

## CHAPTER I

### INTRODUCTION

In recent years polymer/clay nanocomposites have attracted interest, because they exhibit improvement in materials properties when compared with virgin polymer or conventional composites. These improvements include high modulus, increased strength and heat resistance, decreased gas permeability and flammability, and increased biodegradability of biodegradable polymers.

The majority of polymers are non-polar but silicate clays are hydrophilic. That is why organomodification of clay is an important step in the preparation of polymer/clay nanocomposites. The purpose is to increase the interlayer space and render hydrophobic silicate clay to the intercalation of polymers in the interlayer. Many researchers (Kawasumi *et al.*, Hasegawa N. *et al.*, and García-López *et al.*) have studied on dispersing montmorillonite in polypropylene (PP), which is an important commodity polymer due to its attractive combination of properties and low cost but non polar. As expected, because of the absence of any strong interaction, it has been a scientific challenge to disperse silicate clays in polypropylene.

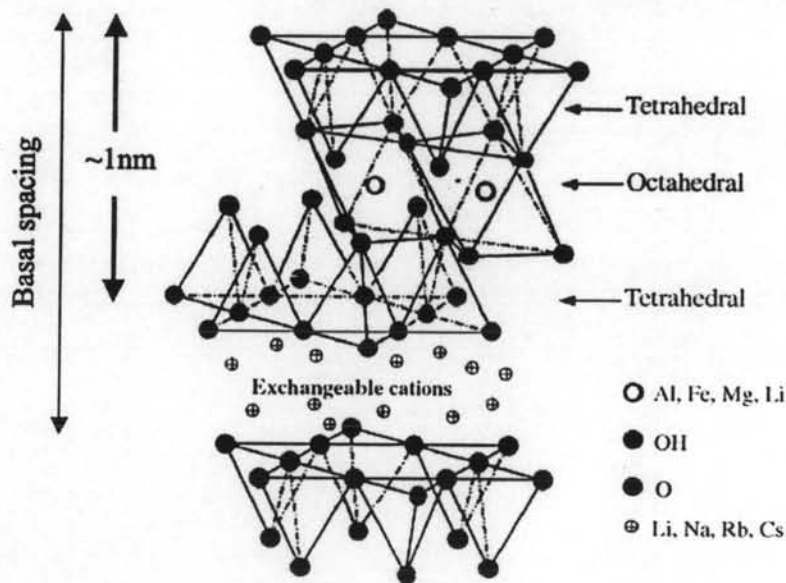
#### 1.1 Structure of Silicate Clays

The silicate clays commonly used in nanocomposites belong to the structural family known as the 2:1 phyllosilicates. Their crystal lattices consist of two-dimensional layers where a central octahedral sheet of alumina or magnesia is fused to two external silica tetrahedrons (the oxygen from the octahedral sheet belonging to the silica tetrahedral). The layer thickness is around 1 nm and the lateral dimensions of these layers may vary from 300 Å to several microns or larger depending on the particular clay. These layers stack with a regular van der waals gap in between them called the interlayer or the gallery. Isomorphic substitution within the layers (for example,  $\text{Al}^{3+}$  replaced by  $\text{Mg}^{2+}$  or by  $\text{Fe}^{2+}$  in montmorillonite, or  $\text{Mg}^{2+}$  replaced by  $\text{Li}^+$  in hectorite) generates negative charges that are counterbalanced by alkali or alkaline earth cations (such as  $\text{Na}^+$ ,  $\text{Li}^+$ , and  $\text{Ca}^{2+}$ )

situated in the interlayer. As the forces that hold the stacks together are relatively weak, the intercalation of small molecules between the layers is easy.

Montmorillonite, hectorite, and saponite are the most commonly used silicate clays. Their structures are given in Figure 1.1 and their chemical formulas are shown in Table 1.1.

This type of clay is characterized by a moderate negative surface charge (known as the cation exchange capacity, CEC and expressed in meq/100 g). The charge of the layer is not locally constant as it varies from layer to layer and must rather be considered as an average value over the whole crystal. Proportionally, even if a small part of the charge balancing cations is located on the external crystallite surface, the majority of these exchangeable cations is located inside the galleries. When the hydrated cations are ion-exchanged with organic cations such as more bulky alkylammoniums, it usually results in a larger interlayer spacing.



**Figure 1.1** Structure of 2:1 phyllosilicates.

**Table 1.1** Chemical formula and characteristic parameter of commonly used 2:1 phyllosilicates

2:1 phyllosilicates	Chemical formula	CEC (mequiv/100 g)	Particle length (nm)
Montmorillonite	$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$	110 *	100–150
Hectorite	$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$	120	200–300
Saponite	$M_xMg_6(Si_{8-x}Al_x)Si_8O_{20}(OH)_4$	86.6	50–60

M: monovalent cation; x: degree of isomorphous substitution (between 0.5 and 1.3)

## 1.2 Bentonites

Bentonite is a plastic clay generated frequently from the alteration of volcanic ash, consisting predominantly of smectite minerals, usually montmorillonite, and its chemical formula is  $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$ . The CEC values have been in the range of 70-100 meq/100 g depending on source of bentonites. There are three main types of bentonite.

### 1.2.1 Natural Sodium Bentonite

Natural sodium bentonite or sodium montmorillonite: natural sodium bentonite as the name suggests occurs with sodium as the predominant exchange cation, derived from volcanic ash that was deposited in marine environment. Sodium bentonites are characterized by high swelling, high liquid limit and high thermal durability.

### 1.2.2 Natural Calcium Bentonite

Natural calcium bentonite or calcium montmorillonite: the extensive majority of the montmorillonites occurring in abundance world wide is of the calcium type and referred to as calcium bentonites, which evolved from volcanic ash deposited in freshwater environment. They are often characterized by much lower swelling and liquid limit values compared to natural sodium bentonite.

### 1.2.3 Sodium Activated Bentonites

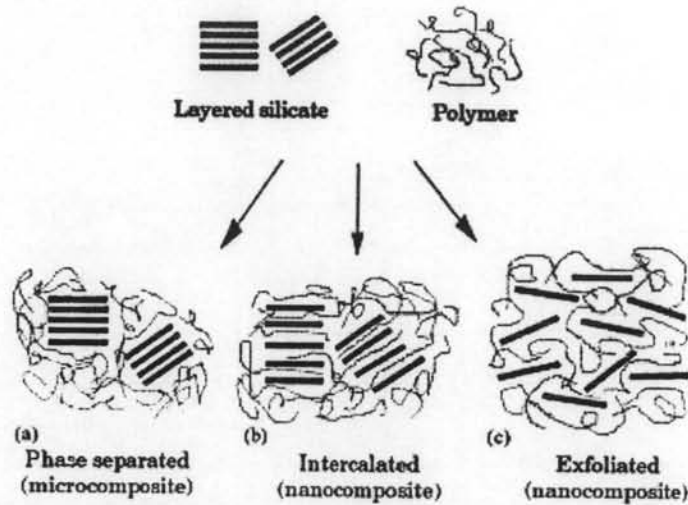
Sodium activated bentonites or sodium activated montmorillonites: sodium activated bentonites are produced by the substitution of calcium ions by sodium ions. This transformation can be achieved by the addition of a soluble sodium salt to calcium bentonite. They have greater swelling and gelling properties to calcium bentonites and are produced to simulate the properties of natural sodium bentonites.

## 1.3 Organomodification of Silicate Clays

The majority of polymers are the non polarity polymers. They are difficult to get the exfoliated and homogeneous dispersion of the silicate clay layer at the nanometer level in the polymers. This is mainly due to the fact that the silicate clays layers have polar hydroxyl groups and are compatible only with polymers containing polar functional groups, such as poly(ethylene oxide) (PEO) or poly(vinyl alcohol) (PVA). In order to render these hydrophilic clays more organophilic, the hydrated cations of the interlayer can be exchanged with cationic surfactants such as primary, secondary, tertiary, and quaternary alkylammonium or alkylphosphonium (onium). The modified clay being organophilic, its surface energy is lowered and is more compatible with organic polymers. These polymers may be able to intercalate within the interlayer. Additionally, the alkylammonium or alkylphosphonium cations can provide functional groups that can react with the polymer matrix, or initiate the polymerization of monomers to improve the interaction between the inorganic and the polymer matrix.

## 1.4 Nanocomposites Structure

Depending on the materials used (clay, organic cation and polymer matrix) and the method of preparation, three main types of composites may be obtained when a silicate clay is associated with a polymer (Figure 1.2).



**Figure 1.2** Scheme of different types of composite arising from the interaction of layered silicates and polymers: (a) phase separated microcomposite; (b) intercalated nanocomposite; and (c) exfoliated nanocomposite (Alexandre and Dubois, 2000).

#### 1.4.1 Phase Separated Composite

Polymer is unable to intercalate between the clay layers (Figure 1.2a). Their properties are the same range as traditional microcomposites.

#### 1.4.2 Intercalated Nanocomposites

Polymer chain is intercalated between the silicate clay layers resulting in a well ordered multilayer morphology built up with alternating polymeric and inorganic layers (Figure 1.2b). Intercalated nanocomposites are normally interlayer by a few molecular layers of polymer. Properties of the composites resemble those of ceramic materials.

#### 1.4.3 Exfoliated Nanocomposites

The individual clay layers are separated in a continuous polymer matrix by an average distance that depends on clay loading (Figure 1.2c). Usually, the clay content of an exfoliated nanocomposite is much lower than that of an intercalated nanocomposite.

## 1.5 Nanocomposite Preparation

Several methods have been considered to prepare polymer-clay nanocomposites. They include four main processes (Oriakhi, 1998):

### 1.5.1 Exfoliation-Adsorption

The clay is exfoliated into single layers using a solvent in which the polymer (or a prepolymer in case of insoluble polymers such as polyimide) is soluble. The polymer adsorbs onto the delaminated sheets and when the solvent is evaporated (or the precipitation of mixture), the sheets reassemble, sandwiching the polymer to form, in the best case, an ordered multilayer structure. Under this process are also gathered the nanocomposites obtained through emulsion polymerization where the silicate clay is dispersed in the aqueous phase.

### 1.5.2 In Situ Intercalative Polymerization

The silicate clay is swollen within the liquid monomer (or a monomer solution) so the polymer formation can occur in between the intercalated sheets. Polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator or by an organic initiator or catalyst fixed through cationic exchange inside the interlayer before the swelling step by the monomer.

### 1.5.3 Melt Intercalation

The silicate clay is mixed with the polymer matrix in the molten state. Under these conditions and if the layer surfaces are sufficiently compatible with the chosen polymer, the polymer can crawl into the interlayer space and form either an intercalated or an exfoliated nanocomposite. This method has great advantages: first, this method is environmentally benign due to the absence of organic solvents. Second, it is compatible with industrial process, such as extrusion and injection molding. The melt intercalation method allows the use of polymers which were previously not suitable.

### 1.5.4 Template Synthesis

The silicates are formed in situ in an aqueous solution containing the polymer and the silicate building blocks has been widely used for the synthesis of double-layer hydroxide-based nanocomposites but is far less developed for layered



silicates. In this technique, based on self-assembly forces, the polymer aids the nucleation and growth of the inorganic host crystals and gets trapped within the layers as they grow.

Normally, the preparation of PP/clay nanocomposite by melt intercalation used maleic anhydride grafted PP (PP-g-MA) as the compatibilizer. However, PP/clay nanocomposites used PP-g-MA as compatibilizer have mechanical properties lower than the native polypropylene. Because the addition of PP-g-MA can result in lower mechanical properties of the final composite. Hence, there is the new way to prepare nanocomposites by using a co-intercalation agent, reducing PP-g-MA content in the nanocomposites and enhancing the properties of the nanocomposites.

### **1.6 Scope of Research Work**

In this research work, two different nanoclays were modified with four different types of alkylammonium cationic surfactant. They are called organoclay and characterized. Organoclays were modified with a co-intercalation monomer which was methacrylic acid. Then, they were melted and blended with PP in twin screw extrusion to generate PP-graft-modified organoclay. The co-intercalation monomer is unsaturated so it could react with PP backbone by a grafting reaction. Finally, pure PP was mixed with PP-graft-modified organoclay to obtain PP/clay nanocomposites. The effect of alkylammonium cationic surfactant structure on organoclay structure and PP/clay nanocomposites was investigated. The effect of cationic surfactant on different types of nanoclays between sodium activated bentonites from Thailand and sodium montmorillonites from Japan was compared. Finally, the properties of PP/clay nanocomposites which were prepared by modified organoclays with a co-intercalation monomer were determined.