

CHAPTER I

INTRODUCTION

Polymer nanocomposites are generally defined as the combination of a polymer matrix and inorganic particles, which have nanometric dimensions dispersed in a single phase or a multiphase polymeric matrix, which act as a nano-reinforcement. Recently, the development and characterization of clay mineral-polymer nanocomposites have gained spacial attention because of the advantages in comparison to the traditional polymer composites. The presence of nano-reinforcement of nanoclay (<10 wt%) in nanocomposites can significantly enhance the mechanical, thermal, fire retardancy and barrier performance properties due to the large contact area between polymer and clay on a nanoscale (Arau'jo *et al.*, 2004). Nanoclays have more attracted than other nano-reinforcement because of their low cost, ready availability and non-isometric structure derived from a high aspect ratio, which can maximize the reinforcing effect (Ton-That *et al.*, 2004).

The most commonly used clay to prepare nanocomposite is from the smectite group, such as montmorillonite (MMT). It is a 2:1 phyllosilicate, which has layered and crytalline structure. In this clay mineral the silicate layers are joined through relatively weak dipolar and Van der Waals forces and the cations Na^+ and Ca^{2+} located in the interlayers or gallery (Arau'jo *et al.*, 2004).

Since the surfactant used as templates for synthesizing M41S can be intercalated into the interlayer galleries of clays, templated synthesis could be applied for the synthesis of highly porous clays. In 1995 the discovery of a new porous materials known as porous clay heterostructure (PCH) has been reported (Galarneau *et al.*, 1995). The approach is the combination of the conventional pillaring process and the liquid crystal templating mechanism, affording materials with uniform pore diameters in the supermicropore to small mesopore range (1.5 – 3.0 nm), with high specific surface areas and high thermal stability. These materials were prepared by the surfactant-directed assembly of mesostructured silica within the two-dimensional galleries 2:1 mica type layered silicate such as in fluorohectorite, synthetic saponite, montmorillonite and vermiculite (Polverejan *et al.*, 2000).

In the first step of preparation of PCH, the clay is expanded by exchange with a cationic surfactant as a template to allow an easier access to the interlayer region. A neutral amine as co-template is then intercalated. Subsequently, a silica source is formed in situ by polymerizing around templates. By either calcination or solvent extraction, the templates are removed from the solid and are replaced by protons (Benjelloun *et al.*, 2001). The advantages of this approach are that the pore volume can be controlled by the volume of the template constituents and the pore size is controlled by the size of the surfactant micelles (Zhu *et al.*, 2002).

Polypropylene (PP) is one of the most widely used plastics in large volume which is a fast growing thermoplastic that dominates the industrial applications due to its good processibility, great recyclability and low cost. However, many disadvantages of PP, such as low toughness and low service temperature (Ding *et al.*, 2005), are needed to improve the properties of PP. Many research works have reported on dispersing nanoclay in polypropylene to maximize their physical and mechanical properties (Chen *et al.*, 2003). However, PCH is an interesting materials in addition to nanoclay. To date, no research studies about PCH used as a filler in polymer matrix. This makes a great opportunity to study and develop the polymer nanocomposites due to the availability of local clay minerals.

In this research work, we have focused on the synthesis of porous clay heterostructures from the two different clay minerals (commercialized-montmorillonite and local-bentonite) and the investigation of the surfactant chain length effects on the pore size, pore volume and specific surface areas. Moreover, the different methods of surfactant removal have been studied to compare the surface areas and the pore characteristic. Subsequently, PCH was blended with PP for nanocomposite fabrication. The gas barrier and thermal properties of PP-clay nanocomposites was investigated.

Clay Minerals

Clay consists of silicate layers held together by weak ionic forces. Generally, it can be classified into many types according to differences in structures and compositions such as talc, mica, smectite. Among several types of clays, the smectite

one is usually used as a filler in polymer composites because of its reinforcing properties and economic reason.

Smectite clay is a group of clay mainly composed of montmorillonite (MMT) that is a naturally occurring 2:1 phyllosilicate, which has layered and crystalline structure. Its crystal lattice consists of 1 nm thin layers, with a central octahedral sheet of alumina fused between two external silica tetrahedral sheets (in such a way that the oxygens from the octahedral sheet also belong to the silica tetrahedra). These layers organize themselves in a parallel fashion to form stacks with a regular gap between them, called *interlayer* or *gallery* (Manias *et al.*, 2001). Moreover, the stacks of clay layers are held tightly together by Van der Waals forces, as shown in Fig. 1.1.

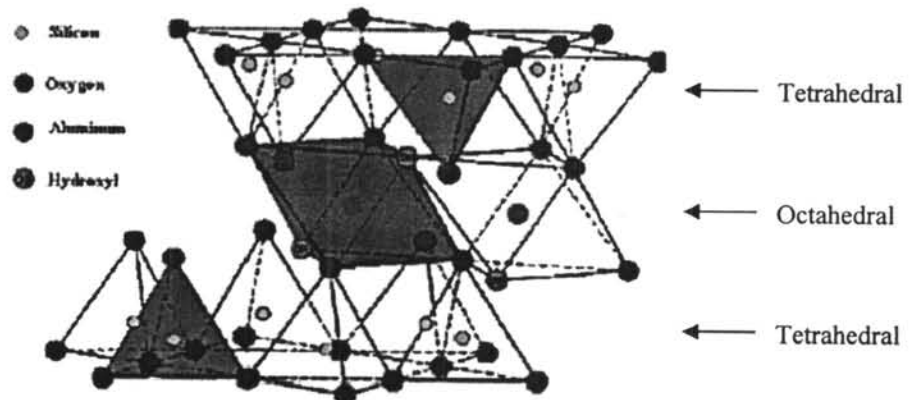


Figure 1.1 Structure of montmorillonite (Morlat *et al.*, 2004).

Isomorphic substitution within the layers (for example, Al^{3+} replaced by Mg^{2+} or Fe^{2+} , or Mg^{2+} replaced by Li^+) generates a negative charges that are counterbalanced by alkali and alkaline earth cations (Na^+ , Li^+ , Ca^{2+}) situated inside the galleries. This is characterized by a moderate surface charge known as the cation exchange capacity (CEC) and generally expressed as mEq/100g. For MMT is typically 76.4-119 mEq/100g. These charges are not locally constant, but varies from layer to layer and must be considered as an average value over the whole crystal (Manias *et al.*, 2001; Sinha Ray and Okamoto, 2003).

Bentonite is a clay generated frequently from the alteration of volcanic ash, consisting predominantly of smectite minerals, usually montmorillonite. Depending on the nature of their genesis, bentonites contain a variety of accessory minerals in addition to montmorillonite. These minerals may include quartz, feldspar, calcite, gypsum and other metal oxides. The presence of these minerals can impact the industrial value of a deposit, reducing or increasing its value depending on the application.

Porous Clay Heterostructures (PCH)

The discovery of porous clay heterostructures (PCH) has transcended the traditional pore size limitations of pillared clays, affording materials with uniform pore diameters in the supermicropore to mesopore range (1.5 to 3.0 nm). Porous clay heterostructures are prepared by the self-assembly of framework silica around surfactant micelles intercalated within the galleries of the phyllosilicate host. The assembly process is analogous to the surfactant-directed assembly of mesoporous molecular sieves, except that the framework silica is constructed in the two dimensional gallery of the host, rather than in three dimensions. The surfactants can be removed from the as-synthesized PCH by calcination or by chemical extraction, producing a stable clay mesoporous silica hybrid with porosity characteristics similar to those of mesoporous molecular sieve (Mercier and Pinnavaia, 1998).

Polypropylene and Maleic Anhydride Grafted Polypropylene

Polypropylene (PP) is a non-polar or hydrophobic polymer which is not miscible with clay. Therefore, it is difficult for non-polar PP macromolecules to enter between silicate layers, since the reaction is thermodynamically unfavourable (Tidjani *et al.*, 2003). The presence of a maleic anhydride grafted Polypropylene (PP-g-MA) oligomer can act as compatibilizer. The PP-g-MA oligomer can interact with layers of the clay through strong hydrogen bonding between the polar functional group of PP-g-MA and the oxygen group of silicates. It has been reported that the intercalated PP-g-MA hybrid can be easily dispersed in the polypropylene matrix to

form nanocomposites, provided miscible PP-g-MA with the polypropylene (Galgali *et al.*, 2001).

Polypropylene/Clay Nanocomposites

The most recent methods to prepare polymer–clay nanocomposites have been developed by several groups and are divided into three main methods (Sinha Ray and Okamoto, 2003).

- *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 involves annealing, statically or under shear, a mixture of the polymer and organically modified layered silicate above the softening point of the polymer. 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. Second, it is compatible with current industrial process, such as extrusion and injection molding.

Two terms (*intercalated* and *delaminate*) are used to describe the two general classes of nanomorphology that can be prepared as presented in Fig. 1.2 (Gilman, 1999).

(1) *Intercalated* structures are well ordered multi-layered structures where the extended polymer chains are inserted into the gallery space between the individual silicate layers.

(2) *delaminated* (or *exfoliated*) structures result when the individual silicate layers are no longer close enough to interact with the adjacent layers' gallery cations.

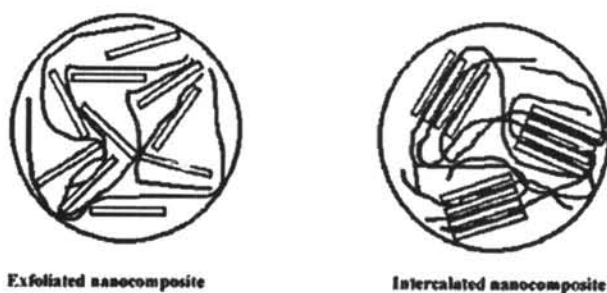


Figure 1.2 Nanocomposite Structures (Morlat *et al.*, 2004).