction. On the contrary, the clay platelets that are parallel to ND-FD and ND-TD planes partially rotate to the direction parallel to the FD-TD plane. Thus, after hot drawing, the orientation of the clay is less random with more clay platelets parallel to the FD-TD plane.

In 2D WAXS patterns of the stretched PET/IMC-MMT specimen (Figure 5.10b), it is evident that on hot stretching, the equatorial peaks became stronger when the X-ray beam is incident on the FD-TD plane. At the same time, strong, almost uniform diffraction rings and meridional peaks are observed when the beam is incident on the ND-FD and ND-TD planes respectively. The results implies that on hot stretching, a substantial amount of clay platelets in PET/IMC-MMT that were originally arranged perpendicular to the injection direction rotate and align in the stretching direction but their normals are randomly oriented in the ND-TD plane (Scheme 5.3). The re-alignment of the clay platelets in the nanocomposites is possible because the stretching force is higher than the shear force during injection molding processing. The polymer chains are aligned during the stretching process and consequently, the polymer chain alignment forces the clay platelets to rotate.

Scheme 5.3. Clay orientation states in stretched (a) PET/Na-MMT/Tsp-POSS and (b) PET/IMC-MMT specimens. It is noted that the clay orientation state in (a) has been exaggerated to better illustrate the difference between the clay orientation states in (a) and (b).

As the relative oxygen permeability is also highly dependent on the orientation of clay in the polymer matrix, the discussion above suggests that the highly oriented clay observed in PET/Na-MMT/Tsp-POSS offers an opportunity to achieve improved barrier property; a property that is critical in packaging materials. This characteristic gives PET/Na-MMT/Tsp-POSS an advantage over conventional polymer/organoclay nanocomposites.

5.3.4 Thermal & Thermo-oxidative Stability

The degradation of organic surfactants can induce and accelerate thermal and thermo-oxidative degradations of polymers, resulting in poor mechanical properties. This limits the property enhancements of the PET/clay nanocomposites as well as restricts its recycling via melt compounding. To reveal if the surfactant-free nanocomposites can really resolve the degradation issues, thermal and thermo-oxidative stabilities exhibited by PET/Na-MMT, PET/Na-MMT/Tsp-POSS and PET/IMC-MMT were characterized.

Thermal degradation temperatures in both nitrogen and air were determined via TGA. As expected, the presence of Tsp-POSS in PET/Tsp-POSS does lead to increased T_d in air owing to its chain extender function (Table 5.3). It is also observed that degradation temperatures (T_d) of the nanocomposites with clay were raised by at least 10 °C in air compared with that of the neat PET. The T_d s of PET/Na-MMT/Tsp-POSS, PET/Na-MMT and PET/IMC-MMT however exhibit no significant difference in both nitrogen and air atmospheres. An explanation for this observation is the same as that discussed in chapter 4, whereby well dispersed clay in PET/IMC-MMT may hinder the evaporation of the decomposition products so that its T_d is not significantly lower. It is noted that despite better clay dispersion state, the decomposition products can induce degradation of PET, consequently leading to reduced molecular weight and poorer mechanical properties. Herein, TGA is unable to reflect this effect as although PET chains are shortened, they do not contribute to the weight loss.

Table 5.3. Degradation temperatures (T_d) of the nanocomposites measured in nitrogen and air using TGA.

Sample	T_d (°C)	T_d (°C)
	In Nitrogen	In Air
PET	393	368
PET/Tsp-POSS	392	374
PET/Na-MMT	389	380
PET/Na-MMT/Tsp-POSS	390	380
PET/IMC-MMT	386	378

The OOT results are presented in Figure 5.11. The thermograms of PET, PET/Tsp-POSS, PET/Na-MMT and PET/Na-MMT/Tsp-POSS display relatively flat baselines after the melting peak (Figure 5.11a), allowing the estimation of OOT (marked in the figure). The OOTs are in the following ascending order: PET, PET/Tsp-POSS, PET/Na-MMT and PET/Na-MMT/Tsp-POSS. PET/Tsp-POSS exhibits a higher OOT than PET as Tsp-POSS can act as chain extenders to connect PET chains. Generally, the incorporation of surfactant-free clay enhances the thermo-oxidative stabilities of the nanocomposites as the clay can act as thermal barriers that slow down the increase in temperature and heat transfer. At the same time, clay can limit the diffusion of oxygen into PET and hence lower the rate of oxidation [126]. Different from that of surfactant-free clay, the OOT thermogram of PET/IMC-MMT (Figure 5.11b) displays an obvious exothermic peak (highlighted by an arrow) immediately after the melting endotherm, which resembles the thermogram of PET/commercial alkylammonium-modified clay nanocomposite. As discussed in chapter 4, it implies that oxidative decomposition of the long alkyl chain in the organic surfactants often occurs at

temperatures below the typical processing temperature of PET. It is worth noting that a weaker exothermic peak is also observed in PET/Na-MMT thermogram immediately after the melting, while it almost diminishes for PET/Na-MMT/Tsp-POSS. It implies that Na-MMT may also induce degradation of PET [81-83], but the clay-induced chain scission of PET chains can be compensated by the chain extension reaction of PET with Tsp-POSS to some extent.

Figure 5.11. The OOT thermograms of (a) PET, PET/Tsp-POSS and the surfactant-free clay nanocomposites and (b) PET/IMC-MMT and PET/Cloisite30B-MMT.

To confirm the above results, DSC experiment was also carried out under isothermal conditions to determine oxidation induction time (OIT). In this work, the isothermal temperature had been chosen to be 280 °C, i.e., the processing temperature of PET. For PET/IMC-MMT, upon switching from nitrogen to air during the OIT test at 280 °C, a strong exotherm appears immediately that extends to very long reaction time (Figure 5.12). In contrast, PET/Na-MMT and PET/Na-MMT/Tsp-POSS exhibit much weaker exotherms. In

comparison with that of PET/Na-MMT, the enthalpy change of PET/Na-MMT/Tsp-POSS owing to oxidative degradation is smaller. This verifies that Tsp-POSS can indeed act as a “stabilizer” to inhibit oxidative reaction.

Figure 5.12. The OIT thermograms of the polymer/clay nanocomposites held isothermally at 280 °C.

In order to further verify that the active hydroxyl groups on Tsp-POSS can undergo a melt reaction with the carboxyl end groups in PET, the inherent viscosities (η_{inh}) of PET/Na-MMT and PET/Na-MMT/Tsp-POSS were determined and compared. The inherent viscosity measurements before and after compounding are listed in Table 5.4. Generally, a greater inherent viscosity signifies a higher molecular weight or branching due to the chain extension function of Tsp-POSS. It was found that PET/Na-MMT/Tsp-POSS before and after

compounding displayed evidently the highest inherent viscosities. The results established the PET chain extension/branching function of Tsp-POSS. One of the reasons for the improved thermo-mechanical property of PET/Na-MMT/Tsp-POSS therefore, may also be its higher molecular weight or incorporation of POSS cage into the chains.

Unsurprisingly, the inherent viscosity of PET/Na-MMT decreases after compounding. However, after compounding, whilst the presence of Tsp-POSS may promote PET chain extension, the inherent viscosity of the PET/Na-MMT/Tsp-POSS also decreases. This may probably be because the compounding process herein does not have sufficient time for the melt reaction to take place unlike in in-situ polymerization [101]. At the same time, Na-MMT can induce degradation of PET to negate the effects of Tsp-POSS to some degree. Nonetheless, it is demonstrated that the clay-induced chain scission of PET chains can be compensated by the chain extension reaction of PET with Tsp-POSS to some extent, such that the inherent viscosity of PET/Na-MMT/Tsp-POSS after compounding is still higher compared to PET and PET/Na-MMT before compounding.

Table 5.4. The inherent viscosity (η_{inh}) measurements of PET and the nanocomposites before and after compounding.

Samples	η_{inh} (dL/g)	
	Before compounding	After compounding
PET	0.59	0.57
PET/Na-MMT	0.61	0.51
PET/Na-MMT/Tsp-POSS	0.78	0.66

* For reference, the inherent viscosity of PET/IMC-MMT was found to be 0.41 dL/g.

The inherent viscosity measurements augment the oxidative stability trend observed in the OOT and OIT tests and support that PET/Na-MMT/Tsp-POSS exhibits the highest thermo-oxidative stability among the nanocomposites studied. It is emphasized that the advantage of this system is that it is able to simultaneously enhance the stiffness and thermo-oxidative stability of the nanocomposites, and due to the chain extension function of Tsp-POSS, reasonable mechanical properties may be retained upon multiple processing steps

5.4 Conclusions

Surfactant-free PET/clay nanocomposites have been readily prepared. The degree of clay dispersion in PET/Na-MMT is successfully enhanced by adding a very small amount of Tsp-POSS as spacers, and an extent of clay intercalation comparable to that of PET/IMC-MMT nanocomposite is achieved. This is because Tsp-POSS spacers not only maintain the separation of clay platelets, they are also able to draw BHET molecules into clay intergalleries so that the in-situ polymerization occurs within the clay intergalleries. Moreover, Tsp-POSS can participate in a melt reaction during polymer processing and further facilitate clay delamination. Herein, the chain extension function of Tsp-POSS had been verified by the inherent viscosity measurements. The storage modulus of PET/Na-MMT/Tsp-POSS is found to be greater than both PET/Na-MMT and PET/IMC-MMT. The evident reinforcement effect observed in PET/Na-MMT/Tsp-POSS is attributed to its better clay dispersion than that of PET/Na-MMT and higher degree of flow-induced clay orientation than that in PET/IMC-MMT. Simultaneously, PET/Na-MMT/Tsp-POSS also exhibits improved thermo-oxidative stability owing to the chain extension function of Tsp-POSS.

A typical route for recycling PET is to convert it to BHET by glycolysis. The BHET from recycled PET may be aptly used to prepare PET/Na-MMT/Tsp-POSS. Another method to reduce environmental footprint that is left behind by PET products is recycling PET via melt compounding [126]. This requires minimization of processing-induced molecular weight reduction of PET so that it can retain reasonable mechanical properties. PET/Na-MMT/Tsp-POSS can hence, potentially benefit recycling of PET owing to its superior mechanical and thermo-oxidative properties than that of PET and PET/organoclay nanocomposites.

6 Conclusions & Recommendations for Future Research

In this thesis, novel systems of PET/clay nanocomposites with POSS incorporated as either a surfactant or a spacer were developed to resolve the degradation issues of conventional surfactants used to modify clay. The limitations and advantages of using POSS as a dispersant were evaluated in terms of their effects on the level of clay dispersion and properties of the resultant nanocomposites. A systematic study to compare surfactant-free PET/Na-MMT nanocomposites and PET/organoclay nanocomposites whereby both have comparable state of clay exfoliation was also carried out to examine the impact of eliminating surface modification of clay on the structure and properties of the nanocomposites. In this chapter, the major findings and important contributions from the abovementioned studies will be summarized. Consequently, the knowledge gained from this research work can be applied to further develop PET/clay/POSS nanocomposites or be extended to other polymer/clay/POSS nanocomposites. Interesting aspects revealed from this research work that attracts further exploration will therefore also be discussed.

6.1 Conclusions

As a prelude to the preparation and evaluation of PET/POSS-modified clay nanocomposites, the packing behaviors of two types of POSS-imidazolium surfactant with different molecular rigidities and at various surfactant loadings were examined. The POSS-

modified clays exhibit large d -spacing not only due to the bulky structure of the POSS compound but also largely due to the inherent bilayer packing tendency of the POSS-imidazolium surfactants as evidenced by WAXS and molecular modeling studies. The bilayer packing structure of the POSS-imidazolium surfactants is also verified for the first time by direct visualization of the POSS-rich regions in the clay intergalleries via TEM.

The different packing structures of the POSS-imidazolium surfactants with relatively flexible and rigid molecular conformations were proposed and verified experimentally. WAXS and DSC results indicate that with a flexible ethane spacer between POSS cage and benzene ring, the relative flexible POSS-imidazolium surfactants are able to form a two-dimensionally ordered structure in clay, while the relative more rigid POSS-imidazolium surfactant with a direct linkage between the POSS cage and the benzene ring displays a disordered packing in clay. As a result of less free surfactants due to the disordered packing structure and lower organic content, the more rigid POSS-imidazolium surfactant also exhibits higher thermal and thermo-oxidative stabilities. In addition, contrary to traditional views where the d -spacing decreases with surfactant loading in organoclays, the POSS-modified clays do not exhibit decreased d -spacing with reduced surfactant loadings, instead its d -spacing even increases.

Based on the aforementioned results, a hypothesis is proposed whereby it is believed that the loose and random packing of the rigid POSS-imidazolium surfactant renders a relatively weaker interaction between the POSS cages and hence may likely to favor the exfoliation of POSS-modified clay in PET. However, PET/POSS-modified clay hybrids prepared from the rigid POSS-imidazolium surfactant at reduced surfactant loading was obtained with extremely poor clay dispersion and no polymer intercalation despite the clay's large d -spacing. It is established that the poor POSS-modified clay dispersion in PET is probably attributed to the gluing effect of the POSS-imidazolium surfactants within the clay

intergalleries and the poor compatibility between the surfactant and PET. At the same time, from compatibility studies performed on POSS-modified clay nanocomposites prepared from polymer matrices such as PVDF, PAN and PEO, it is found that even with large d -spacing of the clay, strong polymer/clay or polymer/surfactant interactions is necessary to obtain good clay dispersion. The results suggest that to aid clay dispersion, the interaction between polymer and the POSS-modified clay can be improved by introducing compounds with polar groups.

In order to improve the dispersion of POSS-modified clay, trisilanolphenyl POSS (Tsp-POSS) was added as a spacer in a very small amount to weaken the interactions of POSS cages and to aid polymer/surfactant interaction via the active silanol groups. This approach consequently yielded PET/dual POSS-modified clay nanocomposites with significantly improved clay dispersion compared to PET/POSS-modified clay microcomposites. However PET/dual POSS-modified clay nanocomposites unlike in PET/organoclay nanocomposites, exhibit only small enhancements in storage modulus and thermo-oxidative stability. Clearly, this is because PET/dual POSS-modified clay nanocomposites display mostly clay tactoids such that the extent of clay intercalation is far from satisfactory compared to PET/organoclay nanocomposites, which exhibit intercalated/exfoliated clay morphologies. Overall, it is garnered that utilizing POSS compounds as surfactants to surface treat clay for preparation of PET/clay nanocomposites may not be straightforward and can be extremely challenging.

On the other hand, it was found that Tsp-POSS proves to be useful in improving clay dispersion and thermo-oxidative stability. Hence, an alternative novel approach to resolve the degradation issue of organic surfactants in PET/organoclay nanocomposites is to prepare surfactant-free PET/Na-MMT nanocomposites and introducing only Tsp-POSS as a spacer to prevent the recombination of clay into stacks and to increase the interlayer spacing of clay. Encouraging results were obtained for PET/Na-MMT/Tsp-POSS nanocomposites such that

clay dispersion state comparable to PET/organoclay nanocomposites was achieved. The incorporation of Tsp-POSS aids clay dispersion in two ways. Firstly, Tsp-POSS are able to effectively draw BHET molecules into clay intergalleries so that in-situ polymerization occurs within the clay intergalleries. Secondly, Tsp-POSS has a PET chain extender function that can participate in reactive compounding to further delaminate the clay. The lack of surface treatment of the clay also led to a higher degree of flow-induced clay orientation and stronger nucleating effect on the crystallization of PET. These structural behaviors consequently result in a simultaneously evident reinforcement effect and improved thermo-oxidative stability in the PET/Na-MMT/Tsp-POSS nanocomposites. In fact, their properties are better than PET/organoclay nanocomposites. It is worth noting that although Na-MMT may induce degradation of PET, the adverse consequences can be compensated by the chain extension reaction of PET with Tsp-POSS to some extent. Owing to its superior mechanical and thermo-oxidative properties, the nanocomposites may be able to retain reasonable mechanical properties after recycling via melt compounding. Moreover, BHET obtained from glycolysis of waste PET may be aptly used to prepare PET/Na-MMT/Tsp-POSS, which makes it a potentially green approach.

6.2 Recommendations for Future Research

6.2.1 Barrier Properties of PET/Clay/POSS Nanocomposites

In PET/Na-MMT/Tsp-POSS, the absence of surface treatment of the clay has led to a high degree of flow-induced clay orientation. It is well-known that the orientation distribution of the clay can greatly influence the barrier properties of the nanocomposites. As discussed in chapter 2, the slow down in transmission of gases in nanocomposites was achieved by creating a tortuous path for the diffusion of gas molecules. This means that compared to

PET/organoclay nanocomposites which has a more random clay orientation, PET/Na-MMT/Tsp-POSS nanocomposites which has most of the clay platelets aligned parallel to the flow direction (i.e. high order parameter, S) is anticipated to display higher barrier properties. In order to verify this effect, it is necessary to determine the oxygen permeability of the nanocomposites to have a better evaluation of their performance in their prospective applications.

6.2.2 More In-depth Studies on Crystallization Behaviors of PET/Clay/POSS Nanocomposites

PET has a slow rate of crystallization, which limits its application and adversely affects its processing cycle, such as during injection molding. PET/clay nanocomposites can help to resolve this issue. The addition of clay not only improves the mechanical properties of the nanocomposites due to its high modulus, the silicate layers are also known to have a nucleating effect, which leads to higher overall crystallization rates. This usually correlates to higher crystallinity, and hence better mechanical and thermal properties. However, some modifiers used to treat clay surfaces are reported to inhibit crystallization of polymers. From the results presented in chapter 5, better nucleating effects of the surfactant-free clay compared to organoclay was demonstrated. In addition, it was found that organoclays disperse better in PET and led to smaller PET crystals formed and surfactant-free clay disperse relatively poorer in PET and resulted in larger PET crystals. However, as crystal growth/size is known to be anisotropic and also indicated by the disparity in sharpness of the crystalline peaks when X-ray beam is incident on the various planes of the PET/Na-MMT/Tsp-POSS specimen, the influence of crystal sizes on mechanical properties is not clear and requires further investigation. Indeed, the normal spherulitic growth of neat polymer and the lamellar organization can be affected by the clay platelets. This could lead to

preferred alignment of clay and the anisotropic arrangement of crystalline lamellae, thus consequently reinforcing the nanocomposites in a specific direction. The importance of the effects of different surface characteristics of the clay on the crystalline morphological changes of PET and their potential impact on the mechanical and barrier properties of the nanocomposites emphasizes the need to have a clearer understanding in this area. 2D WAXS and small angle X-ray scattering (SAXS) can be thus carried out to study the crystal orientation and size.

6.2.3 Recycling via Melt Compounding of PET/Clay/POSS Nanocomposites

In order to reduce environmental footprint that is left behind by PET products, PET can be recycled via melt compounding. However, this will require the PET to minimize processing-induced molecular weight reduction and retain reasonable mechanical properties and physical properties, such as minimal discoloration. PET/Na-MMT/Tsp-POSS can be aptly applied owing to its superior properties and Tsp-POSS's chain extension function. In order to assess if PET/Na-MMT/Tsp-POSS can indeed be recycled via melt compounding without losing its mechanical integrity and exhibiting severe discoloration like in PET/organoclay nanocomposites, it is essential to perform more characterization, such as to subject the nanocomposites through several extrusion cycles and then determine their molecular weight. Using the Ubbelohde viscometer, the molecular weight can be obtained by measuring the intrinsic viscosity and substituting into the Mark-Houwink equation.

6.2.4 Other Polymer/POSS-modified Clay Systems

Despite the limited success attained in PET/POSS-modified clay, the potential of using this strategy on other polymer systems, such as PVDF and PEO had been demonstrated in chapter 4. Indeed, POSS-modified clay had been found to be able to exfoliate well in PVDF

and PEO matrices. Currently ionic liquids are increasingly used as electrolytes due to their high ionic conductivity and high thermal stability in various electrochemical devices. However, they have lower viscosity compared to gel electrolytes, which can result in leakage problem and consequently a decrease in ionic conductivity. Thus, they are often blended with polar polymers such as PVDF which act as a host for these ions. Nevertheless, the compatibility between PVDF and the ionic liquids are not yet ideal and on solvent evaporation can lead to phase separation [127]. It is proposed that the POSS-imidazolium surfactants being amphiphilic can be introduced as a “compatibilizer” to improve the compatibility between PVDF and the ionic liquids. The prerequisite is that the POSS-imidazolium surfactants do not crystallize and form a homogeneous dispersion in PVDF. In order to do so, POSS-imidazolium surfactants can be added through POSS-modified clay such that the sandwich of the POSS surfactants between clay platelets may prevent its agglomeration. At the same time, the ionic conductivities of nanocomposite gel polymer electrolytes have been reported to increase with clay loading due to higher electrolyte uptake as a result of the strong affinity of clay and the electrolytes [128]. Hence, PVDF/POSS-modified clay nanocomposite gel polymer electrolyte can be potentially used in electrochemical devices and further investigation in this area can be carried out.

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