

CHAPTER I

INTRODUCTION

Polymer-clay nanocomposites have attracted much attention because of their superior physical and mechanical properties even at low clay content by comparison with more conventional polymer-microcomposites. Among the many properties that are modified, the observed improvement include increased modulus and strength, heat resistance and decreased gas permeability and flammability (Sinha Ray and Okamoto., 2003). In order to obtain good interfacial adhesion and mechanical properties the hydrophilic clay needs to be modified prior to its introduction in most polymer matrices which are organophilic (Minisini *et al.*, 2005).

Recent studies have been shown that organically modified clay can be efficiently exfoliated in polar polymers like polyamide using appropriate melt processing techniques and conditions (Fornes *et al.*, 2004). Polypropylene (PP) is one of the most widely use polymers. It shows a very positive combination of properties, including relatively high stiffness as well as good thermal and chemical resistance, as compared to other thermoplastics of similar price, so PP/clay hybrids have attracted great research interest. However, PP is a nonpolar polymer incompatible with polar-clay and consequently difficult to get the exfoliated and homogeneus dispersion of the clay particles at the nanometer level in the polymer (García-López *et al.*, 2003). The ways to resolve the difference in polarity between the polyolefins and the clay have been proposed. The addition of polar functional groups like maleic anhydride to the polyolefin backbone for use as the matrix polymer or as a compatibilizer significantly increases the polarity and thus, improves exfoliation in polypropylene (Hotta *et al.*, 2004). Another approach is to copolymerize the olefin monomer with polar monomers like methacrylic acid or acrylic acid. Ionomers are polymers containing small amount of ionic groups where some of the acid groups are neutralized with metal ions such as sodium or zinc provide an extension of this option (Capek, 2004). The advantages of this approach are improving the toughness and clarity of the polymer, the ionic groups also offer the possibility of favorable interactions with the organoclay (Shah *et al.*, 2005).

The availability of local clay minerals and domestic-produced polymers provides us a great opportunity to study and develop our own commercialized polymer nanocomposite materials. In this study, the Na-bentonite (local clay mineral) and Na-montmorillonite were treated with several kinds of quaternary alkylammonium cations to obtain “organoclays” for use as a nano-reinforcement in polymer matrix. The effect of molecular structure and functional groups of the surfactant on organoclays were investigated. Then the organoclays were melt-blended with polypropylene in twin screw extruder and Surlyn[®] ionomer was used as a reactive compatibilizer. The clays dispersion in the nanocomposites were investigated by X-ray diffraction (XRD).

1.1 Structure of Silicate Clays

The silicates clays commonly used in nanocomposites belong to the structural family known as the 2:1 phyllosilicates. Their crystal lattice consists of two-dimensional layers where a central octahedral sheet of alumina or magnesia is fused to two external silica tetrahedron (the oxygen from the octahedral sheet also belong 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, Al^{3+} replaced by Mg^{2+} or by Fe^{2+} in montmorillonite, or Mg^{2+} replaced by Li^+ in hectorite) generates negative charges that are counterbalanced by alkali or alkaline earth cations (such as Na^+ , Li^+ , 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 structure is given in Fig. 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 are 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.

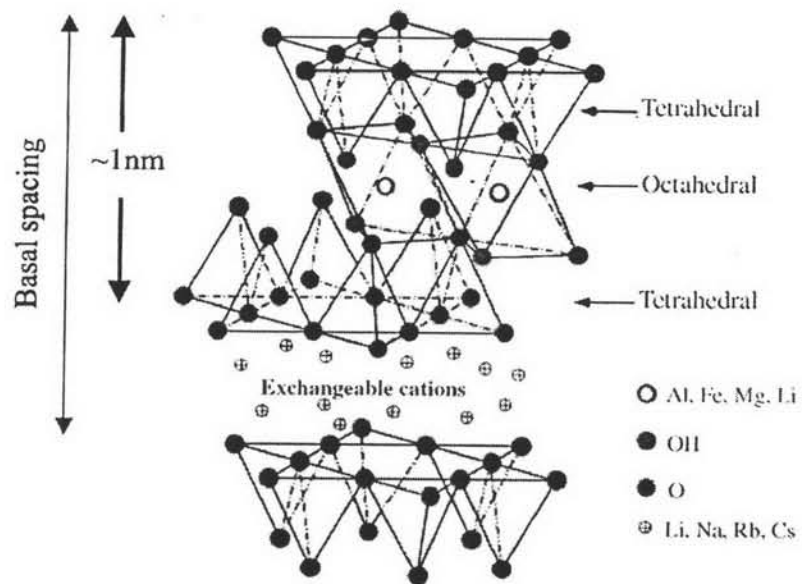


Figure 1.1 Structure of 2:1 phyllosilicates.

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	$M_x(\text{Al}_{4-x}\text{Mg}_x)\text{Si}_8\text{O}_{20}(\text{OH})_4$	110	100–150
Hectorite	$M_x(\text{Mg}_{6-x}\text{Li}_x)\text{Si}_8\text{O}_{20}(\text{OH})_4$	120	200–300
Saponite	$M_x\text{Mg}_6(\text{Si}_{8-x}\text{Al}_x)\text{Si}_8\text{O}_{20}(\text{OH})_4$	86.6	50–60

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

Bentonite is clay generated frequently from the alteration of volcanic ash, consisting predominantly of smectite minerals, usually montmorillonite, its chemical formula is $\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2\cdot \text{H}_2\text{O}$. The CEC value has been in the range of 70-100 meq/100 g depending on source of bentonites. There are three main types of bentonite.

1. Natural Sodium Bentonite or Sodium Montmorillonite: Natural sodium bentonite as the name suggests occurs with sodium as the predominant exchange cation. Sodium bentonites are characterized by high swelling, high liquid limit and high thermal durability.

2. 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. They are often characterized by much lower swelling and liquid limit values compared to natural sodium bentonite.

3. 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.

1.2 Organomodification of Silicate Clays

The physical mixture of a polymer and layered silicate may not form a nanocomposite. This situation is analogous to polymer blends, and in most cases separation into discrete phases takes place. In immiscible systems, which typically correspond to the more conventionally filled polymers, the poor physical interaction between the organic and the inorganic components leads to poor mechanical and thermal properties. In contrast, strong interactions between the polymer and the layered silicate in polymer/ clay nanocomposites lead to the organic and inorganic phases being dispersed at the nanometer level. As a result, nanocomposites exhibit unique properties not shared by their micro counterparts or conventionally filled polymers.

Pristine layered silicates usually contain hydrated Na^+ or K^+ ions. Obviously, in this pristine state, layered silicates are only miscible with hydrophilic polymers, such as poly (ethylene oxide) (PEO), or poly (vinyl alcohol) (PVA). To render layered silicates miscible with other polymer matrices, Organomodified clay is an important step in order to make clay organophilic and more likely disperse in the polymer matrix. Generally, this can be done by ion-exchange reactions with cationic surfactants including primary, secondary, tertiary, and quaternary alkylammonium or alkylphosphonium cations. Traditional structural characterization to determine the orientation and arrangement of the alkyl chain was performed using wide angle X-ray diffraction (WAXD). Depending on the packing density, temperature and alkyl chain length, the chains were thought to lie either parallel to the silicate layers forming mono or bilayers, or radiate away from the silicate layers forming. In addition, for longer chain length surfactants, the surfactants in the layered silicate can show thermal transition akin to melting or liquid-crystalline to liquid-like transitions upon heating.

1.3 Polymer/ Clay Nanocomposites

In general, using nanoclay as filler in thermoplastic polymer matrices has many points of interest. Because of they exhibit improvement properties when compare with virgin polymer, such as:

- increased tensile strength and modulus (probably because the layers contribute to partially immobilize a certain amount of polymer phase);
- increased dynamic stiffness;
- accelerated crystallization (almost certainly because the clays act as nucleating agents);
- not affected crystal structure of the PP matrix;
- improved flame retardancy;
- enhanced barrier to gas (oxygen and carbon dioxide), water and hydrocarbons (gasoline, methanol, and organic solvents) permeation.

The most recent methods to prepare polymer–clay nanocomposites have been developed by several groups and are divided into three main methods.

- *Intercalation of polymer or pre-polymer from solution.* This is based on a solvent system in which the polymer or pre-polymer is soluble and silicate layers are swellable. The layered silicate is first swollen in a solvent, such as water, chloroform or toluene. When the polymer and layered silicate solutions are mixed, the polymer chain intercalate and displace the solvent within the interlayer of the silicate. Upon solvent removal, the intercalated structure remains, resulting in polymer/layered silicate nanocomposite.

- *In situ intercalative polymerization method.* In this method, the layered silicate is swollen within the liquid monomer or a monomer solution so the polymer formation can occur 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 cation exchange inside the interlayer before the swelling step.

- *Melt intercalation method.* This method, the silicate layer is mixed with polymer in molten state under shear. In order for this method to be effective the silicates needed to be previously surface treated through the organo-modification. This method has great advantages over either in situ intercalative polymerization or polymer solution intercalation. First, this method is environmentally benign due to the absence of organic solvents and chemical reaction. Second, it is compatible with current industrial process, such as extrusion and injection molding.

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 silicate clay is associated with a polymer (Fig. 1.2).

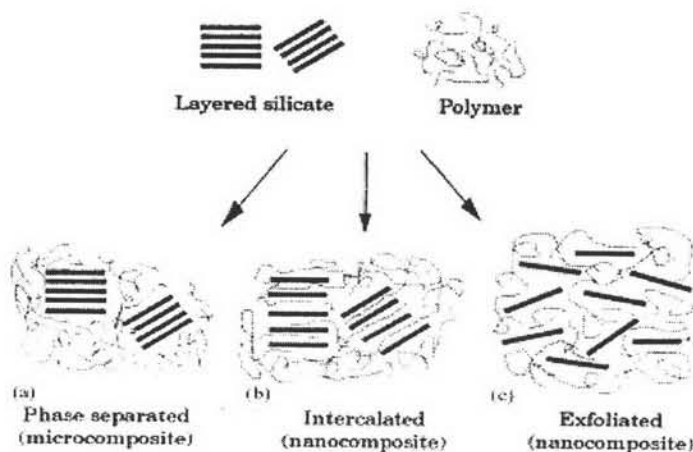


Figure 1.2 Scheme of different types of composite arising from the interaction of layered silicates and polymers: (a) phaseseparated microcomposite, (b) intercalated nanocomposite and (c) exfoliated nanocomposite.

a. phase separated composite: when the polymer is unable to intercalate between the clay layers (Fig. 1.2a). Their properties are the same range as traditional microcomposites.

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

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

1.4 Polypropylene (PP)

Polypropylene (PP) is one of the most widely used polyolefin polymers. Since PP does not have any polar groups in its backbone, it is not compatible with clay and homogeneous dispersion of the silicate layer in PP matrix cannot be realized

using modified hydrophobic MMT. To make the clay dispersed well in the PP matrix, two major methods for preparing PP/ clay nanocomposites have been developed. The first method is melt intercalation using a polar functional oligomer as a compatibilizer. In this method, the organoclay is first blended with the compatibilizer in melt, and then the resulting pre-intercalated clay is melt-blended with PP. When the miscibility of the oligomers with PP is sufficient, exfoliation of the pre-intercalated clay takes place. The second method is intercalating polymerization with a catalyst (TiCl_3 or a metallocene) supported on the modified clay. Although the second method is very promising, the most versatile and environmentally friendly method is based on direct polymer melt blending with modified clay.

1.5 Compatibilizer

The use of a compatibilizer, namely a chemical able to render compatible two different materials, made it possible for the melt intercalation technique to be accepted as the most promising approach leading to polymer/ clay nanocomposites formation. The advantages of this technique are absent of solvents that make an environmental friendly and compatible with current industrial such as extrusion and injection molding.

Through the surface treatment of clay it is possible to change the interlayer structure of silicate layer both increasing the gallery gap and modifying the silicate surface in an organic form, but this is not enough to render compatible matrix and filler. The 'polarizing' compatibilizer needs to be introduced in the system to solve the problem of poor miscibility between PP and clay.

The functionalization of polyethylene with a small amount of ionic groups is a particularly attractive way of compatibilizing because the ionic groups also offer the possibility of favorable interactions with the organoclay. Ionomer are the thermoplastic polymer containing a small mole fraction of ionic groups and the most common commercial type of ionomer is marketed by DuPont under Surlyn[®] trade name. Surlyn[®] is a family of ethylene methacrylic acid (E-MAA) copolymer, in

which some part of methacrylic acid is neutralized with metal ions such as zinc (Zn^{2+}) or sodium (Na^+). The structure of this ionomer is shown in Fig. 1.3.

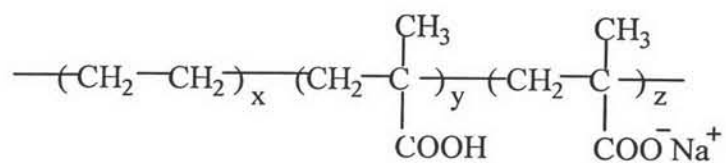


Figure 1.3 Structure of sodium-neutralized ethylene-methacrylic acid (E-MAA) ionomer.