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DEVELOPMENT OF CLAY MODIFICATIONS FOR POLYMER/CLAY NANOCOMPOSITES

by

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Thesis submitted in partial fulfilment of the requirements for the degree Doctor of Philosophy

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ABBREVIATIONS

20  Diffraction angle
15A  Cloisite 15A
30B  Cloisite 30B
APS  3-aminopropyltriethoxysilane
BDA  Benzyldimethyl(2-hydroxyethyl) ammonium chloride
CEC  Cation exchange capacity
DOT  Decomposition temperature
DSC  Differential scanning calorimetry
DTDMA di-tallow dimethyl ammonium chloride
d  d-spacing
E  Elastic module
FTIR Fourier transform infrared spectroscopy
HTP  Hexyltriphenylphosphonium
MMT Montmorillonite
Mw  Molecular weight
Na  Cloisite Na+
NCH Polyamide clay hybrid
ODA Octadecyl amine
O-MMT Organo-montmorillonite
PA  Polyamide
PBT Poly(butylene terephthalate)
PLSN Polymer layered silicate nanocomposite
POSS Polyhedral oligomeric silsesquioxanes
AP-POSS Aminopropylisoctyl-POSS
OA-POSS Octaammonium-POSS
PP  Polypropylene
PP-g-MA Maleic anhydride grafted polypropylene
PS  Polystyrene
Tg  Glass transition temperature
TEM Transmission electron microscopy
TGA Thermogravimetric analysis
WAXD Wide angle X-ray diffraction
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ABSTRACT

Three commercial clays: Cloisite Na⁺, Cloisite 30B and Cloisite 15A were used to melt compound with a number of polymer matrices, including polypropylene (PP), poly(butylene terephthalate) (PBT) and polyamides (PA). X-ray diffraction (XRD), contact angle measurement and thermogravimetric analysis (TGA) showed small interlayer space, poor compatibility and low thermal stability of these nanocomposites, resulting in poor mechanical properties in composites. A number of modifications of commercial clays were carried out, including silylation and introduction of thermally stable surfactants, e.g. alkyl quaternary phosphonium cations and polyhedral oligomeric silsesquioxane (POSS). It was found that poor compatibility between polymer matrices and organically modified clays, especially in those POSS modified clays, again restricted the formation of exfoliated structure in polymer matrices. A mode of dual-surfactant modification for clay was developed, and large interlayer spacing (>3.2 nm), good thermal stability (decomposed at ~300°C) and improved surface properties for those dual-surfactant modified clays promoted a better dispersion of clays in polymer matrices and consequently better mechanical properties. For example, the tensile moduli of PP, PBT and PA 12 were improved from 515 MPa, 1065 MPa and 490 MPa to 1020 MPa, 1470 MPa and 800 MPa of their nanocomposites containing 3 wt% dual-surfactant modified clays, respectively. However, the dispersion of these organoclays varied in different polymer matrices, due to the different compatibility and the existence of polar type interactions between organoclays and polymer matrices. In order to further address the effect of polymer matrix on clay dispersion, three polyamide matrices (PA 6, PA 11 and PA 12) were employed, and PA 6 based nanocomposites showed the most effective exfoliation and mechanical enhancements due to the strong polar type interactions between the polymer and the organoclays.
CHAPTER 1 INTRODUCTION

In this chapter, a general introduction of nanoscience and nanotechnology is given, in addition to the development of polymer nanocomposites and their advantages. A number of challenges, especially for polymer/clay nanocomposites are pointed out based on current development. Aims and objectives of this project are also outlined.

1.1 Background

1.1.1 Nanoscience and Nanotechnology

The term of nanoscience and nanotechnology is primarily originates from the materials worked within the nanometer scale, and these materials are characterised by at least one dimension in the nano range \((1\text{nm} = 10^{-9}\text{m})\). The uniqueness of the structural characteristics, energetics, response, dynamics and chemistry of a nanostructure constitutes the basis of nanoscience. Suitable control of the properties and response of the nanostructure has led to new technology, referred to as nanotechnology [1]. In recent decades, nanoscience and nanotechnology have developed explosively due to the availability of methods of synthesis of nanomaterials and the techniques of characterisation and manipulation, as showed in Table 1.1.
Nanomaterials are different from either molecular or bulk materials, which is due to their spatial structure and shape, phase changes, energetics, electronic structure, chemical reactivity, catalytic properties of large, finite systems, and their assemblies [1]. All of these will potentially change people’s views on the properties of those bulk materials and promote the development of nanotechnology. There are some important issues relate to nanoscience, including size effects, shape phenomena, quantum confinement and response to external electric and optical excitations of individual and coupled finite systems. Among these, size effect is an essential aspect of nanomaterials, which determines the evolution of structure, thermodynamic, electronic, spectroscopic and chemical features. This is because nano-scaled materials possess a high surface-volume ratio, and the surface and surface properties substantially control many important chemical and physical interactions at materials surface [2]. The shape of nanomaterials also plays a role in determining properties, such as reactivity and electronic spectra.

### 1.1.2 Polymer Nanocomposites

Polymer nanocomposites are polymer matrix composites in which the fillers are smaller than 100 nm in at least one dimension. In contrast to traditional polymer composites with high loadings of micrometer-sized filler, polymer nanocomposites...
are being developed with very low loadings (normally less than 5 wt.%), and they exhibit extraordinarily interesting properties. A defining feature of polymer nanocomposites is that the nano-sized fillers have the potential to provide a dramatic increase in interfacial area compared to traditional composites, which creates a relative large volume fraction of interfacial polymer with properties different from the bulk polymer even at low loadings [3]. Polymer nanocomposites have been dramatically developed in the last two decades due to the new fillers’ emergence. For example, polyamide/nanoclay composites were developed for automotive applications [4], transparent conducting polymer/nanotube composites were developed for solar cell electrodes [5], and nanoparticles have been strong candidates for enhancing matrix properties of traditional composites in order to increase and add conductivity and sensing capabilities [6]. Several reasons make polymer nanocomposites so attractive in recent years, for both academic and industrial purpose. First, nanoscale fillers often have very different properties from the bulk materials of the same composition. Second, nanoscale fillers are smaller defeats in a matrix, while microscale fillers are similar in size to the critical crack size that causes early failure [7, 8]. This property will prevent early failure, leading to polymer nanocomposites with enhanced ductility and toughness [9, 10]. Third, nanoscale fillers provide a large surface area, and, in turn, a large fraction of interfacial matrix materials in polymer nanocomposites will be formed with very different performances from bulk polymer.

### 1.1.3 Problems and Challenges

As long as a series of advanced performances of polymer nanocomposites are achievable, the difficulties and challenges in controlling and predicting these properties of polymer nanocomposites are in turn arise. The properties of a polymer nanocomposite are influenced by many factors, including the ratio of dispersed fillers, the size of these component phases and the degree of mixing between the two
phases. In addition, the nature of the components used, (e.g. layered silicate or nanofiber, cation exchange capacity, and polymer matrix), and the preparation method, will also lead to the differences in composite properties [11].

In the case of polymer/clay nanocomposites, the potential superior performances strongly rely on a high degree of exfoliated clay structure in polymer matrices, and it is not easy to achieve in most commercially important polymers, excepted for polyamide 6. One of the challenges is that most commercial organoclays are synthesized, with excess, low thermally stable organic surfactants, which will be easily decomposed in melt processing, especially with higher melting engineering plastics. Other challenges include a lack of guidelines about the compatibility between organoclays and polymer matrices to effectively formulate various types of polymer/clay nanocomposites. In addition, industry’s preferred melt processing is associated with slow penetration of polymer into clay’s interlayers in nanocomposite preparation. The formation of a high degree of exfoliated clay structure in a polymer matrix, will only be achieved at appropriate processing conditions.

1.2 Aims and Objectives

The aim of the project is to develop appropriate organoclays for high performance polymer/clay nanocomposites, especially in terms of mechanical properties. In order to achieve it, several objectives are addressed:

1) To evaluate several commercial organoclays in terms of interlayer spacing, thermal stability and surface properties, and to further surface treatment for commercial organoclays with silane coupling agents.

2) To produce organoclays with more thermally stable organic surfactants, e.g. alkyl phosphonium cations and polyhedral oligomeric silsesquioxane (POSS).
3) To develop surface modification method for organoclays, with good thermal stability and compatible surface properties.

4) To prepare polymer/clay nanocomposites via melt compounding method, with several important polymer materials, including polypropylene, poly(butylene terephthalate) and polyamides.

5) To characterise the organoclays and their polymer nanocomposites in order to find out the influences of clay modifications and polymer matrices on the formation of polymer/clay nanocomposites.
CHAPTER 2 LITERATURE REVIEW

The development of polymer/clay nanocomposites in last two decades is briefly outlined in this chapter. Emphases on clay modification (i.e. the effect of surfactants) and melt compounding method (i.e. the affecting factors) are described. Polymer/clay nanocomposites, based on three polymer matrices (i.e. polypropylene, poly(butylene terephthalate) and polyamides), are reviewed from their preparation methods to their mechanical properties and applications.

2.1 Introduction

Since the Toyota research group announced the advanced properties obtained from Polyamide-6/montmorillonite (MMT) nanocomposites in early 1990s [12], polymer/clay nanocomposites have emerged as a new class of materials and have attracted considerable interest and investigations on a worldwide level. Due to their new and often much improved mechanical, thermal, electrical and optical properties compared to their micro- and macro- counterparts, various polymer/clay nanocomposites are made by dispersing the nanoclays into either thermoplastic or thermoset polymers.

 Earlier attempts of preparing polymer/clay composites can be found in the patent literature [13, 14] fifty years ago. However, the dispersion of silicate particles was so poor that mechanical properties of the composites were disappointing. A major reason for this failure can be attributed to the incompatibility between hydrophilic clay and hydrophobic polymer matrix. A major breakthrough was brought through a detailed study on polymer/clay nanocomposites by Fukushima and Inagaki [15]. They found that the replacing of inorganic cations in clay galleries by alkyl-ammonium surfactant, successfully enabled them compatible with hydrophobic
polymer matrix. Thereafter, an exfoliated PA-6/clay nanocomposite was successfully prepared via in-situ polymerisation of ε-caprolactam, in which alkyl ammonium modified MMT was thoroughly dispersed in the polyamide matrix. Once the nano-scale was achieved, the mechanical properties of the nanocomposites were significantly improved. It was concluded that the exfoliation of silicate particles depends not only on the surface modification of the clays, but also on the compatibility between organoclay and polymer matrices, and other aspects, such as preparation methods and processing conditions, etc.. Since then, other different polymer systems including epoxies [16, 17], unsaturated polyesters [18], poly(ε-caprolactone) [19], poly(ethylene oxide) [20], silicone rubber [21], polystyrene [22], polyimide [23], poly(ethylene terephthalate) [24], polyurethanes [25], and polypropylene [26, 27], were also investigated.

The objective of this literature survey is to review the different techniques used to fabricate polymer/clay nanocomposites based on several different polymer systems, and the improved properties that those materials then display. Additionally, the effects of clay modification on clays and their polymer nanocomposites will be taken into account.

2.2 Clay Minerals

Clay minerals used for polymer nanocomposites, can be classified into three groups in terms of structure, as shown by Figure 2. 1. 2:1 type clays belong to the smectite family and, consist of ~1 nm thick layers of alumina octahedral sheet sandwiched in between two silicate tetrahedral sheets, which will be described in detail in the following section. 1:1 type clays consist of one alumina octahedral sheet and one silicate tetrahedral sheet. The layers are held together by hydrogen bonding between hydroxyl groups in the octahedral sheets and oxygen in the tetrahedral sheets, but without any charges at silicate surface due to the absence of isomorph substitution
occurring either in octahedral sheet or in tetrahedral sheet. The layered silicic acids clays basically are composed of silicon tetrahedral sheets and interlayer hydrated alkali metal cations with various layer thickness. These kind of clays can be natural or synthesised [28]. Among them, montmorillonite (MMT), a 2:1 type clay, is the most popular clay used in industry and academic contexts so far. The reasons for the application of montmorillonite in polymer nanocomposites are its rich intercalation chemistry, good swelling ability, high strength and stiffness, large aspect ratio and surface area, abundance in nature and low cost [28, 29].

![Diagram of clay minerals](image1)

**Figure 2.1** Structure of clay minerals represented by montmorillonite (2:1 type), kaolinite (1:1 type) and kanemite (layered silicic acid) [28].

### 2.2.1 Structure of Montmorillonite

As illustrated in Figure 2.2, a repeat structure of montmorillonite (MMT) consists of three layers: one octahedral alumina layer is sandwiched by two tetrahedral silica layers. These three layers form one silicate sheet with ~1 nm in thickness and 100 nm to several microns in lateral dimensions. These organise themselves to form stacks with a regular van de Waals gap in between, called an interlayer or gallery. Isomorphous substitution occurs in the galleries, like Al$^{3+}$ replaced by Fe$^{2+}$ or Mg$^{2+}$.
and Si\(^{4+}\) replaced by Al\(^{3+}\), resulting in the negative charged silicate surface that is subsequently counterbalanced by alkali or alkaline earth cations situated in the galleries, such as Na\(^{+}\) and Ca\(^{2+}\). Typically, the chemical formula of a MMT is Na\(_{1/3}\)(Al\(_{5/3}\)Mg\(_{1/3}\))Si\(_{4}\)O\(_{10}\)(OH)\(_{2}\) [30]. The clay is characterised by a moderate negative surface charge, named by cation exchange capacity (CEC) which is an average value over the whole crystal. The higher the value of the negative charge of a layered silicate, the stronger the capacity is for hydration, swelling and dispersion of the clay [31]. Therefore, the parameter CEC is very important in evaluating the quality of the clay minerals.

![Structure of montmorillonite (MMT)](image)

**Figure 2.2 Structure of montmorillonite (MMT) [32].**

The unique layered structure and high intercalation capabilities of MMTs allow these to be modified chemically in order to be compatible with polymers. The forces that hold silicate layers are relatively weak, which enables with relative ease, for the intercalation of small molecules between the layers [33], and even to be exfoliated into nanometer platelets with a thickness of about 1 nm and an aspect ratio of 100-1500 and surface areas of 700-800 m\(^2\)/g [28]. As inorganic clay is extremely stiff (~178 GPa [34]), it can act as a very strong reinforcement in polymer matrix and
enables the achievement of equivalent improved properties with very low percentage of clay, compared with that of the conventional composites.

## 2.2.2 Clay Modification

In general, a simple physical mixture of a polymer and MMT may not form a nanocomposite [35]. This is because MMT is inherent hydrophilic which makes it unsuitable for hosting most organic molecules without treatment. Therefore, except for some hydrophilic polymers, such as poly(ethylene oxide) (PEO) or poly(vinyl alcohol) (PVA) etc. [35-37], organic modification of the clay surface is a vital process in obtaining conditions for the polymer/clay nanocomposites. The organic modification is often accomplished via ion-exchange reactions of alkali cations at the silicate surface and clay galleries with desired organic cations, such as alkyl-ammonium, alkyl-phosphonium or alkyl-imidazolium cations. The role of organic surfactant used in organic modification, is to lower the surface energy of inorganic silicate, to match the clay polarity with the polarity of the polymer, and to create an expanded interlayer spacing for intercalation [38, 39]. Additionally, some functional groups with the organic cations can also be introduced which can react with the polymer matrix to improve the strength of the interfacial between the inorganic clay and its polymer matrix. Currently, there are several methods used for the ion-exchange dispersion reactions. The most common approach is carried out in solutions based on polar solvents such as water, acetone, and ethanol, in the presence of MMT and the surfactant. Also, the ion-exchange reaction can occur by mechanical milling, or the melt between organic compounds and MMT to form organoclays [30].
2.2.2.1 Models for Surface Modification

As negative charges are generated on the silicate surface, the cationic head groups of the organic surfactant molecules preferentially reside at the layer surface, leaving the organic tails radiating away from the surface. As a result, four alkyl chain aggregation models have been proposed by Lagaly based on WAXD results [40]. In terms of the density of the negative charges, the geometry of the surface and the degree of exchange, the surfactant molecules can lie flat on the silicate surface in monolayer (a) and bilayer (b), or paraffin-type arrangements, with the molecular chains radiating away from the interlayer surface (d); see Figure 2. 3. Also, a pseudotrimolecular arrangement (c) in which some molecular chain ends are shifted above one another, can be formed as illustrated in Figure 2. 3.

![Figure 2. 3 Alkyl chain aggregation in clay galleries: (a) monolayer, (b) bilayer, (c) pseudotrimolecular layer of chains lying flat on the surface, and (d) paraffin-type monolayer [40].](image)

Vaia and co-workers [41] presented a more realistic description based on the FTIR spectroscopy in association with WAXD. It was found that the intercalated alkyl chains existed in states varying with the degree of order. A disordered, liquid-like
structure will form as the interlayer packing density or the molecular chain length decreases, or as the temperature of the system increases. On the other hand, some orientational order similar to liquid crystalline structure can be attained when the available area per molecule is within a certain range, as presented in Figure 2.4. This was confirmed by molecular dynamic (MD) simulations which showed a strong layering behaviour with a disordered, liquid-like arrangement in clay galleries [42].

![Figure 2.4](image.png)

**Figure 2.4** Alkyl chain aggregation model: short alkyl chain (left), lateral monolayer; intermediate length of alkyl chain (middle), in-plane disorder and interdigitation to form quasi bilayer; longer alkyl chain (right), increased chains’ order to form paraffin-type arrangement [41].

### 2.2.2.2 Surfactants

a) Quaternary alkylammonium salts

The quaternary alkylammonium salts are cationic surfactants that are mostly used for organoclay preparation, due to the absence of hydrolysis and reduced adsorption of free alkylamine [43], compared to the primary alkylammonium salts. For polymer nanocomposites, the presence of quaternary alkylammonium salts influences the affinity between the clay minerals and the polymer. Consequently, for non-polar polymers such as polypropylene or polyethylene, dialkyl dimethylammonium halides are usually modified with the clay minerals, while for polar polymers, such as polyamides, the clays are modified with alkyl benzyl dimethylammonium halides or alkyl hydroxyethylammonium halides [43]. For instance, for the first ever
successful polymer/clay nanocomposite prepared by Toyota in 1990s, an ammonium cation based organic compound was chosen for the clay modification [44]. In addition, most commercial organoclays currently are all quaternary alkylammonium salts based, such as Cloisite®, Nanomer®, Nanofil®, Somasif®, Bentone® etc.

b) Quaternary alkylphosphonium salts
One of the reasons for the use of quaternary alkyl-phosphonium surfactants in clay modification is their relatively good thermal stability. Since polymer/clay nanocomposites are commonly prepared by melt compounding, the thermal stability of the organoclay is of paramount importance. Quaternary alkylammonium compounds are particularly susceptible to decomposition near the temperature of polymer processing, which is about 200°C for polypropylene [45], which could catalyse polymer degradation, causing a variety of undesirable effects during processing and in the final products. Alkyl-phosphonium based surfactants were found to have substantially higher thermal stability than alkylammonium based surfactants [46]. Additionally, phosphonium compounds could enhance the flame retardancy of the composite [47]. For the same purpose of improving thermal stability of organoclays, stibonium [48] and imidazolium surfactants [49] were also investigated.

c) Silane coupling agents
Silane has been used as a clay modifier for a long time. This is because the interaction between silane and swelling clays could be occurred at interlayer, external surface and broken edges. The interlayer grafting within the clay galleries results in the increase of the basal spacing of the clay, (see Figure 2.5), which makes intercalation of polymer molecules easier. In the meantime, the interaction between hydrophobic molecules and clay surfaces can be greatly enhanced by the simple grafting of hydrophobic groups onto the layer surface, as was done using a silane [50]. Because of the capability of grafting on an external surface and broken edges of clay layers, silane coupling agent can be used as a second surfactant, which makes
organoclays more compatible with hydrophobic polymers. As illustrated in Figure 2. 6, although hydrophilic interlayer surface was converted by ion-exchange reaction from organic surfactants, there are still a number of hydrophilic surface exposed, the use of a silane coupling agent could overcome this issue.

![Chemical Structures](image)

**Figure 2. 5** The hypothetical diagram for the intercalation and silylation of silane in clay galleries and the possible silane molecules arrangement [51].

![Diagram](image)

**Figure 2. 6** Schematic diagram for the twice functionalised organoclay [52].
d) Polyhedral Oligomeric Silsesquioxanes (POSS)

Recently, POSS has emerged as a clay modifier for polymer/clay nanocomposites. This is because compared to clays or conventional fillers, POSS is superior in terms of monodisperse molecular weight, low density, high-temperature stability (>300°C), no trace metals, sufficient interfacial interactions between composite particles and polymer segments, good biocompatibility, recyclability, as well as non-flammability [53]. Relating to its structure, a POSS molecule is an organic/inorganic structure containing a basic polyhedral silicon-oxygen nano-structured cage with a precisely Si-Si side length of ~0.5 nm [54, 55]. Eight Si atoms present at the corners of cubic cages, and surrounded by eight or more organic groups for further reaction, as shown by Figure 2.7. The POSS derivatives containing amine groups can potentially play the role of surfactant to modify clay minerals, and this has been modelled by Yei et al. in Figure 2.8. The major reason for these researchers using POSS as the clay modifier is due to the high thermal stability of POSS. In addition, the combination of POSS and clay may result in new nano-reinforcement effects for the preparation of high performance polymer nanocomposites.

Figure 2.7 The anatomy of a POSS nanostructure [55].
2.3 Nanocomposite Structure and Characterisations

2.3.1 Nanocomposite Structure

Generally, three main types of polymer/clay composite structures may be obtained, depending on the nature of silicate layers, organic surfactants and polymer matrix, as well as the method of preparation, (as shown in Figure 2. 9).
Figure 2.9 Scheme of different types of composites arising from the interaction of layered silicate and polymers: (a) phase separated microcomposite, (b) intercalated nanocomposite, (c) exfoliated nanocomposite [35].

*Phase separated microcomposite:* when polymer is unable to penetrate into the clay galleries, the layered silicates remain in stacks, and separated from polymer matrix. Consequently, its properties are in the same range as the traditional microcomposites, as illustrated by Figure 2.9a.

*Intercalated nanocomposite:* in intercalated nanocomposites, the intercalation of polymer chains into layered silicate structure, results in a well ordered multilayer morphology built up with organic polymer and inorganic silicate layers, regardless of the ratio between silicates and polymer (Figure 2.9b).

*Exfoliated nanocomposite:* in an exfoliated nanocomposite, originally ordered silicate structure is broken by intercalated polymer chains, and the individual silicate layers are uniformly and completely dispersed in the continuous polymer matrix and the average distance depends on the clay content (Figure 2.9c).
2.3.2 Characterisation

The chemical composition, structure, morphology, thermal properties and mechanical properties of the clay/polymer nanocomposites have been characterised by using different characterisation techniques, including X-ray diffraction, transmission electron microscopy, infrared spectroscopy, gel permeation chromatography, differential scanning calorimetry, thermogravimetric analysis, dynamic mechanical analysis and tensile testing etc.

2.3.2.1 Wide Angle X-Ray Diffraction (WAXD)

Wide angle X-ray diffraction (WAXD) is widely used to characterise the microstructure of nanocomposite normally exhibited as intercalated and exfoliated forms, which can be identified in terms of the position, shape and intensity of the basal reflections of distributed layered silicates. According to the Bragg’s law:

$$2d\sin\theta=n\lambda,$$

where $d$ is the spacing between atomic planes in the crystalline phase, $\lambda$ is the wavelength of X-ray and $2\theta$ is the diffraction angle of the diffracted x-ray, the XRD patterns can be converted to $d$-spacing.

Generally, a well ordered, layered silicate may possess sharp and intense peaks at high basal angle, while intercalation of clay interlayer will shift the peaks to relative low angle, and no peak will present for an exfoliated structure. However, XRD can only provide the structure information of layered silicate. It is difficult to conclude the spatial distribution of the clays in the polymer matrix. In addition, some layered silicates initially do not exhibit well defined basal reflections: peak broadening and intensity decrease are very difficult to study systematically. Therefore, conclusions based solely on WAXD results are only tentative when evaluating the nanocomposite structure and formation [56]. Figure 2. 10 displays the WAXD data showing the
intensity of several organoclays, which demonstrates three types of nanocomposite structures characterised via XRD patterns.

2.3.2.2 Transmission Electron Microscopy (TEM)

TEM is normally used, incorporate with XRD, in order to complement analyses by WAXD. As shown in Figure 2.10, TEM micrographs provide a qualitative understanding of the internal structure as well as spatial distribution of various phases via direct observation. Therefore, based on the TEM images, not only the structure of layered silicate, but also the dispersion of the silicates can be observed. However, TEM is a relatively time consuming process, and the quality of a TEM image significantly depends on the sample preparation.

![Figure 2.10 WAXD patterns (left) and TEM images of three different nanocomposite structures (right) [35].](image-url)
2.3.2.3 Other Techniques

Apart from above two main techniques for the characterisation of polymer layered silicate nanocomposites (PLSN), a few other techniques may also be used. Fourier transform infrared spectroscopy (FTIR) can be used for component identification and analysis interfacial interactions and orientation of polymers. Differential scanning calorimetry (DSC) is useful for the investigation of the melting and crystallisation behaviour of polymer/clay composites. Thermogravimetric analysis (TGA) is the technique that was mostly used for thermal stability analysis. Mechanical properties can be obtained by tensile testing, etc. [28].

2.4 Preparation of Polymer/Clay Nanocomposites

The key to the successful development of clay containing nanocomposites, is to develop an exfoliated structure of silicate platelets in the polymer matrix. These have been developed over time, with a large number of PLSN preparation methods being reported [19, 35, 39, 57, 58]. Among these, the three major methods to prepare polymer/clay nanocomposites are in-situ polymerisation of initial intercalated monomers, intercalation of polymer from solution and direct polymer melt intercalation.

2.4.1 In-situ Polymerisation

In this method, a clay is swollen within a liquid monomer or monomer solution. The monomers easily penetrate into the clay galleries due to their small molecular size. Subsequently, polymerisation takes place due to a catalyst which was fixed inside galleries before swelling step. Therefore, polymer chains can form between silicate layers, as illustrated in Figure 2.11. In-situ polymerisation has been found to be very effective in the formation of PLSN. However, the requirement of a suitable
monomer/solvent pairs, high cost of catalyst and batch size limits its commercial application.

![Diagram of PLSN obtained by in-situ polymerisation](image)

**Figure 2.11** Scheme of PLSN obtained by in-situ polymerisation [36].

### 2.4.2 Solution Intercalation

This approach requires that the polymer is soluble and the layered silicate is swellable in a suitable solvent. When the layered silicate is dispersed in the polymer solution, the polymer molecular chains intercalate and displace the solvent within the clay galleries. Upon solvent evaporation or polymer precipitation, the intercalated structure remains, which results in the formation of polymer layered silicate nanocomposite. This process is illustrated in Figure 2.12. The biggest drawback of this technique is the usage of solvent. Some polymers are not readily soluble in solvent. In addition, the use of large quantity of the solvent results in high cost, disposal and environmental impact issues.
2.4.3 Melt Intercalation

For most technologically important polymers, both in situ polymerisation and solution intercalation are restricted because either a suitable monomer or a compatible polymer-clay solvent system are not always available. Moreover, these solvents are not always compatible with current polymer processing methods. These drawbacks are driving the development of direct melt intercalation methods. In this method, polymer and layered silicate mixture is heated in either static or shearing conditions, above the glass transition or melting temperature of the polymer. Upon heating, molecular chains diffuse from the molten polymer into the clay galleries to produce either intercalation or exfoliation, depending on the degree of penetration of the molten polymer (Figure 2. 13). Unlike the above two methods, no solvent is
involved in melt intercalation, which has led to it emerging as the mainstream method for industrial manufacturing polymer/clay nanocomposites in recent years [56]. In addition to that, the nanoclay filled polymers can be processed using conventional processing techniques for plastics, such as extrusion and injection. However, this method results in a relatively slow penetration of polymer into the confined clay galleries. Only partial success was achieved so far, e.g., the concentration of exfoliated silicate greater than 4% has not been achieved [56].

![Scheme of the formation of PLSN by melt intercalation](image)

**Figure 2.13** Scheme of the formation of PLSN by melt intercalation [36].

### 2.4.3.1 Factors affecting polymer melt intercalation

Predicting whether or not a polymer/clay nanocomposite will lead to intercalation or exfoliation by melt compounding is not easy, as a number of factors influence the outcome. These include energy changes, the expansion of the interlayer space, and/or the intermolecular interaction between clay surface, surfactant and polymer [39].

**a) Thermodynamic aspects**

A mean-field, lattice-based model was developed by Vaia and Giannelis [59] in order to investigate the formation of polymer/clay nanocomposites thermodynamically.
Basically, the core part of this theory that is widely accepted by other researchers, can be summarised as follows: because of the existence of electrostatic forces between silicate layers, they are held together and the spacing between them is on the order of 1 nm, which is smaller than the radius of normal polymer molecules. There is obviously a large entropic barrier preventing the polymer from penetrating and blending with the clay [60, 61]. However, the entropy loss, associated with the intercalation of a polymer melt into the clay’s galleries is not prohibitive to the formation of nanocomposites, as an entropy gain, associated with layer separation and greater conformational energy of the aliphatic chains of organic surfactants, will balance the entropy loss of polymer intercalation, resulting in a zero net entropy change. Therefore, according to the above theory, the formation of polymer/clay nanocomposite via melt intercalation depends on energies factors which may be determined from the surface energy of the polymer and organoclay. In other words, the characteristics of the polymer and the organoclay, including the nature of the polymer, the type, packing density and size of the surfactant, strongly affect the formation of an exfoliated or intercalated nanocomposite or a conventional microcomposite [62, 63].

b) The effect of clay modification
As reported by Vaia and Giannelis [58], the interlayer structure of the organoclay should be optimised to maximise the configurational freedom of the functional chains upon interlayer separation, and also to maximise the potential interaction sites at the interlayer surface in order to achieve exfoliation during the melt intercalation. Therefore, as already mentioned in the section on clay modification, organic modification of clay including the type of surfactant, the chain length and the packing density, will be very relevant for the formation of exfoliated or intercalated structures. Reichert et al. [64] investigated the effectiveness of the chain length ranging from butyl (C4) to octadecyl (C18) amine on the formation of PP nanocomposites in the presence of maleic anhydride grafted PP. They observed that the alkyl chain length must exceed 8 carbon atoms in order to permit the formation
of an intercalated nanocomposite, and that the C18 cation had yielded the highest level of exfoliation.

Fornes and co-workers [65] did a detailed research, by selecting a series of organic amine salts in different structures and exchange levels relative to the clay. They found that decreasing the number of long alkyl tallow tails from two to one, by the use of methyl rather than hydroxyl-ethyl groups along with the surfactant. Also by the use of an equivalent amount of surfactant with the montmorillonite rather than an excess amount, led to greater extents of clay exfoliation and better mechanical properties in polyamide 6/clay nanocomposites. The detailed organic modifiers and their comparisons are summarised in Figure 2. 14.

However, Hotta and Paul’s [66] research on PE/clay nanocomposites gave a different view, where nanocomposites based on the organoclay with two long alkyl chains were superior to the nanocomposites based on the organoclays having one alkyl chain, in terms of clay dispersion. This was confirmed by Ton-That and co-workers [67], who found that the surfactants with two alkyl tails appeared to be more suitable for the polyolefin and also more thermally stable. Therefore, the conditions favouring exfoliation may be differ, depending on the polymer system used.
As mentioned in the clay modification section, the arrangement of surfactant molecules varies, from disordered monolayer to a solid-like paraffinic structure with the increase of packing density. Viva and Giannelis’s [58] research, found that there is an optimal interlayer structure that favours the formation of nanocomposite, which is a chain arrangement slightly greater than a pseudo-bilayer, and an intermediate between a disordered monolayer and a solid-like paraffinic arrangement. However, the difference stems from primary or quaternary ammonium head groups did not show as a major factor that determines the formation of the PS/clay nanocomposites.

Figure 2. 14 Molecular structure and nomenclature of amine salts used to organoclay by ion exchange. [65].
Bakazs and co-workers [68] developed a theoretical model by using self-consistent field calculation (SFC) to study the effects of the surfactant-matrix enthalpic interactions, surfactant packing density and surfactant length on morphological behaviour of the polymer/clay nanocomposites. Basically, longer surfactants promote intercalation of matrix molecules in the clay galleries, and a very high degree of surfactant coverage on the clay surface makes intercalation and exfoliation unfavourable. Based on this implication, Kurian et al. [69] created a mixed coverage at silicate surface by a mixture of PS-based surfactants with different lengths. However, only phase-separated structure was formed in the corresponding PS/clay composites. This suggested that a small fraction of longer surfactant molecules did not provide sufficient compensation to entropic gain that would promote intercalation. Moreover, as illustrated by Figure 2. 15c, the longer surfactant did not stretch away from the silicate surface, and instead remained as a brush of chemically similar molecules which behaved as a dense brush making intercalation difficult.

![Figure 2.15](image)

**Figure 2.15** Illustration, for a bimodal surfactant brush, of one possible outcome on longer surfactant conformation of the densely packed brush of a shorter surfactant [69].

It is also important to note that the amount of clay incorporated in the polymer matrix is another crucial factor, to determine the formation of intercalated or exfoliated silicate structure. Exfoliated structures were normally obtained at low clay loadings, typically lower than 5 wt%. Only intercalation of polymer molecules in the
clay galleries or even phase-separated structures were observed for higher amounts of clay [34].

c) The effect of polymer matrix

The polymer molecular weight is thought to be important for the resulting melt compounded polymer/clay nanocomposites. Fornes et al. [65] prepared polyamide 6/clay nanocomposites with three different molecular weight grades of polyamide 6 (i.e. low, medium and high), by the melt intercalation method. Overall, nanocomposites based on high molecular weight polyamide 6 exhibited higher degrees of exfoliation and better mechanical properties than nanocomposites formed from the low molecular weight or medium molecular weight polyamide 6, regardless of the organoclay used.

However, the existence of polar type interactions between a polymer and clay is thought to be more critical for the formation of nanocomposites via polymer melt intercalation [39], as polymers containing polar groups are capable of associative type interactions, such as Lewis acid-base interactions or hydrogen bonding, which promotes the intercalation of polymer molecules into clay galleries [58]. A good example is the formation of EVA-based nanocomposites through melt compounding. Studies [70] focused on the effect of the vinyl acetate content on the formation of EVA/clay nanocomposites, concluded that the higher the vinyl acetate content the higher the polarity of the polymer and the easier to form intercalated or exfoliated clay structures in EVA matrix.

On the other hand, no polar reaction between polymers and clays will make clays difficult to be intercalated. This can be compensated by introducing a compatibiliser. Exfoliation of the silicate layers will be formed if the interactions between the oxygen atoms at the clay surface (or galleries) and the polymeric compatibiliser are stronger than the interactions between the clay surface (or galleries) and the surfactant [71]. Maleic anhydride grafted polypropylene (PP-g-MA) is the most used
compatibiliser for polypropylene/clay systems [72-74]. When more maleic anhydride groups are attached to a compatibiliser molecular chain, the potential for multiple interactions with clay surface will enhance the ability of the compatibiliser to enter the clay galleries and lead to more effective mechanical separation of the silicate layers. An optimum amount of compatibiliser is required to obtain delaminated silicate layers, as reported by Marchant and Jayaraman [75], was found to be 2:1 (wt.) respective compatibiliser to clay; this was also claimed by other researchers [67]. However, a 3:1 (wt.) ratio of compatibiliser to clay was used to obtain PP/clay nanocomposites in Kawasumi et al.’s [76] work. It is also important to note that although higher maleic anhydride content in PP-g-MA compatibiliser is desirable for favourable interaction with silicate surface, low molecular weight resulting from the higher amount of maleic anhydride, will make maleated PP easy to degrade and lead to less improved mechanical properties. Apart from PP-g-MA, hydroxyl [77] and ammonium groups [73], grafted polypropylenes were also used as the compatibiliser for polypropylene nanocomposites. Ristolainen et al. [74] revealed that a compatibiliser of hydroxyl grafted PP was effective in the formation of a desired nanostructure at relative high content, while it was not as good as maleic anhydride grafted PP at low content. In addition, the low molecular weight forms of this kind of compatibiliser had the same limitations as PP-g-MA. Wang et al. [73] developed a novel compatibiliser, an ammonium group terminated polypropylene, and it resulted in an exfoliation of silicate layers in the polypropylene matrix. The use of this kind of compatibiliser could permit the omission of organic surfactant in order to promote the compatibility between PP-t-NH$_3^+$ and the silicate surface.

d) The effect of processing conditions
Melt processing conditions are also of importance in order to achieve high degrees of exfoliated structures in polymer/clay nanocomposites. Extruders and mixers are the most popular shear devices used for polymer nanocomposite preparation, among which twin screw extruder is widely accepted as the most effective for exfoliation and dispersion of silicate layers [65]. Cho and Paul [78] made a comparison between
an intermeshing co-rotating twin screw extruder and a single screw extruder in the preparation of polyamide 6/clay nanocomposites. They found that full exfoliation was not achieved for the composite prepared by single screw extrusion, while uniform dispersion and exfoliated structure were obtained for the composites prepared by twin screw extrusion. This is attributed to insufficient shear force and the short residence time of single screw extrusion, compared to that of twin-screw extrusion. In addition, co-rotating twin screw extrusion was more effective than counter-rotating twin screw extrusion, as reported by Strong [79]. However, this does not mean that single screw extruder or mixer cannot be used for nanocomposite preparation. It depends much on the polymer matrix used. For example, McNally and co-workers [80] successfully prepared polyamide 12/clay nanocomposites using conventional single screw melt compounding. Internal mixers are also successfully used for the preparation of exfoliated nanocomposites based on a poly(ether imide) (PEI) matrix [81, 82].

Moreover, for a given shear device, processing conditions such as shearing speed, processing temperature, residence time etc. will strongly affect the final outcome. Modesti et al. [83] determined that the shear stress exerted on the polymer is more influential on the extent of intercalation and delamination, than the residence time, and better results were obtained at higher screw speed and lower barrel temperature for polypropylene/clay nanocomposites. Médéric and co-workers [84] reported a similar conclusion, that long mixing times and high rotational speed led to a good dispersion and a well exfoliated structure in polyamide 12/clay nanocomposites. However, there appears to be an optimum extent of mixing and an optimum shear stress as excessive shear stress or mixing apparently caused poorer delamination and dispersion [81].

The influence of incorporated carbon dioxide and ultrasonic during melt compounding were studied by Nguyen and Baird [85] and Li et al. [86], respectively. PP nanocomposites prepared via melt compounding with CO₂, exhibited better
mechanical properties and a higher degree of dispersion of nanoclay than these no CO₂ incorporated. Similarly, the combination of extruder and ultrasonic power was found to improve the processibility of polymer materials, and enhance the degree of exfoliation of the organoclays, though only for specific matrices.

e) Thermal degradation
Thermal degradation problems may be involved in melt compounding, since polymer/clay nanocomposites have to be prepared above certain temperatures. Apart from the polymer matrix degradation, thermal degradation will take place in the organo-montmorillonite (O-MMT) if the processing temperature exceeds the thermal stability of the O-MMTs. Therefore, high onset temperature of decomposition of the organic surfactant is important in order to make a polymer/clay nanocomposite, especially for those high-temperature engineering plastics. In addition to common detrimental aspects of degradation, the resulting decomposed products may play a major, but yet to be determined role, in the formation of exfoliated nanostructures [87].

Xie et al. [87] studied the effect of organic surfactants on the thermal decomposition of O-MMTs by TGA and found that this decomposition for O-MMT was quite different from that of the unmodified MMT. Generally, four steps can be considered for the decomposition of O-MMT: (1) the release free water below 200 ºC; (2) the region where organic surfactants decompose in the temperature range 200 to 500 ºC; (c) the remove of structural water in the temperature range 500 to 800 ºC; and (d) a region between 800 and 1000 ºC where organic carbon reacts in some yet unknown way. The most distinguishing difference between the sodium montmorillonite (Na-MMT) and the O-MMT, is in the temperature range of 200 to 500 ºC as the organic surfactants in the organoclay start to decompose at around 200 ºC, which is the temperature that most polymers are processed [88, 89]. Some detrimental effects of thermal decomposition have already been identified in literature, e.g. discoloration of polycarbonate/clay [90] and polyamide 6/clay [91] composites, and in
plasticisation and reduction of glass transition temperature of crosslinked epoxy/clay system [92]. However, these authors did not observe the effect of thermal decomposition on clay dispersion.

Dharaiya and Jana [89] investigated the effect of decomposition of alkyl ammonium ions on clay surface energy, which may exert detrimental effects on the dispersion of clay particles and on the final morphology of polymer composites. They concluded that surface energy was very sensitive to the decomposition of alkyl ammonium ions in organoclays: the change of surface energy as well as surface polarity of clay during the heat treatment on O-MMT, had a direct influence on the affinity to polymer matrix and hence on clay dispersion within polymer matrix. On the other hand, in order to reduce the thermal decomposition, a number of high thermally stable O-MMTs were developed, i.e. Chang et al. [93] developed a thermally stable organoclay through ion-exchange reaction between Na\(^+\)-MMT and dodecyl triphenyl phosphonium chloride. Gilman et al. [94] produced PA 6 based nanocomposites, where MMT was modified with trialkylimidazolium cations. Recently, Yei et al. [54] used inorganic polyhedral oligomeric silsequioxane (POSS) as a surfactant to enhance the thermal stability of O-MMTs.

2.5 Polymer/Clay Nanocomposites

2.5.1 Polyamide/Clay Nanocomposites

2.5.1.1 Manufacture

A Polyamide 6/clay nanocomposite was the first polymer nanocomposite that was developed successfully by Usuki et al. of the Toyota Research Group [12, 57], through in-situ polymerisation method in 1990, which has been used by the automotive industry because of significant improvements in mechanical and thermal
properties using small amounts of layered silicate loadings. Polyamide 6/clay nanocomposites were obtained by swelling 12-aminododecanoic acid modified Na-MMT with ε-caprolactam monomer at 100°C, which was subsequently polymerised through a ring opening polymerisation. This process route can be described by the following Figures 2.16 and 2.17.

Figure 2. 16 Schematic representation of the swelling behaviour of 12 amino acid modified MMT by ε-caprolactam monomer [12].

Figure 2. 17 Schematic illustration of polymerisation of ε-caprolactam in the presence of 12-amino acid modified MMT [57].

A one-pot polymerisation method was proposed by Kojima et al. [95] who mixed the Na-montmorillonite, monomer (ε-caprolactam) and catalyst (phosphoric acid)
simultaneously, to promote polymerisation so as to obtain PA 6/clay composites. Surprisingly, the dispersion and mechanical properties of the obtained products by this method are the same as those made by in-situ polymerisation of 12-amino acid modified MMT and ε-caprolactam, as described previously. However, this method had proved to be sensitive to the type of the acid used to promote the intercalation of ε-caprolactam [35].

Direct melt compounding methods have also developed to prepare polyamide nanocomposites by a number of researchers [65, 78, 96, 97]. In all of their studies, MMT was organically modified, which indicates that surface modification of Na-MMT is necessary to obtain successfully exfoliated structure. In Liu et al.’s work [96], polyamide 6/clay nanocomposites with C18 modified MMT were prepared in a twin-screw extruder. WAXD analysis of the nanocomposites with various amounts of MMT indicated that polyamide nanocomposites with less than 10 wt.% MMT loadings resulted in exfoliated structures, while those over 10 wt.% MMT contents led to the formation of intercalated structures.

Fornes et al. [65, 97] used a similar method to prepare the polyamide 6/clay nanocomposite, using a Haake co-rotating, intermeshing twin-screw extruder, which was operated at 240 °C with a screw speed of 280 rpm. In their studies, they revealed that the molecular weight of the polymer, the surfactant molecule’s length, the organic functional group and the adsorbed surfactant density had significant effects on the morphological structure of the MMT within the polyamide 6. As illustrated in Figure 2. 18 and Figure 2. 19, the extent of exfoliation increased with increasing polymer molecular weight. In addition, those surfactants having one long alkyl tail on the ammonium cation rather than two, a methyl group on the amine rather than 2-hydroxyl-ethyl group and an equivalent rather than excessive amount of amine surfactant on the clay surface, led to greater degrees of exfoliation, higher stiffness and yield strength of the resulting polyamide 6/clay nanocomposites.
Figure 2. 18 WAXD spectra of (HE)2M1R1 organoclay and its nanocomposites, based on low molecular weight (LMW), medium molecular weight (MMW) and high molecular weight (HMW) polyamide 6 matrices containing ~ 1.5 wt% MMT [97].

Figure 2. 19 TEM images of melt compounded polyamide 6 nanocomposites containing 3 wt% of MMT, a) HMW, b) MMW, and c) LMW [97].

In order to reduce the cost arising from organic modification, Hasegawa et al. [98] developed a novel solution intercalation method, to prepare polyamide 6/clay nanocomposites. In this method, an uniformly swollen and suspended aqueous clay slurry was mixed into a molten polyamide 6 resin during extrusion, as shown in
Figure 2.20. Exfoliated and uniformly dispersed polyamide 6/clay nanocomposites were produced successfully using this method, and Figure 2.21 shows the principle of understanding in this process. Initially, the clay suspension is pumped into the molten polymer under intensive shearing (a); the water in the aqueous clay slurry begins to evaporate and the clay slurry is reduced to finer drops during blending due to the heating (b and c); an uniform dispersion of silicate layers in polyamide 6 matrix, in the form of a monolayer or a few layers (d), is obtained after water evaporation.

**Figure 2.20** Illustration of the compounding process for preparation of polyamide 6-MMT nanocomposites, via clay suspension [98].
From the commercial application point of view, the masterbatch method or so-called two-step process was developed by Shah and Paul [99]. Using the technical knowledge reported by Fornes et al. [97], that a higher degree of exfoliation of organoclays can be achieved with a high molecular weight (HMW) grade of polyamide 6 than with a low molecular weight (LMW) grade. However, apparently low melt viscosity of the LMW grade of polyamide 6 makes it favourable for certain commercial applications. Therefore, HMW grade polyamide 6 was first melt compounded with a high content of organoclay, to form a masterbatch and to promote exfoliation. Then the masterbatch was diluted with LMW polyamide 6, which is easy to process because of low melt viscosity, to the desired MMT content. The TEM images (Figure 2. 22) show that the polyamide 6 nanocomposites, prepared via the masterbatch method, is in between full exfoliation because of the HMW polyamide 6 and intercalation because of LMW polyamide 6. Additionally, this method offers significant reductions in melt viscosity and only a small reduction
in modulus, compared to nanocomposites prepared directly from melt compounding HMW polyamide 6.

**Figure 2.22** TEM micrographs of nanocomposites containing ~2.0 wt% montmorillonite based on (a) HMW polyamide 6 (b) HMW masterbatch containing ~20 wt% montmorillonite diluted down with LMW (c) LMW polyamide 6 [99].

Besides polyamide 6, a few other types of polyamide nanocomposites, such as those polyamide 6,6, polyamide 11 and polyamide 12 have also been developed or in development. In Liu et al.’s study [100], polyamide 6,6/clay nanocomposite was prepared via a melt compounding method in a twin-screw extruder. The silicate layers were homogeneously dispersed and with a high degree of exfoliation in the polyamide 6,6 matrix, due to the organoclay which was co-intercalated by an epoxy resin and hexadecyl trimethyl ammonium cation into Na-MMT. Chavarria and Paul [101] investigated the differences between nanocomposites based on polyamide 6 and polyamide 6,6, which were melt compounded in the same conditions. The
CHAPTER 2 LITERATURE REVIEW

resulting polyamide 6 nanocomposites showed superior mechanical properties than those made from polyamide 6,6, mainly because polyamide 6 nanocomposites were better exfoliated than the polyamide 6,6 nanocomposites which exhibited a mixture of exfoliated and intercalated structures.

Liu et al. [102] also used the melt compounding method in a twin-screw extruder to prepare polyamide 11/clay nanocomposite. It was found that exfoliation of silicate layer was obtained at low clay concentrations, (less than 4 wt%), and a mixture of exfoliated and intercalated structures of silicate layer were formed at high clay concentrations. The superior thermal and mechanical properties were obtained from polyamide 11 nanocomposites with low clay loadings, which was attributed to the exfoliation and the finer dispersion of the organoclay in the matrix. Zhang et al. [103] prepared a polyamide 11/clay nanocomposite via in-situ polymerisation, with the 11-aminoundecanoic acid intercalated Na-MMT. Similarly, exfoliation was obtained at low clay concentrations (less than 4 wt%), and both exfoliated and intercalated silicate layers were formed at higher clay contents.

Preparation of polyamide 12/clay nanocomposite carried out by Kim et al. [104] had the same principle as Zhang et al.’s [103]. The TEM images revealed that the silicate layers were uniformly dispersed in the polyamide 12 matrix, and an intercalated structure was obtained. Phang et al. [105] used the melt compounding method to fabricate the polyamide 12/clay nanocomposite, in a twin-screw extruder. The XRD diffraction indicated the dominance of the exfoliated silicate layers formed in a continuous polymer matrix, in accordance with TEM observations, as illustrated in Figure 2.23.
2.5.1.2 Properties

When an exfoliated polyamide 6/clay nanocomposite was first developed by the Toyota Research Group [12, 57], via in-situ intercalative ring-opening polymerisation of ε-caprolactam, it was reported that this kind of material has a double increase in modulus and 50% increase in tensile strength, compared with the polyamide 6 alone. The main reason for the dramatic property enhancements of polyamide 6, was attributed to the fine dispersion of nano silicate layers, which strongly interacted with the polymer matrix via the formation of hydrogen bonding, as illustrated in Figure 2. 24.
Figure 2.24 Schematic illustration of the formation of hydrogen bonding in polyamide 6/MMT nanocomposites [35].

According to Kojima et al.’s research [106], the extent of improvement in tensile modulus directly depends on the average length of the dispersed silicate layers, and in turn the aspect ratio, as well as the clay content. They selected two organoclays with different aspect ratios, and exfoliated them into a polyamide 6 matrix via in-situ polymerisation of ε-caprolactam, at various clay contents. The tensile modulus measured at 120 °C, showed that a larger aspect ratio would result in a higher tensile modulus, and the more clay that was added, the higher the tensile modulus, (see Figure 2.25). Additionally, it was realised that the degree of dispersion of clay in polymer matrix played a vital role in property improvement. Liu et al. [102] proved that the exfoliated polyamide/clay nanocomposites had enhanced stiffness compared with intercalated ones, due to the finer dispersion of the organoclay in the polymer matrix.
Figure 2.25 Effect of clay content on tensile modulus in case of polyamide 6/MMT nanocomposites prepared via melt extrusion [106].

Polyamide 6/clay hybrids prepared by one-pot method [95], with various acids as the polymerisation catalysts, showed superior tensile properties to those previously reported polyamide 6/clay hybrids, synthesised by MMT intercalative with 12-aminolauric acid, and polyamide 6, as summarised in Table 2.1. Furthermore, homopolymer polyamide 6 was obtained by a one-pot method, while in the case of ring-opening polymerisation method, a small amount of polyamide 12 may be formed, which could lower the modulus of final composites. Also, Kojima et al. [95] investigated the effect of various acid catalysts during the one-pot synthesis of polyamide-clay hybrid (NCH) and revealed that phosphoric acid was the best promoter for efficient dispersing and exfoliating silicate layers, and consequently resulted in the highest tensile modulus of the composites.
Table 2.1 Mechanical properties of one-pot NCH synthesised in the presence of phosphoric acid [95].

<table>
<thead>
<tr>
<th>Property</th>
<th>Method</th>
<th>One-pot NCH(^a)</th>
<th>NCH(^b)</th>
<th>Polyamide 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Modulus</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(GPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23°C</td>
<td>ASTM D638M</td>
<td>2.25</td>
<td>1.87</td>
<td>1.11</td>
</tr>
<tr>
<td>120°C</td>
<td>JIS K7113</td>
<td>0.67</td>
<td>0.61</td>
<td>0.19</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(MPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23°C</td>
<td>ASTM D638M</td>
<td>102</td>
<td>97.2</td>
<td>68.6</td>
</tr>
<tr>
<td>120°C</td>
<td>JIS K7113</td>
<td>34.7</td>
<td>32.3</td>
<td>26.6</td>
</tr>
</tbody>
</table>

\(^a\) MMT=4.1 wt%; \(^b\) MMT=4.7 wt%, prepared by in-situ polymerisation method.

The tensile properties of melt compounded polyamide/clay nanocomposites were systemically investigated by Fornes et al. [97], using three molecular weight grades of polyamide 6. For all three grade polyamides, the addition of organoclay resulted in a substantial increase in both tensile modulus and strength in the composites. Interestingly, three grades of polyamide 6 based composites showed similar increasing rate in stiffness at any given clay concentrations, despite the modulus of the unfilled polyamide 6 being almost equivalent (Figure 2.26a). The yield strength of polyamide 6 nanocomposites exhibited similar trends as the tensile modulus, with the dependence on the clay loadings and molecular weight, as shown in Figure 2.26b. However, the improvement in strength for pure polyamide 6 varied with the molecular weight of the polymer. The HMW and MMW based polyamide 6 nanocomposites showed a steady increase in strength, as the MMT loading increased, while a lower increasing rate was observed for LMW based polyamide 6 nanocomposites. The elongation at break decreased with MMT contents for the three grades of polyamide 6 matrices (Figure 2.26c). Similar to modulus, the ductility of the composites increased with the increase of the molecular weight of the polymer matrix, i.e. the HMW polyamide base nanocomposites showed the highest ductility at any given clay contents.
Figure 2. The effect of MMT content on tensile modulus (a), yield strength (b) and elongation at break (c) for LMW, MMW and HMW polyamide 6 based composites [97].
Figure 2. 27 Modulus (left) and elongation at break (right) of nanocomposites based on HMW polyamide 6 and organoclays showing the effects of (a, a’) quaternary amines having one vs. two alkyl tails, (b, b’) tertiary amines having one vs. two alkyl tails, (c, c’) the effect of 2-hydroxyl-ethyl versus methyl groups, and (d, d’) the effect of surfactant density (MER) [65].
The effect of the organoclay structure on the mechanical properties of polyamide nanocomposites was also investigated by Frones et al. [65]. Figure 2. 27 shows that the surfactant with one long alkyl tail, rather than two alkyl tails, promoted better enhancement in modulus; the use of methyl rather than hydroxyl-ethyl groups, and the use of an equivalent amount of surfactant with the clay rather than excessive amount, led to increased moduli, higher yield strength and lower elongation at break.

![Graphs](image)

**Figure 2. 28** Effect of montmorillonite content and polyamide repeat structure on the modulus, yield strength and elongation at break of nanocomposites based on PA 6, PA 11 and PA 12 and the organoclay M3(HT)1 [34].

The comparison in mechanical properties between polyamide 6, polyamide 11 and polyamide 12 layered silicate nanocomposites was studied by Frones and Paul [34]. An “exfoliation index” was used in this research and it was found that nanocomposites based on polyamide 6 exhibited a near perfect exfoliation efficiency, particularly at low clay concentrations, whereas those based on polyamide 11 and
polyamide 12 showed relatively lower efficiencies. Increasing the number of methylene units in the polyamide from 5 to 10, i.e., polyamide-6 vs. polyamide-11, resulted in a great effect on modulus, yield strength and elongation at break, while the change from 10 to 11 had little effect, as shown by Figure 2. 28.

Phang and co-workers [105] reported that the improvements of elastic modulus and the hardness of melt compounded PA 12 nanocomposites, were 52% and 67%, respectively, with a clay concentration increased from 0 to 5 wt%. However, decreased impact strength (by about 25%), was observed as the clay loading increased, indicating development of embrittlement due to clay addition. This is believed to stem from the weak interfacial adhesion between the layered silicates and the polymer matrix, which was consistent with Fornes and Paul’s work [34].

![Figure 2. 29](image)

**Figure 2. 29** Tensile modulus (E) and yield strength (\(\sigma_y\)) of PA11/clay nanocomposites as a function of clay concentration [102].

The tensile properties of melt compounded PA11/clay nanocomposites were reported by Liu and co-worker, as shown in Figure 2. 29. It can be seen that both the elastic
modulus and the yield strength of polyamide 11/organoclay nanocomposites were enhanced significantly compared to unfilled polyamide 11 and a higher degree of reinforcement was observed mainly at low clay contents (< 4 wt. %). However, both yield strength and modulus were lower than others reported, which was considered to be due to the compression moulding method associated with tensile bar sample preparation.

2.5.2 Polypropylene/Clay Nanocomposites

2.5.2.1 Manufacture

The melt compounding method was widely used to prepare polypropylene clay nanocomposites, which was typically carried out in a twin screw extruder. Kawasumi et al. [76] from the Toyota Research Group reported that polypropylene/clay nanocomposites had been prepared by simple melt mixing of three components, PP, maleic anhydride modified polypropylene oligomers (PP-g-MA) and stearylammonium modified clay, at 210 °C, using a twin-screw extruder. By changing the clay type and the amount of maleic anhydride, a partially exfoliated and homogenous dispersion of the silicate layers was obtained. A schematic representation of the mixing process of those three components is illustrated in Figure 2. 30. It is believed that the driving force of the intercalation derives from the maleic anhydride group and the oxygen groups of the silicate, through hydrogen bonding [35].
Regarding the fact that maleic anhydride is able to intercalate into the clay galleries due to the polar interactions with silicate surfaces, Hasegawa et al. [27] made a modification to the above approach. Organically modified clay was first melt compounded with maleic anhydride grafted PP, in order to obtain compatible silicate surface and larger interlayer distance. The pre-melt compounded hybrids were then melt compounded with bulk PP at 200 °C in a twin-screw extruder, resulting in efficient dispersion of silicate particles in PP matrix at the nanometer level. The particles became smaller and a more uniformly dispersion as the ratio of PP-g-MA to the clay was increased. A similar result was obtained by Ham et al. [107], who used
the same approach as Hasegawa et al.’s to prepare the polymer nanocomposites. In their study, the formation of nearly exfoliated silicate layers was observed with low MMT loading (2 wt%), and intercalated structures were obtained with higher MMT loading (>4 wt%).

The above mentioned two-step method is highly favoured for industrial applications, as a large quantity is required. Therefore, masterbatch method has been proposed, in which larger amounts of MMT are pre-intercalated with the compatibilisers and diluted with bulk PP to PP/clay nanocomposites with the desired clay percentage. Lan et al. [108] prepared masterbatch up to 50 wt% of MMT, which was then mixed with bulk PP, leading to a better dispersion than that obtained by direct compounding.

Tjong et al. [109] prepared polypropylene/vermiculite nanocomposites with an in-situ polymerisation approach, using maleic anhydride both as the reactive reagent for in-situ polymerisation and as a modifier for the silicate. After swelling and intercalating the vermiculite using the maleic anhydride, in-situ reaction of polypropylene with MA-pretreated vermiculite in the presence of the catalyst dicumyl peroxide occurred during extrusion in a twin-screw extruder. Both WAXD patterns and TEM micrographs showed the formation of intercalated and exfoliated nanocomposites. Garcia et al. [110] reported a novel method of preparing polypropylene/silica nanocomposites in a slurry phase polymerisation reactor. Initially, the reactor was filled with hexane to suspend the Ziegler-Natta (4th) catalyst, using mechanical stirring with the temperature was controlled at 100 °C, silica powders were added in the meantime. When the system reached equilibrium at constant temperature and pressure, the propylene monomer was injected into the reactor to react to form nano-silica contained polypropylene composites. The processing route is illustrated in Figure 2. 31.
Kato and his co-workers [111] developed a solution based method to prepare polypropylene/clay nanocomposites, in which water was injected directly into a mixture of melted polypropylene and the layered silicates in a twin-screw extruder, due to the fact that clay is exfoliated in water. By controlling the pressure of the water vapour, the exfoliated and uniformly dispersed silicate layers were achieved in the bulk PP. The resulting polypropylene nanocomposites had the same excellent properties as those conventionally prepared PP/clay nanocomposites.

2.5.2.2 Properties

The relationship between tensile properties and clay loading in intercalated PP nanocomposites was studied by Svoboda and co-workers [112], and the results are shown in Figure 2. 32. A steady increase in the tensile modulus was observed as a function of clay loadings, which was less dependent on the molecular weight of the compatibiliser, PP-g-MA. The tensile strength of the composite increased sharply by
about 12% at a clay loading of 1 wt.% and levelled off after 5 wt.% loading. However, the tensile strength of intercalated PP nanocomposites was reduced significantly by the addition of low molecular weight PP-g-MA, and similar results have been reported by other researchers [71].

Figure 2.32 Tensile properties as a function of clay content for intercalated PP/PP-g-MA/Cloisite 20A organoclay composites, prepared by twin screw compounding with a 1:1 wt. ratio of PP-g-MA to clay: a) tensile modulus; b) tensile strength [112].

Manias et al. [71] investigated the tensile properties of PP nanocomposites obtained from unfilled/unmodified PP and a semi-fluorinated organic modified MMT (f-MMT). Figure 2.33 shows the comparison between an unfilled-PP/f-MMT nanocomposite and a PP/2C18-MMT conventional composite, as a function of clay content. There is a sharp increase in Young’s modulus for unfilled-PP/f-MMT nanocomposite at a low clay concentration (< 3wt.%), followed by a slower increase beyond a clay loading of 4 wt.%. However, tensile strength does not change markedly with the increase of clay content, compared to that of bulk PP, and there was only a small decrease in elongation at break.
Figure 2. 33 Tensile characterisation of the PP/f-MMT nanocomposites (■). For comparison, conventionally filled PP/2C18-MMT ‘macro’ composites are also shown (○) [71].

Table 2.2 Results of the tensile test for various PP/clay composites [27].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus (MPa)</th>
<th>Strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>$780^{+16}_{-10}$ (1.00)</td>
<td>$32.5^{+0.1}_{-0.2}$ (1.00)</td>
<td>$&gt;150$</td>
</tr>
<tr>
<td>PP/C18-Mt(^a)</td>
<td>$830^{+22}_{-40}$ (1.06)</td>
<td>$31.9^{+0.1}_{-0.2}$ (0.98)</td>
<td>$105^{+35}_{-30}$</td>
</tr>
<tr>
<td>PP/C18-Mt/PP-MA-1/1(^b)</td>
<td>$838^{+22}_{-40}$ (1.07)</td>
<td>$29.5^{+0.5}_{-0.2}$ (0.91)</td>
<td>$7.5^{+0.4}_{-0.5}$</td>
</tr>
<tr>
<td>PP/C18-Mt/PP-MA-1/2(^c)</td>
<td>$964^{+13}_{-12}$ (1.23)</td>
<td>$34.6^{+0.2}_{-0.2}$ (1.06)</td>
<td>$8.6^{+0.5}_{-0.6}$</td>
</tr>
<tr>
<td>PP/C18-Mt/PP-MA-1/3(^d)</td>
<td>$1010^{+25}_{-42}$ (1.29)</td>
<td>$31.7^{+0.2}_{-0.2}$ (0.98)</td>
<td>$5.6^{+0.3}_{-0.3}$</td>
</tr>
</tbody>
</table>

\(^a\) MMT=4.37 wt%; \(^b\) MMT=5.00 wt%; \(^c\) MMT=4.66 wt%; \(^d\) MMT=4.83 wt%.
The effect of a PP-g-MA compatibiliser in PP nanocomposites was investigated by Hasegawa et al. [27], and findings are summarised in Table 2.2. There show that the use of PP-g-MA increased the modulus of the PP nanocomposites, and the rate increased with an increased amount of compatibiliser. 1:2 of MMT/PP-g-MA was optimised to behave with the best performance at ratios of 1:1, 1:2 and 1:3, based on the tensile properties. However, other ratios between MMT and PP-g-MA, such as 1:3 [76] and 1:6 [111] were also reported.

![Figure 2.34](image_url)

*Figure 2.34* Young’s modulus (a) and yield strength (b) as a filler content of compounds of MEC8 and MEC12, where E is compatibiliser PP-g-MA (2.9 wt% MA and 8800 molecular weight); H is compatibiliser PP-g-MA (4.2 wt% MA and 4000 molecular weight) [64].

In addition, Reichert et al. [64] reported that the tensile properties were sensitive to the MA content of the compatibiliser PP-g-MA, as well as the alkyl length of the surfactant (Figure 2.34). This was similar to Hasegawa et al.’s results [27], the addition of compatibiliser, PP-g-MA afforded substantially higher stiffness. Moreover, clay modified with longer alkyl length (C12) gave much improved
stiffness than those with shorter alkyl length (C8). However, the MA content of the PP-g-MA only had minor influence on the modulus, as shown in Figure 2. 34b. However, yield strength of the PP nanocomposites increased significantly when the PP-g-MA contained a higher amount of MA.

Ton-That and co-workers [67] also did research on the influence of the surfactant and the compatibiliser molecular weight on the mechanical properties of PP/clay nanocomposites (see Figure 2. 35). It was found that at a higher molecular weight of PP-g-MA compatibiliser, resulted in higher tensile modulus and tensile strength, which was different to the results reported by Reichert et al. [64]. This could be due to the different montmorillonite contents studied. Additionally, Ton-That et al. [67] found that organoclay with two long alkyl chains performed better than those with one long alkyl chain, on the mechanical properties of PP nanocomposites.

![Figure 2. 35 Tensile properties of PP, PP blends with PP-g-MA and PP nanocomposites with a 2:1 ratio of PP-g-MA to clay, at concentration of 2 wt% [67].](image)

In addition to the degree of dispersion, the strength of coupling between the polymer matrix and the silicate surface, have also been found to affect the tensile modulus values. Taking a silane coupling agent for an example, it was found to limit the
dispersibility of the silicate layers [113], but with a more careful selection of the silane coupling agent type, can produce increases in tensile modulus, as reported by Kumar and Jayaraman [114]. These authors reported that the silane reacted primarily with the hydroxyl groups on the edges of the silicate layers, leading to much better coupling with the matrix and thus to higher modulus. This has been illustrated in Figure 2.36, in which further silane modified C18 clay exhibits higher tensile modulus.

![Figure 2.36 Tensile module of polypropylene and PP nanocomposites by melt compounding with 10 wt% of a fixed PP-g-MA and 5 wt% of MMT with different surface treatments including additional silane treatment [115].](image)

2.5.3 Poly(butylene terephthalate)/Clay Nanocomposites

2.5.3.1 Manufacture

Poly(butylene terephthalate) (PBT) is a conventional semi-crystalline engineering polymer with good tensile strength, flexural modulus, and dimensional stability, but low impact strength. Rubber-like polymers have been blended with PBT to improve
its impact strength. However, it sacrifices other properties such as stiffness, which can be overcome by introducing nanoclay. As with polyamide and polypropylene layered silicate nanocomposites, melt compounding, solution and in-situ polymerisation methods have been used in the preparation of PBT/clay nanocomposites.

Li and co-workers [116] prepared PBT/clay nanocomposites via melt compounding in an internal batch mixer. Three different organoclays, Cloisite 6A, 10A and 30B were selected in order to investigate the effects of clay modifications, i.e. with various polar interactions, on the nanostructure of the PBT hybrids. An intercalated structure was only obtained when PBT was directly melt compounded with organoclays, despite the extent of intercalation varying among these organoclays. Following this, a third component, an epoxy resin, was added to act as a compatibiliser to the PBT matrix and organoclays, and as a result, the dispersion and intercalation extent of the PBT/clay systems changed. For the organoclay 30B, its use leads to enhanced intercalation and further exfoliation, while for 6A and 10A, no changes or even worse intercalation were observed. This indicated that this sort of compatibiliser only worked in the right conditions. Xiao et al. [117] also used a batch mixer to prepare PBT/clay nanocomposites, but with a higher thermally stable organoclay (i.e. cetyl pyridium chloride (CPC) modified montmorillonite). They found that the CPC modified clay was more suitable for PBT/clay nanocomposite fabrication at a high processing temperature, compared to other alkyl ammonium modified clays, and a mixture of intercalated and exfoliated structures in the organoclay were obtained from the PBT nanocomposites. Chang et al. [118] and Scatteia et al. [119] used twin-screw extrusion to melt compound PBT/clay nanocomposites. It was observed that PBT intercalated into the organoclay, and the intercalation occurred more extensively for the PBT matrix with a high viscosity, indicating the importance of the level of shear stress in the preparation of polymer nanocomposites, via a melt compounding method.
Tripathy and co-workers [120] prepared PBT/clay nanocomposites using an in-situ polymerisation method, with cyclic PBT oligomer, c-PBT (Figure 2. 37). Organically modified clay, Cloisite 20A was swollen with constant stirring for about 20 h at 80 °C in a solution of catalyst cyclic stannoxane and antioxidant, Irganox 1010. c-PBT was dissolved in toluene at above 80 °C and then incorporated into the mixture of clay and catalyst, under constant stirring for another 20 h at 80 °C. The final mixture was obtained after solvent evaporation and vacuum drying at 80 °C. The polymerisation of c-PBT was conducted directly on the above dried mixture in a vial at 190 °C for 6 min, under sealed conditions. WAXD results suggested that an exfoliated nanostructure before polymerisation and an intercalated structure after polymerisation, which were confirmed by TEM observations.

![Figure 2. 37 Schematic diagram of the chemical structure of cyclic poly(butylene terephthalate), (c-PBT) [121].](image)

Chang et al. [122] used the PBT monomer to prepare ‘one-pot’ in-situ polymerised PBT/clay nanocomposites. This process is illustrated by Figure 2. 38. The resulting PBT nanocomposites appeared to be dominated by intercalated structures. Although relative good dispersion was observed at low MMT loading (<4 wt.%), some agglomerated clay particles formed in the PBT matrix, especially at high MMT loading (> 4 wt.%).
Figure 2.38 Flow diagram of the in-situ polymerisation of PBT nanocomposite [122].

2.5.3.2 Properties

<table>
<thead>
<tr>
<th>Clay (wt%)</th>
<th>Ult. Str. (MPa)</th>
<th>Ini. Mod. (GPa)</th>
<th>E. B. a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (pure PBT)</td>
<td>41</td>
<td>1.37</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>1.66</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>1.76</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>53</td>
<td>1.80</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>49</td>
<td>1.86</td>
<td>7</td>
</tr>
</tbody>
</table>

* E elongation percentage at break.

The tensile properties of PBT/clay nanocomposites summarised by Chang et al. are given in Table 2.3. The tensile strength of the PBT/clay nanocomposites increases from 41 MPa to 60 MPa with the addition of clay up to a critical loading (about 3 wt.%), and then decreased to 49 MPa at 5 wt.% loading, which can probably be attributed to an agglomeration of the organoclays in the PBT matrix. Chang and co-workers [118] also worked on melt compounded PBT/clay nanocomposites, with
respect to two grades PBT matrices. They found that nanocomposites based on the high viscosity PBT (PBT-B) showed a higher degree of exfoliation of the clay and a higher reinforcing effect compared to the composites based on the low viscosity PBT (PBT-A) (Figure 2. 39). In addition, higher crystallisation temperature were also obtained from the high viscosity PBT based PBT/clay nanocomposites, it was proposed to be due to better dispersion and high degree of exfoliation.

![Figure 2. 39](image)

**Figure 2. 39** Relative tensile modulus $E_{\text{hybrid}}/E_{\text{PBT}}$ (a) and elongation at break (b) as a function of organoclay content [118].

Thermal stability was enhanced by adding organoclays into PBT matrix, as reported by Tripathy et al. [120] that 2 wt.% organoclay C20A loading in-situ polymerised PBT, showed an 8 to 10 °C increment in the onset temperature of degradation, compared with the polymerised c-PBT without any clay. This observation is very much consistent with other nanocomposite systems reported [25, 123]. In addition, there is an optimum amount of clay for improving the thermal stability of the PBT, as it was found that higher organoclay content in the nanocomposites could reduce the thermal stability slightly. However, slightly different results were obtained in melt compounded PBT/clay nanocomposites. [117]. It was reported that the thermal stability decreased slightly from 371.0 °C of pure PBT to 366.5~370.0 °C of PBT/clay nanocomposites, and similar results were also found from Acierno and Scarfato’s work [124]. This may be the result of an antagonistic effect of silicate layers themselves, and the catalytic activity of adsorbed water and the hydroxyl...
groups accelerating the decomposition of the polyester [125]. The crystallisation temperature and degree of crystallinity of the melt compounded PBT/clay nanocomposite were both increased compared to that of pure PBT, which was probably attributed to the heterogeneous nucleation effect of the clay particles [24].

2.6 Applications

Polymer nanocomposites are emerging as a new class of materials and alternatives to conventional composites, due to the nanometer level dispersion of silicate layers in polymer matrix, which remarkably improves performance in mechanical, thermal, barrier, optical, electrical and other physical and chemical properties. These improved properties are generally attained at lower filler content in comparison with conventionally filled systems. Therefore, polymer/clay nanocomposites are lower in density, which makes them quite competitive for specific applications [35]. Furthermore, the development of melt compounding method for polymer/clay nanocomposites enables polymer nanocomposites capable with conventional processing (e.g. extrusion, injection or compression moulding). Therefore, polymer/clay nanocomposites are amenable to most of the common processing techniques in today’s industrial practice, which enables easier commercialisation. In addition, traditional composite formulations require trade-offs between desired performance, mechanical properties, cost and processibility, which can be overcome by polymer nanocomposite technology [126]. Because of the aforementioned attractive characteristics of polymer/clay nanocomposites, a number of industrial applications are involved: automotive (gas tanks, bumpers, interior and exterior panels), construction (building sections and structural panels), aerospace (flame retardant panels and high performance components), food packaging (e.g. with good barrier properties), textiles, electrochemical devices, drug delivery, sensors, medical devices, miscellaneous applications etc. [28, 36, 127-131]. It is for this reason that many companies have taken a strong interest and have invested in developing
nanoclays (Table 2.4) and polymer nanocomposites (Table 2.5).

| Table 2.4 Selected commercial nanoclays [28]. |
|-----------------|-----------------|-----------------|-----------------|
| **Product**     | **Characteristics** | **Applications** | **Producer**    |
| Cloisite        | Organophilic     | Additives to enhance flexural and tensile modulus, barrier properties and flame retardancy of thermoplastics | Southern Clay Products |
| Nanomers        | Microfine powder | Nylon, epoxy, unsaturated polyester, engineering resins | Nanocor |
| Masterbatches   | Pellet           | Thermoplastic olefin and urethane, styrene-ethylene butylene-styrene, ethylene vinyl acetate | PolyOne Corporation, RTP Company |
| Bentone         | With a broad range of polarity | Additives to enhance mechanical, flame retardancy and barrier properties of thermosets and thermoplastics | Elementis Specialties |
| Nanofil         | Improve the mechanical, thermal and barrier properties | Thermoplastics and thermosets | Sud-Chemie |
| PlanoColors     | Nanopigments, e.g. blue, red, green, yellow, high UV-stability | Decorative coloring, UV-stable coloring, heavy metal free coloring | TNO |
| PlanoCoatings   | Additive, excellent transparency and improved barrier properties | Transparent packaging materials, protective coatings, transparent barrier coating | TNO |
Table 2.5 Selected commercial polymer nanocomposites [28].

<table>
<thead>
<tr>
<th>Product</th>
<th>Characteristics</th>
<th>Applications</th>
<th>Producer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon nanocomposites</td>
<td>Improved modulus, strength, heat distort temp., barrier properties</td>
<td>Automotive parts (e.g. timing-belt cover, engine cover, barrier fuel line), packaging (e.g. cosmetics, food, medical electronics), barrier film</td>
<td>Bayer, Honeywell Polymer, RTP Company, Toyota Motors, Ube, Unitika</td>
</tr>
<tr>
<td>Polyolefin nanocomposites</td>
<td>Stiffer, stronger, less brittle, lighter, more easily recycled, improved flame retardancy</td>
<td>Step-assist for GMC safari and Chevrolet Astro vans, heavy-duty electrical enclosure</td>
<td>Basell, Blackhawk Automotive Plastics, General Motors, Gitto Global Corporation, Southern Clay Products,</td>
</tr>
<tr>
<td>M9™</td>
<td>High barrier properties</td>
<td>Juice or beer bottles, multi-layer films, containers</td>
<td>Mitsubishi Gas Chemical Co.</td>
</tr>
<tr>
<td>Durethan KU2-2061 (PA 6)</td>
<td>Doubling of stiffness, high gloss and clarity, reduced oxygen transmission rate, improved barrier properties</td>
<td>Barrier films, paper coating</td>
<td>Bayer</td>
</tr>
<tr>
<td>Aegis™ NC (PA 6/barrier PA)</td>
<td>Doubling of stiffness, higher heat distort temperature, improved clarity</td>
<td>Medium barrier bottles and films</td>
<td>Honeywell Polymer</td>
</tr>
<tr>
<td>SET™ Nanocomposites (PA 12)</td>
<td>Improved stiffness, permeability, fire retardancy, transparency and recycling</td>
<td>Catheter shafts and balloons, tubing, film and barrier, flexible devices</td>
<td>Foster Corporation</td>
</tr>
<tr>
<td>Forte™ nanocomposites</td>
<td>Improved temperature resistance and stiffness, very good impact properties</td>
<td>Automotive, furniture, appliance</td>
<td>Noble Polymer</td>
</tr>
</tbody>
</table>

2.7 Summary

As presented in this literature review, it is clear that polymer/clay nanocomposites have demonstrated significantly superior mechanical properties, compared with unfilled polymer matrices and conventional polymer composites. In addition, very
low loadings of clay typically present in a polymer nanocomposite makes the overall density as low as the unfilled polymer, which increases the processing capability of the resulting polymer nanocomposite. Therefore the applications of polymer/clay nanocomposites will further expand from the current automotive, packaging, coatings and pigments industrial sectors to other areas, including electrics and electronics, building materials and medical devices etc..

However, it should also be noted that large scale production is still in its infancy. The main reason is due to the lack of a basic guidelines for surfactant selection and clay modification, for the purpose of targeting specific polymer matrices [28]. More specifically, although a lot of research has been done on the modification of clays, few of the reports have explained the performance of an organoclay in different polymer matrices; few of these reports have outlined the basic considerations for clay selection with respect to a polymer matrix. Furthermore, although many thermally stable organoclays have been produced for polymer/clay nanocomposites, most of these were not particularly compatible with some important polymer matrices (e.g. PP, PBT etc.). Therefore investigations reported below, will examine these gaps in understanding and so, will further promote the development of polymer/clay nanocomposites.
CHAPTER 3 EXPERIMENTAL WORK

A basic flowchart of the experimental routes undertaken in this research program is presented in Figure 3.1. This shows that clay underwent modification with surfactant materials before being melt compounded and made in test materials. This also indicates the important characterisation and mechanical testing came out organoclays made and their polymer nanocomposites.

Figure 3.1 A flowchart of experimental work.
3.1 Materials

The nanoclays selected for in this study were montmorillonite (MMT). Scanning electron image of representative MMT particles are shown in Figure 3.2. As a starting point, three commercial nanoclays, one sodium montmorillonite (Na-MMT) (Cloisite Na⁺), and two organoclays modified with quaternary ammonium salts (Cloisite 30B and Cloisite 15A) purchased from Southern Clay Product (USA), were used as received. Their properties are summarised in Table 3.1

![FEGSEM image of montmorillonite as received, layered silicates are stacked together by van der Waals forces.](image)

Figure 3.2 FEGSEM image of montmorillonite as received, layered silicates are stacked together by van der Waals forces.
Table 3.1 The main characteristics of commercial nanoclays.

<table>
<thead>
<tr>
<th>Nanoclay</th>
<th>Cloisite Na⁺</th>
<th>Cloisite 15A</th>
<th>Cloisite 30B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supplier</td>
<td>Southern Clay Product</td>
<td>methyl tallow</td>
<td>dimethyl dihydrogenated tallow onium ion where HT is hydrogenated tallow (~65% C18; ~30% C16; ~5% C14)</td>
</tr>
<tr>
<td>Organic modifier</td>
<td>NA</td>
<td>dimethyl dihydrogenated tallow onium ion where HT is hydrogenated tallow (~65% C18; ~30% C16; ~5% C14)</td>
<td>bis-(2-hydroxyethyl) alkyl quaternary ammonium chloride, where HT is tallow (~65% C18; ~30% C16; ~5% C14)</td>
</tr>
<tr>
<td>Structure of organic modifier</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CEC (meq/100g)</td>
<td>92</td>
<td>125</td>
<td>90</td>
</tr>
<tr>
<td>d-spacing, d₀₀₁ (nm)</td>
<td>0.98</td>
<td>3.10</td>
<td>1.80</td>
</tr>
</tbody>
</table>

A series of organic surfactants were chosen for the surface treatment stage, in order to enhance the MMTs compatibility with the polymer matrix. The silane coupling agent, 3-aminopropyltriethoxysilane (APS, Mw≈221.0), was mainly used for further surface modification, and was purchased from Aldrich (UK). It is hydrolytically unstable, with high water solubility of 7.6x10⁵ ml/g (at 25 °C). Ammonium-based surfactants, benzyldimethyl(2-hydroxyethyl) ammonium chloride (BDA), octadecyl amine (ODA) and di-tallow dimethyl ammonium chloride (DTDMA), were used as a second surfactant and purchased from Sigma-Aldrich (UK) and China Resources Oleochem (PR China), respectively. Phosphonium based surfactant, hexyltriphenylphosphonium bromide (HTP) (CH₃(CH₂)₅P(C₆H₅)₃Br) was purchased from Sigma-Aldrich (UK), and the novel surfactants, aminopropylisooctyl polyhedral oligomeric silsesquioxane (AP-POSS) and octaammonium POSS were purchased from Hybrid Plastic Co. (USA). Their molecular structures are shown in Figure 3.3.
CHAPTER 3 EXPERIMENTAL WORK

(a) 3-aminopropyltriethoxysilane

(b) benzylidimethyl(2-hydroxyethyl) ammonium chloride

(c) octadecyl amine

\[
\text{R= tallow fatty alkyl (hydrogenated); including } \sim 65\% \text{ C18; } \sim 30\% \text{ C16; } \sim 5\% \text{ C14}
\]

(d) ditallow dimethyl ammonium chloride

(e) hexyltriphenylphosphonium bromide

(f) aminopropylisooctyl polyhedral oligomeric silsesquioxane

(g) octaammonium polyhedral oligomeric silsesquioxane

Figure 3. 3 Molecular structures of organic surfactants: (a) APS; (b) BDA (Mw=215.7); (c) ODA (Mw=269.5); (d) DTDMA (Mw=556.0); (e) HTP (Mw=429.4); (f) AP-POSS (Mw=1267.3); and (g) OA-POSS (Mw=1173.2).
Polymers matrices used in this study were non-polar propylene homopolymer (PP1013H1), which is an unfilled and widely used PP resin that can be used in medical and pharmaceutical applications, together with maleated polypropylene (PP-g-MA) with graft efficiency of 0.5 to 1.0 wt.% (PO1020) used as a compatibiliser, between reinforcing clays and polypropylene. These polymers were supplied by ExxonMobil Chemical (Belgium). Polar matrix poly(butylene terephthalate) (PBT Celanex 2002-2), is a partially crystalline thermoplastic polyester and produced by melt polycondensation of terephthalic acid dimethylester with 1,4-butanediol. This was supplied by Ticona (UK). Its chemical structure is shown in Figure 3.4b. Polyamide-6 (AKULON), polyamide-11 (BESNO-TL), and polyamide-12 (AESNO-TL) were purchased from DSM and Arkema Canada Inc., respectively, and their chemical structures are also illustrated in Figure 3.4. The basic properties of polymer matrices are summarised in Table 3.2.

![Chemical structures](image)

**Figure 3.4** Chemical structures of (a) homopolymer polypropylene, (b) poly(butylene terephthalate) and (c-e) polyamide-6,-11,-12.
Table 3. 2 Basic properties of the polymers involved in the study.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>PP</th>
<th>PP-g-MA</th>
<th>PBT</th>
<th>PA</th>
<th>PA-11</th>
<th>PA-12</th>
</tr>
</thead>
<tbody>
<tr>
<td>grade</td>
<td>PP1013H1</td>
<td>PO1020</td>
<td>Celanex 2002-2</td>
<td>PA-6 (Akulon)</td>
<td>PA-11 (Besno-TL)</td>
<td>PA-12 (Aesno-TL)</td>
</tr>
<tr>
<td>Supplier</td>
<td>ExxonMobil</td>
<td>Ticona</td>
<td>DSM</td>
<td>Arkema</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mw(g/mol)</td>
<td>&gt;250k</td>
<td>50k~200k</td>
<td>~25k</td>
<td>19K-25K</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Flow property&lt;sup&gt;a&lt;/sup&gt;</td>
<td>7.5</td>
<td>~430</td>
<td>20&lt;sup&gt;b&lt;/sup&gt;</td>
<td>23.5</td>
<td>20.0</td>
<td>18.0</td>
</tr>
<tr>
<td>T&lt;sub&gt;m&lt;/sub&gt; (˚C)</td>
<td>160</td>
<td>160</td>
<td>220-225</td>
<td>215</td>
<td>189</td>
<td>177</td>
</tr>
<tr>
<td>Density (g/cm&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>0.9</td>
<td>0.9</td>
<td>1.31</td>
<td>1.08</td>
<td>1.02</td>
<td>1.01</td>
</tr>
</tbody>
</table>

<sup>a</sup>Melt Flow Index (MFI) measured at H=2.16 kg, T=230˚C

<sup>b</sup>Volume Flow Rate (MVR) measured at H=2.16 kg, T=250 ˚C

3.2 Surface Modification for Montmorillonite

Before clay modification, Na-MMT particles were all heat dried with an air-circulating oven at 100˚C for 16 hours in order to eliminate the adsorbed water from the silicate surface.

3.2.1 Silylation

Typically organoclay (4g) was dispersed in anhydrous ethanol (150 ml) and was stirring continuously and intensively for 2 hours at 20 ˚C in order to swell the nanoclay. A series of different amounts of silane coupling agent APS (1 wt.%, 3 wt.% , 5 wt.%, 10 wt.%, 30 wt.%, 50 wt.%, 100 wt.% and 250 wt.% in the ratio of clay weight) were added into the suspension and stirred at 70˚C for 16 hours. The precipitates were subjected to repeated intensive washes by three cycles of filtration and re-dispersion in ethanol/deionised water solution. The silicate powders were obtained by thermal drying at 70 ℃ for 24 hours and followed by grinding. These are referred to as XAPS-30B /XAPS-15A (X=1, 3, 5, 10, 30, 50, 100, 250). As a comparison, organoclay was washed at the same conditions as silylation, but without...
using silane coupling agent.

### 3.2.2 Surface Modification with Single Surfactant

2 wt.% MMT suspension was prepared and stirred at 20°C for 2 hours in order to swell the silicate layers. HTP/deionised water solutions with various concentrations from 0.3 to 3.0 times of cation exchange capacity (CEC) of MMT, were added into the clay suspension, respectively. The mixtures were intensively stirred at 20°C overnight to achieve the equilibrium. The suspension samples were subsequently centrifuged at 3500 rpm for 50 min to separate the clay particles and supernatant. The clear supernatants were collected for UV spectroscopy measurements (using a Perkin-Elmer Lambda 2, UV/Vis spectrophotometer), and spectra were recorded at \( \lambda = 286 \) nm, through which the equilibrium concentration of the supernatant would be obtained, and consequently the amount of adsorbed surfactant could be calculated by the following equation:

\[
a = \frac{W_s - C_e V}{W_c}
\]

where \( W_s \) and \( W_c \) are the amount of initial surfactant and clay used, respectively. \( C_e \) (g/ml) is the equilibrium concentration of surfactant in the supernatant, and \( V \) is the volume of clay suspension.

The separated organoclay particles were collected and heat dried (70°C for 24 hours). These are referred to as \( X \)HTP/MMT \((X=03, 05, 07, 10, 12, 14, 15, 17, 20 \text{ and } 30)\), respectively.

The POSS modified clays were prepared by a displacement of the sodium cations of Na-MMT with the ammonium ions of the POSS molecule. Similarly, 250 ml of 2 wt.% Na-MMT/deionised water suspension was stirred at 20°C for 2 hours in order
to swell the layered silicates. Then, 10 ml protonated AP-POSS/acetic acid/ethanol solution was added dropwise into the Na-MMT suspension, in which AP-POSS concentration was controlled variously from 0.2, 0.4, 0.6, 0.8 and 1.0 CEC of Na-MMT. The mixed suspension was stirred at 70°C for 16 hours in order to obtain the organoclays denoted as $X$AP-POSS/MMT (where $X$=02, 04, 06, 08, 10). OA-POSS/MMT was prepared in the same way, except that OA-POSS did not need to be protonated by acetic acid.

### 3.2.3 Surface Modification with Dual Surfactants

Typical dual-surfactant modified Na-MMTs were prepared as follows: two separate anhydrous ethanol solutions (10 ml) containing 0.4 CEC POSS and 0.8 CEC of DTDMA, respectively, were magnetically stirred to dissolve the surfactants, followed by the addition of the same molar ratio of acetic acid at 20°C and then stirred for a further 1 hour for protonation. The two separate protonated surfactant solutions then were added dropwise into the Na-MMT suspension at 70°C, with vigorous stirring. The mixture was stirred at 70°C for 16 hours and the dual-surfactant modified clays obtained were denoted as 04AP-POSS/08DTDMA/MMT and 04OA-POSS/08DTDMA/MMT, respectively.

### 3.3 Sample Preparation

#### 3.3.1 PP/Clay Nanocomposites

PP and PP-g-MA pellets were heat dried with an air-circulating oven at 80°C for 16 hours and physically mixed with clays before melt compounding, which was carried out in a Haake internal mixer (Haake Rheocord 9000, Haake Co., Germany), at 190°C barrel temperature, 60 rpm of rotor speed and 30 minutes of residence time. The obtained samples were then compressed into sheets with 1 mm thickness, at
190°C under 10 tonne/100 cm² pressure for 3 minutes. The PP nanocomposite samples prepared are summarised in Table 3.3.

### Table 3.3 PP samples prepared with various organo-montmorillonites.

<table>
<thead>
<tr>
<th>Composites</th>
<th>PP (wt.%)</th>
<th>PP-g-MA (wt.%)</th>
<th>Clays (ppg)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP/Na</td>
<td>100</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>PP/30B</td>
<td>100</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>PP/15A</td>
<td>100</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>PP/MP3/15A</td>
<td>97</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>PP/MP4.5/15A</td>
<td>95.5</td>
<td>4.5</td>
<td>3</td>
</tr>
<tr>
<td>PP/MP6/15A</td>
<td>94</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>PP/MP10/15A</td>
<td>90</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>PP/MP10/Na</td>
<td>90</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>PP/MP10/APS-Na</td>
<td>90</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>PP/MP10/30B</td>
<td>90</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>PP/MP10/APS-30B</td>
<td>90</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>PP/MP10/APS-15</td>
<td>90</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>PP/MP10/04APP-MMT</td>
<td>90</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>PP/MP10/04APP-08BDA-MMT</td>
<td>90</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>PP/MP10/04APP-08ODA-MMT</td>
<td>90</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>PP/MP10/04APP-08DTDMA-MMT</td>
<td>90</td>
<td>10</td>
<td>3</td>
</tr>
</tbody>
</table>

* pp: parts per gram (i.e. 3 g clays per 100g polymers)

### 3.3.2 PBT/Clay Nanocomposites

PBT pellets were heat dried with an air-circulating oven at 100°C for 16 hours and physically mixed with selected clays, which were subjected to melt compounding in a Haake internal mixer (Haake, Rheocord 9000, Haake Co., Germany), at 240°C barrel temperature, 60 rpm of rotor speed and 15 minutes residence time. The resultant samples were compressed at 235°C for 5 min under the pressure of 10 tons/100 cm², and then subjected to further testing. The PBT composites samples prepared are listed in Table 3.4
### Table 3.4 PBT samples prepared with various organo-montmorillonites

<table>
<thead>
<tr>
<th>Composites</th>
<th>PBT 2002-2 (wt.%)</th>
<th>Clays (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBT</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>PBT/Na</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>PBT/30B</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>PBT/15A</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>PBT/APS-30B</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>PBT/HTP/MMT</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>PBT/04AP-POSS/MMT</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>PBT/04AP-POSS/08BDA/MMT</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>PBT/04AP-POSS/08ODA/MMT</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>PBT/04AP-POSS/08DTDMA/MMT</td>
<td>97</td>
<td>3</td>
</tr>
</tbody>
</table>

### 3.3.3 PA/Clay Nanocomposites

All grades of PA pellets were heat dried with an air-circulating oven at 100 °C for 16 hours before use. The polyamide 6, 11 and 12 layered silicate nanocomposites were prepared in a Haake internal mixer (Haake, Rheocord 9000, Haake Co., Germany), at the barrel temperature of 240 °C, 220 °C and 210 °C, respectively for 15 min residence time and 60 rpm shear speed. These samples are listed in Table 3.5.

### Table 3.5 PA samples prepared with various organo-montmorillonites.

<table>
<thead>
<tr>
<th>Composites</th>
<th>PA6 (%)</th>
<th>PA11 (%)</th>
<th>PA12 (%)</th>
<th>Clays (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA6</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA6/04APP-08DTDMA-MMT</td>
<td>97</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA11</td>
<td></td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA11/04APP-08DTDMA-MMT</td>
<td>97</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA12</td>
<td></td>
<td></td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>PA12/04APP-MMT</td>
<td>97</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA12/04OAP-MMT</td>
<td>97</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA12/04APP-08DTDMA-MMT</td>
<td>99</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA12/04APP-08DTDMA-MMT</td>
<td>97</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA12/04APP-08DTDMA-MMT</td>
<td>95</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA12/04APP-08DTDMA-MMT</td>
<td>90</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA12/04OAP-08DTDMA-MMT</td>
<td>97</td>
<td>3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.4 Characterisation

3.4.1 Infra-red Spectroscopy

Fourier Transform Infra-red (FTIR) is commonly used for qualitative identification of various chemical or molecular functionalities. FTIR can be used to tell us whether the adsorption of organic surfactant at clay surface has occurred. Before testing, a certain amount of organoclays (1 mg) was ground with KBr powder and compressed into pellets in the same conditions. Subsequently, FTIR spectra were recorded in the spectral range 400 to 4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) by a Perkin-Elmer FTIR spectrometer at ambient conditions, after 64 times repeat scans.

3.4.2 X-ray Diffraction

Wide angle X-ray diffraction was commonly used to determine clay minerals in terms of their ‘d’ values. This is because XRD is a very useful technique that can be used to identify the crystalline structures according to the variable structure spacing, following Bragg’s law equation:

\[ 2d\sin\theta = n\lambda, \]

where \(d\) is the spacing between atomic planes in the crystalline phase, \(\lambda\) is the wavelength of X-ray, and \(2\theta\) is the diffraction angle of the diffracted X-ray. Regarding the structure of montmorillonite (Figure 3. 5), the repeating ‘d’ value, basal spacing, consists of the thickness of a silicate layer and the interlayer.
All the XRD spectra of clay and polymer/clay nanocomposite samples were recorded using Cu$_{K\alpha}$ radiation ($\lambda=0.1542$ nm) on a Bruker AXS, D8 Advance Diffractometer operated at 40 kV and 100 mA with a divergence slit of 1.0 ° between 1.0 and 10.0 ° (2θ) at a step size of 1 °/min, and the corresponding basal spacing was calculated from the Bragg’s law equation.

### 3.4.3 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) makes a continuous weighing of a small sample (ca. 10 mg) in a controlled atmosphere (e.g. air or nitrogen) as the temperature is increased at a programmed linear rate. The resultant thermogram records weight loss due to the desorption of gases (e.g. moisture) or decomposition of organic components from the sample. It is very useful for quantitatively analyse of organic content of the organoclay and in turn, indicate the thermal stability of the organoclays. In this study, all the clay samples were analysed with a Setaram TGA 92 Thermobalance, controlled in a nitrogen atmosphere at 10 °C/min heating rate over the temperature range 30 to 700 °C.
3.4.4 Contact Angle Measurement

The surface energies of the clay minerals were measured by using a contact angle system OCA (Dataphysics Instrument GmbH, Germany) via sessile drop method with double distilled water and diiodomethane. Prior to the test, all the clay powders were pressed into platelets (5 mm in radius) with 10 tonne force for 2 minutes at room temperature. Average values of every three drops were taken, and the surface free energies were calculated by the Owens-Wendt-Rabel-Kaelble equation [132, 133]:

\[
\sqrt{\sigma_s^D \sigma_i^D} + \sqrt{\sigma_s^P \sigma_i^P} = \frac{\sigma_i (\cos \theta + 1)}{2}
\]

where \(\sigma_s^D\) and \(\sigma_s^P\) is the disperse and polar component to solid surface energy, respectively; \(\sigma_i^D\) and \(\sigma_i^P\) is the disperse and polar component to liquid surface energy; \(\theta\) is contact angle between solid and liquid phases. The standard surface free energies of the reference liquids measured by Ström et al. [134] were selected for the calculation from the programme.

3.4.5 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a common method of obtaining qualitative information about the dispersion of particles in a polymer matrix. To evaluate the morphology of polymer/clay nanocomposites, all the samples were embedded in cured epoxy blocks and cut at room temperature using an ultramicrotome (Ultracut-1, UK) with a diamond knife. Thin TEM specimens, 50-100 nm, were collected in a trough filled with water and placed on a 200 mesh copper grid. TEM images were obtained on a JEOL 2000FX microscope with an acceleration voltage of \(~120\) kV.
3.4.6 Differential Scanning Calorimetry

A non-isothermal differential scanning calorimeter (Paris 1, Perkin Elmer Co., Norwalk CT) was used for thermal analysis of PA 12 and its nanocomposites at a nitrogen atmosphere. The samples were analysed following temperature program: heated up from 25 ºC to 250 ºC at 20 ºC/min to eliminate the specimen’s heat history; maintained for 1 min at 250 ºC, followed by cooling the specimen to 25 ºC at 10 ºC/min; maintained for another 1 min before heating again to 250 ºC at 10 ºC/min. The degree of crystallinity, Xc, of the samples was calculated according to Eq.3.2

\[ X_c = \frac{\Delta H_m}{\Delta H_m^0(1-\phi)} \times 100\% \]  
Eq. 3.2

where $\Delta H_m$ is the measured heat fusion for the samples, (on second heating) and $\Delta H_m^0$ is the heat of fusion for 100 % crystalline PA 12, which is 209.2 j/g [80].

3.4.7 Tensile Test

Dumbbell specimens for mechanical testing were cut from 1 mm thick hot pressed sheets. Tensile modulus, yield strength, tensile strength and elongation at break were measured at ambient temperature, using a Hounsfield universal testing machine (UK), with a crosshead speed of 50 mm/min for PP/clay and PA/clay nanocomposites, and 5 mm/min for PBT/clay nanocomposites. The average values were calculated from five runs for each sample.
CHAPTER 4 RESULTS AND DISCUSSION

In this chapter, the results of organically modified clays (i.e. silylation, single surfactant modification and dual-surfactant modification), in terms of interlayer spacing, thermal stability and surface properties, are presented and discussed. Their morphological properties in polymer matrices (i.e. PP, PBT and PAs) and corresponding tensile properties of polymer/clay nanocomposites are also conducted.

4.1 The Effect of Surfactants on Interlayer Space of Montmorillonite

4.1.1 Grafting of APS

The IR spectra of silane coupling agent APS, commercial clays before and after silane treatment are presented in Figure 4. 1a. It can be seen from Figure 4. 1a that the characteristic bands at 1084 cm$^{-1}$, 1334 cm$^{-1}$, 1384 cm$^{-1}$, 2850 cm$^{-1}$ to 3000 cm$^{-1}$ and 3440 cm$^{-1}$ corresponding to Si-O-CH$_3$, stretching vibration, C-O, CH$_3$, C-H and OH stretching vibration of adsorbed water for organic compound APS, respectively [135-137]. After silylation to Na-MMT, a new peak appeared at 2931 cm$^{-1}$ and a small shoulder at 2850 cm$^{-1}$ (Figure 4. 1b), due to the asymmetric stretching and vibrations of the methylene groups [138], while the new peaks at 1557 cm$^{-1}$ and 1457 cm$^{-1}$ are attributed to the NH$_2$ vibration [139]. When Cloisite 30B was silylated, the peak at 3430 cm$^{-1}$ (OH from adsorbed water), was significantly reduced. Not much difference was observed from the FTIR spectra of Cloisite 15A before and after silylation (Figure 4. 1d).
Figure 4.1 FTIR spectra of APS and commercial clays before and after silylation.

The principle of silylation can be described in two steps, hydrolysis and polymerisation [140, 141], as shown in the following reactions, (as shown by a and b in Figure 4.2).

\[
\begin{align*}
\text{H}_2\text{N} \equiv \text{Si} &\equiv \text{(OE)}_3 + \text{H}_2\text{O} \quad \rightarrow \quad \text{H}_2\text{N} \equiv \text{Si} \equiv \text{(OH)}_3 + \text{EtOH} & \quad \text{(a)} \\
\text{H}_2\text{N} \equiv \text{Si} \equiv \text{(OH)}_3 + \text{Clay} \quad &\rightarrow \quad \text{Clay} \quad \text{H}_2\text{N} \equiv \text{Si} \equiv \text{(OH)}_2 + \text{H}_2\text{O} & \quad \text{(b)} \\
\text{H}_2\text{N} \equiv \text{Si} \equiv \text{(OH)}_3 &\quad \rightarrow \quad \text{H}_2\text{N} \equiv \text{Si} \equiv \text{(OH)}_2 \quad \text{Si(OH)}_2 \equiv \text{NH}_2 & \quad \text{(c)}
\end{align*}
\]

Figure 4.2 Possible reactions during the silylation on montmorillonite.
CHAPTER 4 RESULTS & DISCUSSION

The hydrolysed silane molecules can combine with the hydroxyl groups by mean of condensation reaction at the clay surface and broken edges to form a siloxane linkage. The successful grafting of the silane coupling agent on the MMT surface can be observed from FTIR spectrum of APS, whose characteristic bands at 2931 cm\(^{-1}\) and 2850 cm\(^{-1}\), are attributed to the asymmetric stretching and vibrations of the methylene groups. Bands at 1557 cm\(^{-1}\) and 1457 cm\(^{-1}\) corresponded to the NH\(_2\) vibration appearing after Na-MMT was silylated with APS, mostly due to the reactions with hydroxyl groups at the broken edges of the silicate layers or the self-condensed form of polysiloxane oligomers adsorbed on the silicate surface (reaction c in Figure 4.2) [142]. However, the intensity of the new peaks was weak, suggesting that the degree of grafting of APS was low and, in turn, the reactive –OH groups at MMT surface or broken edges were not sufficient.

The reduction in relative peak intensity at 3430 cm\(^{-1}\) and 3630 cm\(^{-1}\) for APS-30B infrared spectra, corresponding to OH from adsorbed water and OH from the silicate frame [143], respectively, was due to the reactions between the silane coupling agent APS and OH groups from silicate layers. However, it is difficult to identify the grafting APS for 15A, as shown by Figure 4.1d. 15A clay was modified with an excess amount of organic surfactant, as evidenced by TGA result, (presented in section 4.2), which may isolate the APS from silicate layers and make it difficult to react with the OH groups of silicate frame. Consequently, it is difficult to detect the response of silylation. On the other hand, APS might self-condense and present in the form of polysiloxane oligomer rather than grafting at silicate surface.
Figure 4.3 XRD patterns of commercial clays and their silylated derivatives: a) Cloisite Na⁺, b) APS-Na, c) Cloisite 30B, d) APS-30B, e) Cloisite 15A, and f) APS-15A, where 100 wt.% APS was used for all silylated clays.

The changes in interlayer spacing further evidenced the grafting or adsorbing of APS at the clay surfaces. Figure 4.3 shows the XRD diffraction patterns of both Cloisite Na⁺ and Cloisite 30B, with the characteristic peaks at 2θ=9.3° for Cloisite Na⁺ and 2θ=6.0° for Cloisite 30B, respectively, shifted to lower angles after silylation with APS corresponding to the interlayer spacing, which increased from 0.98 to 1.40 nm for Cloisite Na⁺ and from 1.80 to 1.90 nm for Cloisite 30B, respectively. However, increased diffraction angle (2θ) was observed for Cloisite 15A after silylation, i.e. giving a reduction in the interlayer space from 3.10 nm to 2.50 nm.
In order to find out the reason for this reduction, different amounts of silane coupling agent APS were used to modify Cloisite 15A. Figure 4. 4a presents the influence of different amounts of APS on the interlayer spacing, and it shows that, the interlayer space of Cloisite 15A was reduced from 3.10 nm to ~2.50 nm, regardless the function of APS contents, which is very close to the value of organoclay 15A after washing ($d_{001}$=2.53 nm) as shown in Figure 4. 4b. According to the TGA results presented in section 4.2.1, more than 1.3 CEC organic surfactant was present in commercial organoclay Cloisite 15A, and numbers of surfactant molecules adhere to the surface-adsorbed surfactant cations by van der Waals forces [144], which could be easily dissolved in organic solvent, e.g. ethanol which was used in silylation. The increased sharpness and intensity of the XRD pattern after washing imply that the structure of organoclay is more efficiently ordered than that of unwashed [42]. This is also an indirect evidence of excessive organic surfactants in Cloisite 15A that resulted in disrupted clay structure.
Figure 4.4 (a) The influence of APS concentrations on the interlayer spacing of APS grafted Cloisite 15A; (b) the effect of washing process on the interlayer space of Cloisite 15A.

4.1.2 Phosphonium Surfactant Modified Montmorillonite

The effect of alkyl phosphonium surfactant (HTP) on the interlayer spacing of organically modified MMTs, was investigated by WAXD (Figure 4.5). The interlayer space increased along with the increasing amounts of HTP surfactant until
an adsorption isotherm of organic surfactant reached. The basal space of HTP/MMT increased from 0.98 nm for unmodified MMT (Cloisite Na⁺) to 1.76 nm, suggesting that the organic surfactant HTP molecules were successfully intercalated into the clay galleries. The characteristic reflection at 2θ=5° (corresponding to $d_{001}=1.76$ nm) remained constantly until 1.0 CEC HTP, indicating that the cation exchange in the clay galleries was completed [42]. Once ion-exchange was finished, further adsorption of HTP into clay galleries introduced a pressure between the silicate layers, resulting in the change of surfactant molecules assembly, and finally forcing the gallery to be expanded, resulting in increase of the basal spacing to 1.97 nm above ~1.6 CEC of adsorbed HTP, as illustrated in Figure 4.5.

![Figure 4.5 d-spacing of HTP modified MMT as the function of HTP contents](image)

Based on the data of bond length, atomic radius and the bond angle, the dimensional parameters of the HTP surfactant molecule were calculated by using Chemoffice 2004 and presented in Figure 4.6, where the mauve ball represents the phosphorous
atom, the right part of which is alkyl chain, and three phenyl groups located at the left side. The size of HTP molecule may vary with its orientation. When the plane of the zigzag arrangement of the carbon atom of HTP is perpendicular to the plane of the silicate layer, the height of triphenyl side is ~0.75 nm and that of alkyl side is ~0.323 nm (Figure 4. 6a). These values changed to ~0.75 nm and ~0.287 nm respectively when the plane of the zigzag arrangement of the carbon atoms of HTP is parallel to the plane of silicate layer (Figure 4. 6b). As the thickness of a single silicate layer is about 0.97 nm [145] and two constant basal spacing values of HTP/MMT are 1.76 nm and 1.97 nm, respectively, it can be deduced that the formation of a lateral monolayer arrangement before 1.0 CEC HTP as the interlayer space (1.76-0.97=0.79 nm) is very close to the height of HTP surfactant (~0.75 nm) and an overlapped bilayer arrangement after ~1.6 CEC of HTP surfactant in the clay galleries, respectively, since the interlayer space of >1.6 CEC HTP modified MMT is ~1.00 nm (1.97-0.97 nm), which is close to the height of triphenyl group (0.75 nm) plus the height of alkyl carbon chains (0.29~0.32 nm).
Figure 4.6 Molecular conformation of HTP, (a) plane of the zigzag arrangement of the carbon atoms of HTP is perpendicular to the plane of the montmorillonite layer; (b) the plane of the zigzag arrangement of the carbon atoms of HTP is parallel to the plane of the montmorillonite layer.
4.1.3 Montmorillonite Modified with Polyhedral Oligomeric Silsesquioxane (POSS)

![XRD patterns of Na-MMT, AP-POSS and various amounts AP-POSS modified MMT (a); and OA-POSS and various amounts of OA-POSS modified MMT (b).](image)

**Figure 4.** XRD patterns of Na-MMT, AP-POSS and various amounts AP-POSS modified MMT (a); and OA-POSS and various amounts of OA-POSS modified MMT (b).
The effect of aminopropylisoctyl POSS (AP-POSS) and octaammonium POSS (OA-POSS) concentrations on the interlayer spacing of POSS modified MMTs was investigated and the XRD patterns of AP-POSS and OA-POSS modified clays are shown in Figure 4. 7a and b, respectively. The XRD patterns for Na-MMT, and POSS are also presented in Figure 4. 7 as the corresponding reference. The POSS surfactants show characteristic reflections at ~7.2° for AP-POSS and ~6.9° and ~7.3° for OA-POSS are attributed to the aggregation of POSS molecules [146]. For the AP-POSS modified MMTs, the basal spacing increased from 0.98 nm for unmodified MMT to 1.25 nm for 0.2 CEC AP-POSS/MMT and ~3.40 nm for 0.4 CEC AP-POSS/MMT, indicating the intercalation of AP-POSS surfactant into the clay galleries. Strong (001), (002) and (003) reflections with d-values of >3.4 nm, 1.8 nm and 1.2 nm observed in 0.4 CEC and higher AP-POSS modified MMTs were due to the formation of a percolated structure based on the tactoids as claimed by Burgentzlé et al. [147] and Fox et al. [148]. Similar XRD results were observed in other studies [149, 150]. The basal spacing of over 3.5 nm for AP-POSS modified MMTs suggested that the POSS molecules were arranged in a double layer structure in the interlayer, as the average size of POSS cubic is about 0.5 nm to 1.5 nm [54, 55, 151] depending on the organic functional groups attached at cubic corners, and 1.8 nm basal spacing for a single layer structure [152, 153]. The appearance of a third reflection at ~7.3° (003) implies a greater degree of layered silicate structure than those without the (003) peak [148]. Unlike typical surfactants with long floppy alkyl chains, POSS molecules are really rigid and incompressible, once a bilayer structure has been achieved, the interlayer spacing will not change dramatically due to the strong hydrophobic interactions associated with the POSS cages [154, 155]. This has been shown by the XRD reflections of AP-POSS/MMT in Figure 4. 7a, where 0.4, 0.6, 0.8 and 1.0 CEC AP-POSS modified MMTs appeared to possess similar \( d_{001} \) values between 3.50 and 3.87 nm.

However, different results were observed for OA-POSS modified MMTs whose basal spacing did not change with OA-POSS concentration, remaining at ~1.64 nm.
He and Zhang [151] reported that the dimension of an octaammonium-POSS molecule is about 0.5nm to 0.6nm. Therefore, a single layer arrangement of OA-POSS molecules was formed by OA-POSS/MMT (1.64-0.97=0.67 nm). The molecule of OA-POSS contains eight ammonium groups, present at the corners of cubic POSS surfactant, all of which could be involved in an exchange of Na$^+$ ions in the interlayer. The formation of ionic bonds between silicate layers and OA-POSS molecules may prevent more OA-POSS from penetrating into the interlayer space to generate larger basal spacing, even though larger amounts of OA-POSS were used.

Table 4.1 presents the weight loss of the POSS modified MMTs measured by TGA, the exchange efficiency (the ratio of experimental weight loss to theoretic weight loss), exchange ratio in percentage of exchanged POSS cations to sodium cations based on the ion-exchange capacity of the silicate (92 meq/100g), and the surface coverage calculated based on the number of exchanged POSS molecules, the specific area of MMT (750 m$^2$/g) [2] and the particle size of POSS surfactant (~1.5 nm). It can be seen that a saturated cation exchange was achieved after 0.6 CEC AP-POSS was used to modify MMT since very little weight loss changes (less than 1.0%), were observed between 06AP-POSS/MMT and 10AP-POSS/MMT, compared to
8.8% weight loss between 04AP-POSS/MMT and 06AP-POSS/MMT. Consequently, the exchange efficiency reduced from ~65.0 % for 0.6 CEC AP-POSS/MMT to less than 50.0 % for 1.0 CEC AP-POSS. A similar tendency was observed for exchange ratio and surface coverage, which a constant value (~35.0 % for exchange ratio and ~58.0 % for surface coverage) was achieved for >0.6 CEC AP-POSS modified MMTs.

Although the ion-exchange process is not quantitative, and it was very difficult to control in ideal conditions, the relative low exchange ratio, (compared to those common alkyl ammonium surfactant modified clays), could lead to a number of hydrophilic silicate surfaces being uncovered. This was found to be even worse in OA-POSS modified MMTs at the maximum adsorption reached at 0.2 CEC of OA-POSS, only about 12.2 % of exchangeable Na+ ions were displaced by OA-POSS molecules, leaving about 80 % of the silicate surface uncovered.

The relatively low exchange ratio was probably due to the large molecular size of the rigid POSS, which prevented other POSS surfactant molecules from further exchanging. Also the replacement of the interlayer cations and the covering of the internal surface were often not quantitative during the penetration process, and the increasing number of contacts reduced the mobility of the POSS cations. Hence they could not occupy the whole interlayer space but instead accumulated near the edges without formation of any chemical bonding [152]. Additionally, a very low exchange ratio for the OA-POSS modified MMTs is probably attributed to the formation of chemical bonds between both silicate layers of the interlayer space by a single OA-POSS molecule, which will have restricted the ion-exchange with other free OA-POSS surfactants, as discussed previously. Therefore, both POSS modified MMTs were partially intercalated with some hydrophilic silicate surface areas exposed, which may be unbenefficial for compatibility with the hydrophobic polymer matrix.
4.1.4 Dual-Surfactant Modified Montmorillonite

Both a large interlayer spacing of the modified clay and a good compatibility between the polymer and the modified clays are essential in order to achieve an intercalation/exfoliation of the modified MMT in the polymer matrix. Although a high concentration of POSS modified MMT may provide more coverage on a hydrophilic clay surface, a large amount of rigid and bulky POSS present inside the clay galleries could have also physically inhibited further intercalation of polymer chains. Boo et al. [156] reported that in some cases, the conformational freedom of the intercalating chains is more critical than a large interlayer spacing to form an intercalated and/or exfoliated structure. Therefore this could be an effective way of producing the intercalated or exfoliated structures by using two different structured surfactants. The reason is being that POSS could provide a large interlayer spacing and a second surfactant, with long flexible alkyl chains, could further modify the partially modified silicates and consequently improve the compatibility between polymer and modified clays.

Figure 4. 8 illustrates the mechanism of the ion-exchange for a dual-surfactant modified clay. Because of the physical hindrance effect generated by the large and rigid POSS surfactants, POSS molecules are difficult to exchange with Na\(^+\) cations fully in the clay galleries, resulting in some of the hydrophilic clay surfaces being exposed and there being poor compatibility between the polymer and organoclays. With the introduction of a second, more flexible surfactant, the exposed hydrophilic clay surfaces can be covered by these hydrophobic organic chains, resulting in better compatibility between polymer matrix and organoclays.
The XRD patterns of the modified MMTs, using three different dual-surfactant combinations, are shown in Figure 4.9. Three strong reflections associated with (001), (002) and (003), were weakened or disappeared in the organoclays modified by dual-surfactant, compared with those only AP-POSS modified MMTs. This suggested that the ordered layered structure was disturbed by the introduction of the second surfactant. It can be seen that 04AP-POSS/08BDA/MMT exhibited the largest $d$-spacing of 4.16 nm while 04AP-POSS/08DMDTA/MMT had the smallest $d$-spacing of 3.24 nm.

![Figure 4.8 Schematic illustration of the mechanism of dual-surfactant modified clay](image)

**Figure 4.8** Schematic illustration of the mechanism of dual-surfactant modified clay

![Figure 4.9 XRD patterns of three organoclays](image)

**Figure 4.9** XRD patterns of three organoclays: 04AP-POSS/08BDA/MMT, 04AP-POSS/08ODA/MMT, and 04AP-POSS/08DMDTA/MMT.
Regarding the molecular structures of the second surfactants, BDA has the shortest molecular chain length which better enabled it to penetrate into the inter-space between POSS molecules, to take part in the ion-exchange with the un-reacted Na\textsuperscript{+} cations. This may consequently increase the $d$-spacing. Moreover, the OH group present in BDA molecules may also interacted with OH groups at the edges of silicate layers and disturbed the structure of the layered clays, which was reflected in the broadened peaks and decreased intensity of XRD peak [83, 157]. The 04AP-POSS/08DMDTA/MMT, DMDTA molecule has two long alkyl tallow chains with a large molecular volume, which will have had greater difficulties to penetrate the inter-space between the POSS surfactants during the ion-exchange reactions, resulting in a smaller $d$-spacing. For 04AP-POSS/08ODA/MMT, the chain length and molecular volume of ODA is between that of BDA and DMDTA. The resultant $d$-spacing (3.52 nm) therefore was formed in the middle of the other two organoclays.

As a comparison, the interlayer structure of 04AP-POSS/08DTDMA/MMT and 04OA-POSS/08DTDMA/MMT were studied and presented in Figure 4. 10, together with their single POSS modified MMTs. The (001) reflection of 04AP-POSS/08DTDMA/MMT remained almost the same as that of 04AP-POSS/MMT’s but became broader, the (002) and (003) reflections either disappeared or shifted to lower angles, suggesting that the second surfactant DTDMA was intercalated and presumably covered the unmodified clay mineral surface. The unchanged (001) reflection is mostly due to the formation of a stable bi-layer structure of intercalated AP-POSS.

Different results were observed in OA-POSS/MMT, where the basal spacing was increased from 1.64 nm for 04OA-POSS/MMT to 2.16 nm for 04OA-POSS/08DTDMA/MMT, indicating intercalation of the second surfactant DTDMA. As a large molecular volume was provided by the second surfactant DTDMA, it was most probable that a large pressure was generated between
interlayers which weakened the hydrogen bonding between OA-POSS molecules and silicate surface, and expanded the interlayer space. In the meantime, more unmodified silicate surfaces were covered by the DTDMA while increasing of interlayer space.

Figure 4.10 XRD patterns of four organo-montmorillonites: 04AP-POSS/MMT, 04OA-POSS/MMT, 04AP-POSS/08DTDMA/MMT and 04OA-POSS/08DTDMA/MMT.

4.2 The Influences of Surfactants on Thermal Stability of Organo-Montmorillonites

The thermal stability of organo-montmorillonites (O-MMT) was investigated by use of thermogravimetric (TGA) and derivative thermogravimetric (DTG) analyses, in order to determine the changes in weight in relation to changes in temperature, and to determine the point at which weight loss is most apparent, respectively. Table 4.2
summarises the thermal properties of organoclays, by TGA and DTG, in the temperature range of 200 and 500 °C, in which most organic compounds are decomposed [87]. Based on the weight loss and molecular weights of surfactant, the amount of organic surfactant in O-MMTs was calculated, which was an indirect indication of thermal properties of O-MMTs, as higher amounts of organic compounds will reduce the thermal stability of O-MMTs. The first major decomposition by organic compounds between 200 and 500 °C, from the DTG peak, was taken as an index of the thermal stability of the O-MMTs.

<table>
<thead>
<tr>
<th>Clays</th>
<th>Weight Loss % (200-500°C)</th>
<th>Adsorbed surfactant (CEC)</th>
<th>DTG peak (1st) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloisite Na⁺</td>
<td>0.8</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Cloisite 30B</td>
<td>18.7</td>
<td>0.86</td>
<td>215</td>
</tr>
<tr>
<td>Cloisite 15A</td>
<td>39.8</td>
<td>1.34</td>
<td>233</td>
</tr>
<tr>
<td>APS/MMT</td>
<td>14.5</td>
<td>N/A</td>
<td>262</td>
</tr>
<tr>
<td>APS/30B</td>
<td>28.0</td>
<td>N/A</td>
<td>250</td>
</tr>
<tr>
<td>APS/15A</td>
<td>33.5</td>
<td>0.98</td>
<td>326</td>
</tr>
<tr>
<td>HTP/MMT</td>
<td>29.0</td>
<td>1.07</td>
<td>312</td>
</tr>
<tr>
<td>04AP-POSS/MMT</td>
<td>17.9</td>
<td>0.20</td>
<td>315</td>
</tr>
<tr>
<td>08AP-POSS/MMT</td>
<td>25.7</td>
<td>0.33</td>
<td>318</td>
</tr>
<tr>
<td>04OA-POSS/MMT</td>
<td>10.8</td>
<td>0.12</td>
<td>354</td>
</tr>
<tr>
<td>08OA-POSS/MMT</td>
<td>12.3</td>
<td>0.14</td>
<td>354</td>
</tr>
<tr>
<td>04AP-POSS/08BDA/MMT</td>
<td>22.0</td>
<td>0.50</td>
<td>330</td>
</tr>
<tr>
<td>04AP-POSS/08ODA/MMT</td>
<td>27.0</td>
<td>0.77</td>
<td>220</td>
</tr>
<tr>
<td>04AP-POSS/08DTDMA/MMT</td>
<td>34.4</td>
<td>0.74</td>
<td>295</td>
</tr>
<tr>
<td>04OA-POSS/08DTDMA/MMT</td>
<td>16.0</td>
<td>0.25</td>
<td>270</td>
</tr>
</tbody>
</table>

Generally, the weight loss of O-MMT occurs in three stages: (1) the free water loss in the temperature below 200 °C; (2) degradation and loss of organic compounds in the temperature range of 200 to 500 °C; (3) loss of water from the clay structure in the temperature range of >500 °C. The multiple events are attributed to the nanoscopic dimensions of the interlayer influencing the reaction kinetics, product transfer and volatilisation [46].
4.2.1 Commercial Clays

TGA thermograms of Cloisite Na\(^+\) and other two commercial organoclays show approximately 4 wt.% and 1 wt.% weight loss below 200 °C, and a total weight loss of 8.8 wt.%, 22.0 wt.% and 42.9 wt.% for Cloisite Na\(^+\) and Cloisite 30B and Cloisite 15A, respectively up to temperature of 700 °C (Figure 4.11).

Figure 4.11 TGA and DTG thermograms of commercial clays, Cloisite Na\(^+\), Cloisite 30B and Cloisite 15A.

The weight loss below 200 °C was due to the elimination of free water (water between particles and absorbed on the external surface of clays) and/or water molecules around the exchangeable sites in clay galleries. It was reported that bulk interlayer water is present in natural montmorillonite (Na-MMT), with the inner (primary) hydration shell around the exchangeable cation and the outer (secondary) coordination sphere of the cation due to the hydrated sodium cation [87]. However,
there is no interlayer water in the O-MMT, as the quaternary ammonium salt has been exchanged for the sodium cation in Cloisite 30B and Cloisite 15A. Therefore, only ~1 wt.% (free water) appeared for Cloisite 30B and Cloisite 15A at a lower temperature, below 200 °C. Similar results have been also observed by other researchers [45, 158].

DTG curves indicated that the thermal decompositions of the MMT occurred due to the phase transformation. Apart from a decomposition below 200 °C, there was another decomposition for Cloisite Na⁺ between 500 to 700 °C (~640 °C), which was due to the dehydroxylation of the MMT [159, 160]. Between 200 and 500 °C, Cloisite Na⁺ did not undergo any thermally changes. Therefore, the peaks in this region for Cloisite 30B and Cloisite 15A could be attributed to the organic surfactants [125, 161]. There were two main separated peaks observed for Cloisite 30B at 256 °C and 360 °C. These were attributed to the thermal decomposition of physically adsorbed and intercalated via ion-exchange reaction organic surfactants, respectively.

As Xi et al. [162] described, there are three different molecular environments found in MMTs modified by ammonium based surfactants: (1) surfactant molecules intercalated into clay galleries via ion-exchange reaction; (2) surfactant molecules physically adsorbed on the silicate surfaces; and (3) surfactant molecules adhering to the surfaces of adsorbed surfactants via van der Waals forces, which is normally presented when excess amounts of surfactants are used, and their properties are very similar to those pure surfactants. Therefore a small shoulder at 215 °C was attributed to the small amount of surfactants that self-adhered. Intercalation by the surfactant caused a relatively high phase transformation temperature compared to the surfactant alone [163], since any motion of intercalated surfactant will be restricted by the silicate layers; this was reflected by the decomposition peak at 360 °C. It is also worth mentioning the smaller peak at 274 °C, which can be attributed to the thermal degradation of the organic ions, as the ammonium ions did not completely volatilise
in the first major degradation step (256 °C), and a small amount of carbonaceous residual remained, which was burned at a higher temperature [158, 164]. In the temperature range of 500 to 700 °C, the dehydroxylation temperature of Cloisite 30B was shifted down from 640 °C for Na-MMT to 577 °C, which was due to the penetration of the methyl groups of the intercalated surfactants into the siloxane layer [141].

A more complex situation arose in Cloisite 15A as suggested by several peaks overlapping. This is mostly because a massive amount of organic surfactants was present in Cloisite 15A, not only adsorbed on silicate surfaces, but also located in the clay galleries with and without chemical bonding. All the decomposition temperatures of Cloisite 15A shifted to higher temperatures compared with that of Cloisite 30B, as shown in Figure 4. 11. This can be explained by the molecular structures of their organic surfactants, as Cloisite 30B contains only one tallow chain while Cloisite 15A has two, giving Cloisite 15A better thermal stability [116].

4.2.2 Silylated Commercial Clays

The effect of silylation on the thermal stability of commercial clays is illustrated in Figure 4. 12. Compared with the Cloisite Na⁺, the DTG curve of APS-Na⁺ displays two peaks in the temperature range of 200 to 500 °C. The peak at ~260 °C was reported to be due to the desorption of silane from the external surface; the peak at 390 °C has been attributed to the decomposition of the intercalated silane, while the peak at 573°C corresponded to the co-occurrence of the decompositions of the grafted silane and the dehydroxylation of the clay [51].

100
Figure 4. 12 DTG thermograms of Cloisite Na⁺, Cloisite 30B and Cloisite 15A further modified with 100 wt.% silane coupling agent, APS.

It was noticed that the small peaks at relatively low temperature (200 to 300 °C) for the commercial clay 15A, disappeared after APS modification, which was probably due to the ethanol extraction of excess surfactants adsorbed on the external silicate surfaces during the silylation process. The remained organic surfactants were also mostly located inside the clay galleries supported by observation of the two decomposition temperatures at 326 °C and 404 °C, corresponding to the decompositions of the surfactant cations located within the interlayer and intercalated into the interlayer space through ion-exchanging and bonding to surface via electrostatic interaction, respectively [47].

Different circumstances occurred in Cloisite 30B; initially ~0.85 CEC organic surfactants were presented in Cloisite 30B, and there were still some clay surfaces available for the reactions to occur between APS and silicates. Consequently,
although the degradation peaks at low temperature were eliminated due to ethanol extraction, the peaks at 250 °C and 531 °C have been considered to be due to the decomposition of silane adsorbed at the external silicate surfaces and grafted silane, respectively [51, 141]. It was notable that the decomposition peaks corresponding to the intercalated surfactant had shifted to a higher temperature (from 360 °C to 404 °C) after silylation for both APS-30B and APS-15A. This was probably due to grafted silane restricting the thermal motion of organic molecules within clay galleries [165], resulting in improved thermal stability of the organoclays.

Basically grafting a silane coupling agent onto silicate itself provides good thermal stability to the organoclay. On the other hand, the process of silylation involved an extraction reaction, which removes excess organic surfactant, resulting in an improved thermal stability of organoclays, as the excess organic surfactants presented on the clay reduced its thermal stability [47, 144, 164].

4.2.3 Single Surfactant Modified Montmorillonites

The DTG curves of single surfactant modified MMTs, e.g. HTP/MMT, AP-POSS/MMT and OA-POSS/MMT are shown in Figure 4. 13. The derivative weight loss curves exhibited very similar patterns to these observed for commercial organoclays and APS grafted organoclays. The first maximum decomposition rate at 316 °C for HTP/MMT was considered as the degradation of unconfined HTP, which did not undergo the ion-exchange reaction as the onset decomposition of HTP occurred at ~300 °C [46]. The peak at 476 °C was attributed to the decomposition of the HTP surfactants which had settled inside the clay galleries via ion-exchange, and this was delayed by the barrier effect generated by silicate layers.

It is notable that phosphonium surfactant (HTP) modified MMT, had a higher thermal stability than that of ammonium based organoclays, i.e. Cloisite 30B and
Cloisite 15A, as shown in Table 4.2. Similar results were observed by Xie et al. [46, 125]. Generally, the thermal stability of exchanged MMT is related to the thermal stability of the surfactants used, despite the non-isothermal decomposition of phosphonium-MMT and ammonium-MMT behaves similarly. A much higher initial decomposition temperature of the HTP compared with that of Cloisite 30B and Cloisite 15A, irrespective of the addition effects of the silicate layers, resulted in the higher thermal stability of HTP-MMT. Moreover, in contrast to ammonium modified MMTs, the architecture of the phosphonium cation affected significantly the thermal stability of the HTP/MMT, in which the presence of three phenyl groups was thought to provide the steric resistance inhibiting the bimolecular reaction around the P atom. Alternatively, the possibility of interactions between the P and phenyl groups would result in the delocalisation of the positive charge, which can also diminish the susceptibility of the alkyl chain to elimination, enabling high thermal stability of HTP/MMT, compared to that of ammonium modified MMTs [46].

![Figure 4.13 DTG analysis of 1.5 CEC HTP, 0.4CEC AP-POSS, 0.8CEC AP-POSS, and 0.4CEC OA-POSS modified MMTs.](image-url)
For 0.4CEC AP-POSS and 0.8CEC AP-POSS modified MMTs, a large weight loss peak was observed for 04AP-POSS/MMT at the temperature below 200 °C, which was due to the evaporation of absorbed water. It also showed that AP-POSS/MMT was partially intercalated, leaving numbers of hydrated sodium cations un-exchanged, as shown in Table 4. 2. Again, multi-decomposition was observed for these POSS modified MMTs. The peak at approximately 315 °C for both 04AP-POSS and 08AP-POSS modified MMT, was attributed to the decomposition of the attached POSS surfactant on the surfaces of MMT [159, 166]. The decomposition peak at about 387 °C was mainly due to the decomposition of the ion-exchanged POSS surfactant, as intercalation of the surfactant caused a relatively high phase-transformation temperature with respect to the free surfactant [163]. It is notable that the decomposition temperature of AP-POSS surfactant was reduced from 412 °C (Figure 4. 14) to 315 °C for AP-POSS modified MMT (Figure 4. 13). The decrease in the thermal stability of the surfactant was attributed to the presence of Lewis and Brønsted acid sites within the aluminosilicate layer [46, 125].

Slightly different results were obtained from 0.4CEC OA-POSS modified MMT (Figure 4. 13). About 4 % weight loss was observed at the temperature of below 200°C, which is even higher than unmodified MMT, suggesting that 04OA-POSS/MMT is more hydrophilic than Na-MMT. Regarding the molecular structure of OA-POSS (Figure 3.2), eight amino groups are presented at the corners of POSS cubic structure, making it more hydrophilic. Similar to that of AP-POSS modified MMTs, two degradation peaks at ~330 °C and ~427 °C for 04OA-POSS/MMT are due to the decompositions of physically adsorbed and chemically ion-exchanged OA-POSS, respectively, as the thermal decomposition temperature of OA-POSS was occurred at 331 °C, as illustrated in Figure 4. 14. The weakened DTG peaks intensity of 04OA-POSS/MMT in comparison to that of 04AP-POSS/MMT is attributed to the fact that fewer POSS molecules were intercalated, as shown in Table 4. 2.
Both AP-POSS and OA-POSS modified MMTs exhibited higher thermal stability than alkyl ammonium modified MMTs, i.e. Cloisite 30B and Cloisite 15A. This is because the POSS molecule is very thermally stable, with a degradation temperature greater than 300 °C [55]. As mentioned previously, the thermal stability of exchanged MMTs is related to the thermal stability of the surfactants used [46].

The thermal degradation of ammonium salts follows a Hoffmann elimination reaction (or an S_N2 nucleophilic substitution), that occurs in the presence of basic anions, such as hydroxyl groups, which extract hydrogen from the alkyl chains of the quaternary ammonium [47], as shown in Figure 4. 15. Both POSS and alkyl ammonium modified MMTs degraded mainly in this manner, but the presence of Si-O bond (111 kcal/mol) [46] in the POSS cages is relatively stronger compared to the C-C bond (72 kcal/mol) [167] in alkyl chains, as representative R group in Figure 4. 15, enabling higher thermal stability of POSS modified MMTs.

Figure 4. DTG analysis of AP-POSS and OA-POSS.
The difference between AP-POSS/MMT and OA-POSS/MMT in thermal stability could be derived from two aspects. First, as shown in Table 4.2, more AP-POSS molecules (0.20 CEC) were intercalated in MMT than OA-POSS (0.12 CEC), and the thermal stability of exchanged MMTs normally decreases as the increase of the amount of organic surfactants in MMTs [144]. Second, the decomposition of OA-POSS/MMT involves more than two Hoffmann elimination reactions respect to that of AP-POSS/MMT. As discussed earlier, the low exchange ratio and small interlayer spacing of OA-POSS/MMT were mostly due to the amino groups of OA-POSS molecule ion-exchanged with both sides of silicate layer in clay galleries. Therefore, a Hoffmann elimination reaction would have occurred at both sides of interlayer during thermal decomposition of OA-POSS/MMT, which required more energy than that for the decomposition of AP-POSS/MMT, where only one amino group is available for degradation. Additionally, the free amino groups presented at OA-POSS molecules enabled it to eliminate the degradation catalyst (the Lewis and Brønsted acid sites within the aluminosilicate layer), making it less active in thermal decomposition.

Figure 4.15 Schematic diagram of Hoffmann elimination reaction for ammonium salts.
4.2.4 Dual Surfactant Modified Montmorillonites

In order to improve the hydrophobic properties of partially exchanged POSS modified MMT, a second surfactant with flexible alkyl chains was introduced, and the thermal properties are also summarised in Table 4.2. The TGA results showed that the weight loss for those dual surfactant modified clays was increased from 17.9% for 04AP-POSS/MMT and to 22.0%, 27.0%, 34.4% for 04AP-POSS/08BDA/MMT, 04AP-POSS/08ODA/MMT and 04AP-POSS/08DMDTA/MMT, respectively, in the temperature range of 200-500 °C, due to the addition of the second surfactant. Based on the calculation of the amounts of adsorbed surfactant in O-MMTs, fewer molecules of surfactant BDA were adsorbed/intercalated (~0.30 CEC) in 04AP-POSS/08BDA/MMT, which was likely to be due to the OH groups in surfactant molecules reacted with the hydroxyl groups at the broken edges of silicate layers, and with other surfactants by forming hydrogen bonding, as reported from our previous work [168]. The excess salt accumulated in the interlayer space might be easily desorbed by washing with water due to its polar cations [159]. On the other hand, having long chain molecules with less polar cations, such as ODA (0.57 CEC) and DTDMA (0.54 CEC), are likely to be much more resistant to the washing process [169], resulting in higher adsorption on an external clay surface.
Figure 4.16 Derivative thermogravimetric thermograms of (A) 04AP-POSS/08BDA/MMT, (B) 04AP-POSS/08ODA/MMT, and (C) 04AP-POSS/08DTDMA/MMT.

Figure 4.16 shows the DTG analysis of the dual surfactant modified MMTs. The first thermal decomposition at a temperature of around 220 ºC present for 04AP-POSS/08ODA/MMT, mostly due to the decomposition of the second alkyl ammonium surfactant adsorbed on the clay’s surface. The decompositions which occurred at 330 ºC for 04AP-POSS/08BDA/MMT and 295 ºC for 04AP-POSS/08DMDTA/MMT, were probably a combination of the decomposition of the intercalated BDA(DTDMMA) surfactant and the adsorbed POSS molecules, while the decomposition peaks at about 400 ºC and 570 ºC for all these dual surfactant modified clays, corresponded to the decomposition of ion-exchanged POSS surfactant and structural dehydroxylation of the montmorillonite, respectively [153].

Among them, 04AP-POSS/08BDA/MMT exhibited the best thermal stability as the first decomposition peak was about 330 ºC, which was very close to that of 0.4 CEC
AP-POSS modified MMT. Regarding the fact that a low percentage of BDA was adsorbed/intercalated in 04AP-POSS/08BDA/MMT, the signal for adsorbed BDA decomposition may have been so weak that it could not be identified from its DTG thermogram. On the other hand, the BDA molecule was more likely to be intercalated inside the clay galleries due to its small molecular size, as well as undergone chemical grafting onto the edges of layered MMT. A broadened decomposition peak at \(~220\ \degree\text{C}\) was observed for 04AP-POSS/08ODA/MMT, corresponding to excessive, less thermally stable, adsorbed alkylammonium surfactant. As mentioned previously, a long chain surfactant with a low polarity will have not been easy to remove by water, so the excess second surfactant could still adsorb with other surfactants by hydrogen bonding. This was considered as a negative factor in the preparation of polymer/clay nanocomposites, since it may plasticise the polymeric matrix and so degrade the final properties of composites [159]. The decomposition peak for 04AP-POSS/08DMDTA modified MMT was around 295 \degree\text{C}, suggesting a good thermal stability still remained despite the presence of a second surfactant, in contrast to Cloisite 15A and Cloisite 30B, which decomposed as low as 210 to 230 \degree\text{C} (Table 4.2)

The weight loss for OA-POSS based, dual-surfactant modified MMT (04OA-POSS/08DTDMA/MMT), was increased from 10.8 \% for 04OA-POSS/MMT to 16.0 \%, indicating that about 0.14 CEC DTDMA was intercalated or adsorbed into the MMT. Two peaks in its DTG thermogram (Figure 4.17), in the temperature range of 200 to 500 \degree\text{C}, mainly corresponded to the degradation of intercalated DTDMA molecules at the lower temperature (\(~270\ \degree\text{C}\)) and the decomposition of adsorbed or intercalated OA-POSS at the higher temperature (342 \degree\text{C}). It was shown clearly that the decomposition temperature of intercalated OA-POSS molecules was reduced from \(~430\ \degree\text{C}\) (Figure 4.13) to \(~350\degree\text{C}, after dual-surfactant surface modification.
As discussed early, the interlayer space was expanded by introducing the DTDMA surfactant, from 1.64 nm for 04OA-POSS/MMT to 2.16 nm for 04OA-POSS/08DTDMA/MMT (Figure 4. 9), which will have broken one side of the ionic bond between the OA-POSS molecule and the silicate layer. The energy required for a Hoffmann elimination reaction [47] consequently was reduced dramatically during the thermal decomposition of 04OA-POSS/08DTDMA/MMT. In addition, the thermal degradation of ammonium salts generated an olefin and an amine, and left an acid proton on the surfaces of the MMT [125]. This acid site probably had a catalytic effect during the initial stages of decomposition of organic compounds in the organo-montmorillonite [170]. This effect was even enhanced by the presence of a number of free amino groups from the OA-POSS molecules.

Figure 4. 17 DTG thermograms for 04AP-POSS/08DTDMA and 04OA-POSS/08DTDMA modified MMTs, respectively.
It is also obvious that the thermal stability of 04OA-POSS/08DTDMA/MMT was lower than that of 04AP-POSS/08DTDMA/MMT, as shown in Figure 4. 17, with two decomposition temperatures of 270 °C and 342 °C for 04OA-POSS/08DTDMA/MMT, corresponding to 295 °C and 399 °C for 04AP-POSS/08DTDMA/MMT, respectively. Besides the reason given above, the bilayer structure formed by AP-POSS led to the second surfactant DTDMA having difficulty releasing from the clay galleries once it is intercalated. This restricted the thermal motion of lower thermally stable DTDMA molecules especially at the early stage of decomposition, while the impeding effect of the single layer structure formed in OA-POSS/MMT, was less than that of AP-POSS modified MMT.

4.3 The Influence of Surface Modification on Surface Properties of Organo-Montmorillonite

4.3.1 Surface Free Energy

The purpose of surface treatment for montmorillonite is to reduce its relatively high surface free energy (SFE) [171, 172] which had been considered to be the force keeping silicate layers strongly together, and to convert the hydrated sodium cations with organic compounds to match the polymer matrices, making possible the uniform dispersion and exfoliation of the clays in polymer matrices [71, 173, 174]. SFE measurement is used as an indication of hydrophilicity, i.e. the higher value of the SFE the more hydrophilic of a material. In addition, SFE can be divided into dispersive and polar components, the latter of which determines the relative polarity of solids.
Table 4.3 Surface free energies of various polymer matrices and organoclays.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface free energy (mN/m)</th>
<th>Polarity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma_s$</td>
<td>$\gamma_d$</td>
</tr>
<tr>
<td>PP</td>
<td>32.1</td>
<td>32.0</td>
</tr>
<tr>
<td>PP-g-MA</td>
<td>34.2</td>
<td>33.6</td>
</tr>
<tr>
<td>PBT</td>
<td>35.5</td>
<td>28.1</td>
</tr>
<tr>
<td>PA 6</td>
<td>44.9</td>
<td>36.7</td>
</tr>
<tr>
<td>PA 11</td>
<td>41.1</td>
<td>35.0</td>
</tr>
<tr>
<td>PA 12</td>
<td>32.0</td>
<td>28.0</td>
</tr>
<tr>
<td>Cloisite Na+</td>
<td>66.5</td>
<td>29.1</td>
</tr>
<tr>
<td>Cloisite 30B</td>
<td>38.3</td>
<td>29.7</td>
</tr>
<tr>
<td>Cloisite 15A</td>
<td>34.6</td>
<td>27.5</td>
</tr>
<tr>
<td>APS-15A²</td>
<td>42.2</td>
<td>35.3</td>
</tr>
<tr>
<td>HTP/MMT³</td>
<td>41.6</td>
<td>33.2</td>
</tr>
<tr>
<td>04AP-POSS/MMT</td>
<td>34.8</td>
<td>25.2</td>
</tr>
<tr>
<td>08AP-POSS/MMT</td>
<td>36.6</td>
<td>32.9</td>
</tr>
<tr>
<td>04OA-POSS/MMT⁴</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>04AP-POSS/08BDA/MMT</td>
<td>22.3</td>
<td>19.9</td>
</tr>
<tr>
<td>04AP-POSS/08ODA/MMT</td>
<td>26.6</td>
<td>25.2</td>
</tr>
<tr>
<td>04AP-POSS/08DTDMA/MMT</td>
<td>27.7</td>
<td>27.3</td>
</tr>
<tr>
<td>04OA-POSS/08DTDMA/MMT</td>
<td>40.1</td>
<td>36.1</td>
</tr>
</tbody>
</table>

¹ all samples were dried at 80 °C overnight before test
² the amount of APS used for silylation is 100 wt.% of organoclay
³ the amount of HTP is 1.5 CEC
⁴ sample was too hydrated to be measured accurately using deionised water

The SFEs for polymers, commercial clays and organically modified clays were measured using contact angle tests, and the results are shown in the Table 4.3. The SFE for most polymer matrices varied in the range of 30 to 45 mN/m, which is almost half of that of unmodified MMT (Cloisite Na+), whose SFE was as high as 66.5 mN/m. By employing organic compounds in order to modify the MMT, the SFE of all O-MMTs were reduced significantly but varied depending on the surfactants used. The polarity of MMT was also reduced following with surface modification, from 56.3 % for Na-MMT to ~20 % for commercial organoclays (Cloisite 30B and Cloisite 15A), to even as low as less than 10 % for dual-surfactant modified MMTs.
The decreased SFE and polarity, after surface modification, was due to the change of hydrophilicity and polarity of the silicate surfaces, which were covered by hydrophobic and so less polar surfactants. The different SFE values among these O-MMTs were mostly due to the different surfactants used for modification with different concentrations, molecular weights and characteristics [172]. For example, the SFE of Cloisite 30B was 38.3 mN/m, which is higher than that of Cloisite 15A (34.6 mN/m), indicating that Cloisite 30B was more hydrophilic. Relating to the TGA results summarised in Table 4.2, the fact that more surfactants were presented in Cloisite 15A (1.37 CEC) than Cloisite 30B (0.86 CEC), higher surface coverage associated within Cloisite 15A led to lower SFE [172, 175]. Moreover, lower SFE will be reflected from weaker forces between the silicate layers as long as the interlayer distance increases. As reported in section 4.1.1, two long alphatic chains from Cloisite 15A’s surfactant enable it with much larger interlayer space (3.10 nm) than that of Cloisite 30B (1.80 nm), which possessed only one long alkyl chain, which also contributed to a lower SFE in Cloisite 15A.

Upon silylation of the Cloisite 15A, excess organic surfactant was removed, leaving surface exchanging down to less than 1.0 CEC and interlayer space reducing from 3.10 nm to 2.50 nm. As a result, an increased SFE value was observed for APS-15A (42.2 mN/m). Since the silane coupling agent mostly reacted with the hydroxyl groups at the edges of silicate layers [52, 176], the polarity of Cloisite 15A consequently reduced from 20.5% to 16.3% with the APS grafted Cloisite 15A.

Both 04AP-POSS/MMT and 08AP-POSS/MMT were partially exchanged, leaving ~0.8 CEC and ~0.6 CEC of hydrated sodium cations un-exchanged, respectively, although a large interlayer space (>3.4 nm) was formed in AP-POSS/MMT. In addition, as the major composition of POSS surfactant was the relative hydrophilic Si-O unit, leaving the SFE of AP-POSS/MMT at a relative high value (34.8 to 36.6 mN/m). Even lower surface exchange (~0.12 CEC) of 04OA-POSS/MMT and more hydrophilic nature derived from eight amino groups of OA-POSS surfactant, lead to
a higher SFE value of 04OA-POSS/MMT, which adsorbed water very easily. On the other hand, due to the relatively large proportion of polar silicate surfaces being uncovered in POSS modified MMTs, the polarity of POSS/MMT was relatively high (27.6 % for 04AP-POSS/MMT). This was reduced by introducing more AP-POSS surfactant, with the polarity of 08AP-POSS/MMT was lowered to 10.1 %.

For the dual-surfactant modified clays, even lower SFE values were observed, i.e. 22.3 to 27.6 mN/m for AP-POSS based dual-surfactant organoclays, compared to ~35 mN/m for 04AP-POSS/MMT. As calculated in Table 4.2, much more hydrated sodium cations were ion-exchanged by the introduction of a second surfactant to AP-POSS modified MMTs, and more hydrophilic silicate surfaces became hydrophobic. In the meantime, a large interlayer space resulted in a reduction of SFE. All of these factors contributed to the lowered SFE of AP-POSS/second surfactant/MMTs. Although a reduced SFE value was also observed for 04OA-POSS/08DTDMA/MMT, compared to that of 04OA-POSS/MMT, its SFE was still relatively high (i.e. 40.1 mN/m), which had to be attributed to its low surface coverage (only ~0.25 CEC Na⁺ cations were exchanged), and relatively smaller interlayer space than that of the AP-POSS modified MMTs.

### 4.3.2 Interfacial Free Energy

In general, in order to form intercalated/exfoliated montmorillonite particles in a polymer matrix, it is necessary to have similar surface properties between clay minerals and polymers, especially polarity [153]. It can be seen that PP is a non-polar polymer, with polarity as low as 0.3 %. Because of the absence of any strong polar-polar interactions, it has been a challenge to disperse silicate clays in the highly apolar PP. The general approach for improving the compatibility of PP with MMT, has been the addition of polar functional groups to the PP polymer, for instance, employing a commercially available maleic anhydride grafted PP
(PP-g-MA) polymer. By introducing the polar groups derived from maleic anhydride to PP, its polarity slightly increased to ~1.8 % and although this was very dependent on the amount of MA present. However, higher polarity PP-g-MA resulting from a high proportion of MA would likely change the structure and reduce the crystallinity of PP, which unfortunately, significantly reduces polymer mechanical properties [76]. On the other hand, PBT and PAs are both polar polymers of commercial importance, with polarities of 20.8 % and 12.5% to 18.3 %, respectively. There is a slight difference between polyamides’ (PA6, PA11 and PA12) surface properties, which is mostly due to the polarity of the repeat structure. The lower the hydrocarbon content of the polyamide, the more polar the polymer [34]. Therefore, PA12 exhibits the lowest polarity with ~12.5 % and PA6 the highest with ~18.3 %. As there are different polarities for PP, PBT and the PAs, then it was apparently there would be different requirements on modified MMTs, in order to create favourable compatibility between polymer matrices and MMT.

Poor dispersion and lack of adhesion at the interface in polymer/clay nanocomposites, generally leads to poor mechanical properties, which may even be worse than those of conventional polymer composites. Determining the polymer-filler interfacial free energy (IFE) enabled us to predict the compatibility between fillers and polymer matrices, which should be useful for organoclay selection. Therefore, the interfacial free energy, \( \gamma_{mf} \) is an important parameter in predicting the strength of interactions formed at the filler/polymer interfaces, which can be calculated using the equation [173] below:

\[
\gamma_{mf} = \gamma_f + \gamma_m - \frac{4\gamma_f^d\gamma_m^d}{\gamma_f^d + \gamma_m^d} - \frac{4\gamma_f^p\gamma_m^p}{\gamma_f^p + \gamma_m^p}
\]

\[\text{Eq. 4-1}\]

Subscripts \( m \) and \( f \) denote matrix and filler, respectively, and \( \gamma^d \) and \( \gamma^p \) are the dispersive and polar components of surface free energy, respectively. A minimal value, tending to zero, of interfacial free energy will result in effective adhesion.
between filler and matrix [177].

Table 4. 4 Interfacial free energies of various polymer/clay pairs

<table>
<thead>
<tr>
<th>Samples</th>
<th>Interfacial free energies $\gamma_{mf}$ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PP</td>
</tr>
<tr>
<td>Cloisite Na$^+$</td>
<td>37.2</td>
</tr>
<tr>
<td>Cloisite 30B</td>
<td>8.4</td>
</tr>
<tr>
<td>Cloisite 15A</td>
<td>7.1</td>
</tr>
<tr>
<td>APS-15A</td>
<td>6.8</td>
</tr>
<tr>
<td>HTP/MMT</td>
<td>17.1</td>
</tr>
<tr>
<td>04AP-POSS/MMT</td>
<td>10.1</td>
</tr>
<tr>
<td>08AP-POSS/MMT</td>
<td>3.4</td>
</tr>
<tr>
<td>04OA-POSS/MMT$^a$</td>
<td>-</td>
</tr>
<tr>
<td>04AP-POSS/08BDA/MMT</td>
<td>4.9</td>
</tr>
<tr>
<td>04AP-POSS/08ODA/MMT</td>
<td>1.9</td>
</tr>
<tr>
<td>04AP-POSS/08DTDMA/MMT</td>
<td>0.6</td>
</tr>
<tr>
<td>04OA-POSS/08DTDMA/MMT</td>
<td>4.0</td>
</tr>
</tbody>
</table>

$^a$ this clay specimen was too hydrated to be measured accurately using deionised water

Table 4. 4 summarises the IFEs between several polymer matrices and various O-MMTs. Among all the polymer/clay pairs, the highest interfacial free energy (>20 mN/m) was found from those containing unmodified MMT (Cloisite Na$^+$), indicating that it was very incompatible with most polymer matrices, which has already been proved by other means. However, there are still some differences between these high IFEs calculated between polymer matrices and Na-MMT. By introducing the polar group MA into the PP’s alkyl chains, the IFE was slightly reduced from 37.2 mN/m for PP/MMT to 36.0 mN/m for PP-g-MA/MMT, suggesting that a slightly improved compatibility would be achieved for maleated PP than bulk PP. For the polar polymer matrices, this value was significantly reduced for both PBT and PAs, due to their relatively inherent high polarity. It is noticeable that PA6/MMT had a lower IFE value than those for PA 11 and PA 12; this supports the fact that PA 6 possesses the highest polarity of the three different polyamide matrices.
For PP/clay pairs, the IFE reduced (so compatibility increased) with the decreasing polarity of clays. As can be seen from Table 4. 4, an IFE value of over 7.0 mN/m was observed from most PP/clay pairs containing single surfactant modified MMTs, while an IFE value as low as 0.6 mN/m was obtained for these PP/clay pairs containing dual-surfactant modified MMTs. The lowest IFE value was achieved by 04AP-POSS/08DTDMA/MMT with only 0.6 mN/m, indicating that better compatibility would be achieve between PP and dual-surfactant modified clays, especially for 04AP-POSS/08DTDMA/MMT than other PP/clay pairs.

Comparisons between the two commercial organoclays, PP/Cloisite 15A showed a slightly lower IFE (7.1 mN/m) than that for PP/Cloisite 30B (8.4 mN/m), corresponding to the lower polarity of Cloisite 15A than that of Cloisite 30B, implying that Cloisite 15A could be better dispersed in PP matrix than Cloisite 30B. By grafting silane coupling agent at the edges of silicate layers, so consuming the polar hydroxyl groups of silicate, resulted in reduced polarity of APS-15A, and consequently, PP/APS-15A exhibited an even lower IFE value than that of PP/Cloisite 15A. After modification with 0.4 CEC AP-POSS, the IFE value between the modified clays and PP, remained relative high at 10.1 mN/m, which was reduced to 3.4 mN/m when the concentration of AP-POSS was increased, which corresponded to a reduction of polarity from 27.6 % for 04AP-POSS/MMT to 10.1 % for 08AP-POSS/MMT.

By adding a second surfactant to 04AP-POSS/MMT, in which its un-exchanged hydrophilic and polar silicate surfaces were further covered by the second surfactant, which resulted in the reduction in the surface energy and the polarity, as presented in Table 4. 3. Because ODA and DMDTA are both long chain surfactants with low polarity and good hydrophobic character, dual surfactant modified MMTs formed by them showed relatively low polarity of 5.3 % and 1.5 %, respectively, and consequently good compatibility with PP matrix, as indicated by low IFE values as presented in Table 4. 4. However, due to the presence of –OH groups in BDA
surfactant, 04AP-POSS/08BDA/MMT still possessed relative high polarity, making it less compatible with PP. In comparison, 04OA-POSS/08DTDMA/MMT although it contained less polar DTDMA surfactant, OA-POSS was relatively hydrophilic as a polar surfactant, the OA-POSS based dual-surfactant modified MMTs were still rather polar, (10% polarity) and not particularly compatible with the non-polar PP.

On the other hand, not only the polarity, but also the surface free energy will affect the compatibility of clays in polar polymer matrices [173, 178]. Similar polarity and surface free energy will result in better compatibility between polymers and clays. Taking poly(butylene terephthalate) (PBT) as an example; PBT is a polar polymer with 20.8 % polarity. The high polarity of 56.3 % for the unmodified MMT, resulting incompatibility with PBT as predicted from the IFE value (20.1 mN/m), given in Table 4.4. The compatibility was significantly improved by an organic modification to MMT, as the IFE between PBT and commercial organoclays was reduced significantly to 0.2 mN/m and ~0.0 mN/m for Cloisite 30B and Cloisite 15A, respectively. After silylation, the SFE and polarity of Cloisite 15A increased to 42.2 mN/m and decreased to 16.3 % respectively, which probably corresponded to the removal of excess organic surfactant and grafting of the silane coupling agent at broken silicate edges. The IFE between PBT and APS-15A was increased slightly from ~0.0 mN/m before silylation to 0.8 mN/m after silylation, suggesting that a relatively poorer compatibility would result in PBT/APS-15A than in PBT/15A. Similar results should be expected in a PBT/APS-30B system.

For the AP-POSS modified MMTs at low AP-POSS concentration (0.4 CEC), due to the close SFE and polarities between organoclay and PBT matrix, a relatively low IFE value (0.4 mN/m) was calculated for PBT/(04AP-POSS/MMT). When the concentration of AP-POSS was increased, the compatibility between the modified clays and PBT was not as good as expected, because of the larger surface coverage reduces the polarity of 08AP-POSS/MMT to as low as 10.1 %, which therefore resulted in increased IFE value (to 1.6 mN/m), and made 08AP-POSS/MMT less
compatible with PBT, as showed in Table 4. 4. However, it is notable that the IFE values between dual-surfactant modified MMTs and PBT were not as low as these single surfactant modified MMTs/PBT pairs, e.g. PBT/Cloisite 15A (Cloisite 30B) or PBT/04AP-POSS/MMT according to the calculation by Vrsaljko’s equation [159]. This could be attributed to the relative low SFE values and polarities of these dual-surfactant modified MMTs.

As a comparison, other three polar polymer matrices: PA 6, PA11 and PA 12 with varying SFE values and polarities, having different compatibilities with organoclays, were used for further investigation. Basically, due to their relatively high SFE values and polarities, these were more compatible with the more polar organoclays with slightly higher SFE. As predicted by IFE calculation, similar to that obtained from PBT/clay pairs, a better compatibility of PA 6 (PA 11 or PA 12) could be achieved with commercial organoclays and APS grafted commercial organoclays, respectively, rather than with those dual-surfactant modified MMTs.

However, it should be taken into account that the SFE and polarity of O-MMTs may change at elevated temperatures [89, 179] and thermal decomposition of the surfactants could occur during melt compounding, especially in high temperature processing, e.g. high temperature processing required in PBT and PAs, which could have great effect on the surface properties of O-MMT. In addition, as mentioned earlier the replacement of the interlayer cations and the covering of the internal surfaces are often not quantitative during the ion-exchanging process, especially in those POSS modified MMTs as the increasing number of contacts reduces the mobility of the surfactants. Therefore, compatibility prediction by IFE can only provide basic indications, while thermal stability as well as interlayer conformation of the O-MMT, should all be included for melt dispersion consideration.
4.4 Microstructure and Morphology of Organically Modified Montmorillonite in Polymer Matrices

4.4.1 Commercial Clays

The interlayer spacing of three commercial clays which had been melt compounding with polypropylene (PP) in the presence of compatibiliser PP-g-MA, was measured by WADX, and is presented in Table 4.5. The main reflections of Cloisite Na\(^+\), 30B and 15A at position of 2θ=9.04\(^\circ\), 6.14\(^\circ\) and 3.19\(^\circ\), corresponding to the basal spacing with 0.98 nm, 1.44 nm and 2.74 nm, respectively, remained or even shifted to higher diffraction angles compared to their diffraction patterns prior to melt compounding. The unchanged interlayer space for Cloisite Na\(^+\) and even the reduced interlayer space for Cloisite 30B and 15A after melt compounding, indicated that the immiscible/intercalated montmorillonite structure was formed in PP matrix, and similar results were also observed by Qin et al. [180].

**Table 4.5** Basal spacing of three commercial clays before and after melt compounding with PP, the PP nanocomposites were prepared in weight ratio of 45/5/1.5 (PP/MAPP/clay).

<table>
<thead>
<tr>
<th>Clays</th>
<th>Bragg angle (2θ)</th>
<th>Interlayer spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloisite Na(^+)</td>
<td>9.03</td>
<td>0.98</td>
</tr>
<tr>
<td>PP/MAPP/Na</td>
<td>9.04</td>
<td>0.98</td>
</tr>
<tr>
<td>Cloisite 30B</td>
<td>4.92</td>
<td>1.80</td>
</tr>
<tr>
<td>PP/MAPP/30B</td>
<td>6.14</td>
<td>1.44</td>
</tr>
<tr>
<td>Cloisite 15A</td>
<td>2.86</td>
<td>3.10</td>
</tr>
<tr>
<td>PP/MAPP/15A</td>
<td>3.19</td>
<td>2.74</td>
</tr>
</tbody>
</table>

Despite both basal spacing of Cloisite 30B and Cloisite 15A being reduced, the extent of the decrease between 15A and 30B was different; i.e. 11.6 % reduction for 15A and 20 % for 30B. This had to be related to the structure of organic surfactants present in clay galleries. As illustrated in Figure 4.18, original Cloisite 15A probably adopted a paraffin-like bilayer (3.10 nm) structure with two tallow chains stretching within the galleries and expanding the space, while Cloisite 30B adopted a lateral...
bilayer (1.80 nm) structure with only one tallow chain lying on the silicate layers. After the releasing of organic surfactants during melt compounding, Cloisite 15A will have still adopted a paraffin-type monolayer (2.74 nm) while Cloisite 30B will have formed a lateral monolayer (1.44 nm) [181], suggesting that Cloisite 15A with two tallow chains was relatively stable compared to than that of Cloisite 30B with only one tallow chain [116]. On the other hand, excess organic surfactants were present in Cloisite 15A and these were less stable, (i.e. starting to degrade at as low as ~180 ºC [87]), due to the weak interactions between them, especially at the initial stage of melt compounding. As discussed in section 4.1.1, Cloisite 15A will not be stable until the basal spacing reaches 2.50 nm. This means Cloisite 15A may also be intercalated by PP due to the expanded interlayer space from 2.50 nm to the finally obtained 2.74 nm.

![Cloisite 15A and 30B before and after melt compounding](image)

**Figure 4.18** Schematic illustration of the interlayer structure of Cloisite 15A and 30B before and after melt compounding.

TEM analysis provided more visible evidence of clay morphology in the PP matrix. As shown in Figure 4. 19, the dark lines are the cross sections of silicate layers. In the case of PP/MAPP/Na-MMT (Figure 4. 19a), the silicate layers agglomerated into large particles with particle size up to 1.5 μm, and no intercalation of PP occurred, which agreed well with the XRD results. This was thought to be due to the lack of
the affinity between the polar clay and the highly non-polar polymer matrix [85].

Considering the surface properties of Cloisite Na\textsuperscript{+} as discussed in the previous section, Cloisite Na\textsuperscript{+} is a relative pure MMT, that is strongly hydrophilic with high polarity and high surface energy, so it will lack compatibility with the hydrophobic PP matrix. The prediction made from IFE value between PP and Cloisite Na\textsuperscript{+} also matches well with what is indicated by the TEM micrographs.

![Figure 4.19 TEM micrographs of (a) PP/MAPP/Na\textsuperscript{+}, (b) PP/MAPP/30B and (c) PP/MAPP/15A (all in the weight ratio of 45/5/1.5).](image)
In the case of PP/MAPP/30B, a slightly better dispersion level was observed, (see Figure 4. 19b). Clearly the size of the aggregates was reduced and a few small particles are observed. It is apparent from this observation that surface modification of MMT has a positive effect on the dispersion of the clay in PP matrix. However, this effect varies with the chemistry, structure, thermal property etc. of the surfactants. As shown in the PP/MAPP/15A composite (Figure 4. 19c), 15A particles were fairly well dispersed and the clay was evenly distributed throughout the PP matrix. Although a few thick stacked silicate layers were still present, a number of particles had been intercalated and even exfoliated into single layers. TEM observation confirmed the formation of intercalated/exfoliated structures in PP/MAPP/15A, which was likely to be attributed to the relative large interlayer space of Cloisite 15A, allowing better intercalation by the PP chains. Furthermore, it was imperative that the surface properties between polymer and organoclay should be matched in order to get a fully wetted and intercalated structure [38]. PP/Cloisite 15A exhibited closer surface properties (i.e. lower IFE) than Cloisite 30B and Cloisite Na⁺, which will have further promoted the formation of intercalated structures or even exfoliated structures in PP/MAPP/15A.

On the other hand, the formation of immiscible structures (forming aggregates) will have resulted from the silicate layer collapse, which could be due to the poor thermal stability of the organic surfactant. Thermal decomposition of organic surfactants made the surface character of O-MMTs less organophilic, in addition to the decreased of the interlayer spacing that increases the entropic hindrance for polymer confinement. Therefore, both melt intercalation and thermal decomposition occurred simultaneously during melt compounding; only the clay intercalated in the initial stage could be collapsed since the thermally decomposed organoclays do not satisfy the condition for melt intercalation any more [182]. This was found to be even worse in PP/MAPP/30B, as Cloisite 30B has even lower thermal stability and smaller interlayer spacing than that of Cloisite 15A, and both were evidenced in TEM micrographs.
Unlike that of non-polar PP, the polarity (from the carboxyl groups) present in PBT may enhance the attractions between polar polymer matrix and O-MMTs. As illustrated in Figure 4. 20, the XRD diffraction peak of Cloisite 30B before and after melt compounded with PBT polymer shifted from the original peak of Cloisite 30B at 4.92° (1.80 nm) to 2.64° (3.35 nm), and a broader peak appeared at 5.74° (1.54 nm), indicating that the PBT molecules were intercalated into the clay galleries. The relatively broad peaks obtained from PBT/clay nanocomposites suggested that the relative disordered silicate structure was formed in the PBT matrix.

![Figure 4. 20 XRD patterns of Cloisite 30B and PBT/30B nanocomposite (97/3 wt./wt.)](image)

From the high magnification of the TEM images presented in Figure 4. 21, the primary particles of Cloisite 30B can be seen to be partially exfoliated as single silicate layers and/or partially intercalated as multi-layers in the polymer matrix. It was clear that the dispersion of silicate layers was disordered and reasonably uniform within the PBT matrix.
As mentioned previously with respect to the PP/clay nanocomposite, it was essential to match the surface properties of organoclay with these of PBT matrix in order for PBT to be fully wetted and to intercalate the organoclay tactoids [38]. As suggested in Table 4.4, the compatibility between Cloisite 30B and PBT matrix is extremely good, as the IFE value of the PBT/Cloisite 30B was as low as 0.2 mN/m, which would suggest the promoting the formation of intercalated/exfoliated structures in the PBT matrix. In addition, polar interactions between a polymer matrix and O-MMTs are also critical for the formation of intercalated, especially exfoliated, nanocomposites by melt compounding [59]. In the case of Cloisite 30B, the existence of hydroxyl groups in alkylammonium cations promoted strong polar interactions between organic surfactants and carboxyl groups presented in PBT chains, which further enhanced the penetration of PBT chains into the clay galleries and the formation of intercalated/exfoliated PBT/Cloisite 30B nanocomposites. However, the presence of these polar hydroxyl groups in the alkylammonium cations also enhanced the interaction of the organic surfactant with the silicate surfaces, where hydroxyl groups were also available. Consequently, covering the silicate surface with PBT chains will be less favourable, impeding the extensive intercalation and exfoliation of Cloisite 30B in PBT matrix [183]. Furthermore, for PBT
nanocomposites, the high processing temperature, employed for melt compounding, would have induced thermal decomposition of the relative low thermally stable Cloisite 30B [125], resulting in the change of the interface between the MMT and PBT matrix. As a result, a few immiscible particles were also observed to be present in the PBT matrix (Figure 4. 21).

As a comparison, the morphological properties of the commercial organoclay Cloisite 15A are presented in Figure 4. 22. Where uniform dispersion of organoclays was obtained, in melt processing, there was with a large proportion of intercalated silicates stacked in numbers of silicate layers. Large aggregated immiscible clay particles were also observed, suggesting the dispersion of Cloisite 15A was not as good as Cloisite 30B, although it possessed better thermal stability and a larger interlayer space. As predicted by the IFE values, compatibility between PBT and Cloisite 15A was similar to that of PBT/Cloisite 30B. The lack of polar reactions between surfactants and the PBT matrix will have led to a relative poor dispersion of Cloisite 15A in PBT matrix, compared to Cloisite 30B.

![Figure 4. 22 TEM of PBT/Cloisite 15A nanocomposites containing 3 wt.% organoclays.](image-url)
4.4.2 Silylated Commercial Organoclayes

Figure 4. 23 shows the XRD patterns of three silylated (with 100 wt.% APS) commercial clays, before and after melt compounding with PP, in the association of compatibiliser PP-g-MA. The basal spacing of APS-MMT (Figure 4. 23a) did not change and remained at ~1.40 nm after melt compounding, suggesting that the PP chains, in most cases, were not intercalated into the clay galleries. This was because the grafting silane coupling agent APS was not sufficient to convert the hydrophilic silicate surface to hydrophobic, as most grafting occurred at the edges of silicate layers rather than in the clay interlayer [176]. In comparison, the basal spacing of APS-30B was slightly reduced from 1.90 nm to 1.86 nm after melt compounding with PP (Figure 4. 23b), indicating that collapsed silicate structures were formed in PP/MAPP/APS-30B composites. An intercalated silicate structure was expected for PP/MAPP/APS-15A nanocomposites, as the XRD reflection peak of APS-15A was slightly shifted to lower angle after melt compounding with PP and the basal spacing was slightly increased from 2.50 nm to 2.57 nm (see Figure 4. 23).
Figure 4. 23 XRD patterns of silylated organoclays compounded with polypropylene with compatibiliser PP-g-MA: A) APS-Na filled PP composites, B) APS-30B filled PP composites, and C) APS-15A filled PP composites (with 3 wt.% of organoclays).

Similar results were obtained from PBT/APS-30B nanocomposites, as shown in Figure 4. 24, in which the original peak of APS-30B at 4.69° (1.90 nm) was shifted to 4.58° (1.93 nm) after melt compounding with PBT polymer, indicating that APS-30B remained in its original ordered layer structure undergoing only a small expanded interlayer distance, i.e. an immiscible/intercalated structure was formed in PBT matrix.
Figure 4: XRD patterns of APS-30B and PBT/APS-30B nanocomposite (97/3 wt./wt.), where 100 wt.% APS was used.

The reduction in interlayer spacing of APS-30B after melt compounding PP composites, was thought to be due to the same reasons as that which occurred in Cloisite 30B during melt compounding, i.e. due to the thermal decomposition of the organic surfactants. However, the extent of interlayer spacing reduction of APS-30B (0.04 nm) was well below that of Cloisite 30B (0.36 nm), after melt compounding with PP and PP-g-MA in the same processing conditions. As shown in Table 4.2 that APS-30B was ~30 °C more thermally stable than Cloisite 30B with respect to thermal degradation, silylation on the O-MMTs enabled higher thermal stability. Similar results were also reported in Lee et al.’s work [182], and the reason for the decrease of the interlayer space with the increasing of the temperature here was suggested to be due to the release of organic molecules by thermal decomposition of complex-desorption of organic ions [184] and the thermal decomposition of the intercalated organic molecule itself [185].
On the other hand, although enhanced thermal stability and improved surface properties were obtained for both APS-15A and APS-30B, their dispersions in PP and PBT matrices were not as improved as expected, compared to the PP/MAPP/15A and PBT/30B nanocomposites, respectively. This was confirmed by the TEM observations in Figure 4. 25, where the dispersion of APS-15A in PP matrix appeared to be reasonably uniform with some proportion of the silicate layers being intercalated, while a number of aggregated particles were still present in the PP matrix, and the primary particles of APS-30B were agglomerated into large particles with poor dispersion in PBT matrix (Figure 4. 25b). It was obvious that the silicate layers were still stacked together in their original structure, and only slightly intercalation has taken place. This supports the results obtained from XRD analysis.

![TEM micrographs](image)

**Figure 4. 25** TEM micrographs of (a) PP/PP-g-MA/APS-15A (45/5/1.5 wt.) and (b) PBT/APS-30B (47.5/1.5 wt.) nanocomposites.

However, there was slightly difference from the prediction indicated by IFE calculation, as $\gamma(PP/APS-15A)$ was lower than $\gamma(PP/15A)$, which suggested that APS-15A should have better compatibility with PP than Cloisite 15A. Apart from the reactions expected to occur between APS and hydroxyl groups on the edges and surfaces of the silicate layers, silane coupling agents may also have self-condensed
in the presence of adsorbed water to form a silica coverage on the clay surface, or a linkage to bond adjacent to the silicate layers altogether, (as shown in Figure 4.26), thus preventing the silicate layers from peeling apart [168]; i.e. the grafting of silane may also restrict the intercalation of PP or PBT regardless of compatibility. This did not happen in Cloisite 15A and Cloisite 30B during melt intercalation, although they possessed lower thermal stability.

![Organoclay and Silylated organoclay](image)

**Figure 4.26** Schematic graph of silylation for organoclay.

### 4.4.3 Single Surfactant Modified Organoclays

The change of interlayer space of HTP/MMT before and after melt compounding with PP and PBT, respectively, is presented in Table 4.6. It can be seen that the interlayer spacing of HTP/MMT was reduced from 1.90 nm to 1.87 nm and 1.84 nm after melt compounded with PP and PBT, respectively, suggesting that less intercalation occurred in both PP/HTP-MMT and PBT/HTP-MMT composites.

**Table 4.6** Basal d-spacing of HTP/MMT before and after melt compounding with PP and PBT, respectively.

<table>
<thead>
<tr>
<th>Matrices</th>
<th>Basal d-spacing ($d_{001}$) of HTP/MMT$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before melt compounding</td>
</tr>
<tr>
<td>PP</td>
<td>1.90 nm</td>
</tr>
<tr>
<td>PBT</td>
<td>1.90 nm</td>
</tr>
</tbody>
</table>

$^a$ HTP/MMT was modified with 1.5 CEC HTP.
TEM observations (Figure 4. 27) on the dispersion of HTP/MMT in polymer matrices confirmed it was extremely poor and serious aggregation had occurred. As predicted by the IFE between HTP/MMT and PP (PBT) that compatibility between these was poor ($\gamma_{\text{PP/HTP-MMT}}>15 \text{ mN/m}$ and $\gamma_{\text{PBT/HTP-MMT}}>10 \text{ mN/m}$), conditions were not favourable for polymer molecules to penetrate into the clay galleries rather gathering alongside of silicate surfaces, the increasing pressure at the clay surface led to the shrinkage of interlayer space. The relatively small interlayer space (~1.90 nm) occupied by the relative large and rigid HTP surfactant, a large proportion (~1.0 CEC) of which were presented in the clay galleries (Table 4. 2), further restricting the intercalation of polymer chains, as the conformational freedom of the intercalation chains, is also very important in some cases [58, 59, 186]. Furthermore, an excessive adsorption of the stable organic surfactant HTP on the clay’s surface will cause aggregation of clay particles and will have increased the steric effect [187] during melt compounding.

![TEM micrographs](image)

**Figure 4. 27** TEM micrographs of (a) PP/PP-g-MA/HTP-MMT (45/5/1.5) composites and (b) PBT composites containing 3 wt.% HTP/MMT.

Slightly better results were observed for these AP-POSS modified MMTs, as shown in Figure 4. 28. Here the interlayer spacing of 04AP-POSS/MMT was increased
from 3.40 nm to 4.23 nm and from 3.40 nm to 3.55 nm, after melt compounding with PP and PBT, respectively, suggesting the formation of intercalated silicate structures in the PP and PBT matrices. The existence of (001), (002) and (003) reflection peaks in both XRD patterns of PP and PBT nanocomposites, indicated that the flocculated structures had remained [188]. Corresponding TEM micrographs (Figure 4.29) of PP and PBT nanocomposites containing 3 wt.% 04AP-POSS/MMT show improved dispersion of the modified MMTs in polymer matrices, compared to the dispersion of unmodified MMT (Figure 4.19a) and HTP/MMT (Figure 4.27). While the dispersion of 04AP-POSS/MMT was reasonably uniform, a number of aggregates were evident in the PP matrix, and even larger aggregated 04AP-POSS/MMTs were formed in PBT matrix.

![Figure 4.28 XRD patterns of 04AP-POSS/MMT and 08AP-POSS/MMT before and after melt compounded with PP and PP-g-MA.](image-url)
CHAPTER 4 RESULTS & DISCUSSION

Figure 4. 29 TEM micrographs of (a) PP/clay nanocomposites and (b) PBT/clay nanocomposites, both containing 3 wt.% of 04AP-POSS/MMT.

As summarised in Table 4. 3, the surface properties of AP-POSS modified MMT were dramatically changed, compared to these of unmodified MMT. The polarity of MMT was reduced from 56.3 % for Na-MMT to 27.6 % for 04AP-POSS/MMT, and as well as the reduced surface free energy (from over 60 Nm/m to ~35 Nm/m), making AP-POSS/MMT more compatible with PP and PBT than unmodified MMT, as predicted by IFE calculation that >35 mN/m for PP/Na-MMT was lowered to ~10 mN/m for PP/04AP-POSS/MMT and 0.4 mN/m for PBT/04AP-POSS/MMT (see Table 4. 4). Considering that 04AP-POSS/MMT was partially exchanged (~0.2 CEC) and that the surface modification was not quantitative, leaving some of the hydrophilic and polar silicate surfaces unmodified, (evidenced by the (002) and (003) diffraction peaks), this resulted in the formation of immiscible clay particles as shown in Figure 4. 29. On the other hand, due to the large interlayer space formed in 04AP-POSS/MMT, early melt intercalation of PP and PBT chains was achieved to some extent, which was shown by the increased basal $d$-spacing ($d_{001}$) in Figure 4. 28.
In addition, it is known that a three-dimensional ‘card house’ structure will be formed at the early stages of clay modification, and the number of silicate layers gathered in this kind of structure will determine the final clay particle size. Surface modification by organic surfactant reduces the interactions between silicate layers and thereby reduces the number of platelets in the ‘card house’ structure [189]. However, due to the cage structure of AP-POSS, a relatively small degree of coverage on silicate surfaces will result in a higher number of platelets still in the ‘card house’ structure, forming large clay particles that are more difficult to be intercalated than those finer clay particles [190, 191]. Moreover, steric hindrance generated by the rigid AP-POSS surfactant, in addition to low viscosity of molten PBT matrix, will have further restricted the intercalation of O-MMT, although 04AP-POSS/MMT was calculated as having strong compatibility with PBT.

When the concentration of AP-POSS was increased, the compatibility between PP and 08AP-POSS/MMT was further improved (IFE= ~3 mN/m), and improved dispersion of modified MMT in the PP matrix was observed (see Figure 4.30a). Most clay particles were assembled with several silicate layers having an average size of 10 to 20 nm. However, XRD results presented in Figure 4.30b indicated that little intercalation had occurred in 08AP-POSS/MMTs, as the interlayer spacing only increased from 3.64 nm to 3.68 nm after melt compounding. This could stem from the rigid and large molecular structure of the AP-POSS surfactant, as a large amount of POSS molecules inside clay galleries could physically inhibit the intercalation of PP molecules, as conformational freedom is important for intercalation, and despite a high concentration of AP-POSS, modified MMT may have provided more surface coverage on the hydrophilic clay surfaces.
4.4.4 Dual-Surfactant Modified Clays

Although both the large interlayer spacing of the modified clay and the good compatibility between polymer and modified clays are essential in order to achieve the intercalated/exfoliated structure in polymer matrix, the conformational freedom of the intercalating chains is more critical in forming an intercalated and/or exfoliated structure in some cases [156]. AP-POSS based dual-surfactant and modified MMT remain large in terms of interlayer spacing. Further improved compatibility between the polymer and modified MMTs, and reduced physical hindrance in clay galleries generated by a large amount of rigid POSS molecules, will be exhibited by dual-surfactant modified MMTs. As shown in Figure 4. 31, the organoclays, 04AP-POSS/08ODA/MMT and 04AP-POSS/08DTDMA/MMT, formed much better dispersions in PP matrices, thin layered MMT particles in which intercalation, and with a few exfoliations were observed.
Figure 4.31 TEM micrographs of PP/PP-g-MA/clay nanocomposites in the ratio of 45/5/1.5 (wt./wt./wt.): (a) 04AP-POSS/08ODA/MMT, (b) 04AP-POSS/08DTDMA/MMT, and (c) 04AP-POSS/08BDA/MMT.

As indicated by the increased ion-exchange ratio presented in Table 4.2, by adding a second surfactant to 04AP-POSS/MMT, its un-exchanged hydrophilic surfaces will be covered by the second surfactant, resulting in a reduction in its SFE and the polarity. Based on the IFE values calculated and given in Table 4.4, 04AP-POSS/08ODA/MMT and 04AP-POSS/08DTDMA/MMT were more compatible with PP matrix, as suggested by their low IFE values, which was largely due to the long chain surfactant ODA and DTDMA with low polarity and good
hydrophobic character.

Conversely, the AP-POSS based dual-surfactant modified MMTs with a different second surfactant, i.e. 04AP-POSS/08BDA/MMT, exhibited a relatively poor dispersion in the PP matrix compared to the former two dual-surfactant modified MMTs, as shown by the fact that a few aggregates were still visible in TEM and there was a large average distance between dispersed clay particles (Figure 4. 31c). This has to be connected to the –OH groups present in the BDA organic compounds, and a relatively low exchange ratio (0.50 CEC) compared to that of 04AP-POSS/08ODA/MMT and 04AP-POSS/08DTDMA/MMT (~0.75 CEC), which contributed to relatively high polarity [192], and consequently making 04AP-POSS/08BDA/MMT less compatible with non-polar PP. Furthermore, the formation of large silicate particles because of the low surface coverage, made intercalation difficult because of an incompatible PP matrix, although large interlayer spacing was also obtained in 04AP-POSS/08BDA/MMT.

Different results were observed for PBT nanocomposites that contained dual-surfactant modified MMTs. Figure 4. 32 shows the XRD results of the PBT/clay nanocomposites containing 3 wt.% of dual-surfactant modified MMTs. It can be seen that the XRD analyses were dependent on the kind of O-MMTs used. The broaden diffraction peak corresponding to 4.13 nm interlayer space for 04AP-POSS/08BDA/MMT disappeared after melt compounding, while the peak at higher diffraction angle, (corresponding to 1.50 nm) remained, implying that a number of silicates were intercalated or even exfoliated in the PBT, and some proportion of silicates formed intercalated/immiscible structures. The original peaks \(d_{001}\) of 04AP-POSS/08ODA/MMT and 04AP-POSS/08DTDMA/MMT have shifted to lower diffraction peak values corresponding to the increased interlayer space after melt compounding with PBT. This indicated that the PBT was intercalated into the clay galleries, and the increased reflection intensities also indicated the formation of more ordered silicate structures, but the degree of
intercalation varied with the O-MMTs.

![X-ray Diffraction patterns](image)

**Figure 4.** X-Ray Diffraction patterns of (a) 04AP-POSS/08BDA/MMT, (b) 04AP-POSS/08ODA/MMT, (c) 04AP-POSS/08DTDMA/MMT and their PBT nanocomposites containing 3 wt.% of dual-surfactant modified montmorillonites.

TEM studies further confirmed the dispersion states of the various dual-surfactant modified MMTs in the PBT matrix. It was obvious that the PBT/04AP-POSS/08BDA/MMT nanocomposite showed a better dispersion level than the others. The primary particles of 04AP-POSS/08BDA/MMT were partially exfoliated into single layers and thin multi-layer stacks were randomly and uniformly dispersed in the PBT matrix, along with a few big aggregates (Figure 4. 33a). In comparison, PBT/04AP-POSS/08DTDMA/MMT showed relative uniform dispersion but little intercalation, as a large proportion of silicates were stacked and
aggregated (Figure 4. 33b).

**Figure 4. 33** TEM pictures of PBT/clay nanocomposites containing 3 wt.% of dual-surfactant modified MMT: (a) PBT/04AP-POSS/08BDA/MMT, (b) PBT/04AP-POSS/08DTDMA/MMT.

The difference between these dual-surfactant modified MMTs comes from their varying surface properties, as matched surface polarity between polymer and organoclay was imperative for the polymer to be fully wetted and so intercalate the silicate layers [38]. 04AP-POSS/08BDA/MMT showed the biggest initial interlayer spacing (>4 nm), allowing for an easier intercalation by the PBT chains. Its relatively high polarity (>10 %) matched to the polar PBT matrix and high thermal stability (i.e.
first DTG peak at ~330 °C) maintained the surface properties during high temperature melt compounding, which in turn favoured extensive intercalation. In addition, strong polar-type interactions between hydroxyl groups from BDA surfactant and carboxyl groups present in PBT, further promoted the intercalation of PBT chains and the formation of PBT/clay nanocomposites. However, the presence of the hydroxyl groups also enhanced the interaction of the BDA with the silicate surfaces. As a result, replacement of the surface contacts by PBT chains will be less favourable, impeding the extensive intercalation and further exfoliation of 04AP-POSS/08BDA/MMT in PBT matrix [116]. Moreover, relatively low degrees of surface coverage calculated for 04AP-POSS/08BDA/MMT, leading to the formation of large silicate particle size and a high degree of hydrophilicity, restricting further intercalation and full exfoliation, as evidenced by the peak at 1.50 nm in Figure 4.32.

On the other hand, although a big initial interlayer spacing (~3.2 nm) of 04AP-POSS/08DTDMA/MMT enabled an early intercalation of PBT chains, relative low polarity (1.5 %) made it less compatible with PBT matrix (IFE>6 mN/m). Furthermore, the lack of strong polar interactions between organic surfactants and PBT molecules further discouraged the intercalation of PBT chains. Similar explanations can be applied to PBT/04AP-POSS/08ODA/MMT. In addition to its low thermal stability (first DTG peak at ~220 °C), which badly affected their surface properties in melt processing and made these less compatible with PBT matrix, resulting in relative poor dispersion and only giving intercalated clay structures in PBT. It was again demonstrated that that interlayer spacing and thermal stability of O-MMTs, compatibility and optimum interactions between polymer matrix, organic surfactants and the silicate layer surface were crucial to the formation of intercalated and especially exfoliated polymer/clay nanocomposites [193].
As a comparison, the dispersion of O-MMTs into another polar polymer matrix of PA 12 was also investigated. Figure 4.34 shows the XRD patterns of two dual-surfactant modified MMTs, PA 12 and their nanocomposites. The basal reflection (001) of 04OA-POSS/08DTDMA/MMT (Figure 4.34A) shifted from 4.1° (2.16 nm) to 2.8° (3.19 nm) after melt compounding with the PA 12 matrix, indicating that intercalated MMT particles were formed in the polymer matrix. The appearance of a reflection at 2θ=5.1° (d=1.75nm), could be due to either the (002) reflection of neat PA 12 or due to the collapse of the montmorillonite particles [105].

In the 04AP-POSS/08DTDMA/MMT filled PA 12 nanocomposite (Figure 4.34B), its basal spacing was increased from 3.24 nm to over 4.0 nm, and the shape of the reflection shifted to a shoulder-like and low intensity peak, suggesting the formation of a more disordered or partially exfoliated structure in the polymer matrix [83, 194].
Figure 4. XRD patterns of PA 12, 04OA-POSS/08DTDMA/MMT and their nanocomposites (a), PA12, 04AP-POSS/08DTDMA/MMT and their nanocomposites (b).
TEM examination confirmed the formation of intercalated and partially exfoliated MMT particles in the PA 12 matrix for two dual-surfactant modified MMTs (04OA-POSS/08DTDMA/MMT and 04AP-POSS/08DTDMA/MMT), respectively, as shown in Figure 4.35. 04OA-POSS/08DTDMA/MMT did not disperse very well and a small proportion of O-MMT remained as thin platelets with several layers which presumably were intercalated. In comparison, 04AP-POSS/08DTDMA/MMT showed uniform dispersion with a number of exfoliated particles, although some small particles with thickness of several nanometers remained.

Figure 4.35 TEM micrographs of (a) 04OA-POSS/08DTDMA/MMT filled PA 12 nanocomposites and (b) 04AP-POSS/08DTDMA/MMT filled PA12 nanocomposites, both in the weight ratio of 97/3 (PA12/MMT)
However, the results obtained by XRD and TEM appeared not quite consistent with the interfacial free energy calculations which predicted that the better compatibility would be achieved between 04OA-POSS/08DTDMA/MMT and PA 12, as the system had a lower IFE value (IFE= 1.0 mN/m). This was probably due to the thermal stability of these O-MMTs. As discussed previously, 04OA-POSS/08DTDMA/MMT possessed lower thermal stability compared to that of 04AP-POSS/08DTDMA/MMT, which could induce some degradation of the surfactants during the melt compounding (at 220 °C for 15 min). Additionally, the degradation of the relatively large proportion of the second surfactant DTDMA in the dual-surfactant formulation of 04OA-POSS/08DTDMA/MMT, led to changes in the surface properties of the modified MMTs, making it more hydrophilic.

For 04AP-POSS/08DTDMA/MMT, although thermal decomposition occurred on DTDMA, most of the hydrophilic surfaces of the clay mineral were still covered by the more hydrophobic AP-POSS and intercalated DTDMA, resulting in better compatibility of 04AP-POSS/08DTDMA/MMT in PA 12. In addition, a relatively large initial interlayer spacing of 04AP-POSS/08DTDMA/MMT (3.22 nm) compared to that of 04OA-POSS/08DTDMA/MMT (2.16 nm) led to an easier intercalation of PA 12 chains. Moreover, the low degree of surface coverage for 04OA-POSS/08DTDMA/MMT, resulted in the formation of larger sized silicate particles that were difficult to further intercalate by the PA 12 molecules. The morphology of partially exchanged 04AP-POSS/MMT in the PA 12 matrix, (see Figure 4. 36) further confirmed that low surface coverage would result in difficulties in intercalation, and consequently poor dispersion of O-MMTs, as several large aggregates were observed, although a number of silicates appeared to be intercalated or partially exfoliated. Therefore, both the high thermal stability and compatibility of the modified clays with the polymer matrix were essential for achieving a good dispersion and full exfoliation [179].
Figure 4.36 TEM micrograph of 04AP-POSS/MMT filled PA 12 nanocomposites containing 3 wt.% organoclays.

The different dispersion states of 04AP-POSS/08DTDMA/MMT in PBT and PA 12 matrix have to be addressed in terms of the compatibilities between them. As summarised in Table 4.4, higher IFE value was calculated for PBT and 04AP-POSS/08DTDMA/MMT, due to the relative high polarity of the PBT matrix, suggesting that 04AP-POSS/08DTDMA/MMT would be more compatible with PA 12 than PBT. The temperature used for melt compounding PA12 nanocomposites (at 220 °C) was lower than that of PBT nanocomposites (at 240 °C), which would have reduced the risk of thermal degradation of the organic surfactants so maintaining relatively good surface properties of O-MMT, leaving to the formation of partially exfoliated structures in the PA 12 matrix. More importantly, in comparison to the lack of strong polar interactions between the silicates and the PBT matrix, the existence of amine groups and carboxylic acid units in PA 12 chains, promoted physically interactions between silicate surfaces and PA 12, which increased the silicate surfaces to be contacted by PA 12 chains and promote the formation of exfoliated silicate layers, (as shown in Figure 4.37) [35]. In addition, the higher viscosity of molten PA 12 than that of molten PBT enhanced shearing forces that were applied on O-MMTs and further encouraged the formation of PA12 nanocomposites.
In order to further address the effect of a polar polymer matrix on the clay dispersion, PA 11 and PA 6 nanocomposites containing 3 wt.% 04AP-POSS/08DTDMA/MMT, respectively, together with 3 wt.% 04AP-POSS/08DTDMA/MMT loaded PA 12 nanocomposites were analysed by WAXD and TEM. Figure 4. 38 shows X-ray diffractions with low 2θ values for nanocomposites formed from PA 6, PA 11 and PA 12 and the O-MMT: 04AP-POSS/08DTDMA/MMT. Nanocomposites based on PA 6 exhibited relatively smooth scattering profiles, with an absence of any basal reflections, which indicated the disruption of the ordered silicate layers, and the formation of high degree exfoliated structures in PA 6 matrix. While a broadened and low intensity peak was observed both for PA 11 and PA 12 based nanocomposites, at low diffraction angles (corresponding to $d_{001}=\sim4$ nm), suggesting partially exfoliation of silicate layers was achieved for both PA 11 and PA 12 matrices.
Figure 4.38 XRD patterns of (a) 04AP-POSS/08DTDMA/MMT; (b) PA 12/clay nanocomposites; (c) PA 11/clay nanocomposites; and (d) PA 6/clay nanocomposites containing 3 wt.% 04AP-POSS/08DTDMA/MMT, respectively.

The TEM photomicrographs in Figure 4.39, provide more conclusive evidence of the extent of clay dispersion, while supporting the interpretation of the XRD results given above. Nanocomposites based on PA 6 (Figure 4.39a) exhibited a well-exfoliated morphology, consisting predominantly of single silicate layers dispersed uniformly throughout the PA 6 matrix. Nanocomposites based on PA 11 (Figure 4.39b), and PA 12 (Figure 4.35b), also showed a high degree of exfoliation. However, the extent of delamination was less than that of PA 6 based nanocomposites, due to the formation of relatively few aggregated clay particles.
Figure 4. TEM micrographs of (a) PA 6/organoclay and (b) PA 11/organoclay nanocomposites containing 3 wt.% 04AP-POSS/08DTDMA/MMT, respectively.

As polarity of a polymer matrix is an important factor that determines the level of the interaction with an organoclay, the increasing number of methylene units in the polyamide repeat structure relative to PA 6 results in lower polarity of PA 11 and PA 12, with 14.9 % and 12.5 %, respectively, which in turn reduce the thermodynamic affinity between the polymer and organoclay [34]. Although poor compatibility was calculated for the PA 6 and 04AP-POSS/08DTDMA/MMT combination due to a higher IFE value (~8.5 mN/m), compared to that of PA 11/O-MMT (IFE=6.0 mN/m) and PA 12/O-MMT (IFE=2.9 mN/m), the interactions appeared to be dominated by polymer-silicate interactions rather than polymer-surfactant interactions, due to the
existence of the amine groups and carboxylic acid units, which were capable of physically interacting with the silicate surface. The higher polarity of PA 6 (18.3 %) enabled strong interactions to occur between silicates and polymer matrix, resulting in a well-exfoliated clay structure in PA 6 matrix.

4.5 Tensile Properties of Organo-Montmorillonite/Polymer Nanocomposites

4.5.1 PP/Organo-Montmorillonite Nanocomposites

4.5.1.1 The Effect of Compatibiliser PP-g-MA

![Graph showing the influence of PP-g-MA concentration on the tensile properties of PP/O-MMT nanocomposites](image)

**Figure 4.** The influence of PP-g-MA concentration on the tensile properties of PP/O-MMT nanocomposites, containing 3 wt.% organoclays.
The effect of compatibiliser PP-g-MA on the tensile properties of PP/clay nanocomposites is presented Figure 4.40. Comparing the compatibilised and non-compatibilised PP/clay nanocomposites, the modulus of non-compatibilised PP/clay nanocomposite was enhanced as compatibiliser PP-g-MA was used, and increased with increased loading of PP-g-MA. As much as a 36.5% increase in modulus was observed for the compatibilised PP/O-MMT+10%MAPP from 720 MPa of non-compatibilised PP/O-MMT nanocomposites to 990 MPa. As the modulus is determined at a low stress level, the quality of organo-montmorillonite (O-MMT) dispersion plays an important role. The finer (nanometer-sized) dispersion of silicate layers in the PP matrix, led to improved modulus [195]. When more PP-g-MA was involved in PP/clay composites, there were more chances for silicate layers to be intercalated. This is because only the PP-g-MA can intercalate into the clay galleries at the first stage of the mixing process due to the driving force originating from the strong hydrogen bonding between the maleic anhydride group and the oxygen groups of the silicates [76]. Upon the intercalation of PP-g-MA, the interlayer spacing of the clay increased, and the interaction of the layer should have been weakened, allowing the PP to more easily penetrate into the clay galleries. By forming a fine dispersion of the intercalated or exfoliated silicate structure within the polymer matrix, good mechanical properties would have resulted.

Conversely, the concentration of PP-g-MA did not have a considerable effect on the tensile strength of the PP/clay nanocomposites, which only slightly increased from 33 MPa of non-compatibilised PP/O-MMT to 35 MPa of PP/O-MMT+6%MAPP nanocomposites. This suggests that MMT particles did not adequately exfoliate into the PP matrix, which supported the TEM findings.
Although PP/O-MMT+10%MAPP nanocomposites possess higher modulus, the tensile strength was slightly decreased from the 35 MPa of PP/O-MMT+6%MAPP to 34 MPa of PP/O-MMT+10%MAPP, which implies that the addition of PP-g-MA into pure PP will degrade its mechanical properties. As shown in Figure 4.41, both the tensile modulus and strength were reduced with increasing loadings of PP-g-MA. This was mostly due to the grafting of MA on the PP chains reducing its molecular weight and crystallinity of PP [196, 197], and decreasing the mechanical properties of PP. Therefore, a correct selection of the PP-g-MA concentration has a significant effect on the dispersion of O-MMTs in PP matrix, and in turn the mechanical properties of PP/clay nanocomposites.

Figure 4.41 The effect of compatibiliser PP-g-MA concentration on the tensile properties of polypropylene.
4.5.1.2 The Influence of Organo-Montmorillonite

The effect of various organically modified MMTs on the tensile properties of PP/clay nanocomposites is summarised in Table 4.7. The tensile modulus of PP was increased from 410 MPa for PP/MAPP to as high as 1020 MPa of 04AP-POSS/08DTDMA/MMT filled PP nanocomposites, but varied with different modified clays. While the tensile strength values remained very similar when organoclay was added, the elongation properties of PP were reduced dramatically from over 500 % to less than 25 % of PP/O-MMT nanocomposites, suggesting that the dispersion of O-MMT was not good enough to fully exfoliate in PP, which was supported by morphology studies, discussed previously.

Mechanical properties of polymer nanocomposites were found to be very dependent on their morphology, which has to be related to the structures of organic surfactants, making the tensile modulus vary between different O-MMTs filled PP nanocomposites. It was reported that two distinct aspects have to be considered during the organic modification of the MMTs: minimisation of the platelet-platelet cohesion forces and of the interaction between the polymer and clay surface [58, 59, 62, 63]. The minimisation of the platelet-platelet cohesion forces is proportional to the increase of the interlayer space. On the other hand, the minimisation of the unfavourable interaction between polymer and clay surface is proportional to the degree of surface coverage.


Table 4. 7 Tensile properties of PP and its nanocomposites with various O-MMTs.

<table>
<thead>
<tr>
<th>matrix</th>
<th>Fillers (3 wt.%)</th>
<th>Modulus (MPa)</th>
<th>Strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td></td>
<td>515±35</td>
<td>35</td>
<td>560</td>
</tr>
<tr>
<td>PP/MAPP</td>
<td></td>
<td>410±5</td>
<td>34</td>
<td>560</td>
</tr>
<tr>
<td>PP/MAPP</td>
<td>Cloisite 15A</td>
<td>550±51</td>
<td>34</td>
<td>15</td>
</tr>
<tr>
<td>PP/MAPP</td>
<td>APS-15A</td>
<td>690±91</td>
<td>33</td>
<td>16</td>
</tr>
<tr>
<td>PP/MAPP</td>
<td>HTP/MMT</td>
<td>530±57</td>
<td>37</td>
<td>18</td>
</tr>
<tr>
<td>PP/MAPP</td>
<td>04AP-POSS/MMT</td>
<td>920±10</td>
<td>33</td>
<td>24</td>
</tr>
<tr>
<td>PP/MAPP</td>
<td>04AP-POSS/08DTDMA/MMT</td>
<td>1020±52</td>
<td>35</td>
<td>19</td>
</tr>
</tbody>
</table>

1. The reference PP samples were processed at the same melt compounding conditions as other formulation of PP.
2. The percentage of PP-g-MA was chosen with 10 wt.%. 
3. Commercial organoclay Cloisite 15A was used as received.
4. The percentage of silane coupling agent APS was optimised at 5 wt.%.

In the case of Cloisite 15A, both interlayer space (~3.1 nm) and clay surface coverage (1.37 CEC) were high enough to achieve good dispersion and intercalation. However, a large amount of organic fraction from Cloisite 15A, could have acted as a plasticising agent at temperatures above Tg [198], which reduced its mechanical properties. Moreover, the compatibility between Cloisite 15A and PP was not relatively good as calculated by IFE (6.1 to 7.1 mN/m). This was improved by silylation of the Cloisite 15A, the reduced IFE value (5.3 to 6.8 mN/m) between APS-15A and PP indicate the potential for better compatibility between matrix and clay fillers, although interlayer space (2.5 nm) was slightly reduced after silylation, due to the release of excess organic surfactant. The silicate surface exchange still remained as high as 0.98 CEC, which was of great importance in order to minimise the unfavourable interaction between PP and organoclays. On the other hand, the loss of organic surfactants during silylation lowered the organic fraction of organoclay, which reduced any plasticisation effects during melt compounding and improved the thermal stability of organoclay as well. In addition, a grafted silane coupling agent was found to have a reinforcing effect when it was mixed with polymers [199].
However, the phosphonium surfactant HTP modified MMT only generated 1.90 nm interlayer space, although 1.07 CEC HTP was present in MMT. Additionally, the presence of polar functional groups (-OH) in the HTP molecules made it more polar and so not very compatible with non-polar PP matrix, resulting in a poor dispersion of HTP/MMT in PP matrices (as shown in Figure 4.27), and dramatically reduced tensile modulus compared to APS-15A filled PP nanocomposites.

For PP/MAPP/04AP-POSS/MMT, the organoclay was partially exchanged (0.20 CEC), due to the large molecular structure of AP-POSS surfactant, leaving some clay surfaces uncovered and less compatible with PP matrix ($\gamma_{mf}=9.1-10.1$ mN/m). However, the 04AP-POSS/MMT particles still dispersed in a reasonably uniform manner and formed intercalated structures in the PP matrix, due to its large interlayer spacing (3.4 nm) and strong thermal stability, (over 300 ºC). The tensile modulus was improved significantly from 410 MPa of PP/MAPP to 920 MPa of PP/MAPP/04AP-POSS/MMT. By introducing the second surfactant DTDMA to 04AP-POSS/MMT, the coverage of MMT was increased to 0.74 CEC, and its compatibility with PP matrix was also improved ($\gamma_{mf}=-0.7$ mN/m). In the meantime, the interlayer space of 04AP-POSS/08DTDMA/MMT still remained large enough at 3.22 nm and its thermal stability, did not be sacrificed by the second surfactant DTDMA, maintaining at ~295 ºC. Physically, two structures of surfactants (AP-POSS vs. DTDMA) could provide more conformational freedom for further intercalation and/or exfoliation of O-MMTs during melt compounding [153, 156]. The dispersion of 04AP-POSS/08DTDMA/MMT in PP matrix was even better and a partially exfoliated structure was observed (Figure 4.30b). As a result, the highest tensile modulus was achieved from PP/MAPP/04AP-POSS/08DTDMA/MMT nanocomposites.

It was noticeable that POSS modified MMT filled PP nanocomposites showed much better tensile modulus than those generated by conventional organic surfactants (i.e. alkylammonium or alkylphosphonium cations) modified MMTs. This could be due...
to the reinforcing effect of POSS molecules at low concentration (<10 wt.%) [200, 201] besides the reinforcement generated from MMT. Unlike other conventional organic surfactants, AP-POSS has a rigid inorganic silicon oxygen cubic structure which provides nanoscale reinforcement to the PP matrix, resulting to the increase of mechanical properties of PP nanocomposites.

A careful choice of a second surfactant to AP-POSS modified MMT is also important for the mechanical properties of PP nanocomposites, due to its effect on the compatibility between polymer matrix and MMT. As shown by Figure 4. 42, the best mechanical properties were achieved from 04AP-POSS/08DTDMA/MMT filled PP nanocomposites with 1020 MPa in modulus and 35 MPa in tensile strength. While regard to previous reported TEM morphology and interfacial properties, 04AP-POSS/08ODA/MMT and 04AP-POSS/08DTDMA/MMT showed relatively smaller IFE values compared with other dual-surfactant modified MMTs (04AP-POSS/08BDA/MMT), indicating good compatibility between O-MMT and PP matrix, and this was confirmed by TEM micrographs which showed good dispersion with partial exfoliation for 04AP-POSS/08DTDMA/MMT in PP matrix (Figure 4. 30).
Figure 4.2 Influence of various dual-surfactant modified MMTs on mechanical properties of PP nanocomposites, containing 3 wt.% of A) 04AP-POSS/08BDA/MMT, B) 04AP-POSS/08ODA/MMT and C) 04AP-POSS/08DTDMA/MMT.

4.5.2 PBT/Organo-Montmorillonite Nanocomposites

The effect of organically modified MMT on the tensile properties of PBT/clay nanocomposites are presented in Table 4.8. It can be seen that the dispersion of the O-MMTs on the nanometer scale (as shown in Figure 4.33) provides the PBT/clay nanocomposites with improved mechanical properties, and the most significant improvement was observed from PBT nanocomposites containing 3 wt.% dual-surfactant modified clay (04AP-POSS/08BDA/MMT) with the highest tensile modulus (1470 MPa) and tensile strength (55 MPa). In order to compare the reinforcing effect among these PBT/clay nanocomposites more clearly, the relative tensile moduli of the nanocomposites to that of unfilled PBT are shown in Figure 4.
43. It shows that all the PBT/clay nanocomposites exhibited higher modulus than pure PBT, but the degree of modulus enhancement varied with O-MMTs used, and up to a 38% increase was obtained for PBT/04AP-POSS/08BDA/MMT nanocomposites.

**Table 4.8** Tensile properties of various PBT/O-MMT nanocomposites containing 3 wt.% of organoclays (tested according to ASTM D638, at 5 mm/min crosshead head speed).

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Fillers (3 wt.%)</th>
<th>Modulus (MPa)</th>
<th>Strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>PBT</td>
<td>1070±107</td>
<td>54</td>
<td>130±95</td>
</tr>
<tr>
<td>B</td>
<td>PBT</td>
<td>1270±24</td>
<td>50</td>
<td>13</td>
</tr>
<tr>
<td>C</td>
<td>PBT</td>
<td>1240±81</td>
<td>49</td>
<td>10</td>
</tr>
<tr>
<td>D</td>
<td>PBT</td>
<td>1230±97</td>
<td>46</td>
<td>21</td>
</tr>
<tr>
<td>E</td>
<td>PBT</td>
<td>1240±31</td>
<td>49</td>
<td>14</td>
</tr>
<tr>
<td>F</td>
<td>PBT</td>
<td>1470±111</td>
<td>55</td>
<td>21</td>
</tr>
<tr>
<td>G</td>
<td>PBT</td>
<td>1310±20</td>
<td>54</td>
<td>20</td>
</tr>
<tr>
<td>H</td>
<td>PBT</td>
<td>1210±20</td>
<td>52</td>
<td>17</td>
</tr>
</tbody>
</table>

1 Melt compounded at the same conditions as other PBT/clay nanocomposites
2 The concentration of APS was used as 100 wt.% of organoclay.

**Figure 4.43** Relative tensile modulus ($E_{hybrid}/E_{PBT}$) of various PBT/clay nanocomposites containing 3 wt.% of organoclays, B: Cloisite 30B, C: APS-30B, D: HTP/MMT, E: 04AP-POSS/MMT, F: 04AP-POSS/08BDA/MMT, G: 04AP-POSS/08ODA/MMT, and H: 04AP-POSS/08DTDMA/MMT, respectively.
As discussed early, introducing montmorillonite (~178 GPa) [202] with an extremely large modulus into a relatively soft polymer matrix will give a high composite modulus, following a simple additivity rule, despite some O-MMTs not being well dispersed in PBT matrix, as evidenced by TEM observations. It is recognised that the degree of modulus enhancement experienced in polymer/clay nanocomposites is proportional to the aspect ratio of the dispersed silicate particles, which is directly related to the extent of clay dispersion [34]. The interfacial areas between polymer and inorganic clays are increased tremendously with the increasing degree of dispersion of the silicate layers, and the resultant huge interfacial interactions can induce significant improvements in the mechanical properties of the polymer/clay nanocomposites, especially for those containing exfoliated silicate structures [118]. The greatest stiffening effect in the 04AP-POSS/08BDA/MMT filled PBT nanocomposites had to be correlated with the finer dispersion of silicate layers, and the formation of partially exfoliated structures in the PBT matrix (Figure 4. 33a) compared to other O-MMTs. Although a reasonably fine dispersion was observed in PBT/Cloisite 30B nanocomposites, small molecules, i.e. α-olefins, amines or intermediates [125], generated by degradation of a lower thermally stable Cloisite 30B, under high temperature processing, could affect the polymer matrix [91, 92]. Hence, plasticisation of the PBT, negatively affecting the properties of PBT to relatively low tensile modulus (1270 MPa) was obtained for PBT/Cloisite 30B nanocomposites.

Similar trends were also observed for the tensile strength of PBT/clay nanocomposites (Table 4. 8). Of the PBT/clay nanocomposites, PBT/04AP-POSS/08BDA/MMT exhibited the highest tensile strength of 55 MPa, due to its fine dispersion and partially exfoliated silicate structure. However, lower tensile strength values were obtained for most PBT/clay nanocomposites as compared to that of pure PBT (54 MPa), which was mainly attributed to the poor dispersion of the clay in the PBT nanocomposite, especially for the HTP/MMT that has the lowest tensile strength (46 MPa). As tensile strength is very sensitive to the
degree of clay dispersion in polymer matrix [102], the large aggregated particles formed in APS-30B, HTP/MMT and 04AP-POSS/MMT filled PBT composites, may have acted as crack initiators so degrading the mechanical properties of the composites. In addition to the slightly better dispersion of those dual-surfactant modified MMTs in PBT matrix, the reinforcing effect of POSS molecules at low concentration (<10 wt.%) [200, 201] may also contribute to the superior tensile strength properties of those dual-surfactant modified MMTs filled PBT nanocomposites than those single-surfactant modified MMTs filled PBT composites.

Furthermore, a higher crystallinity of the polymer may lead to an increase in the strength and stiffness of the material [203]. It is well accepted that clay layers may serve as additional nucleation sites which accelerate the crystallisation and hence higher crystallinity of polymer matrix [204]. The finer dispersion of silicate layers, provides large amounts of heterogeneous nucleation sites for the crystallisation of PBT, thus even higher crystallinity would be achieved in high degree exfoliated PBT/clay nanocomposites [168], which also contributed to the larger enhancement of PBT/04AP-POSS/08BDA/MMT nanocomposites.

4.5.3 PA/Organo-Montmorillonite Nanocomposites

4.5.3.1 The Effect of Organo-Montmorillonites

The moduli of all O-MMT filled PA12 nanocomposites (Table 4. 9) were improved compared to that of bulk PA12. The highest improvement was achieved by 04AP-POSS/08DTDMA/MMT filled PA12 nanocomposites with ~60 % increase from 490 MPa for bulk PA 12 to 790 MPa for PA 12/04AP-POSS/08DTDMA/MMT nanocomposites, which contained 3 wt.% of organoclay. The enhancement of the tensile properties may be attributed to the exertion of the strong clay mineral particles themselves, a good dispersion of the silicate layers and strong interaction
between polymer and O-MMTs [205, 206]. The different improvements in the moduli between the four O-MMTs are most likely to be due to the differences in dispersion in the PA12 matrix, as shown by the XRD (Figure 4. 34b) and TEM (Figure 4. 35b) results.

Table 4. 9 Tensile properties (at RT) of PA12 and various O-MMTs loaded PA 12 nanocomposites containing 3 wt.% organoclays.

<table>
<thead>
<tr>
<th>Sample1</th>
<th>Modulus (MPa)</th>
<th>Yield Strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA122</td>
<td>490±56</td>
<td>39</td>
<td>290</td>
</tr>
<tr>
<td>PA12/04AP-POSS/MMT</td>
<td>650±98</td>
<td>41</td>
<td>240</td>
</tr>
<tr>
<td>PA12/04OA-POSS/MMT</td>
<td>590±86</td>
<td>41</td>
<td>230</td>
</tr>
<tr>
<td>PA12/04AP-POSS/08DTDMA/MMT</td>
<td>790±155</td>
<td>42</td>
<td>265</td>
</tr>
<tr>
<td>PA12/04OA-POSS/08DTDMA/MMT</td>
<td>650±105</td>
<td>41</td>
<td>260</td>
</tr>
</tbody>
</table>

1 All the PA 12 nanocomposites contain 3 wt.% organo-montmorillonites.
2 It was melt compounded at the same conditions as other PA 12 nanocomposites.

For the tensile yield strength, a similar tendency was observed, and the strength was enhanced from 39 MPa for PA12 to 42 MPa for 04AP-POSS/08DTDMA/MMT filled PA 12 nanocomposite. This was because the yield strength was very sensitive to the degree of clay dispersion in polymer matrix [102]. Elongation properties were normally reduced with increasing stiffness of a composite, especially with less well dispersed fillers in the composites. In these studies, the maximum reduction observed was from the highest value (290 %) for pure PA 12 to the lowest value (230 %) for a 04OA-POSS/MMT filled PA 12 nanocomposite. The best performance was obtained from 04AP-POSS/08DTDMA/MMT filled PA12 nanocomposite, of the four O-MMTs, which was mainly due to its good dispersion as well (Figure 4. 35b).

The effect of O-MMT content on PA 12 mechanical properties was also investigated on 04AP-POSS/08DTDMA/MMT filled PA 12 nanocomposites (Table 4. 10). It was noticed that there was an optimum MMT content around 3 wt.% for improving tensile modulus and yield strength. The decrease in tensile modulus and yield
strength at higher MMT contents, can be attributed to the aggregation of the clay mineral particles at higher contents [207]. This was confirmed by XRD measurements (Figure 4.44), which showed the changes of clay morphology in term of MMT content. At lower concentrations, the XRD pattern was relatively smooth, and the intensity increased with the MMT content until a very sharp reflection appeared, indicating that the nanocomposite structure shifted from exfoliated to intercalated, with the formation of aggregates within the PA 12 matrix.

<table>
<thead>
<tr>
<th>MMT content (wt.%)</th>
<th>Modulus (MPa)</th>
<th>Yield Strength (MPa)</th>
<th>Elongation (%)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>490±56</td>
<td>39</td>
<td>290</td>
<td>20.36</td>
</tr>
<tr>
<td>1</td>
<td>570±92</td>
<td>40</td>
<td>280</td>
<td>20.82</td>
</tr>
<tr>
<td>3</td>
<td>800±147</td>
<td>42</td>
<td>265</td>
<td>23.14</td>
</tr>
<tr>
<td>5</td>
<td>650±64</td>
<td>41</td>
<td>270</td>
<td>23.00</td>
</tr>
<tr>
<td>10</td>
<td>700±130</td>
<td>41</td>
<td>110</td>
<td>21.89</td>
</tr>
</tbody>
</table>

The crystal structure and degree of crystallinity were also important factors that can influence the mechanical properties. A higher crystallinity may have led to an increase in the strength and stiffness of the material [203]. The (200) and (001) reflections located at 2θ≈5.8º and 2θ≈21.4º for pure PA12 and its nanocomposites of the pseudo-hexagonal γ-form of PA12 [208, 209] did not change at all (Figure 4.44), suggesting that no crystal phase transformation or new crystal formation occurred when O-MMTs were introduced into PA12 matrices. There was a little increase in the degree of crystallinity (Table 4.10) from 20.4 % of pure PA12 to 23.1% for 3 wt.% of 04AP-POSS/08DTDMA/MMT loaded PA12 nanocomposite, which also contributed to the better mechanical properties of the nanocomposite.
Figure 4.44 XRD patterns of 04AP-POSS/08DTDMA/MMT filled PA12 nanocomposites as a function of MMT content.

4.5.3.2 The Effect of Polyamide Matrices

Enhancements in mechanical properties associated with the addition of clay provided another means of assessing the effects of polymer matrix on the extent of exfoliation in polyamide nanocomposites. Table 4.11 summarises the effect of polyamide polymer matrices on the tensile properties of PA/clay nanocomposites. It shows that by dispersion of O-MMTs into polymer matrices, the tensile moduli of PA nanocomposites were increased from 720 MPa for pure PA 6 to 1180 MPa, from 430 MPa for pure PA 11 to 550 MPa, and from 490 MPa for pure PA 12 to 800 MPa, corresponding to PA 6, PA 11 and PA 12 nanocomposites, respectively.
Table 4.11 Tensile properties of PA/clay nanocomposites based on PA 6, PA 11 and PA 12 that contain 3 wt.% O-MMTs (04AP-POSS/08DTDMA/MMT).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tensile Modulus (MPa)</th>
<th>Yield Strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA 6(^1)</td>
<td>720±42</td>
<td>66</td>
<td>220</td>
</tr>
<tr>
<td>PA 6 nanocomposite</td>
<td>1180±23</td>
<td>75</td>
<td>26</td>
</tr>
<tr>
<td>PA 11(^1)</td>
<td>430±30</td>
<td>40</td>
<td>320</td>
</tr>
<tr>
<td>PA 11 nanocomposite</td>
<td>550±125</td>
<td>38</td>
<td>250</td>
</tr>
<tr>
<td>PA 12(^1)</td>
<td>490±56</td>
<td>39</td>
<td>290</td>
</tr>
<tr>
<td>PA 12 nanocomposite</td>
<td>800±147</td>
<td>42</td>
<td>260</td>
</tr>
</tbody>
</table>

\(^1\) Samples were melt compounded at the same conditions as its nanocomposites

However, before discussing the effect of polymer matrix, it is important to highlight the fact that an unfilled PA 6 is a stronger polymer matrix than the unfilled PA 11 and PA 12 materials, and low modulus matrices generally offer greater potential for reinforcement than high modulus matrices for a given filler aspect ratio. Therefore, comparing the relative modulus of nanocomposites based on polymer matrices with different moduli may be misjudged if this effect is not considered. On the other hand, due to the fact that the modulus enhancement from polymer/clay nanocomposites is directly related to the degree of clay exfoliation, as discussed earlier, ‘exfoliation efficiency’ [34] was proposed as a value to evaluate the stiffness between different matrices based polymer/clay nanocomposites. The exfoliation efficiency is defined as the experimentally obtained modulus of the nanocomposites divided by the modulus calculated from the theory, assuming perfect exfoliation based on the theory of Halpin-Tsai and modified Halpin-Tsai model [210].

\[
\frac{E_c}{E_m} = \frac{1 + \xi \eta V_f}{1 - \eta V_f} \quad \text{(Eq.4-2)}
\]

\[
\eta = \frac{(E_f/E_m) - 1}{(E_f/E_m) + \xi} \quad \text{(Eq.4-3)}
\]

\[
V_f = \frac{W_f \rho_N}{\rho_{MMT} - W_f (\rho_N + \rho_{MMT})} \quad \text{(Eq.4-4)}
\]
where $E$ is Young’s modulus, with the subscripts $c$, $m$ and $f$ correspond to the modulus of composite, matrix and filler, respectively. $V_f$ and $W_f$ are the volume fraction and weight fraction of filler, respectively, while $\xi$ is the shape factor that determined by filler geometry. $\rho$ refers to the density, whilst subscripts MMT and N correspond to the montmorillonite particles and polyamide matrix, respectively.

Substituting $W_f=0.03$ and the density $\rho_N$ (PA 6=1080 kg/m$^3$, PA 11(PA 12)=1020 kg/m$^3$) into Eq.4-4, the volume fraction of MMT can be calculated as 0.01411 for PA 6 nanocomposites and 0.01332 for PA 11 (PA 12) nanocomposites. The shape factor $\xi$ was simplified to ~200 for MMT [210] in addition to the modulus for MMT is 178 GPa [34], theoretical elastic moduli for polyamides 6, -11 and -12 nanocomposites can be obtained in association with the Eq.4-2 and Eq.4-3, with 1.8 GPa, 1.2 GPa, and 1.3 GPa, respectively. Consequently, the exfoliation efficiency for PA 6, -11 and -12 nanocomposites containing 3 wt.% 04AP-POSS/08DTDMA/MMT are 0.64, 0.46 and 0.59, respectively. Higher exfoliation efficiency obtained for PA 6/clay nanocomposites compare to those based on PA 11 and PA 12 polymer matrices, suggesting that PA6 was most effectively reinforced by 04AP-POSS/08DTDMA/MMT. This corresponded well with the morphologies that PA 6/clay nanocomposites exhibited uniform dispersion and higher degree exfoliated silicate layers, while partial exfoliation was obtained for both PA 11/clay and PA 12/clay nanocomposites. In addition, AP-POSS molecules used as clay modifier may also act as reinforcement for PA nanocomposites due to its nanometer scale, the compatibility between AP-POSS and PA matrices may also affect the modulus enhancement in PA/clay nanocomposites.

Similar structure-property effects were observed from the changes in yield strength. Nanocomposites formed from PA 6 exhibit dramatic improvements from 66 MPa for pure PA 6 to 75 MPa for PA 6/04AP-POSS/08DTDMA/MMT nanocomposites, while the increased yield strength values for PA 11 and PA 12 nanocomposites were less pronounced. In general, introducing clay into polymer matrix resulted in a loss
of ductility for each polymer, however, the extent of reduction was considerably less for PA11 and PA 12 nanocomposites than those based on PA 6, which is most likely related to the higher inherent ductility of the PA 11 and PA 12 polymer matrices.
CHAPTER 5 CONCLUSIONS & FUTURE WORK

5.1 Conclusions

Based on the work conducted for this project, several conclusions can be drawn as follows:

1) Surface modification of montmorillonite is a key factor in the formation of polymer/clay nanocomposites. Commercially available organoclays are mostly alkyl quaternary ammonium cations based with low thermal stability, restricting them for the applications for high temperature processed engineering plastics, e.g. poly(butylene terephthalate) and many polyamides. In order to overcome this problem, silylation with silane coupling agent (APS) for commercial organoclays and the introduction of thermally stable surfactants, i.e. HTP and POSS, were used for the clay modifications. However, all of these organoclays were found to be less favourable for the formation of intercalated/exfoliated polymer/clay nanocomposites, suggesting that the effects of interlayer space, thermal stability and surface properties of organoclay are crucial in the clay selection.

2) Dual-surfactant modified clays with a combination of large interlayer spacing, relative good thermal stability and improved surface properties, were found to be more effective with the dispersion into polymer matrices to form intercalated/exfoliated polymer/clay nanocomposites. This further confirms the three criteria in clay selection, i.e. interlayer space, thermal stability and surface properties.
3) The differences of dual-surfactant modified clays in the formation of PP/clay and PBT/clay nanocomposites, suggest that the existence of polar-type interactions between organoclays and polymer matrices is also important for the formation of polymer/clay nanocomposites.

4) The effect of polar-type interactions on the morphology and mechanical properties of nanocomposites was investigated for PA 6, PA 11 and PA 12 based polymer/clay nanocomposites. The results showed that PA 6/clay nanocomposites were most effectively dispersed, implying that strong polar type interactions between polymer and organoclays were also important for the formation of these nanocomposites, as well as the large interlayer space, good thermal stability and good compatibility.

5) Although dual-surfactant modified clays showed better properties in the formation of polymer/clay nanocomposites, compared with those of conventional organically modified clays, there were occasions when these types of nanocomposites did not have the best properties. Maximising properties strongly depends on the combination of the two surfactants selected with respect to the polymer matrix, as suggested by a comparison between dual-surfactant modified clays, based on two types of POSS surfactants (AP-POSS vs. OA-POSS) and dispersed in PA 12. This study showed that AP-POSS based dual-surfactant modified clays give superior properties in the formation of PA 12/clay nanocomposites, when compared to the OA-POSS based clays.
5.2 Future Work

1. As the importance of surface modification for montmorillonite in the formation of polymer nanocomposites, dual-surfactant modification could be further optimised, e.g. the type of the surfactants, the ratio between two surfactants, the structures of the surfactants etc.

2. A lot of work has been carried out on alkyl quaternary phosphonium cation based, thermally stable organoclays, but good dispersion of this kind of clay has been rarely reported. Dual-surfactant modification may provide another option for those types of thermally stable organoclays.

3. Although the reinforcing effect of single POSS molecules in polymer matrix was reported, the combination of POSS molecules and MMT, especially for those POSS used as cationic surfactants is unknown. More detailed work on this kind of reinforcement will further develop the polymer/clay nanocomposites.
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APPENDICES

Appendix 1 List of Publications


Appendix 2 Abstracts of Published Work

1. Morphology and Properties of Silane-Modified Montmorillonite Clays and Clay/PBT Composites (Journal of Applied Polymer Science)

ABSTRACT: Commercial available organoclay (Closite30B) was modified by 3-aminopropyltriethoxysilane (APS) via a silylation reaction. Sodium clay (Closite Na) was treated by APS directly as a control. Such modified clays were further melt-compounded with polybutylene terephthalate (PBT). The morphology and properties of the modified organoclays and PBT/organoclay composites were characterized with X-ray diffraction, transmission electrical microscopy, Infra-red spectroscopy, contact angle measurement, thermogravimetric analysis and differential scanning calorimetry. The basal spacing of Closite Na was enlarged from 1.01 nm to 1.41 nm after APS treatment, indicating that the APS was intercalated into the clay intergalleries as a monolayer. The basal spacing of Closite 30B increased slightly after APS treatment, partially resulted from the reactions between the APS and hydroxyl groups on the intercalant of Closite30B. Closite 30B was found to be exfoliated disorderly after melt-compounded with PBT. While the APS modified Closite 30B only dispersed as swollen elliptical clay aggregates, in which the silicate layers were orderly-intercalated. TGA results showed that the decomposition temperature at 5% weight loss of Closite 30B was increased from 250°C to 270°C after APS treatment. A significant increase in the degree of crystallinity of PBT was observed in the exfoliated PBT/30B composite.

Keywords: organosilane; clay; silylation; thermal stability; PBT

2. Crystallization Behavior of PBT/POSS Nanocomposites (PPS-24)

ABSTRACT: Poly(1,4-butylen terephthalate)(PBT)/glycidyllsobutyl polyhedral oligomeric silsesquioxane (POSS) nanocomposites wereprepared by in situ ring-opening polymerisation of cyclic butylene terephthalate (CBT). The effects of POSS on the crystalline structure and crystallization behavior of the composites were investigated by wide angle X-ray diffraction and differential scanning calorimetry. The crystallization kinetic parameters were determined according
to the Avrami method. The pCBT/POSS composites exhibited multiple melting peaks only after crystallized at lower temperature. The average Avrami exponent n of the pCBT and composites increased with the addition of POSS (less than 1 wt%). A significant increase in crystallization kinetic constant and a decrease in crystallization half time of pCBT were observed in the presence of POSS particles, indicating a heterogeneous nucleating effect of POSS on crystallization of pCBT. The melting temperature and equilibrium melting temperature of pCBT in the composites decreased with increasing POSS content, which is directly related to the size of pCBT crystals. The difference of pCBT melting enthalpies in the matrix and composites demonstrated that the presence of POSS can effectively enhance the crystallinity of pCBT. The crystallization thermodynamics of pCBT and its composites were studied according to the Hoffman theory.


ABSTRACT: A functionalised organoclay was prepared by surface treatment of commercial organoclay (Cloisite 30B) with silane coupling agent, 3-aminopropyltriethoxysilane (APS), which was subsequently melt compounded with polypropylene (PP) and maleic anhydride grafted polypropylene (MA-g-PP) in a Haake internal mixer. The FTIR, TGA and XRD analysis of the functionalised organoclay APS-30B showed that the chemical interactions were enhanced by the formation of Si-O-Si bond between the silane coupling agent and the organoclay. The thermal decomposition onset temperature of the organoclay was increased by ~20°C upon silane treatment. The effects of the APS on the dispersion of organoclay in PP/30B nanocomposites and its resulted mechanical properties were studied by XRD, TEM and tensile test. It showed that thermal degradation occurred in the organoclay 30B during the melt compounding, resulting in poor mechanical properties. While PP/APS functionalised 30B nanocomposites exhibited much improved thermal stability and mechanical properties of ~33% increase in Young’s modulus, which is probably due to the strong interaction of the coupling bonds between PP matrix and the organoclays. Meanwhile, the investigations on the effects of different amounts of APS on the properties of APS treated organoclay/PP nanocomposites showed that an optimum amount for better mechanical properties was at 3%-5 wt.% of organoclay. The excessive APS may prevent the mechanical
performance due to the blocking effect on the organoclay surface and self-condensed APS at the boundaries of PP matrix and the organoclays.

\textit{Keyword:} Polypropylene nanocomposites; organoclay; silane coupling agent; thermal stability; FTIR; TGA; XRD; mechanical properties


\textit{ABSTRACT:} Cationic surfactant, hexyltriphenylphosphonium bromide (HTP) was selected to modify montmorillonite (MMT) clay (Cloisite Na+) to investigate the effects of surfactant adsorption and drying procedure on the formation of HTP modified clay and its PBT/clay nanocomposites. A series range of surface coverage ratios from 0 to 3.0 CEC of adsorbed HTP to MMT were studied by the UV/vis spectrophotometer and X-ray diffraction (XRD). It was found that the adsorption behaviour of the clay surface was highly dependent on the surfactant concentration and a maximum adsorption of HTP to MMT was achieved at \( \sim 1.5 \) CEC HTP. The intercalation of MMT also varied with the surfactant concentrations as the interlayer spacing remains at 1.76 nm below 1.0 CEC of adsorbed HTP and increases to \( \sim 1.97 \) nm after \( \sim 1.6 \) CEC of HTP. The corresponding surfactant structure inside clay galleries was changed from lateral monolayer to lateral bilayer, based on the calculation of molecular size and interlayer spacing. The FEGSEM micrographs showed that the thermal dried organoclay (HTP-MMT-H) was massive, aggregated and compressed, while freezing dried organoclay (HTP-MMT-F) formed much smaller and loose particles. Both clay powders were melt compounded with PBT polymer in a Haake internal mixer, and the obtained PBT/clay composites were analysed by XRD and TEM, respectively. The effect of adsorption showed that although 1.5 CEC HTP-MMT possessed relative large interlayer spacing, it is difficult to be intercalated. On the other hand, the effect of drying procedure showed that freeze dried powder was easier to be dispersed in PBT matrix compared to the thermal dried organoclay, despite no intercalation in both organoclays.

\textit{Keywords:} Cationic surfactant; Surfactant concentration; Interlayer spacing; Morphology; PBT nanocomposites
5. Surface Characterisation of Polyhedral Oligomeric Silsesquioxane Modified Clay and its application in polymerisation of macrocyclic Polyester Oligomers (Journal of Physical Chemistry B)

**ABSTRACT:** Novel porous aminopropylsooctyl polyhedral oligomeric silsesquioxane (POSS) modified montmorillonite clay complexes (POSS-Mts) with large interlayer distance and specific surface area have been successfully prepared via ion-exchange reaction and followed by freeze-drying treatment. The morphology of the POSS-Mts is highly influenced by the POSS concentration, pH of the suspension and drying procedure, but the interlayer distance of the POSS-Mts does not change much when the POSS concentration is above 0.4 CEC. The POSS-Mts were used as Sn-catalyst supporters to initiate the ring-opening polymerisation of cyclic butyleneterephthalate oligomers (CBT) for the first time. No diffraction peak was detected by wide-angle X-ray diffraction for the polymerized composites (pCBT/POSS-Mt), even at 10 wt % loading of POSS-Mt. A clay network rather than exfoliation structure was observed unexpectedly in the composites by transmission electron microscopy. The pCBT/POSS-Mt composite with 10 wt % POSS-Mt was further melt-compounded with commercial PBT resin as a master batch. The tensile properties of the resultant PBT/POSS-Mt composites were highly improved as compared to the pristine PBT due to the homogeneous dispersion of POSS-Mt in the PBT matrix.


**ABSTRACT:** Polyamide 12/Trisilanophenyl-POSS (PA 12/POSS) composites were prepared via melt-compounding. The effect of POSS on crystalline structure and crystalline transition of PA 12 was investigated by wide-angle X-ray diffraction (WAXD) and real time Fourier transform infrared spectroscopy (FTIR). WAXD results indicated that PA 12 crystallized into γ-form as slowly cooling from melt and the presence of POSS did not influence the crystalline structure of PA12. Both PA 12 and PA 12/POSS composites underwent Brill transitions when they were heated from room temperature to melt point. Real time FTIR patterns showed that an absorption band at 697 cm⁻¹ ascribed to Amide V (α) mode was emerged along with the disappearance of Amide VI (γ) band at 628
cm$^{-1}$ with the increase of the temperature for PA 12 and PA 12/POSS composites, which suggested that the $\gamma$-form crystalline has transformed into $\alpha$ form. The Brill bands were identified and the transformed mechanism was discussed based on the real FTIR results. The addition of POSS enhanced the tensile strength and thermal stability of PA 12.

Keywords: polyamide; POSS; crystalline transition; physical properties

7. Modification of Montmorillonite with Aminopropylisooctyl Polyhedral Oligomeric Silsequioxane (Journal of Colloid and Interface Science)

ABSTRACT: Sodium montmorillonite (Na-MMT) was modified with various amounts of aminopropylisooctyl polyhedral oligomeric silsequioxane (POSS) and a second surfactant (alkyl ammonium based) via ion-exchange reactions. Interlayer spacing, interlamellar structure, thermal and surface properties of these organoclays were characterized by wide angle X-ray diffraction, thermogravimetric analysis and contact angle measurement. The interlayer space of POSS modified clay (POSS-MMT) was strongly dependent on the arrangement of POSS surfactant but less dependent on the POSS concentration. The sodium ions in Na-MMT were only partially exchanged by protonized POSS due to the steric hindrance effect. In addition, the dual surfactant modified clays exhibited increased exchange ratio by controlling the amount of the second surfactant, resulting in a good balance in hydrophobicity and polarity of the modified clays. The resultant organoclays were mixed with polypropylene (PP) via melt-compounding method. It was found that the dual surfactant modified clays with low polarity and similar hydrophobicity to PP were well-dispersed in the PP matrix.

Keywords: montmorillonite, dual surfactant, interlayer spacing, thermal stability, dispersion.


ABSTRACT: Sodium-montmorillonite (MMT) was modified with two types of AP-POSS and OA-POSS and dual-surfactants (POSS with a ditallow-based second surfactant: 04AP-POSS/08DTDMA and 04OA-POSS/08DTDMA), respectively, via ion-exchange reaction. The
interlayer space, interlamellar structure, thermal and surface properties of these organo-montmorillonites were investigated by X-Ray diffraction, thermogravimetric analysis, and contact angle measurement, respectively. The interlayer space of POSS modified clay was strongly dependent on the arrangement of POSS surfactants, but less on the POSS concentration. The POSS modified montmorillonites have partially exchanged silicate surfaces and good thermal stabilities due to steric hindering and thermal stability of the POSS molecules. Dual-surfactant modified montmorillonites showed higher exchange ratio and possessed better compatibility with PA12 due to the lower interfacial free energy. Polyamide 12-montmorillonite nanocomposites were prepared by conventional melt compounding with the four POSS based organo-montmorillonites. The best dispersion of modified montmorillonite was observed for 3 mass % 04AP-POSS/08DTDMA/MMT filled PA12 nanocomposites, which resulted in the best mechanical performance with an increase of 60% in tensile modulus and 10% in yield strength, respectively, compared to that of pure PA12. Compatibility between montmorillonites and polymer was not the only key factor affecting dispersion, thermal stability and interlayer space were also crucial for good dispersion of montmorillonites in polymer matrix.

Keywords: montmorillonite, dual-surfactant, thermal stability, interfacial properties, nanocomposites, mechanical properties