

CHAPTER I

INTRODUCTION

Polymer/layered inorganic nanocomposites represent a new class of materials which generally are defined as a combination of matrix polymer and inorganic particles, which the latter having at least one dimension in the nanometer range. Nanofillers combined with polymer in only small quantities have been shown to dramatically increase in the Young's modulus, flexural modulus and impact strength of the polymer matrix (Manias, 2001; Cheung, 2002; Galgali, 2004). Increase in thermal degradation temperature, decrease in thermal deformation and improvements in barrier properties from neat polymer, have all been recorded (Zanetti, 2002; Zhang, 2006; Ray, 2003).

A wide range of natural and synthetic inorganic fillers can be used and are susceptible to intercalation by macromolecules (Alexandre and Dubois, 2000) among them layered silicates are really the most employed (particularly with polyolefin matrices) due probably to their availability (as natural clay) and ease of surface treatment, and they have been studied for a long time (Okawa and Kuroda, 1997) and recently reviewed (Paul *et al.* 2005). Other interesting inorganic layered materials are layered double hydroxides, often synthetic substrates characterized by similar shape and structure to natural clay that have more recently appeared in the field of polymer nanocomposites (Constantino and Pinnavaia, 1995).

Since the layered inorganic clay are naturally hydrophilic and incompatible with most polymers, especially polyolefins. Therefore, the surface treatment of both layered inorganic clay is necessary to render their surface more hydrophobic, which facilitates an exfoliation structure. Generally, this can be done by ion-exchange reaction with the organic species: the cationic surfactants, i.e. primary, secondary, tertiary and quaternary alkylammonium cations (Le *et al.* 2002) are widely employed for layered silicate, while the anionic surfactants are widely used for layered double hydroxides. These voluminous organic ions increase the interlayer distance, lower the surface energy by improving the wetting characteristic of the clay layers and make intercalation with polar polymers is possible.

This modification also leads to expand the basal spacing between the silicate layers due to the presence of alkyl chain intercalated in the interlayer. For polymer containing polar functional groups, an alkylammonium surfactant is adequate to promote the nanocomposite formation. However, in the case of polyolefins, i.e. PE, PP, it is frequently necessary to use a compatibilizer, such as maleic anhydride modified polypropylene (PP-g-MA). Kawasumi *et al.* (1997), Kato *et al.* (1997) and Hasegawa *et al.* (1998) showed that there are two important factors to achieve the exfoliation of the clay layer silicates: (i) the compatibilizer should be miscible with the polypropylene matrix, and (ii) it should include a certain amount of polar functional groups in a molecule. Generally, the polypropylenes modified with maleic anhydride (MA) fulfill the two requirements and are frequently used as compatibilizer for polypropylene nanocomposites. However, they have mechanical properties lower than the native polypropylene, due to chain scission during grafting. Therefore, the addition of PP-g-MA can result in lower mechanical properties of the final composite. Hence, it is important to investigate the effect of PP-g-MA on the degree of dispersion, to optimize its concentration.

As for the case of microcomposites, to achieve the abovementioned improvements, good dispersion of organoclay in the polymer matrix and a good interface between the two phases are essential. Since the hydrophilic clay layers tend to strongly bond to each other, these goals are not always easy to achieve, especially for hydrophobic matrices like polyolefins (i.e. PE, PP). There has been much interest in polyolefins-based nanocomposites for different applications because of their low cost, low density, and the high specific properties of the PP matrix itself. As a result, several different approaches have been used to overcome the problems involved. These include modification of the clay surface by organo-intercalant to reduce the interaction between the clay platelets while at the same time making them more compatible with the polymer matrix, or the modification of polyolefin matrixes by adding a compatibilizing agent, or the modification of both phases. Modifications of compounding equipment and processing conditions have also been considered. Nevertheless, full dispersion of organoclays (so-called exfoliation) in polyolefin matrixes has remained difficult to achieve by melt blending; the usual result is instead rather poor intercalation, where the clay layers remain in stacks with

expanded galleries. At this point, the question arises as to why it is so difficult to achieve full exfoliation in polyolefin. As discussed earlier, the incompatibility between the matrix and the clays is one of the reasons.

The use of organoclay nanoadditions to polymers may change their decomposition temperature, flame resistance, gas and water permeability, elasticity, and tensile strength. Orientation ordering of polymer chains in clay layers increases the elastic modulus of the material. The magnitude of these effects depends on the nature of the interaction between the polymer chains and clay layers. To date, considerable insight has been gained into the structure and basic properties of nanocomposite polymers, significant advances have been made in techniques for engineering and characterizing such materials, and many related processes have been generally understood. It has now become clear that polymer intercalation into interlayer spaces of layered clays is one of the most effective approaches to the fabrication of hybrid nanocomposites. This area of research is now making rapid progress. At the same time, many important issues, especially those pertaining to the intercalation mechanism, guest–host interactions, interfacial processes, and strength–structure relations have not yet been fully clarified. In intercalated nanocomposites, the inorganic layers inherit their structural properties from the parent polysilicate (or another layered material), and the organic. Significant research is needed to figure out the behavior of nano-interfaces, and this field can still be considered to be in its beginnings. In particular, the development of accurate nanomechanical models, and understanding of the properties of the polymer at the interface are required to address the outstanding issues of the polymer nanoparticle interface and thus optimize the mechanical performance of polymer nanocomposites. It is believed that one of the main issues in preparing good polymer nanocomposite samples is the good dispersion of the nanoparticles in a polymer matrix.

Based on the above considerations, the main objective of this research study was to prepare and study the structure–properties relationships of polyolefins nanocomposites based on two types of inorganic layered clays: (i) polypropylene (PP)/layered silicate nanocomposites and (ii) low density polyethylene (LDPE)/layered double hydroxide nanocomposites. Several aspects were studied such as structure of the both cationic and anionic surfactants used for modification

layered clays and organoclay loading. The structure-property relationships, thermal stability, and mechanical of intercalated nanocomposites have been discussed as a function of both the organoclay loading and types of modifying agent.

A general introduction about the dissertation is given in Chapter I together with its significance and the objectives of the study. Chapter 2 discusses in detail the structure and modifications of two layered inorganic clays: layered silicate (MMT) and layered double hydroxide (LDH). This is followed by a literature review focusing on polypropylene (PP) based layered silicate nanocomposites and polyethylene (PE) based layered double hydroxide nanocomposites. The various materials used in the present study and their basic features are described in Chapter 3. The experimental methods and analytical tools used for characterization of both layered inorganic clays and their nanocomposites are also presented. Chapters 4, 5 and 6 explain the properties of PP/layered silicate nanocomposites. Chapter 4 discusses in detail the effect cationic surfactant structure (i.e. alkyl chain length) and the organoclays loading on morphological, thermal, crystallization and mechanical properties of PP nanocomposites. The morphology/property relationships, development/establishment of exfoliated, intercalated and even mesoscopic structures as a function of the organoclay content was studied regarding to the confinement effects, are well discussed in Chapter 5. The effects of the shear stress, testing temperature, and filler concentration on the melt rheology and extrudate swell of PP/layered silicate nanocomposite using capillary rheometry are explained in Chapter 6. Studying the properties of new LDPE/layered double hydroxide nanocomposites with different organic modifying and amount of organoclay content is explained in Chapter 7. Finally, Chapter 8 presents the conclusion and recommendations of both polyolefins based nanocomposites.