

CHAPTER II

LITERATURE REVIEW

Polymer/layered inorganic nanocomposites (PLNs) generally refer to a particle-filled material where nanoparticles have at least one dimension in the nanometer range. These fillers usually exist in the form of sheets of one to a few (1–3) nanometres thick, and hundreds and even several thousand nanometres long, thus with very high aspect ratios. Layered inorganic materials can be considered as active fillers able to swell the interlayer spaces (under specific conditions) and to modify their structure from microsized particles to nanodispersed particles owing to the intercalation/exfoliation processes by polymer chains (supported by using an intercalating agent). The characteristic properties of nanocomposites thus formed are generally reported as remarkably improved when compared to those of pristine polymers or traditionally microfilled composites. Improvements include higher modulus, increased strength and heat resistance and decreased gas permeability and flammability, all properties significantly depending on the degree of nanodispersion of layered inorganic substrates modulated by tuning the interfacial interaction with the polymer matrix. The use of these particular fillers overcomes the limited commercial availability of anisotropic nanofillers and the potential health hazards related to their handling and inhalation. 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).

2.1 Layered Silicates Based Nanocomposites

2.1.1 Background

The generic term layered silicates can be referred not only to natural clays but also to synthesized layered silicates such as magadiite, mica, laponite (Munzy *et al.* 1996), and fluorohectorite (Lan and Pinnavaia, 1996). Both natural clays and synthetic layered silicates have been successfully used in the synthesis of polymer nanocomposites. In this present study, we focus on the use of natural clay from the smectite family: montmorillonite. Because of its suitable layer charge density and disc-like structure with a very high aspect ratio that can serve as an effective reinforcing material, montmorillonite is nowadays the most widely used clay as nanofiller. Montmorillonite is a common clay mineral with numerous worldwide localities. It has, in most cases, been formed by the weathering of eruptive rock material, usually tuffs and volcanic ash, known as bentonite (Deer and Howie, 1962). Depending on their genesis, bentonite may contain a variety of accessory minerals such as cristobalite, zeolites, biotite quartz, feldspar, calcite, gypsum and other metal oxides found in volcanic rocks. The presence of these minerals influences the grade and some properties. Therefore, a purification (Earley *et al.* 1953) of the clay is required prior to nanocomposite synthesis.

2.1.2 Structure and Characteristics of Layered Silicates

The silicate clays commonly used in nanocomposites belong to the structural family known as the 2:1 phyllosilicates. Their crystal lattice, proposed by Hoffmann *et al.* (1933), 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, the source of the clay and the method of preparation. Therefore, the aspect ratio of these layers (ratio length/thickness) is particularly high, with values greater than 1000 (Alexandre and Dubois, 2000). 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 structures are given in Figure 2.1 and their chemical formulas are shown in Table 2.1. 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.

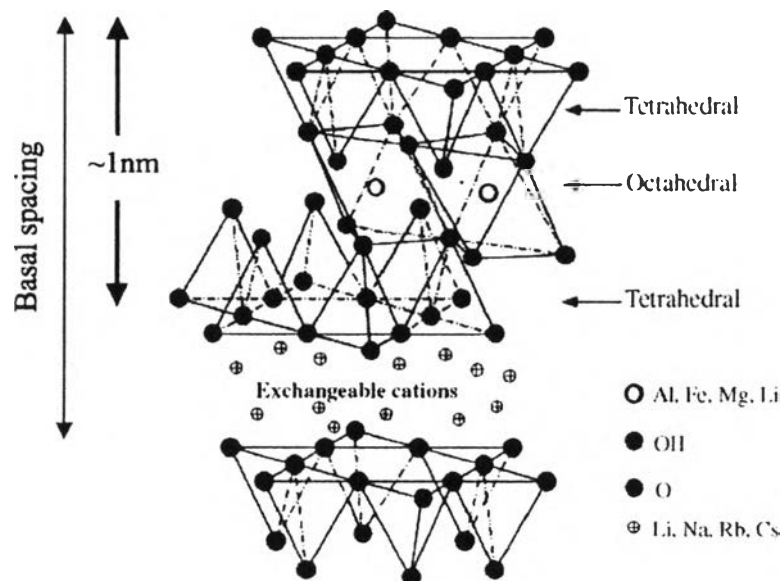


Figure 2.1 Structure of 2:1 phyllosilicates (Hoffmann *et al.* 1933).

Table 2.1 Chemical formula and characteristic parameter of commonly used 2:1 phyllosilicates (Alexandre and Dubois, 2000)

2:1 phyllosilicates	Chemical formula	CEC (mequiv/100 g)	Particle length (nm)
Montmorillonite	$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$	110.0	100–150
Hectorite	$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$	120.0	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)

The sum of the single layer thickness (9.6 Å) and the interlayer represents the repeat unit of the multilayer material, so called *d*-spacing or basal spacing, and is calculated from the (00*l*) harmonics obtained from X-ray diffraction patterns. The *d*-spacing between the silica-alumina-silica units for a Na-montmorillonite varies from 9.6 Å (for the clay in the collapsed state) to 20 Å when the clay is dispersed in water solution (Mering, 1946).

The crystallographic structure of montmorillonite can be characterized by X-ray diffraction (XRD) as shown in Figure 3. The XRD patterns of clay show basically two categories of information on the crystallographic structure (Brindley and Brown, 1980). One class consists of the basal (00*l*) reflections which depend on the nature of the interlayer cations, the state of hydration of the mineral such as the thickness and regularity of the water layers between the silica sheets - and the presence of other intercalated molecules, i.e. ammonium salts. The second class consists of the two-dimensional *hk* diffraction bands which are characteristic of the structure of the smectite layers themselves and are independent from the basal spacing. These *hk* diffraction bands are the same in all smectites. They are not very useful in structural determination because of the nature of the diffraction process and the fact that each observed band is the summation of several *hk* index pairs.

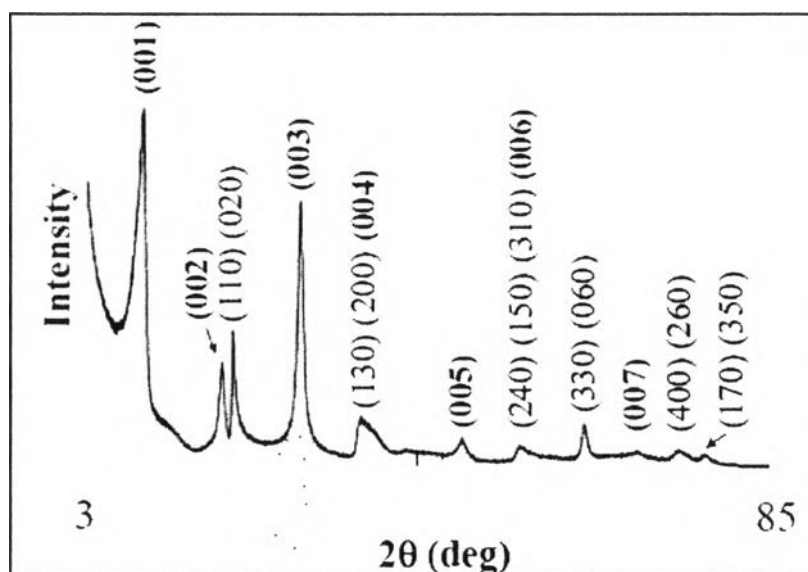


Figure 2.2 X-ray diffraction pattern of Na-montmorillonite showing the (001) basal reflections (in bold) and the (hk0) diffraction bands. In some cases, both reflections are overlapping (Brown, 1972).

2.1.3 Organic Modification of Layered Silicates

As the hydrophilic of layered silicates are generally compatible only with polymers containing hydrophilic parts, such as poly(ethylene oxide) (PEO), or poly(vinyl alcohol) (PVA). To render these clays more miscible with other polymer matrices like polyolefins, the hydrophilic surfaces of silicate clays have to be modified to an organophilic one (Kornmann *et al.* 2001). This challenge can be achieved by exchange the cations of the interlayer (such as Na^+ , Li^+ , Ca^{2+}) with cationic surfactants including primary, secondary, tertiary and quaternary alkylammonium or alkylphosphonium cations (onium) (Figure 2.3). These surfactants are not only lower the surface energy of the silicate clays but improve also the wetting characteristics of polymer matrix (Giannelis, 1996). Moreover, the long organic chains of such surfactants, with positively charged ends, are tethered to the negatively charged surface of silicate layers, resulting in an increase of the basal spacing which is suitable for the intercalation of the polymer molecules (Giannelis, 1996 and Usuki, 1997).

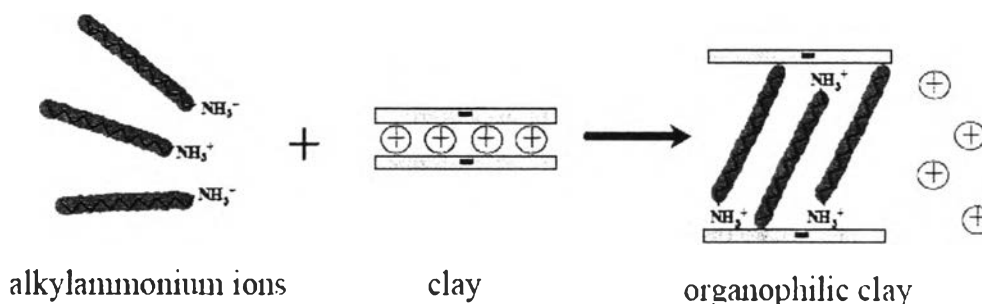


Figure 2.3 Schematic represents the cation-exchange process between alkylammonium ions and cations (i.e. Na^+ , Li^+ , Ca^{2+}) situated in the intercalated between the silicate layers.

It is evidence that the structure of cationic surfactants has a strong influence on basal spacing and the nanocomposite structures. For example, Usuki *et al.* (1993) showed that swelling of montmorillonite modified with ω -amino acids by ϵ -caprolactam increased significantly when the carbon number of the amino acid was greater than 8 as shown in Figure 2.4 (A). This ultimately led to the selection of the proper amino acid needed to form the exfoliated nanocomposite. Lan *et al.* (1995) also found that alkylammonium ions with shorter chains lead to the formation of intercalated nanocomposites whereas alkylammonium ions with chain length larger than eight carbon atoms result to the formation of exfoliated in epoxy nanocomposites. Reichert *et al.* (2000) investigated also how the length of the alkyl group on the amine used to modify sodium fluoromica and addition of maleated polypropylene (PP-g-MA) affected the morphology and mechanical properties of PP nanocomposites prepared by melt processing. A suitable alkyl length of 12 carbons or more was found necessary for promoting exfoliation in conjunction with PP-g-MA. Increasing the anhydride functionality of PP-g-MA also promoted exfoliation.

Moreover, Fornes *et al.* (2002) found from a comparison of different types of inorganic silicates that clays having higher CEC lead to more efficient exfoliation of the silicate platelets as shown in Figure 2.4 (B). For the case of quaternary ammonium salt modified MMT, Wang *et al.* (2001) prepared the organoclays with different alkylammonium chain lengths and also used the organophilic clay, Cloisite 20A, which has two long alkyl chains. They found that

the interlayer spacing increases with the increase in size of alkylamine chain length. The interlayer spacings of C12M, C16 M, C18M (with 12, 16 and 18 carbon atoms in the alkylammonium chain) and 20A were 1.36, 1.79, 1.85 and 2.47 nm, respectively. In summary, both the physical and chemical properties of the layered silicate are important factors that affect the morphology and properties of nanocomposites.

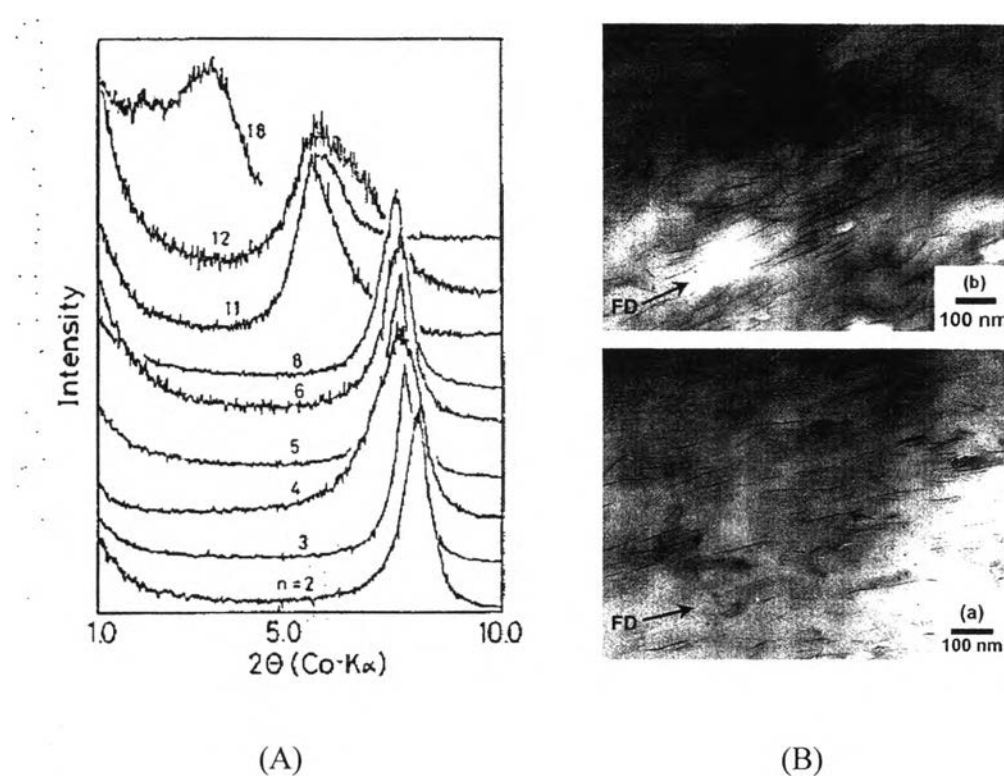


Figure 2.4 (A) X-ray diffraction patterns of Na-MMT as the length of the alkylammonium chain increases (Usuki *et al.* 1993), (B) TEM images of injection molded HMW nylon 6 nanocomposites as different silicate clays; (a) $(\text{HE})_2\text{M}_1\text{R}_1\text{-WY}$ (higher CEC) and (b) $(\text{HE})_2\text{M}_1\text{R}_1\text{-YM}$ (lower CEC) (Fornes *et al.* 2002).

Depending on the charge density of layered silicate and alkyl chain length of the cationic surfactants, the alkyl chains may organize in different ways between the silicate layers: monolayers, bilayers, pseudo-trilayers, and paraffin-type structure. In general, at lower charge densities, the surfactant packs in monolayers and, as the charge density increases, the surfactant can arrange either bilayers or

trilayers as shown in Figure 2.5 (Lagaly, 1986). Moreover, it was found that at very high CECs (>120 meq/100 g) and long chain surfactants (>15 carbons), the paraffin-type structure usually obtain. This is due to the fact that positively charged heads of the alkylammonium molecules preferentially adopt close to the surface of layered silicate, while the organic tails tend to fill at the middle.

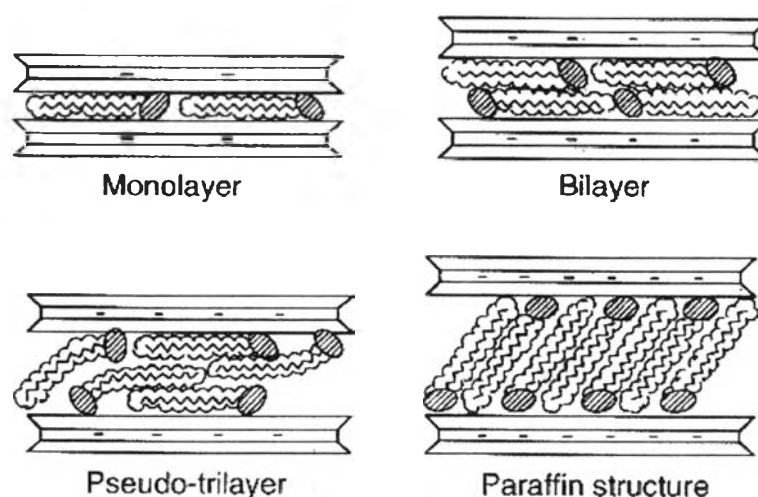


Figure 2.5 Schematic of the orientations of alkylammonium ions in the galleries of layered silicates with different layer charge densities (Lagaly, 1986).

2.1.4 Structure of Polymer Layered Silicate Nanocomposites

In general, the dispersion of silicate particles in a polymer matrix can result in the formation of three different types of polymer/layered silicate nanocomposites as shown in Figure 2.6 (Alexandre and Dubois, 2000). *Conventional composites* contain clay tactoids with the layers aggregated in the unintercalated face-face form. The clay tactoids are simply dispersed as a segregated phase. *Intercalated nanocomposites* are formed when polymer chains reside between the host silicate layers with more or less fixed interlayer distances, generally less than 2–3 nm separation between the layers (Alexandre, 2000; Chin, 2001; Kim, 2001). Intercalation results in a well-ordered multilayered structure and the properties usually resemble those of the host layers. *Exfoliated nanocomposites* are formed when silicate layers are delaminated and dispersed in the polymer matrix. In this case, the polymer expands the clay layers to 8–10 nm or more (Alexandre, 2000;

Chin, 2001; Kim, 2001). The exfoliated state is of particular interest due to it maximizes the polymer–clay interactions providing the entire surface of the layers available for the polymer. This leads to the significant changes in the mechanical and other performance properties (Denis *et al.* 2001). Besides these two well defined structures, other intermediate organizations can exist presenting both intercalation and exfoliation (Giannelis, 1998; Alexandre, 2000; Chin, 2001).

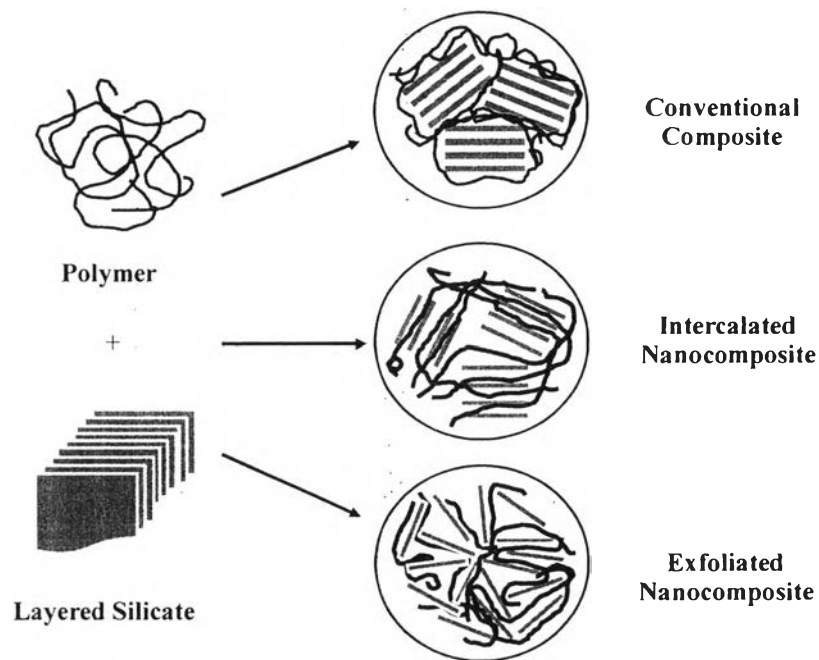


Figure 2.6 Schematic of different types of composite arising from the interaction of layered silicates and polymers: Conventional composite, Intercalated nanocomposite and Exfoliated nanocomposite (Alexandre and Dubois, 2000).

2.1.5 Characterization of Polymer Layered Silicate Nanocomposites

Identification of the silicate morphology within a PLSNs can be accomplished using a number of analytical techniques. The most common analysis technique is wide angle X-ray diffraction (WAXD). Gallery spacing values of the layered silicates can be determined from diffraction peaks and evidence of silicate exfoliation can be characterized from peak intensities. In addition to WAXD, an optical image of the silicate morphology can be produced using transmission electron microscopy (TEM). Moreover, multiple studies on the rheological properties of PLSNs have attempted to find qualitative relationships between silicate morphology and rheology with limited success.

2.1.5.1 Wide Angle X-ray Diffraction (WAXD)

X-ray diffraction is a powerful tool for identifying crystalline structures on the nanoscale. WAXD involves the use of X-ray diffraction at low angles between 1 and 10 degrees where reflections are the result of crystalline structures having length dimension on the order of tens of nanometer. This technique allows the determination of the layer spacing of silicate according to Bragg equation: $2d\sin\theta = n\lambda$, where d is the average basal spacing of the silicate tactoids, θ is one half of the 2θ location of the (001) diffraction peak, n is the wave number normally taken to be 1 and λ is the wave length of the X-ray radiation used in the diffraction experiment (Alexandre and Dubois, 2000). By monitoring the position, shape and intensity of the (001) basal diffraction from the distributed silicate layers, the nanocomposite structure can be identified (Ray and Okamoto, 2003). For conventional composites due to the structure of layered silicate is not changed so that the basal diffraction do not change. However, for intercalated nanocomposites due to the change of layered structure by the intercalation of polymer molecules, the (001) diffraction peak shifts toward lower angle and thus increasing of basal spacing. In such intercalated nanocomposites, the repetitive multilayer structure is well preserved, allowing the interlayer spacing can be observed. In contrast, for exfoliated nanocomposites, no (001) diffraction peaks are seen in the WAXD patterns because of a much too large spacing between the layers (i.e. exceeding 8 nm in the case of

ordered exfoliated state) or the loss ordering structure of layered silicate (Vaia 1997; Alexandre 2000; Beyer, 2002).

2.1.5.2 Transmission Electron Microscopy (TEM)

TEM images can be used to confirm results obtained from WAXD. The primary advantage of TEM over WAXD is the ability to confirm the presence of exfoliation in a PLSN samples. WAXD can be strongly affected by particle size, sample preparation, silicate concentration and sample orientation. WAXD curves indicating exfoliation can be the result of low silicate concentration or poor sample preparation. In the case of a WAXD curve indicating exfoliation, TEM can be used to confirm the presence of exfoliation. A severe limitation to the use of TEM is the highly localized nature of the images that are obtained. The extremely high magnification of TEM means the operator must choose a representative image for the entire sample from only a very small portion of the actual sample. For this reason, levels of intercalation and exfoliation can be highly variable if obtained from TEM images.

2.1.5.3 Rheology

The rheology of PLSNs has been studied for a wide variety polymer and filler types. The primary characteristic of interest in rheological studies is the formation of yield stress behaviour during dynamic oscillatory rheological testing. Krishnamoorti *et al.* (1996) found increasing yield stress behaviour in polyamide-6 PLSNs with increasing silicate loading. This behaviour was attributed primarily to the tethering of polyamide chains to the surface of the layered silicate. Lim and Park (2001) used dynamic oscillatory shear in the linear viscoelastic regime of three different polymer systems in an attempt to identify the behaviour of exfoliated and intercalated PLSNs. In agreement with previous studies the authors found an increase in yield behaviour with clay loading. It was also found that for exfoliated silicate morphologies yield stress behaviour was caused by the formation of a percolated network structure. Intercalated PLSNs showed yield like behaviour at low frequencies only when strong interactions between the polymer and silicate existed.

2.1.6 Preparation of Polymer Layered Silicate Nanocomposites

The methods used in synthesis of nanocomposites have a significant effect on the dispersion of silicate layers and the resulting composite properties. Three methods that have been used successfully in producing nanocomposites are in-situ polymerization, solution mixing and melt intercalation. Each method has advantages as well as disadvantages and much research has been devoted to understanding each of them.

2.1.6.1 Intercalation of Polymer or Pre-Polymer from Solution

In intercalation of polymer or pre-polymer from solution, a common solvent (chloroform, toluene) or solvent mixture is used to disperse the layered silicate and at the same time, dissolve the polymeric matrix. A schematic of this technique is shown in Figure 2.7. Depending on the interaction of the solvent and the layered silicate, the crystallite may be delaminated in an adequate solvent due to the weak van der Waals force to stack the layer together. Polymer chains then can be adsorbed on the delaminated individual layer. However, upon solvent removal, the layers can reassemble to reform the stack with polymer chains sandwiched in between, forming a well ordered intercalated nanocomposites. Few exfoliated nanocomposites were prepared via this method. However, this method is required large amount of solvent, resulting in a higher cost. Also the types of polymers that can be used to prepare nanocomposite ultimately depend on the selection of proper solvent, limiting the applicability of this method.

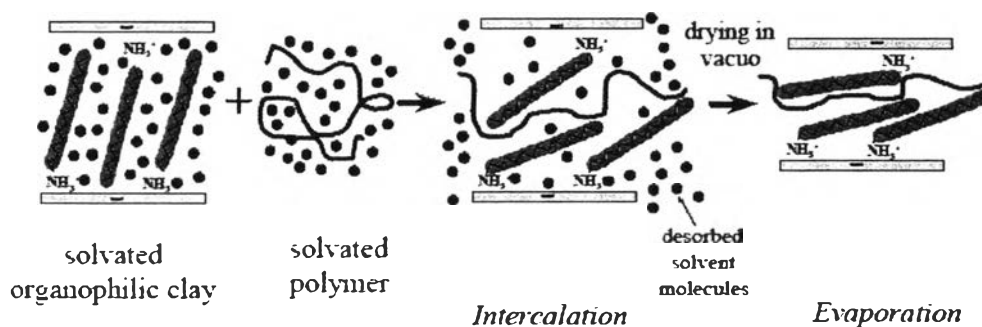


Figure 2.7 Schematic illustrates the intercalation of polymer or pre-polymer from solution.

2.1.6.2 In-Situ Intercalative Polymerization

In in-situ polymerization, monomer is first mixed with layered silicates and then polymerization takes place leading to the delamination of the clay layers. A schematic of this technique is shown in Figure 2.8. Because of the low viscosity of a monomer in comparing to a polymer, it is much easier to break up particle agglomerates using a high shear device, and achieve more uniform mixing of particles in the monomer. In addition, the low viscosity and high diffusivity results a higher rate of monomer diffusion into the interlayer region of layered silicate. Furthermore, it is possible to control nanocomposite morphology through the combination of reaction conditions and clay surface modification. The greatest disadvantage to this technique is the extended processing time as well as the necessity for solvent while polymerization certain types of polymer.

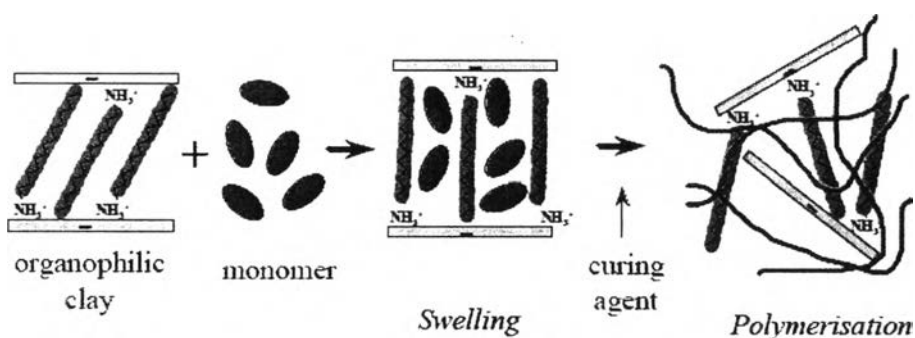


Figure 2.8 Schematic illustrates the in-situ intercalative polymerization.

2.1.6.3 Melt Intercalation

In melt intercalation, the layered silicate is mixed with the polymer matrix in the molten state. More often this technique is carried out in a mixer or an extruder where shear forces are imparted into the composite material. The combination of mobile polymer chains and shear force facilitates either an intercalation or sometime an exfoliated nanocomposite when suitable levels of polymer-clay compatibility exist. Figure 2.9 shows a simple schematic of melt intercalation. Among three methods, melt intercalation has the advantage of being simple, fast and compatible with current industrial techniques.

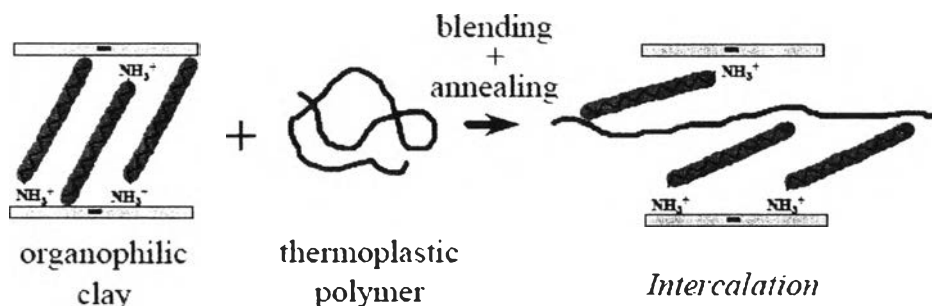


Figure 2.9 Schematic illustrates the melt intercalation.

2.2 Polypropylene Layered Silicate Nanocomposites (PPLSNs)

Polypropylene (PP) is one of the widely used polymers due to its attractive combination of good processability, physical properties and chemical resistance, and therefore finds high-volume applications in many sectors such as automotive, packaging and appliances (Galli and Vecellio, 2003). PPLSNs are of high commercial significance: incorporation of nanoclay into PP is expected to further improve stiffness, strength and barrier performance. As a result, different processing techniques have been developed in an attempt to achieve PPLSNs systems with desired morphologies and properties.

2.2.1 Preparation by Solution Mixing and In-Situ Polymerization

Regarding to the properties of PP which is difficult to dissolve in common solvents, for example chloroform, toluene, or even other expensive one, i.e. dichlorobenzene, xylene. Therefore the solution mixing is not commonly used. However, there are few works reported about preparing PPLSNs via this technique, for example, Avella *et al.* (2005) prepared the PPLSNs with different organomodified clays (C_{16} - C_{18} modified MMT) and clay loadings using *o*-dichlorobenzene as an effective solvent at 180°C . They found that the exfoliated nanocomposite was obtained at lower clay content, i.e. <3 wt%, while at higher clay loading i.e. 5 wt%, a partially collapsed structure was obtained. Mechanical tests showed that the elastic modulus increases of about 20% compared to the neat polymeric matrix value when 1 and 3% of nanofiller was added. Recently,

Ding *et al.* (2006) also prepared PP/MMT nanocomposite by directly dissolving of PP in the modified MMT in xylene system at 130°C.

The in-situ polymerization has been used to prepare PPLSNs. Tudor *et al.* (1996) first prepared a synthetic hectorite with methylaluminoxane (MAO) to remove the acidic protons and to prepare the interlayer spacing for receiving the transition metal catalyst. Using a synthetic fluorinated mica-type layered silicate deprived of protons in the galleries, the metallocene catalyst ($[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Me}(\text{THF})]^+$) was intercalated directly within the silicate layers, without the need of MAO treatment. Later, Sun and Garces (2002) reported the preparation of PPLSNs by this technique using the metallocene/clay as catalysts.

2.2.2 Preparation by Melt Intercalation

Since the possibility of direct melt intercalation was demonstrated by Giannelis (1996) and Vaia (1993), this technique has become the standard for preparing polymer/layered nanocomposites, as well as PPLSNs. This is due to its environmentally and economically favorable method that suitable for current processing, i.e. extrusion or injection processing. In general, an interplay of entropic and enthalpic factors determines the outcome of whether an organically modified montmorillonite (OMMT) will be dispersed intercalated or exfoliated in a polymer. Dispersion of layered silicates in a polymer requires sufficiently favorable enthalpic contributions to overcome any entropic penalties. Favorable enthalpy of mixing for the polymer/OMMT is achieved when the polymer/MMT interactions are more favorable compared to the surfactant/MMT interactions (Vaia, 1997 and Balazs, 1998). For most polar polymers, an alkyl-ammonium surfactant (the most commonly used organic modification) is adequate to offer sufficient excess enthalpy and promote the nanocomposite formation, in the case of olefinic polymers (PE, PP), the polymer/surfactant systems are at the theta conditions, and there is no favorable excess enthalpy to promote nanocomposite formation. Thus, the challenge with polyolefins is to design systems where the polymer/MMT interactions are more favorable than the surfactant/MMT interactions.

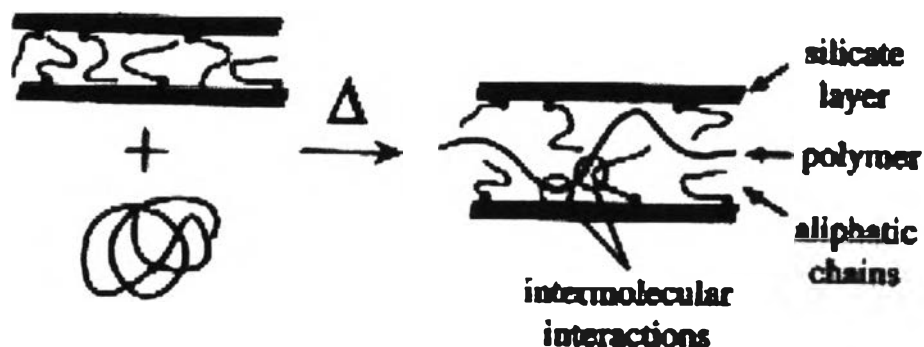


Figure 2.10 Schematic depicting the intercalation process between a polymer melt and an OMLS (Vaia and Giannelis, 1997).

2.2.2.1 The Role of Compatibilizer

For most polar polymers, an alkylammonium surfactant (the most commonly used organic modification) is adequate to offer sufficient excess enthalpy and promote the nanocomposite formation. However in the case of PP, there is no favorable excess enthalpy to promote nanocomposite formation. Thus, the challenge with PP is to design systems where the polymer/layered clay interactions are stronger than the surfactant/layered clay interactions. Many efforts were made to improve the mixing of layered clay in PP by using functional oligomers as compatibilizers. Most authors used low molecular weight PP oligomers to enhance the diffusion of oligomers into clay galleries (Kurokawa, 1997; Kato, 1997; Kawasumi, 1997; Hasegawa, 1998). Usuki *et al.* (1997) first reported a novel approach to prepare PP based nanocomposites using a functional oligomer (PP-OH) with polar telechelic OH groups as a compatibilizer. In this approach, PP-OH was intercalated between the layers of 2C18-MMT, and then the PP-OH/2C18-MMT was melt mixed with PP to obtain the nanocomposite with intercalated structure. Further study by the same group, Kawasumi *et al.* (1997) prepared PP-clay hybrids by simple melt-mixing of three components: PP, maleic anhydride modified PP oligomers (PP-MA), and organoclay (clay intercalated with stearylammmonium). They found two important factors to achieve the exfoliated and homogeneous dispersion of the clay in the hybrids: (i) the oligomers should include a certain amount of polar groups to be intercalated between the clay layers through hydrogen bonding, (ii) the oligomers

should be well miscible with PP. Since the content of polar functional groups in the oligomers should affect the miscibility of it with PP. The driving force of the intercalation originated from the strong hydrogen bonding between the maleic anhydride group (or -COOH group generated from the hydrolysis of the maleic anhydride group) and the oxygen groups of the silicates. The interlayer spacing of the clay increases and the interaction of the layers should be weakened. The intercalated clays with the oligomers contact PP under a strong shear field. If the miscibility of PP-MA with PP is good enough to disperse at the molecular level, the exfoliation of the intercalated clay should take place smoothly, as illustrated in Figure 2.11. Later, Hasegawa *et al.* (1998) also prepared PP based nanocomposites by using a maleic anhydride-modified PP oligomer (PP-MA) as a compatibilizer. PP was melt blended with organophilic clay (C18-MMT) which was intercalated with PP-MA by twin-screw extruder at 200°C. In this system, the silicate layers became smaller and were dispersed more uniformly as the ratio of PP-MA to the clay increased.

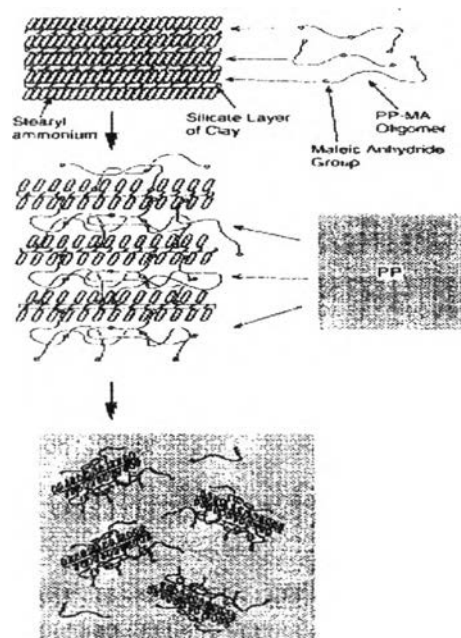


Figure 2.11 Schematic depicting the dispersion process of the organized clay in the PP matrix with the aid of compatibilizer, PP-MA (Kawasumi *et al.* 1997).

It was found the use of compatibilizer mainly based on PP-g-MA has been shown to significantly improve clay intercalation depending on their characteristics as molecular weight and grafting content and on the coupling agent-to-clay ratio. High maleic anhydride (MA) content generally enhances the melt intercalation of PP oligomers into clay layers; however, it may lead to immiscibility with the PP matrix and harm the mechanical properties of the composites (Kato *et al.* 1997). On the other hand, the effect of molecular weight is less clear. However, high molecular weight PP oligomers gave rise to better improvement in mechanical properties (Reichert *et al.* 2000). In fact, there is a critical level for individual maleated PP to be incorporated into the nanocomposite. Moreover, Wang *et al.* (2004) found that low molecular mass and high maleic anhydride content of maleated PP provided good clay dispersion.

2.2.2.2 *The Effect of Processing Conditions*

Melt processing conditions play a key role in achieving high levels of exfoliation. Indeed, nanocomposites have been formed using a variety of shear devices (e.g. extruders, mixers, ultrasonicators, etc.), among which twin screw extruders have proven to be most effective for the exfoliation and dispersion of silicate layers. It was found that most of the PLSNs produced using the twin screw extruder showed complete exfoliation (Cho *et al.* 2005). For the case of PP based nanocomposites, Kawasumi *et al.* (1997 and 1998) prepared PPLSNs by melt compounding of the three components (PP, PP-g-MAH and modified clay) in a twin-screw extruder. Wolf *et al.* (1999) described that the swollen organoclay was compounded with PP in a twin-screw extruder at 250°C to prepare PP/organoclay nanocomposites. In addition, Kaempfer *et al.* (2002) prepared new nanocomposites via melt compounding of syndiotactic polypropylene (sPP) containing OMLS and in situ formed core/shell nanoparticles. Melt compounding of sPP with octadecylammonium modified fluorohectorite in a co-rotating twin-screw extruder represents an attractive new route to reinforced sPP with considerably greater stiffness. Matrix reinforcement is achieved by in situ formation of silicate nanoparticles through exfoliation combined with simultaneous in situ encapsulation of the resulting nanosilicates in a thin shell of iPP-g-MA. The resulting anisotropic core/shell type nanoparticles, containing stacks of organohectorite layers as the core

and iPP-g-MA as the shell, represent a very effective class of nucleating agents for sPP crystallization. Recently, Peltola *et al.* (2006) examined the effect of rotational screw speed on PP layered silicate nanocomposites. A twin screw extruder was used to produce PPLSNs at screw speeds of 200, 500 and 1000 rpms. Results showed an increase in intercalation and a modest increase in exfoliation with increasing screw speed but no improvement in nanocomposite mechanical properties were seen. Modesti *et al.* (2006) carried out an extensive study of the effect of both temperature and screw speed on the morphology and mechanical properties of PPLSNs. Screw speeds of 200 and 350 rpms were used in an intermeshing, co-rotating twin screw extruder. The two different melt temperatures employed were approximately 170°C and 200°C. The results of both the silicate morphology tests and the mechanical properties test were conclusive in showing that the most effective melt compounding condition was that of low temperature and high screw speed. The authors concluded that conditions which maximize the shear stress exerted on the polymer are the most effective at forming highly dispersed and exfoliated PPLSNs. In addition to the effect of temperature and screw speed on silicate morphology, the authors showed also that the effect of residence time was far less influential in achieving silicate exfoliation than shear stress during processing. This conclusion might be expected since the rate of polymer diffusion into silicate galleries is on the same order as the rate of polymer self diffusion. Zhu and Xanthos (2004) investigated the effects of clay chemical modifiers, mixing protocols, and operating conditions upon the clay structure in PP based nanocomposites prepared with a corotating twin-screw extruder. Two mixing methods were used for the nanocomposite preparation: two-step mixing and one-step mixing. Experimental results of MFI showed that C15A composites have higher viscosity (lower MFI) than C30B composites. This indicates that C30B was less exfoliated. The mixing protocols have some effects on the MFI of the composites. Generally, in a two-step mixing method, nanocomposites have lower MFI. That is, the composites prepared by the two-step mixing method have better exfoliation for the nanofillers than one-step mixing method.

In summary, melt intercalation offers a simple way of preparing nanocomposites. However, very careful attention has to be paid to finely modify the

layered silicate surface chemistry to increase the compatibility with polymer matrix. Processing conditions have considerable effects on the structure evolution of polymer nanocomposites by melt intercalation.

2.2.3 Morphological Characteristic of PPLSNs

As mentioned before, morphology and degree of exfoliated silicate layers are generally characterized by a combination of X-ray diffraction (XRD) and transmission electron microscopy (TEM). It has been well established that an intercalated/exfoliated mixed morphology is usually formed in most polymer layered silicate nanocomposites (Giannelis, 1998; Alexandre, 2000; Ray, 2003). Similar evidence was commonly found in the case of PPLSNs system especially using PP-g-MA as a compatibilizer (Kawasumi, 1997; Nam, 2001; Yu, 2004). For example, Figure 2.11(A) shows the XRD patterns of three types of functionalized-PP/2C18-MMT nanocomposites: (a) methylstyrene 1 mol%, (b) maleic anhydride 0.5 mol%, and (c) hydroxyl-containing styrene 0.5 mol%). The diffraction peaks at the low angle region which indicates the *d*-spacing of ordered intercalated and ordered exfoliated nanocomposites. The author also observed the large number of exfoliated layers existing for all nanocomposites, which show no peaks in this region due to the loss of structural registry of the layers and the large *d*-spacing (> 100 nm). Therefore, TEM image was employed to confirm such a structure, as shown in Figure 2.11(B). It is clear from TEM that the intercalated tactoids (indicated as A) and disordered/exfoliated stacks of layers (indicated as B) coexist in the structure. The author suggested this phenomenon might originate from the chemical and size inhomogeneities of the silicate layers (Manias *et al.* 2000).

It worth noting that the characteristic and the compatibilizer (PP-g-MA) content as well as the concentration of clay have strong affects to the structure of PP nanocomposite. PP-g-MA was found to improve the dispersibility of the silicate layer (Hasegawa *et al.* 1998). Lertwimolnun and Vergnes, (2005) studied the effect of PP-g-MA content (0, 5, 15, and 30 wt%) on the PP nanocomposite morphology. It was found that the degree of dispersion is improved by incorporating a maleic anhydride grafted, the morphology was observed by TEM, as shown in Figure 2.12. It is clear that without PP-g-MA, the clay aggregates at a micrometer

level are seen. Practically, no individual silicate layer is dispersed. For the hybrids containing PP-g-MA, the size of aggregates is greatly reduced, although some aggregates still exist. In best conditions (30 wt%), the individual silicate layers are really observed, corresponding to the partial exfoliation of the clay (Jayaraman *et al.* 2002). Moreover, Wang *et al.* (2004) supported that low molecular mass and high maleic anhydride content of PP-g-MA provided good clay dispersion. A suitable silicate clay content (<3 wt%), a considerable well dispersion and exfoliation of the clay in PP nanocomposites is observed. On the other hand, an aggregation (tactoids and macro-aggregates) was obtained at high content of layered clay as shown in Figure 2.12 (Tang *et al.* 2003).

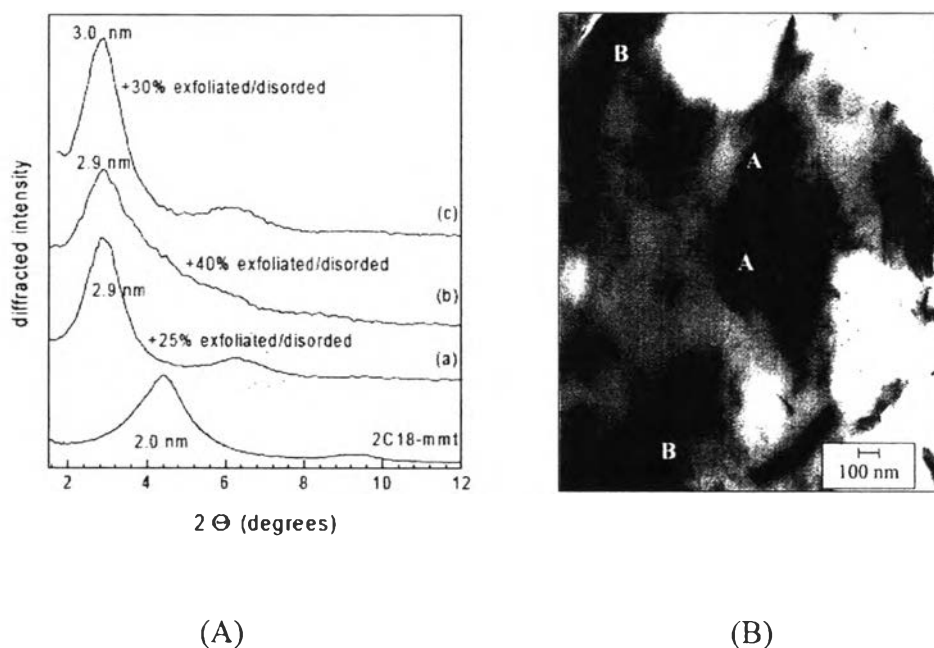


Figure 2.12 (A) XRD patterns of a dimethyldioctadecylammonium-modified montmorillonite (2C18-MMT) and all of the functionalized-PP/2C18-MMT nanocomposites at different functional groups: (a) methylstyrene 1 mol %, (b) maleic anhydride 0.5 mol % and (c) hydroxyl-containing styrene 0.5 mol % and (B) TEM image of the functionalized-PP/2C18-MMT nanocomposite structure (PPr-MA/6 wt % OMMT).

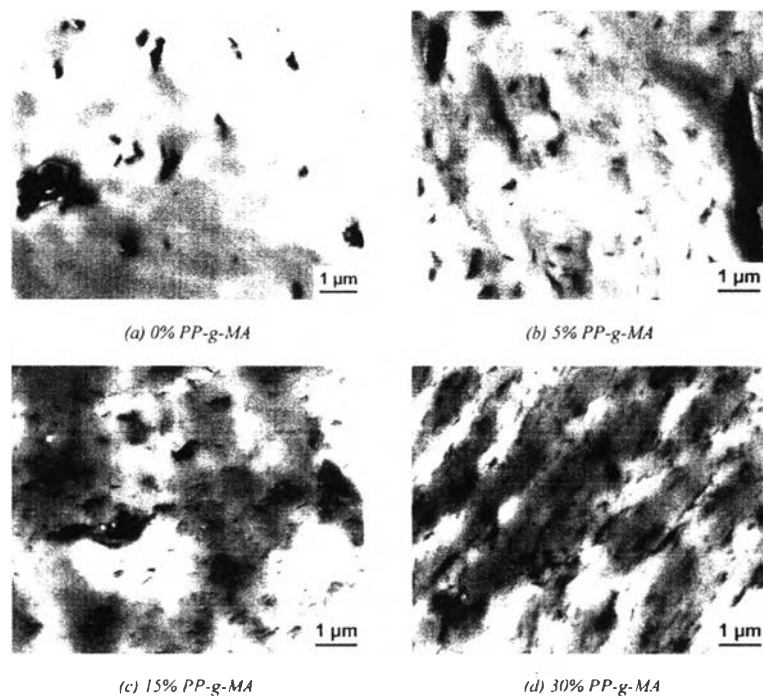


Figure 2.13 TEM micrographs (X10,000) of PP/PP-g-MA/Cloisite®20A composites with different PP-g-MA content.

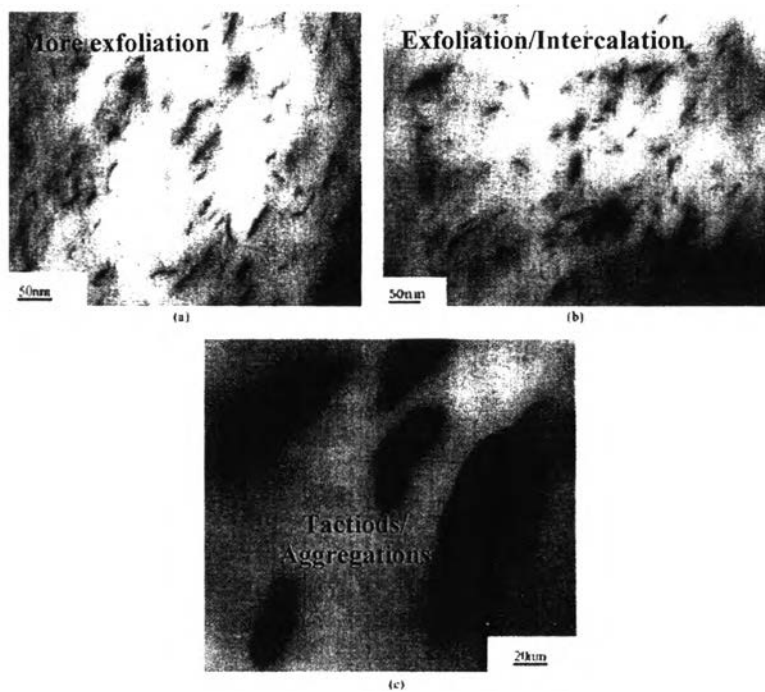


Figure 2.14 TEM images of PP/clay hybrids: (a) PP/MAPP/OMT1, (b) PP/MAPP/OMT2 and (c) PP/MAPP/OMT3.

2.2.4 Properties of PPLSNs

The presence of layered silicates has provided tremendous property enhancement of the PP matrix as well as the presence of polar groups of PP-g-MAH affecting the dispersion of clay layers in the composite and thereby enhances the properties. A number of material properties where enhancements have been reported in the literature include tensile strength and modulus, flexural modulus, glass transition temperature, heat distortion temperature, thermal stability, flame retardant and barrier ability etc.

2.2.4.1 *Mechanical Properties*

In general, the addition of an organically modified layered silicate in a polymer matrix results in a remarkable improvement of mechanical properties, i.e. tensile strength, Young's modulus, but significantly reduced elongation and impact strength. The improvement in mechanical properties requires good exfoliation and dispersion of the silicate layers in the polymer matrix. Most of PP layered silicate nanocomposites reported in literature studied the tensile properties as a function of the layered silicate content (Figure 2.15). A sharp increase of the Young's modulus was observed at very small layered silicate loadings (<4 wt%), followed by a much slower increase beyond layered silicate loadings about 5wt%. With increasing layered silicate content, the yield stress does not change markedly compared to the neat polymer (Manias *et al.* 2000). Similar behavior was found by Svoboda *et al.* (2002). There was a sharp increase of tensile strength from 0 to 1 wt% of clay. Further addition of clay improved the tensile strength only moderately. After reaching the maximum value (about 3 wt%), the further addition of clay decreases the tensile strength. In addition to clay content, the present of compatibilizers in polymer matrix also plays a crucial role in improvement of mechanical properties. It was found that the PP containing compatibilizer (PP-g-MAH) shows large improvement of modulus while the uncompatibilized PP showed no improvement. Manias *et al.* (2000) suggested that when the polymer/inorganic interaction is improved, i.e. when MA functional groups are added to the polymer, the stresses are much more effectively transferred from the polymer matrix to the inorganic clay, and thus an enhancement in Young's modulus is achieved. Similar result was observed by Galgali *et al.* (2004). The same result was found by

Cheung *et al.* (2002) for iPP/OMMT hybrids, both tensile yield strength and the tensile modulus increased, but the elongation at break and the notched Izod impact did not change significantly. In addition, Okamoto *et al.* (2001) showed that the degree of intercalation of the PP-g-MA chains and the aspect ratio of the dispersed clay particles strongly affected the final mechanical properties of the PPLSNs, in their study; the intercalated PPLSNs exhibited an enhancement of the moduli compared with pure PP matrix.

For flexural modulus, for example, Modesti *et al.* (2005) found that the increase in flexural modulus was strongly depended on the compatibilizer. Using a compatibilized PP, about 35% increase in the flexural modulus was realized over the neat PP matrix. Uncompatibilized PP based composite showed a maximum increase of 26% over the neat PP matrix. This difference in flexural modulus between two samples was attributed primarily to an improvement in polymer/clay compatibility. The authors proposed that improvement in polymer/clay interaction should decrease polymer chain mobility and increase the stiffness of the material.

In contrast to tensile strength and modulus, the % elongation of nanocomposites was reduced with increasing the clay content. The reduction of elongation may be due to the greater interaction between filler and polymer matrix, which probably leads to lower polymeric chain mobility, making the material more rigid (Modesti *et al.* 2005).

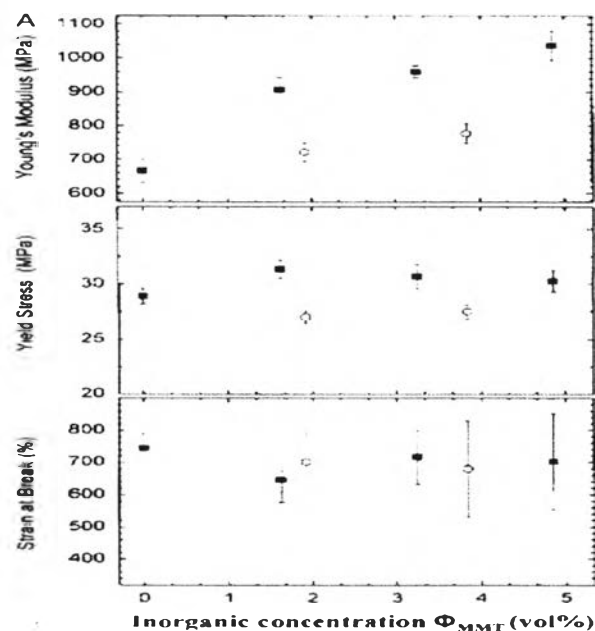


Figure 2.15 Mechanical properties of PPLSNa as a function of clay content.

2.2.4.2 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) measures the response of a given material to an oscillatory deformation (usually tension or three-point bending type deformation) as a function of temperature. DMA results are expressed by the three parameters: (i) the storage modulus (E'); (ii) the loss modulus (E''); and (iii) $\tan \delta$, which is the ratio of E''/E' , useful for determining the occurrence of molecular mobility transitions, such as the glass transition temperature (T_g). It is well known that both storage and loss modulus are improved by the addition of layered silicate in a polymer, in particular at temperature above the T_g . For the exfoliated nanocomposite, the increase in E' is due to the creation of a three-dimensional network of interconnected long silicate layers, strengthening the material through mechanical percolation (Alexandre and Dubois, 2000). Above the T_g , when materials become soft, the reinforcement effect of the clay particles becomes more prominent, due to the restricted motion of the polymer chains and thus the enhancement of E' was observed (Ray and Okamoto, 2003). For the case of PP based nanocomposite, Nam *et al.* (2001) observed a large improve of E' for all PPCNs that influenced from the presence of layered silicate. They found that below T_g , the enhancement of E'

was clear in the intercalated PPCNs nanocomposite. PPCNs showed a shift of $\tan \delta$ curves to higher temperatures at 25°C and another broad peak between 50°C and 90°C. Similar result was reported by Liu and Wu (2001), who prepared PPCNs with EM-MMT as an organoclay. The results show that the incorporation of EM-MMT into the PP matrix results in a remarkable increase in stiffness (Figure 2.15). In general, a shift of T_g to higher temperatures has been observed for PLSNs. It was established that T_g is strongly affected by the addition of nanoparticles and particularly when there is a good polymer–filler interaction, T_g of the amorphous polymer tends to increase by decreasing the size of the particles or by increasing the filler content; this behaviour is generally associated to the confinement effect generating a reduction in chain mobility until suppression of cooperative segmental motions of the confined macromolecules. However, the opposite effect was reported in the case of PP-based nanocomposites (Nam *et al.*, 2001). The authors suggested a decrease of $\tan \delta$ peaks was probably due to the suppression of polymer chain by the presence of the clay. Another interesting phenomenon is that the T_g values of PPCNs do not further decrease above an EM-MMT content of 3 wt%.

In summary, the storage elastic modulus appears to be substantially enhanced at temperatures above T_g for exfoliated nanocomposites filled with layered silicates of high aspect ratio. A possible explanation for such an improvement could be the creation of a three-dimensional network of interconnected long silicate layers, strengthening the material through mechanical percolation.

2.2.4.3 Thermal Stability

The thermal stability of a material is usually assessed by thermogravimetric analysis (TGA). The weight loss due to the formation of volatile products after degradation at high temperature is monitored as a function of temperature (and/or time). When heating occurs under an inert gas flow, a non-oxidative degradation occurs, while the use of air or oxygen allows oxidative degradation of the samples (Ray and Okamoto, 2003). Generally, the incorporation of clay into the polymer matrix was found to enhance thermal stability by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition, as well as by assisting in the formation of char after thermal

decomposition (Zhu, 2001 and Becker, 2004). Zanetti *et al.* (2002) studied the thermal behavior of PP based nanocomposites. They found that both onset temperature (T_{onset}) and the temperature of maximum degradation (T_d) were shifted to higher temperature (under oxidation or non oxidation process). At 10 wt% of clay loading, the T_{onset} significantly increased, which was about 50°C higher than the pure PP. They explained this increase in the thermal stability was due to the barrier effect of the silicate layers. The barrier effect concerns the diffusion of the volatile thermal oxidation products to the gas phase and, at the same time, of the oxygen from the gas phase to the polymer matrix. In fact, this behavior is attributed to the formation of char on the surface of the PLSNs during exposure to high temperature air. The inorganic char is said to be responsible for decreasing degradation by insulating the material beneath it. In addition to having insulating properties, the uniform char formation makes the diffusion of volatile degradation products out of the sample more difficult by increasing the tortuosity of the sample.

It was found that the degradation temperature is improved with the level of the exfoliated layered silicate. Zhang and Wikie (2006), for example, found that PP based nanocomposite containing 1wt% organoclay significantly increased in T_d , which was 45°C higher than pure PP. As the organoclay content exceeded to 3wt% and the 5wt%, which in turn, the T_d value not much increased. From the TEM images, it was seen that at 1wt% revealed the exfoliated state. While at 3 wt% and 5wt% of organoclay content, the intercalated and agglomerated morphology, in stead, was observed. In contrast, Wang *et al.* (2006) found that the T_d at lower OMMT content (i.e. 0.5 and 1 wt%) are lower than that of pure PP, after OMMT content is increased up to 2 wt%, the thermal stability is obviously reinforced (Figure 2.16). The reason is that as OMMT content exceeds 1 wt%, the nanodispersed clay tactoids/sheets progressively establish and complete the mesoscopic network structure. It is conceivable that the mobility and relaxation of iPP chains will be confined by the physically correlated cage comprising layered OMMT tactoids and layers, resulting in the opposite evolution of macroscopic properties after the threshold (1 wt%) of filler content. So, in contrast to the cases of low OMMT content, the role of a percolated filler network created at high OMMT

content is dominant in determining the macroscopic properties, resulting in low melt fluidity, retarded crystallization capability, but an enhanced thermal stability and modulus.

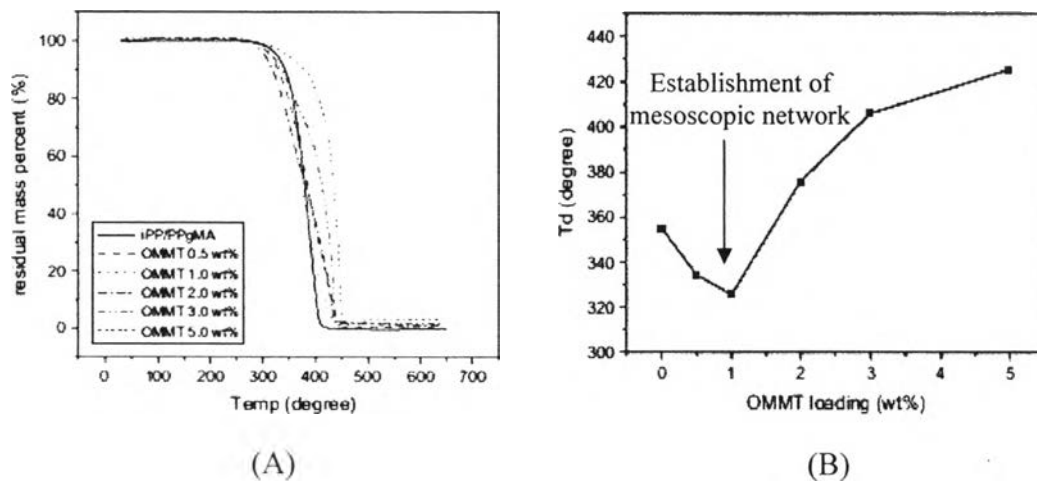


Figure 2.16 (A) TGA curves of iPP/OMMT hybrids containing various OMMT contents and (B) thermal degradation temperatures (T_d) as a function of OMMT content. The datum in (B) was extracted from (A) and corresponded to the values at largest slope of TGA curves (Wang *et al.* 2006).

2.2.4.4 Crystallinity

Crystallization is one of the most effective processes used to control the extent of intercalation of polymer chains into silicate galleries, and hence to control the mechanical and various other properties of the nanocomposites. The effects of the silicate layers on the crystal structure of the PP based nanocomposites have been of interest. For example, Maiti *et al.* (2002) found that although clay particles act as nucleating agents for the crystallization of a PP-MA matrix, the linear growth rate and the overall crystallization rate were not significantly influenced by the presence of clay. In contrast, Li *et al.* (2003) studied the nonisothermal crystallization behavior of PP-g-MA/MMT system and found that the presence of MMT clay resulted in the increase of crystallization rate and the decrease of supercooling degree required for crystallizing nucleation. The activation energy for

the nanocomposites was found to be higher than the matrix, indicating an active heterogeneous nucleation of the clay. Similarly, Modesti *et al.* (2006) reported a remarkable increase of crystallinity and crystallization rate for PP based nanocomposites explained by considering that the nanoclay platelets dispersed in the matrix promote heterogeneous nucleation. In addition, Krump *et al.* (2006) found that with increasing organoclay content, the melting temperature was increased. The author explained this behavior by considering an increase in PP lamellar thickness, at the same time the very small decrease of the associated enthalpy was attributed to the lowering of the total amount of thicker lamellae present in the material, suggesting for this nanocomposite a larger amorphous part and more space for chain movement. However, Wang *et al.* (2006) found that the crystallization temperature of iPP/OMMT hybrid first increased with the addition of OMMT, but then decreased as the clay content exceeds 1 wt%, although in such case the crystallization temperatures of nanocomposites were still higher than that of basal matrix. The author suggested such a phenomenon was attributed to the confined motion of PP chains within clay network, hindering the segmental rearrangement during crystallization and restricting the formation of perfect crystals in the polymer matrix similar with the previous results reported by Lu and Nutt (2003).

2.2.4.5 Heat Deflection Temperature

Heat distortion temperature or heat deflection temperature (HDT) is the temperature at which a polymer sample deforms under a specified load. Thus, it is an index of a polymeric material's heat resistance towards applied load. In general, improvements of HDT are reported by nanocomposite formation. Usually, a significant increase is achieved for clay contents of approximately 5 wt%, and then HDT values level off for higher clay loadings. The nanodispersion of layered silicate in the PP matrix also promotes a higher heat deflection temperature (HDT). For example, Manias *et al.* (2001) reported the HDT of PP and its nanocomposites based on f-MMT and alkylammonium-MMT. In the case of neat-PP/f-MMT there is a marked increase of the HDT, from 109°C for the neat polymer to 152°C for a 6 wt % nanocomposite; beyond 6 wt% of f-MMT the HDT of the hybrid levels off. When the same neat-PP polymer is filled with alkylammonium-modified MMT, the HDT is also increased but to a smaller extent, reflecting the lower exfoliation level of the

inorganic fillers. Moreover, in the latter case, there is a strong dependence of the HDT on the processing conditions during the composite formation, similarly to the tensile properties. The increase of HDT due to MMT dispersion is a very important improvement for PP, not only from the application/industrial viewpoint, but also because it is difficult to achieve similar HDT enhancements by chemical modification or reinforcement by other fillers.

2.2.4.6 Rheology

The study on rheology of polymer layered silicate nanocomposites (PLSNs) is very important due to it offers a way to characterize the state of dispersion of layered silicate, and also provide useful guidelines for optimum processing conditions. It is well known that the rheological properties of PLSNs melt are highly sensitive to the essential microstructure; there exists a dramatic difference between the rheology with and without a percolating clay network. Many researchers instead propose modified models of filler networks for interpreting reasonably the unique rheological properties in PLSNs, for example, Krishnamoorti *et al.* (1996, 1997, 2000) conducted small-strain amplitude oscillatory shear experiments of two series of end-tethered exfoliated nanocomposites based on poly(ϵ -caprolactone), nylon 6, and one series of intercalated nanocomposites based on a disordered diblock copolymer of polystyrene and polyisoprene (PSPI). The storage (G') and loss moduli (G'') of these nanocomposites increased monotonically with the silicate loading at all frequencies. It was found at low frequency that nanocomposites containing high clay loading exhibited a pseudo-solid-like response (i.e. G' exceeded G'' and G' was nearly independent of frequency). This pseudo-solid-like behavior at long times was attributed to randomly oriented stacks of silicate layers that formed a percolated three-dimensional network. The similar low frequency behavior has been observed by Fomes *et al.* (2001) for nylon 6/clay nanocomposites. However, for PP based nanocomposites, many researches have been studied their rheology based on the clay content or even the effect of compatibilizer, usually PP-g-MA. For example, Solomon *et al.* (2000) studied the melt-state linear and nonlinear shear rheological properties of PP based nanocomposites. Above inorganic loadings of 2.0 wt % the nanocomposites exhibited apparent low-frequency plateaus in the linear viscoelastic

moduli. The transient stress in start-up of steady shear scaled with the applied strain. These observations allow features of the PP/clay nanocomposites structure to be deduced. The transient nonlinear rheology is consistent with an anisometric, non-Brownian structure. The demonstration of the sensitivity of melt-state rheological measurements to interparticle structure and chemistry of the hybrid materials indicates the potential usefulness of such studies for the development of new nanocomposite materials. After investigating the same PLSN system, they suggested also that the hybrid network was easily destroyed by deformation, but attractive interparticle interactions would promote reconstitution of the network, giving rise to overshoot in the stress during flow reversal studies. Galgali *et al.* 2001 suggested that the solid-like rheological response of PP/clay nanocomposites originates from strong frictional interactions of the clay tactoids and layers after formation of a percolating filler network. Within this network, the free rotation of clay tactoids is hindered by the adjacent ones. Recently, Wang *et al.* (2006) conducted dynamic melt rheology (under small-amplitude oscillatory shear) to study the effect of layered silicate on the motion and relaxation of PP chains. In their study, the establishment of a mesoscopic clay network was demonstrated as the change of storage modulus (G') and loss moduli (G''). As can be seen from Figure 2.17(a), in the high ω regime (corresponded to the movement within small timescale) not much difference of the G' is seen for the composites with various OMMT contents (0–5 wt%), indicating the movements of partial polymer chains and methyl groups tethered on the backbone were unaffected by OMMT nanoparticles. However, the G' in the low ω regime is significantly dependent on the OMMT content, i.e., the G' of nanocomposites is slightly lower than that of base polymer when the OMMT content is lower than 2 wt%. On the contrary, the G' at high OMMT concentration is higher than that of base polymer. The rheological properties in the low ω regime can be regarded to reflect the relaxation and motion of whole PP chains. The frequency-independence of G' in the low-frequency regime, regarded as a pseudo-solid-like behavior that the terminal slope of $G'-\omega$ curve approaches zero, does not increase monotonically with increasing OMMT content until threshold content is reached, at ~2 wt% OMMT. The terminal slope of $G'-\omega$ curves begins to decrease when the OMMT content reaches 2

wt% indicating that there are adequate number of layered OMMT particles to establish a percolated filler network in which the free movement of PP chains is restricted by the spatially confined geometry, resulting in the incomplete relaxation of the chains upon the applied small amplitude strain over a long time range. The terminal slopes of G'' vs. ω curves are approximately comparable for the iPP/OMMT composites over the full OMMT concentration range as shown in Figure 2.17(b). The increase in the frictional stress, which originates from the difference in the relative motion between silicate particles and basal resin, is limited, even though the percolating filler network has been constructed at high concentration.

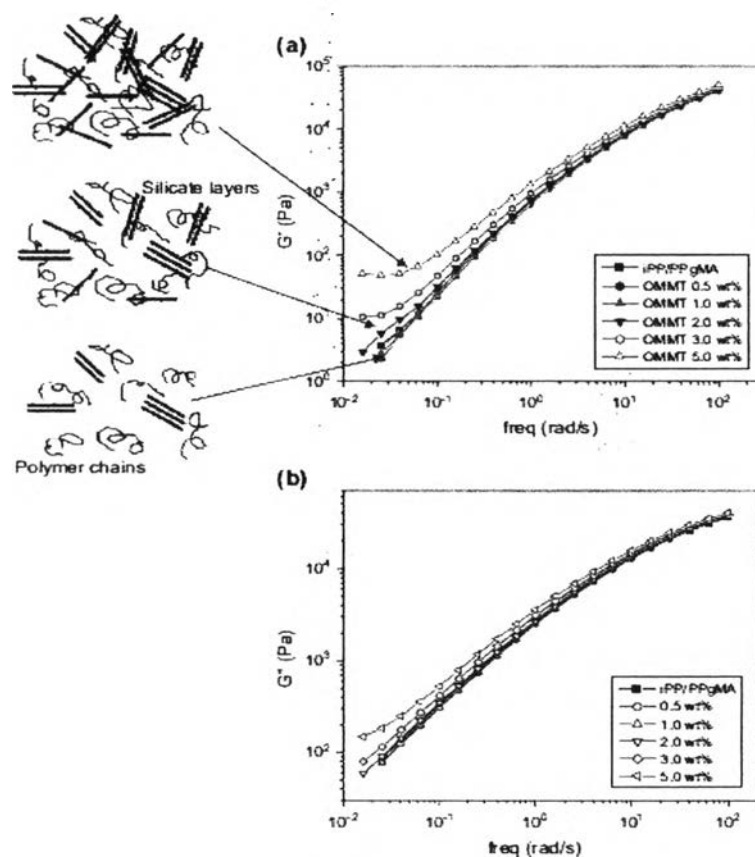


Figure 2.17 Linear melt-state rheological properties as a function of oscillatory frequency: (a) storage modulus (G') and (b) loss modulus (G'') (Wang *et al.* 2006).

Other types of rheological studies have been performed on PPCNs. The significance of compatibilizer (PP-g-MA) on the rheological behavior of PPCNs was studied by Galgali *et al.* (2001). The zero-shear viscosity (η_0) of compatibilized nanocomposites was three-orders of magnitude higher than that of the matrix and uncompatibilized nanocomposites indicating that the presence of PP-g-MA enhanced the exfoliated structure, and η_0 also decreased with annealing time. Salomon *et al.* (2001) also performed non-linear reversing shear flow experiments (shear rate = 0.1 s^{-1} , 300 s, 4.8 wt% clay) in order to study the transient structural evolution during shear and the disorientation kinetics of flow-aligned silicate domains during the annealing period between deformations. The magnitude of stress overshoot was strongly dependent on the rest time. The transient stress in start-up of shear scaled with strain over a wide range ($0.005\text{--}1 \text{ s}^{-1}$) of strain rates. The authors concluded this non-linear rheology was consistent with an anisometric, non-Brownian structure, which was later confirmed by other studies (Li, 2003 and Treece, 2007). Additionally, Gu *et al.* (2004) showed that at lower frequencies, the steady shear viscosities of PPLSNs increased with OMMT content. However, the PPLSNs melts showed a greater shear-thinning tendency than pure PP melt because of the preferential orientation of the MMT layers. The author concluded that PPLSNs had a higher moduli but better processibility compared with pure PP.

2.3 Layered Double Hydroxide Based Nanocomposites

2.3.1 Background

Layered double hydroxides (LDHs) are a class of anionic clay materials. They can be of both synthetic and natural origin. The most commonly known naturally occurring LDH clay is hydrotalcite having chemical formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$. Hydrotalcite is the first mineral of this group whose structure and properties were studied extensively and often taken as the representative of the LDH clay materials. Hence, the LDHs are also known as hydrotalcite-like-compounds. Important features of LDH are the highly tunable intra-layer and inter-layer composition that allow one to fit the properties of the clay to applications in a large number of fields: catalysis and their supports (Constantino *et al.* 1995), adsorbents (You *et al.* 2002), ceramic precursors (Hibino and Tsunashima, 1998), ion exchangers (Xu and Zeng, 1998) electrochemical reactions (Yao *et al.* 1998), medicine stabilizers (Qian and Zeng, 1997) and controlled release of anions (Ambrogi *et al.*, 2001). Very recently, LDHs are considered as a new emerging class of the most favorable layered crystals for the preparation of multifunctional polymer/layered crystal nanocomposites (Leroux and Basse, 2001).

2.3.2 Crystal Structure of LDHs

The general chemical formula of LDHs is written as $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+} (A^{n-})_{x/n} \cdot mH_2O$, where M^{II} is divalent metal ions (i.e. Mg^{2+} , Ca^{2+} , Zn^{2+} , etc.), M^{III} is trivalent metal ions (i.e. Al^{3+} , Fe^{3+} , Cr^{3+} , etc.) and A^{n-} is an anions (i.e. CO_3^{2-} , Cl^- , NO_3^- , etc.). The anions occupy the interlayer region of these layered crystalline materials. Although a wide range of values of x is claimed to provide LDH structure, the pure phase of LDH clays is usually obtained for a limited range as $0.2 < x < 0.33$ (Brown, 1967; Miyata, 1973; Cavani, 1991). The structure of LDHs can best be explained by drawing analogy with the structural features of the metal hydroxide layers in mineral brucite or simply the $Mg(OH)_2$ crystal structure. Brucite consists of a hexagonal close packing of hydroxyl ions with alternate octahedral sites occupied by Mg^{2+} ions. The metal hydroxide sheets in brucite crystal

are neutral in charge and stack one upon another by Van der Waals interaction. The interlayer distance or the basal spacing in brucite has a value of about 0.48 nm. In LDH, some of the divalent cations of these brucite-like sheets are isomorphously substituted by a trivalent cation and the mixed metal hydroxide layers, $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}$, thus formed acquire a net positive charge. This excess charge on the metal hydroxide layers is neutralized by the anions accumulated in the interlayer region. The interlayer region in LDHs also contains some water molecules for the stabilization of the crystal structure (Khan *et al.* 2002). The presence of anions and water molecules leads to an enlargement of the basal spacing from 0.48 nm in brucite to about 0.77 nm in Mg-Al-LDH. A schematic representation comparing the brucite and the LDH structures is shown in Figure 2.18.

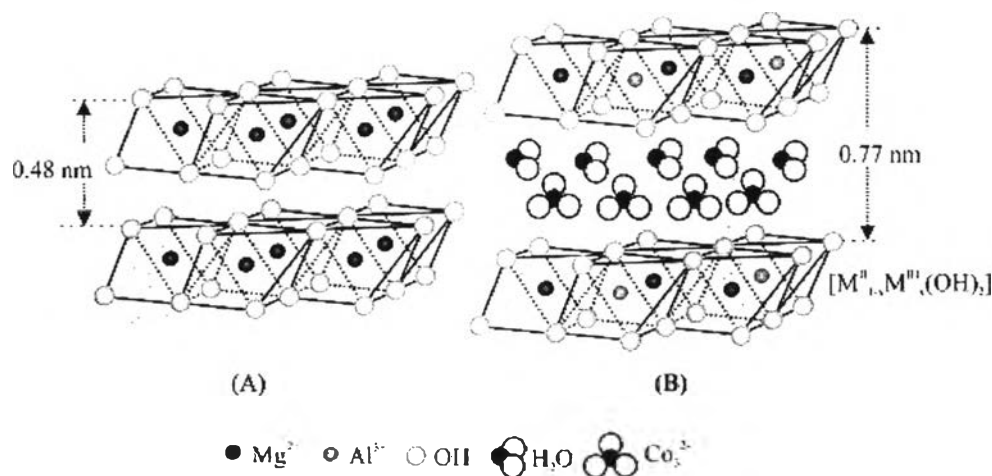


Figure 2.18 Schematic representation comparing the crystal structure of (A) brucite and (B) Layered Double Hydroxides (LDHs) (Khan *et al.* 2002).

2.3.3 LDHs as nanofiller

In recent years, there is a growing interest in using LDHs as novel nanofiller for preparing polymer nanocomposites and in that sense it is a competing material to layered silicates, the most commonly used nanoclays. The characteristics that make LDHs suitable as nanofiller are its layered structure and readily exchangeable interlayer anions with large organic species. In principle, LDHs can be

modified similarly as layered silicates to make polymer nanocomposites. But, LDHs have distinct advantages over layered silicates, as follow.

i. Chemically active: its makes grafting of organic species on inorganic layers (Prevot *et al.* 2001).

ii. Thermally unstable: the endothermic decomposition above decomposition temperature of many polymeric materials helps in improving flame retardancy through active participation in flame inhibition.

iii. Cationic layer charge: can be modified by wide range of anionic species starting from anionic surfactants to large anionic metallic clusters, (polyoxo metalates) or anionic metal complex (Costa *et al.* 2007).

iv. Large anion exchange capacity: theoretical AEC (at $M^{II}:M^{III} = 2:1$) is greater than 400 mmole/100g LDH.

The reactivity of LDHs to wide range of organic and inorganic anionic species makes it an ideal material for designing nanohybrids with diversified applications some of which will be discussed in the following sections.

2.3.4 Modification of LDHs

The potential application of LDHs as nanofiller for preparing polymer nanocomposites has been received considerable attention from both academia and industrial points of view. The unique positive charge of LDHs crystal layers provides a greater flexibility in selecting the suitable organic modifiers. Since, LDHs have high charge density, which is generally 3–4 fold higher than that of layered silicate. The high charge density as well as the high content of interlayer anions and water molecules result in strong interlayer electrostatic interactions between layers and strong hydrophobic properties, and thus prevent both swelling and exfoliation of the LDH layers. Therefore, in order to facilitate the intercalation of LDHs into polymer matrixes and to achieve a good level of dispersion, the interlayer space of LDHs should be chemically modified to eliminate the interaction and obtain the hydrophobic property of LDH layers. There are four general methods reported in literatures for preparing organo-LDHs: (i) anion-exchange of a precursor LDHs; (ii) direct synthesis by coprecipitation; (iii) regeneration method and (iv) thermal

reaction. In this study, we report the synthesis of organo-LDHs via anion-exchange of a precursor LDHs, which are described in the following sections.

2.3.4.1 Anion Exchange of Precursor LDHs

The anion-exchange method has been found to be the most common method for preparation organo-LDHs. Several anionic species such as phosphates, carboxylates, sulfonates, and sulfates have been widely used to modify the layered LDHs via this method (Newman and Jones, 1998). In particular, alkyl sulfates have been found to be the most efficient class of the anionic surfactants for LDHs modification. The exchange reaction is controlled by the selectivity of the layered host for the different anions. The previous study by Miyata *et al.* (1983) has demonstrated the selectivity scale of exchangeable anions as following: $\text{CO}_3^{2-} > \text{SO}_4^{2-} \gg \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{ClO}_4^-$. LDHs containing ClO_4^- , NO_3^- or even Cl^- anions are, therefore, the most suitable precursors for anion exchange syntheses due to the relative ease with which the nitrate anions can be displaced from the interlayer. In general, the anion-exchange reaction is carried out by simply dispersing the precursor LDHs in aqueous solution containing an excess of the organic anion that is to be incorporated. The organic anion of interest must be stable at the pH of exchange and, if the $\text{M}^{2+}/\text{M}^{3+}$ ratio of the precursor LDHs is to be retained in the anion-exchanged LDHs, the hydroxide layers must also be stable. Exchange of interlayer anions by an organic anion (acetate) was first reported by Miyata and Kumura (1973). Later, Boehm *et al.* (1977) reported the anion exchange of a Zn-Cr LDH containing nitrate or chloride anions with short- and long-chain sodium alkyl sulfate anions. Various organo-LDHs can be obtained by incorporation a large variety of organic anions into the LDH interlayer space, i.e. sulfate, sulfonate, carboxylate (Carlino, 1997; Choy, 2001; Khan, 2002; Qiu, 2006).

2.3.4.2 Direct Synthesis by Coprecipitation

The co-precipitation method requires the addition of metal salts solution to a base solution containing the organic anions at a constant pH value (normally from 8 to 10). Hsueh and Chen (2003), for example, prepared MgAl-aminobenzoic acid (AB) LDHs by adding MgAl nitrates solution into the AB solution at the pH value of 10 controlled by NaOH solution.

2.3.4.3 Rehydration of Calcined LDH Precursor

It is well known that most LDH materials show unique phenomenon called “memory effect”, which involves the regeneration of the layered crystalline structure from their calcined form, when the later is dispersed in an aqueous solution containing suitable anion (Miyata, 1980), as shown in Figure 2.19. This property is usually used to synthesize and modify LDHs with different types of organic anions. The ease and extent of reconstruction of the calcined LDHs are controlled by the properties of the matrix cations as well as the temperature of calcinations (Sato, 1988 and Kooli, 1994). In order to improve the crystallinity of the rehydrated product, therefore, Carlino *et al.* (1995) recommended heating the precursor LDHs using a slow ramping technique ($\sim 1^{\circ}\text{C min}^{-1}$). This technique prevents the rapid expulsion of carbon dioxide and water from the LDHs, which occurs upon direct and sudden heating, disrupting the layered structure of the calcined product. However, Chibwe and Jones (1989) even they prepared several organo-LDHs in a nitrogen atmosphere, the carbonate impurity was still observed due to the high affinity of the mixed oxide for carbonate anions. Recently, large variety of organo-LDHs have been prepared via the rehydration route, including LDHs containing sulfate and sulfonate (Costa *et al.* 2005) etc.

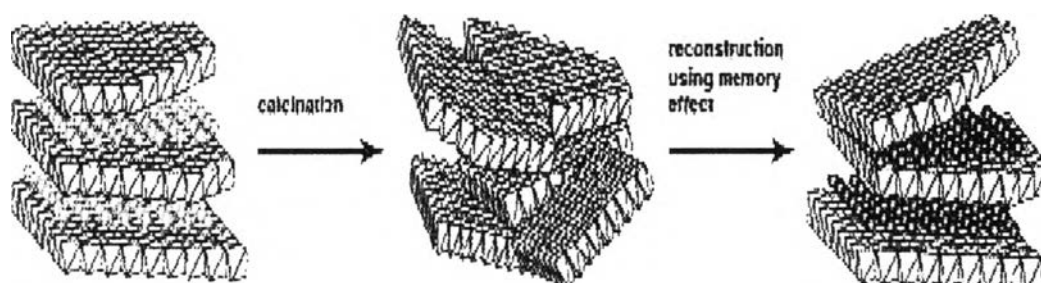


Figure 2.19 Scheme of Rehydration of calcined LDH precursor.

2.3.4.4 Hydrothermal Crystallization Method

Thermal reaction is a relatively new approach to the preparation of organo-LDHs. The procedure was first reported by Carlino and Hudson (1994) who reacted molten sebacic acid with MgAl(CO₃) LDH. In this procedure an intimate mixture of MgAl(CO₃) and sebacic acid was heated at a temperature 20–30°C above the melting point of the acid. In year 1995 and 1996, Carlino *et al.* used the same procedure to incorporate the caprate or phenylphosphonate anions into MgAl-LDH. In addition to the corresponding organo-LDH phase, the thermal reaction product was found to contain in each case an unreacted MgAl(CO₃) phase. Although phase pure organo-LDH products have not been obtained using thermal reaction, this approach nevertheless provides an interesting alternative to the conventional wet methods.

Nevertheless, all method for preparing organo-LDHs commonly have the carbonate contamination, since the carbonate anions are readily incorporated and tenaciously held in the interlayer. Therefore, decarbonated and deionized water is suggested to use through the reaction.

2.4 Polyethylene LDH nanocomposites

2.4.1 Preparation of Polymer LDH Nanocomposites

Similarly with layered silicate based polymer nanocomposites, polymer/LDH nanocomposites can be synthesized by several methods, as shown in Figure 2.20 (Leroux and Besse, 2001). In general, depending on the different dispersion states of the LDH layers in the matrix polymer, two main types of polymer/LDH nanocomposites, intercalated and exfoliated nanocomposites can be obtained. The exfoliated ones usually attract more interest due to they have nanoscale dispersion of high aspect ratio LDH layers in the polymer nanocomposites and thus can exhibit a superior properties compared with micro-dispersed and conventional composites (Choi *et al.* 2001). The detail of each method, particularly the melt intercalation that used to prepare LDPE/LDH nanocomposites in our study, will be discussed in the following section.

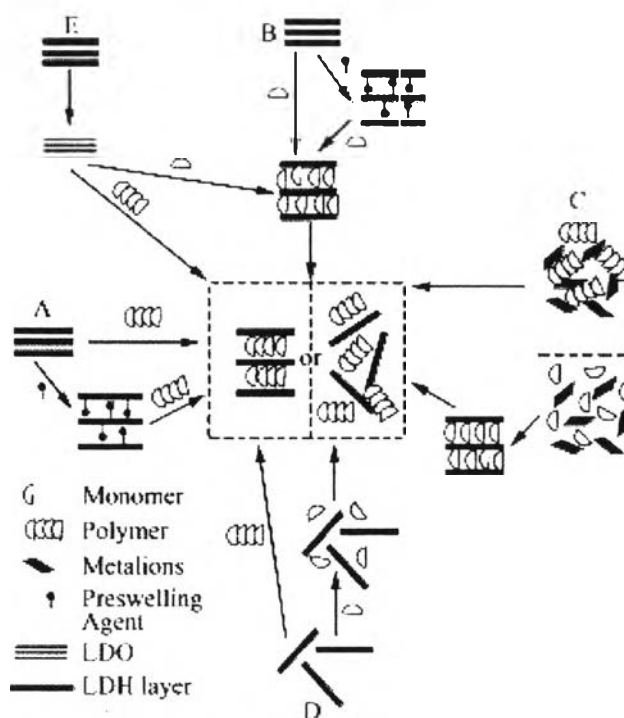


Figure 2.20 Schematic illustrates the preparation method of polymer/LDH nanocomposites: (A) direct intercalation; (B) in-situ polymerization; (C) in-situ synthesis; (D) exfoliation/restacking and (E) reconstruction (Leroux and Besse, 2001).

2.4.1.1 In-Situ Polymerization

In-situ polymerization is the most widely referred technique for preparing polymer/LDH nanocomposites. This method is solution based and is usually carried out in an aqueous system. Various polymers/LDH nanocomposites have been successfully prepared via this method. For instance, Chen *et al.* (2003) have synthesized PMA/ZnAl-LDH nanocomposites with 5wt% ZnAl-DS LDH loading. The XRD and TEM analysis suggested the intercalated structure in which the LDH layers was face-to-face oriented with about 3 nm spacing in the PMA matrix. Since the strong interlayer electrostatic interaction, small gallery space, and hydrophilic property of LDH, few studies were reported on the preparation of exfoliated polymer/LDH nanocomposites. O'Leary *et al.* (2002) have reported that the delamination of dodecyl sulfate modified MgAl-LDH in polar acrylate monomers

with the help of high shearing and subsequent polymerization of the monomers containing the LDH dispersion gave exfoliated polyacrylates/LDH nanocomposites. Hsueh and Chen, (2003) have reported one polyimide/LDH-exfoliated nanocomposite prepared from a solution of polyimide precursor and an amino benzoate-intercalated MgAl LDH using N,N-dimethylacetamide as a solvent.

2.4.1.2 Solution Intercalation

The solution intercalation has been proven an effective method for the preparation of polymer/LDH nanocomposites. To prepare polymer nanocomposites, typically the organo-LDHs are dispersed in a solution containing polymer. The resultant dispersion is then stirred or aged under nitrogen atmosphere to accomplish the polymer intercalation. Several polymers have been prepared via this method, for example, Buniak *et al.* (2002) used DS-LDH to prepare PEO/LDH nanocomposites. The modification of MgAl-LDH was carried out using ion-exchange method and the modified LDH was later treated with aqueous solution of PEO to prepare the nanocomposite. Costa *et al.* (2004) prepared nanocomposites through intercalation of dendrimers (carboxylate terminated polyamidoamide) into LDH. They observed saturation of dendrimer intercalation into host LDH when the mixing ratio of the two ingredients exceeded 1:2 (charge ratio of anionic clay and carboxylate group of the dendrimer). The dendrimers remained densely packed in the interlayer region of LDH with an ellipsoidal shape. When excess dendrimers was used (mixing ratio 1:8), in addition to intercalation they were also adsorbed on the clay surface. Many research works have been focused on polyethylene based LDH nanocomposites, for instance, Chen *et al.* (2003 and 2004) prepared and characterized polyethylene (LDPE)/LDH by this method using dodecylsulfate modified LDH (LDH-DS). The nanocomposites were obtained by refluxing the mixture of LDH-DS and the polymers solution in xylene. The XRD result suggested the exfoliated structure. Later, the linear low density polyethylene (LLDPE)/ZnAl-LDH nanocomposites have also been prepared in a non-polar system and the obtained nanocomposites were characterized by a combination of XRD and TEM. The author suggested that with high amount of organo-LDH loading, the LLDPE chains were not intercalated between the LDH layers. However small amount of organo-LDH, instead, the exfoliated was evidence (Chen *et al.* 2004). In solution

method, it was found that several factors, i.e. LDH loading, refluxing time, and preparation method have influence on the dispersion state of LDHs. For example, the completely exfoliated LDH layers can be achieved by decreasing the content of LDH and elongating the refluxing time. Moreover, it was found that slow evaporation of the solvent only leads to an intercalated structure, while rapid evaporation is in favor of exfoliated structures (Qiu *et al.* 2005).

2.4.1.3 Melt Intercalation

The most challenging method of preparing polymer/clay nanocomposites is the melt compounding method. With non-polar polymers, like polyolefin, it becomes more difficult due to high thermodynamic incompatibility between the non-polar matrix and the polar clay materials. There are not many reports available till today that exclusively deal with the preparation of polymer/LDH nanocomposites using melt-compounding technique. This method has proven technological advantage over the solution method as it can be easily adopted for industrial product manufacture using conventional polymer processing equipments. The melt compounding method used for the preparation of polymer/LDH nanocomposites is similar to that used for conventional polymer/layered silicate nanocomposites. The organo-LDHs are the suitable precursor for this process, which are mixed with molten polymer in the typical plastic processing equipments. Nichols and Chou (1999) first reported the melt compounding for preparing polymer/LDH nanocomposites. Very recently, researchers are showing more interests in this method to prepare nanocomposites based on different types of polymers. For examples, Zammarano *et al.* (2006) prepared polyamide 6/LDH nanocomposites using organically modified MgAl-LDH. They observed that high degree of exfoliation of the LDH particles can be obtained using LDHs with low anion exchange capacity. Lee *et al.* (2006) prepared poly(ethyleneterephthalate)/LDH nanocomposites with MgAl-LDH modified with various organic surfactants. They observed improved thermal and mechanical properties of these nanocomposites as compared to the unfilled polymer. However, a few studies have been reported on melt intercalation technique for preparing polyethylene/LDH nanocomposites, for instance, Costa *et al.* (2005 and 2007) reported the preparation of

intercalated/flocculated LDPE/SDBS-LDH nanocomposites using. A complex morphological feature of dispersed LDH particles was observed with mostly located in the form of thin platelets and agglomerates. The significant changes in linear viscoelastic responses in low frequency region was observed i.e. storage modulus (G') of the composites was higher than pure LDPE even at very low loading (2 phr) of SDBS-LDH suggesting the formation of network-like structure via the interaction between LDHs particles and polymer chains. Du and Qu, (2006) prepared LLDPE/DS-LDH nanocomposites, the morphological analysis by XRD and TEM of such composites did not evidence a homogeneous dispersion and a perfect exfoliation of LDH particles, but the thermal stability and fire resistant properties of these composites were significantly enhanced. The author suggested that this behaviour may be ascribed to the barrier effect of LDH layers on the oxygen diffusion that can shield PE chain segments from thermal oxidation. Similarly result was reported for PE/stearate-LDH nanocomposites (Costatino *et al.* 2005). It is believed that the incorporation of compatibilizer (PE-g-MA) is very necessary to improve the degree of exfoliation of the polyethylene/LDH nanocomposites. Costa *et al.* (2006) has investigated how chemical compatibility of the polymer matrix influenced on the morphological and rheological properties of the composites using two different types of polyethylene matrices: one with unmodified polyethylene and the other with maleic anhydride (MAH) grafted polyethylene. SEM analysis evidenced that the single platelets remained more intensely coated by polymer in MAH grafted polyethylene system, while they trended to form structural association or clusters for the unmodified polyethylene system. This result was supported by the larger increase in the storage modulus in the more polar polymer system, which originated from the differences in the polymer-particle and particle-particle interactions that the matrix polarity favored the dispersion of LDH particles.

2.4.2 Properties of Polyethylene/LDH Nanocomposites

2.4.2.1 Morphological Characteristics

Similar to that of polymer/layered silicate nanocomposites, X-ray diffraction (XRD) and transmission electron microscopy (TEM) are commonly used to identify the morphology and dispersion level of layered double hydroxide in the matrix polymer. In case of PE/organo-LDH nanocomposites, the majority of the nanocomposite structure has found to be intercalated of LDH layers rather than the exfoliated one. For instance, Costa *et al* (2005 and 2006) prepared LDPE/organo-LDH modified with sodiumdodecylbenzene sulfonate (SDBS) and MA-grafted high-density polyethylene (HDPE-g-MA) as a compatibilizer via melt-compounding process in a Brabender mixer. The XRD showed unchanged of the (003) diffraction peak as compared to the pristine organo-LDH for any LDH contents (Figure 2.21(A)). As can be seen from TEM micrographs, the dispersed particles show a tendency to form structural association or clusters with increasing LDH loading (Figure 2.21(B)). In contrast, Costatino *et al.* (2005) observed the disappearance of the (003) diffraction peak for the case of PE/stearate-ZnAl LDH nanocomposites with 5, 10, 15% w/w organo-LDH loading, indicating an exfoliated structure was established, as shown in Figure 2.21(C). Regarding to this, the author found that the thermal stability and fire resistant properties of these nanocomposites were significantly enhanced due to the good barrier effect of the exfoliated LDH layers.

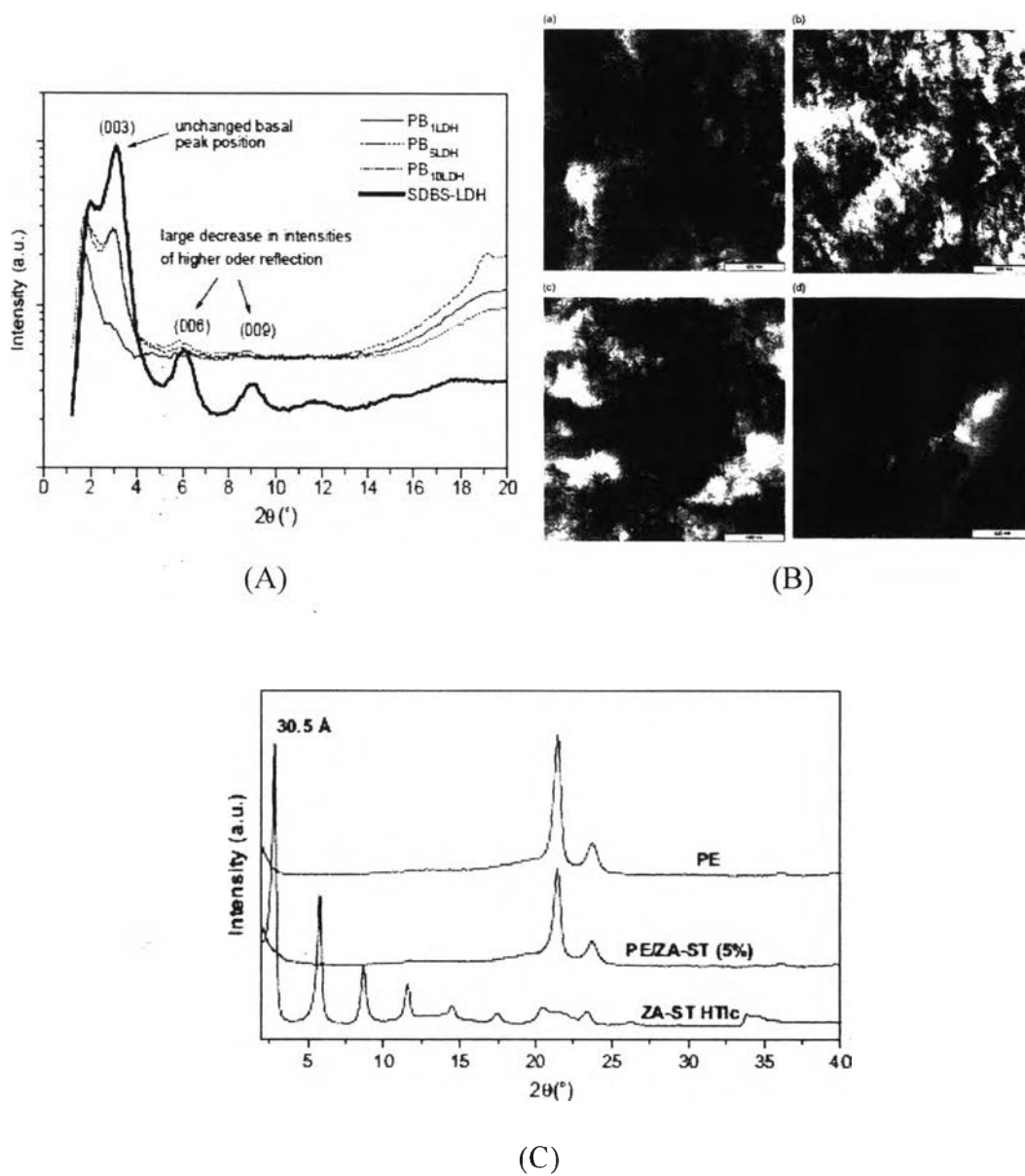


Figure 2.21 (A) XRD spectra, (B) TEM images of HDPE-g-MA/LDH (PB_xLDH) nanocomposites with (a) 0.5 phr, (b) 1.0 phr, (c) 2.0 phr and (d) 10 phr (Costa *et al.* 2006) and (C) XRD patterns of PE/stearate ZnAl LDH nanocomposites (Constatino *et al.* 2006).

2.4.2.2 Mechanical Properties

The addition of nanoparticles to the polymer is expected to improve any specific property of the final composites such as mechanical properties, gas permeability, thermal stability, etc. In case of polymer/LDH nanocomposites, similar improvements are also observed in many occasions. For example, tensile strength and the modulus of epoxy/LDH nanocomposites was significantly increased when a small amount of LDH particles was added, indicating the strong reinforcing nature of LDH in epoxy matrix. This highly reinforcing nature of LDH particles in epoxy was related to their exfoliated structure in the nanocomposite, where the highly anisometric LDH layers remain strongly attached to the polar epoxy matrix. However, for the case of polyolefins/LDH nanocomposites not much works have been reported about the mechanical characterization. For example, Chen *et al.* (2004) studied the tensile properties, i.e. Young's modulus, stress at yield and strength and elongation at break for LLDPE/dodecyl sulfate-LDH system containing 2, 5, 10 and 20 wt% of organo-LDH. A significant increase of Young's modulus over pure LLDPE (59% higher) was observed in the case of 20 wt% organo-LDH loading. However, both the strength and elongation at break much decreased compared to pure LLDPE. From XRD a decrease of the crystallinity was evidenced for all LDH nanocomposites compared with the LLDPE matrix but the critical parameter for these systems appeared to be the degree of dispersion of LDH layers. In this specific case, a certain degree of aggregation of dodecyl sulfate-LDH nanolayers was observed, which could be another possible reason for the decrease of strength and elongation at break. Similar with the results recently reported by Costa *et al.* (2006) for the case of PE/LDH nanocomposites, as shown in Figure 2.22. The tensile strength shows a decreasing trend with an increase in LDH content. However, increasing LDH content brings about steady increase in modulus and also a sharp decrease in the elongation at break. In fact, in the nanocomposites, the amount of low molecular weight compatibilizer (PE-g-MA) is also increased along with the increasing LDH content, which has a deteriorating effect on the tensile strength of the matrix. The author believed that there is a combined effect of the dispersed LDH particles and the compatibilizer in opposite direction to the change in tensile properties of the composites. However, the reinforcing effect of the LDH clay could

actually be realized in the composition containing 15 wt% LDH, when compared with similar unfilled matrix composition (PEPB in Figure 2.22). The comparison further reveals that E-modulus is increased by about 40% and tensile strength is increased from about 12.17 MPa in PEPB to about 15.17 MPa in case of the nanocomposite with 15 wt% of LDH content. However, the elongation at break is reduced drastically, which indicates that at 15 wt% LDH content, the energy absorbed by the nanocomposites drops significantly and the material tends to become more brittle as compared to the composites with lower LDH content and the unfilled matrix.

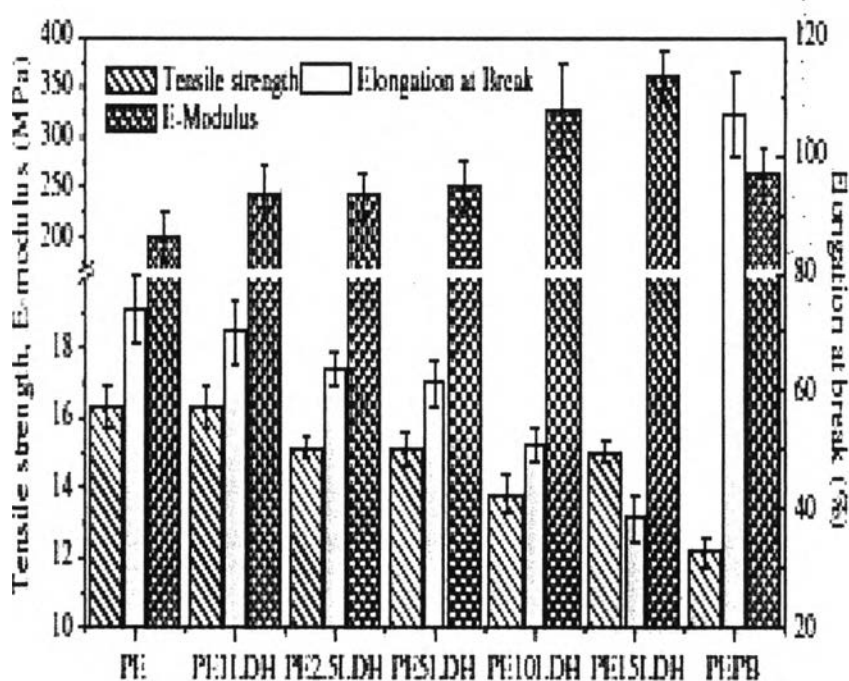


Figure 2.22 The tensile properties of polyethylene/LDH nanocomposites comparison with their unfilled matrix.

2.4.2.3 Thermal and Flame Retardant Properties

Polymer/LDH nanocomposites have unique thermal stability and have been proven to be promising candidates for the fire retardants compared with unfilled polymer and conventional composite. For example, Chen and Qu (2003) observed the thermal decomposition (at 50% of weight loss) of PE-g-MA/LDH nanocomposites with 5wt% MgAl-DS was 60°C higher than that of PE-g-MA. And the nanocomposite has a slower thermal-oxidative rate than PE-g-MA in the range of 200–320°C. Generally, it has been found that the incorporation of LDH into the polymer matrixes can enhance thermal stability by promoting the charring process of polymer matrixes and acting as a superior insulator and mass transport barrier to the volatile product generated during the decomposition. Chen *et al.* (2004) observed a faster charring process in the range of 200–400°C and enhancement thermal stability at above 370°C for LLDPE/ZnAl LDH nanocomposite compared to pure LLDPE. Similar behavior reported by Constatino *et al.* (2005) for PE/stearate-ZnAl LDH nanocomposites with 5, 10, 15% w/w organo-LDH loading was observed.