

CHAPTER III

LITERATURE REVIEWS

In recent years, there has been extensive study of polymer/clay nanocomposites because they enhance the various properties at low clay loading [2-14, 21]. However, clays are hydrophilic and naturally incompatible with a wide range of polymer types, especially polyolefins. Therefore, hydrophilic clay must be treated with organic cation such as an alkyl ammonium ion by ion exchange reaction. By modifying the surface polarity of hydrophilic clay, organic cation is essential to ensure thermodynamically favorable penetration of polymer chains into layered silicates [15].

Numerous studies have focused on the effect of amine salts on the interlayer spacings of clay in organoclay [4-5]. A series of amine salts were selected by interaction into the space between layered silicates of clay. For the increasing of number of long alkyl tail of amine surfactants led to the increasing of interlayer spacings for organoclays [4-5]. For example, interlayer spacings of methyl bis(hydrogenated-tallow) ammonium montmorillonite or $M_1H_1(HT)_2$ -MMT were larger than those of bis(2-hydroxy-ethyl)methyl tallow ammonium montmorillonite or $(HE)_2M_1T_1$ -MMT, which were shown in figure 3.1 [4] and the interlayer spacings of tetraoctadecylammonium bromide-sodium montmorillonite or 4C18-Na-MMT were also higher than those of methyltrioctadecylammonium bromide-sodium montmorillonite or 3C18-Na-MMT [5].

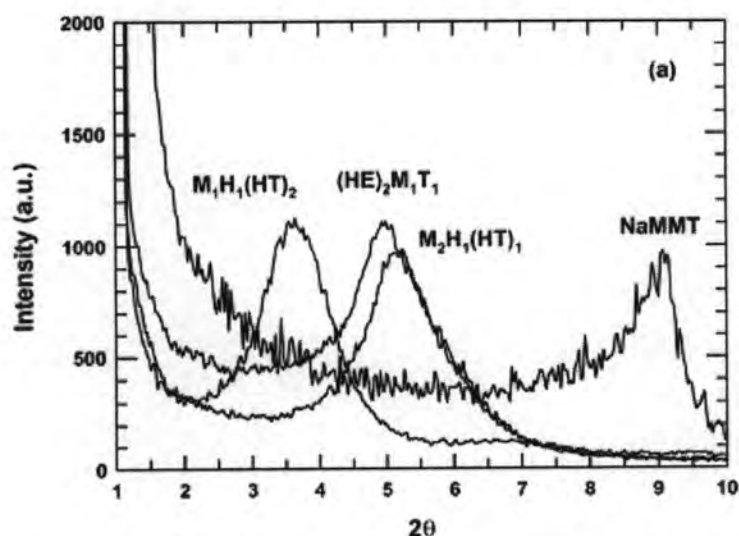


Figure 3.1: WAXS patterns for organoclays and sodium montmorillonite [4].

However, the dispersion of layered silicates in polymer matrix affects strongly on the final properties of polymer/clay nanocomposites [3, 4, 6, 11]. Especially, exfoliated structure of polymer/clay nanocomposites is favorable in enhancing several properties as compared with neat polymer such as mechanical, thermal and gas barrier properties because of the high aspect ratio of layered silicates and high surface area of clay in which the interfacial interaction between polymer matrix and surface of clay would also be high [10].

Many researches have studied the effect of the structure of the organoclay [4], compounding process [6] and molecular weight [11] on dispersion of layered silicates which affects on the final properties of polymer/clay nanocomposites, such as tensile modulus, yield strength, elongation at break, thermal and barrier properties. Polymer/clay nanocomposites can be formed by different methods i.e. in situ polymerization [14], solution method and melt processing technique [4-6, 2, 8-11, 12]. Melt processing technique is the most attractive way due to its low cost, high productivity and compatibility with current polymer processing techniques. By melt processing technique of preparation nylon 6/clay nanocomposites, organoclays which were modified with one long alkyl tail of amine surfactants, equivalent amount of amine surfactants, saturated form of tallow amine surfactants [4] and hydroxyl-ethyl

group of amine surfactant [11] led to the good dispersion or nearly exfoliated structure that were shown in figure 3.2. Especially, nylon 6/clay nanocomposites which based on high molecular weight of nylon 6 ($M_n= 29,300$ [4, 11]) led to a higher dispersion than lower molecular weight of nylon 6 ($M_n= 22,000$ [11] and $M_n= 16400$ [4, 11]) in nylon 6/clay nanocomposites due to the high shear stress during process in the extruder and the high viscosity of high molecular weight of nylon 6 [4, 11] that were shown in figure 3.3. However, linear low density polyethylene (LLDPE) /clay nanocomposites exhibited intercalated structure when organoclay was treated with one long alkyl tail of ammonium salts which were shown in figure 3.4 [12].

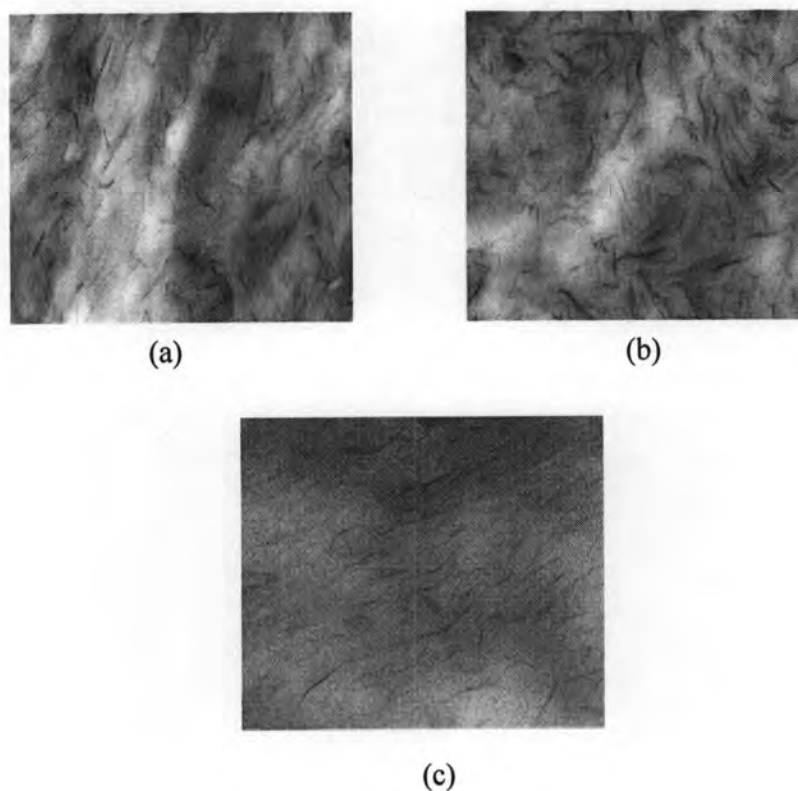


Figure 3.2: TEM micrographs of high molecular weight of nylon 6/clay nanocomposites ($M_n= 29,300$) based on (a) trimethyl hydrogenated tallow ammonium montmorillonite, $M_3(HT)_1$ -MMT [4], (b) trimethyl tallow quaternary ammonium montmorillonite, M_3T -MMT [4] and (c) bis (hydroxyethyl)-methyl-repeseed quaternary ammonium montmorillonite, $(HE)_2M_1R_1$ -MMT [11] at 3 wt% MMT respectively.

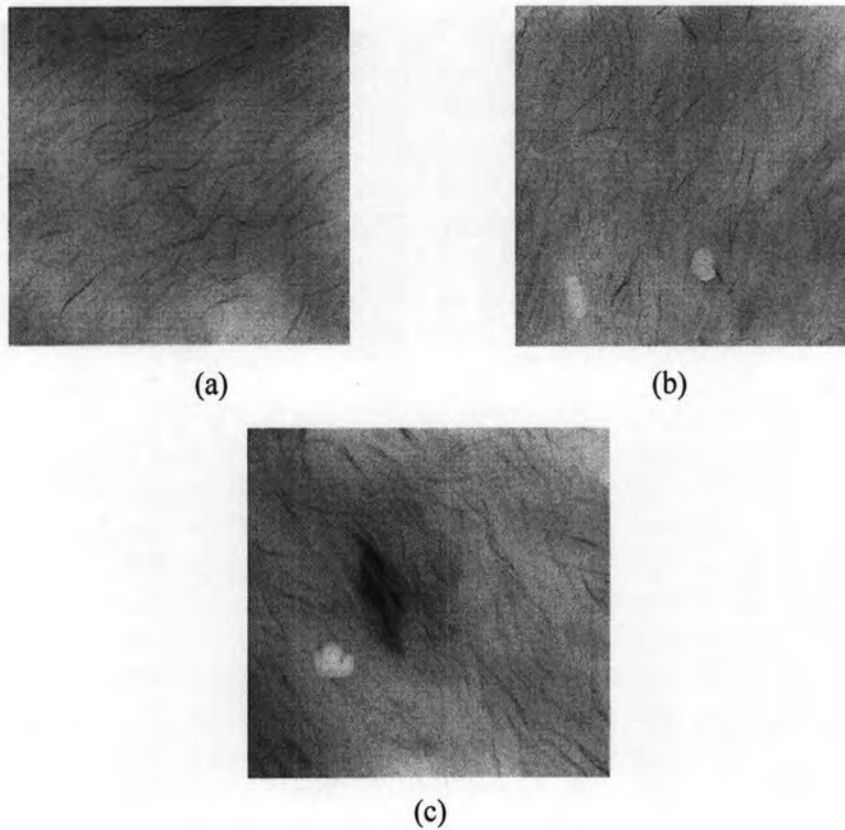


Figure 3.3: TEM micrographs of melt compounded nanocomposites at 3 wt% montmorillonite based on (a) HMW ($M_n=29,300$), (b) MMW, and ($M_n=22,000$) (c) LMW ($M_n=16,400$) nylon 6 [11].

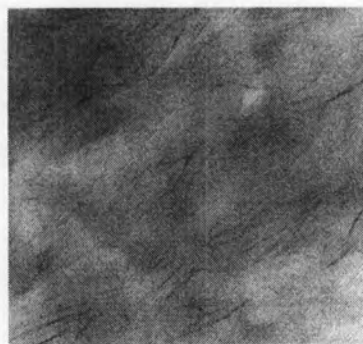


Figure 3.4: TEM micrographs of linear low density polyethylene/clay nanocomposites based on dimethyl (bishydrogenated-tallow) ammonium montmorillonite, $M_2(HT)_2$ -MMT at 4.5–4.9 wt%MMT [12].

Interestingly, compound processing techniques also affected the dispersion of silicate platelets [6]. Figure 3.5 showed XRD patterns of sodium montmorillonite powder (a), nylon 6 with pristine clay (b) and nylon 6/clay slurry (c). Nylon 6 with pristine clay exhibited an intense peak at $2\theta = 7.1^\circ$ corresponding to interlayer spacing of 1.25 nm which was the same as sodium montmorillonite powder or pristine clay. This indicated that nylon 6 segments did not insert into the space of layered silicates. In other words, nylon 6 with pristine clay still contained in aggregated state. However, there was not an intense peak for nylon 6/clay slurry. This indicated that the highly exfoliated structure of nylon 6/clay slurry occurred or nearly exfoliated when nylon 6 was melted mixing with clay slurry that water was evaporated during extrusion process. This observation was confirmed by transmission microscopy (TEM), which was shown in figure 3.6 [6].

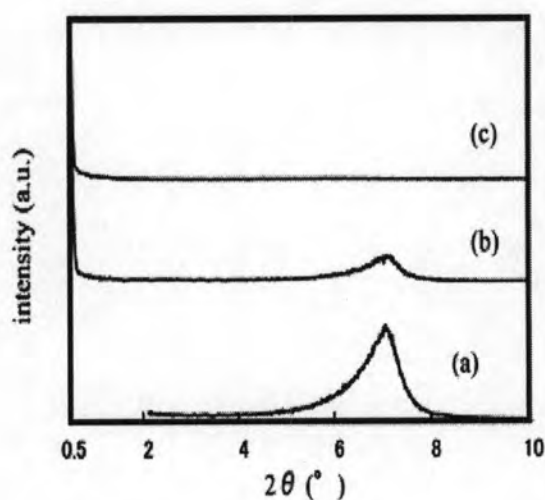


Figure 3.5: X-ray diffraction patterns of sodium montmorillonite powder (a), nylon 6 with pristine clay (b) and nylon 6/clay slurry (c) [6].

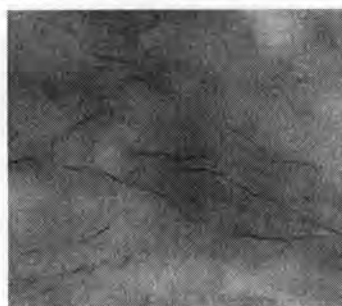


Figure 3.6: TEM micrographs of nylon 6/clay slurry [6].

It is well known that the degree of clay dispersion (intercalation and exfoliation) strongly affects the properties of polymer/clay nanocomposites [2-4, 6, 10-11]. Exfoliated nanocomposite contributes fully to interfacial interactions with polymer matrix. This structural distinction is the primary reason why the exfoliated clay state is especially effective in improving various properties such as mechanical [2-4, 6, 9-12], optical [8], thermal [2, 6-10, 14] and barrier properties [13, 5-6, 8, 12, 14] due to the incorporation of clay platelets with polymer matrix. For example, figure 3.7 showed the effect of clay loading on mechanical properties, i.e. tensile modulus, yield strength and strain at yield of nylon 6/clay nanocomposites. It can be seen that tensile modulus and yield strength of nylon 6/clay nanocomposite films increase with increasing clay loading. In other word, the addition of organoclay loading leads to substantial improvement in stiffness because layered silicates serve as a reinforcement agent [10]. However, young modulus of nylon 6/clay nanocomposites as shown in figure 3.8 decreased with increasing moisture content because nylon 6 was a high polar polymer and was capable of high water content adsorption [2].

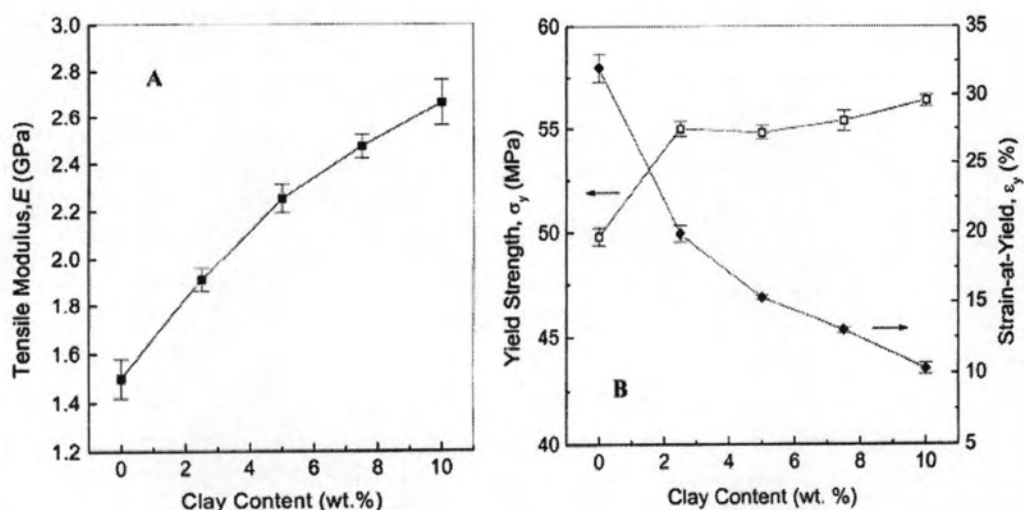


Figure 3.7: Tensile modulus (a), yield strength and strain at yield versus clay content [10].

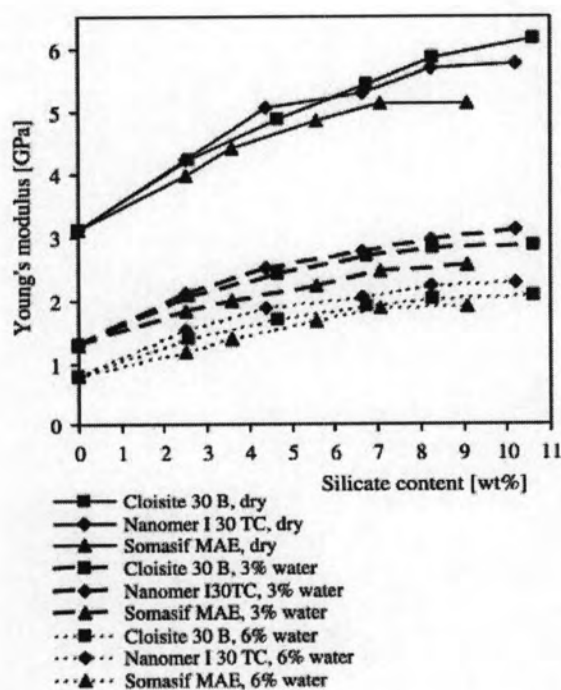


Figure 3.8: Young's modulus as a function of silicate content at different moisture contents [2].

Furthermore, numerous research groups have also described the effect of silicate platelets in polymer/clay nanocomposites on the crystalline phase of polymer

matrix. Many studies have focused on nylon 6/clay nanocomposites because nylon 6 exhibits crystalline structure with two types of stable crystalline phases, monoclinic α and γ crystalline phase that was confirmed by X-ray diffraction (XRD) and differential scanning calorimeter (DSC) [8-10]. In figure 3.9, the diffraction intensity of neat nylon 6 exhibited two diffraction peaks at $2\theta = 20^\circ$ and 24.8° corresponding to α_1 (200) and α_2 (002) crystalline phase of nylon 6 respectively [8-10]. Interestingly, the addition of layered silicates into nylon 6 matrix enhanced the formation of the γ crystalline phase of nylon 6, which peak appears around at $2\theta = 21.4^\circ$, while α crystalline phase of nylon 6 still existed in nylon 6/clay nanocomposites [8-10].

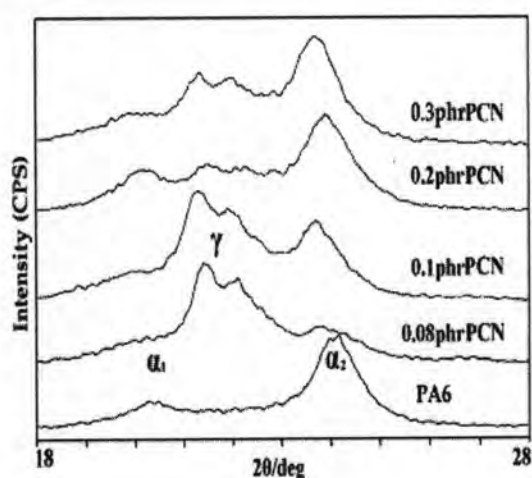


Figure 3.9: XRD patterns of nylon 6 and nylon 6/clay nanocomposites at different of organoclay contents (0.08, 0.1, 0.2 and 0.3 wt% organoclay) [8].

In addition, a resistance of gas permeability [5-6, 12-14] and solvent permeability [8] of polymer/clay nanocomposites with a wide range of polymer matrix, such as low density polyethylene (LDPE) [12], polyethylene terephthalate (PET) [14], nylon 6 [8] and polyethylene [5], has been extensive studied. Barrier properties of polymer/clay nanocomposites increased with increasing the organoclay loading. For example, the oxygen permeability of polyethylene terephthalate/clay nanocomposite films in figure 3.10 decreased by 50 percent when organoclay loading approached to 3 wt%. It is due to layered silicates that were dispersed in polymer matrix created a tortuous pathway [14]. Moreover, the increasing of degree of

crystallinity also affected a resistance of gas permeability because it can reduce the free volume of amorphous phase of polymer matrix such as nylon 6 [8].

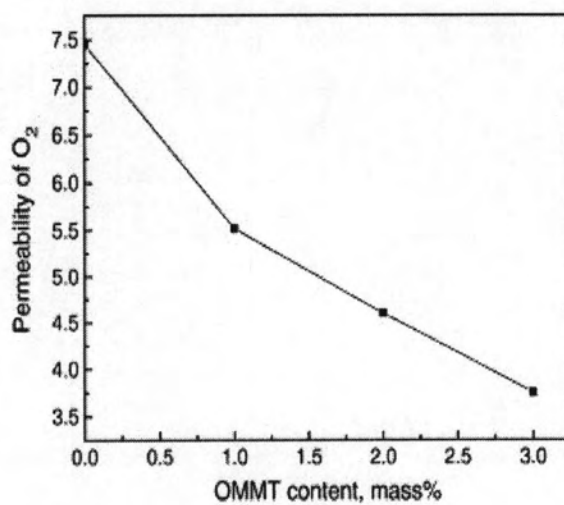


Figure 3.10: Oxygen permeability rate of poly(ethylene terephthalate)/clay nanocomposites [14].