

## CHAPTER II

### LITERATURE REVIEW

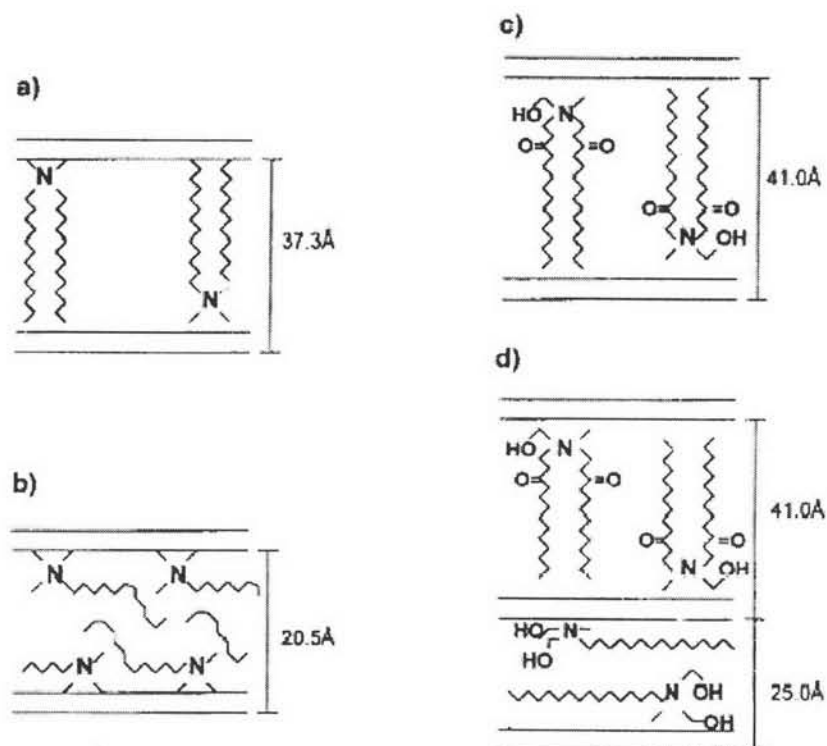
Polypropylene (PP) is one of the most widely used polyolefin; therefore, intense investigation of PP composites reinforced by fillers has been carried out. Since PP does not include any polar groups in its backbone and montmorillonite is hydrophilic, it is difficult to get the exfoliated and uniform dispersion of the clay layers at nanometer level. Therefore it is challenged from the researchers, to study in the preparations which include processing, dispersion of the clay particles, the effect of compatibilizer and modifying agents and their excellent properties.

As the hydrophilic clay is incompatible with polypropylene, compatibilization between the clay and PP is necessary to form stable PP nanocomposites. There are two ways to compatibilize the clay and PP. One is to lower the enthalpy of the interaction between the surfactant and the clay. The other way is to use a compatibilizer, such as functionalize PP with polar group, maleic anhydride grafted PP (PP-MAH). So in 1997 Usuki *et al.* first reported a novel approach to prepare PP/ clay nanocomposites (PPCNs) 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.

In the same year (1997), Kawasumi *et al.* studied the preparation of PP/ clay nanocomposites obtained by melt blending of PP, a maleic anhydride grafted PP oligomer (PP-g-MA), and clays modified with stearylammmonium using a twin-screw extruder. They found that there are two important factors to achieve the exfoliated and homogeneous dispersion of the layers in the hybrids: (1) the intercalation capability of the oligomers in the layers and (2) the miscibility of the oligomers with PP.

Choy *et al.* (1997) prepared organoclay complexes exhibiting hydrophilic as well as organo-philic natures by using several kinds of quaternary alkylammmonium cations with different molecular structure and functional groups, tearyldimethylammmonium chloride (DMDS), methyltriethanoldipalmitylesterammmonium methyl-

sulfate (DCEM), monostearyltrimethylammonium chloride (ODTM), and methyltriethanolpalmitylesterammonium methylsulfate (DHMC), were incorporated into interlayer spaces.



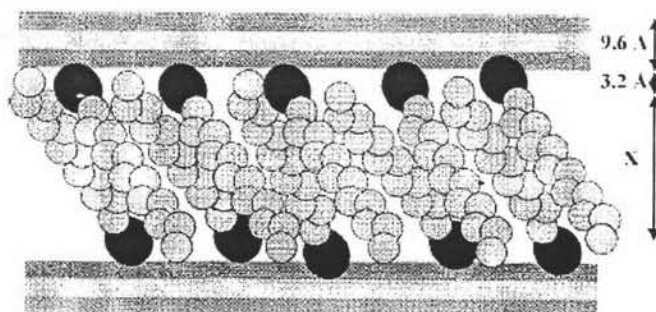
**Figure 2.1** The schematic diagrams of the possible interlayer structures of each quaternary alkylammonium derivative: (a) DMDS-M, (b) ODTM-M, (c) DCEM-M and (d) DHMC-M.

X-ray diffraction patterns for the dried organo-clay complexes. Upon intercalation, the basal spacing of DHMC-M expanded up to  $66 \text{ \AA}$ , indicating the incorporation of large surfactant molecules. On the basis of X-ray diffraction patterns and infrared spectra, the interlayer packing structures were proposed as shown in Fig. 2.1. Among them, the formation of a regular interstratified structure for DHMC molecules (Fig. 2.1d) might be due to the coexistence of DCEM molecules in the starting material as a competing guest species.

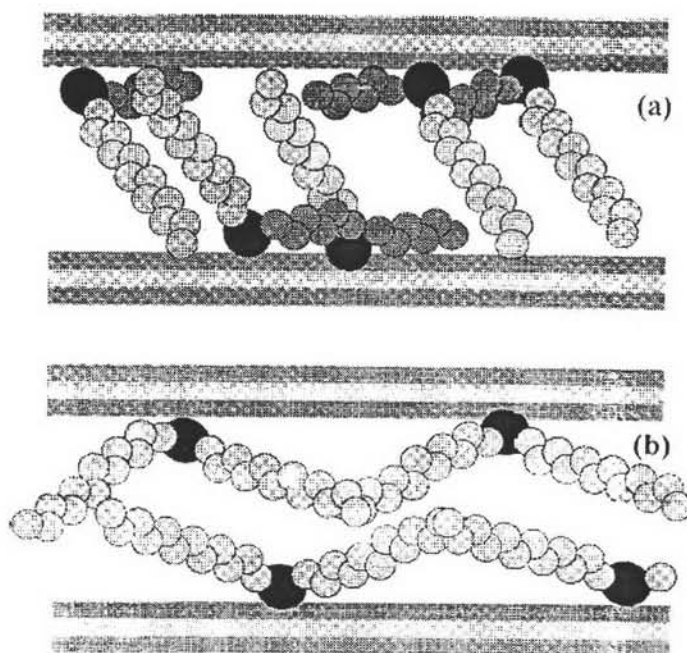
Thajaroen (2000) found in case of primary-alkylamine modified montmorillonites (MMTs), the degree of basal spacing expansion increased with the

length of hydrocarbon part in the structure of modifying agents. For quaternary-ammonium salt modified MMTs, the same trend was obtained but the degree of interlayer expansion was lower than that of primary-alkylamine modified counterparts.

Williams-Daryn and Thomas (2002) measured the dimensions of the interlamellar space following intercalation of a vermiculite (Eucatex) by three series of surfactants, *n*-alkyltrimethylammonium bromides, *N,N*-dialkyldimethylammonium bromides, and the gemini cationic surfactants,  $\alpha,\omega$ -bis (*N*-alkyldimethylammonium) alkanes. X-ray diffraction was used to examine the intercalation by cations of different shape, charge and size, focusing particularly on the space occupied by non-charge-neutralizing species. The arrangement of surfactant was shown in Fig. 2.2 and Fig. 2.3.



**Figure 2.2** Schematic model of surfactant chains used for calculating the expected interlamellar spacings for Eucatex intercalated by *N*-alkyl trimethyl ammonium bromides. The interlamellar spacing is given by  $X = (1.265n + 1.5) \times \sin (54.5)$  where  $n$  is the number of carbon atoms in the *N*-alkyltrimethylammonium bromides.



**Figure 2.3** Possible arrangements of two chains in the interlamellar space of complexes of Eucatex vermiculite and dialkyldimethyl ammonium bromides. In (a) there is space on the surface of the clay for the shorter, secondary chains and the long chain is tilted at  $54^\circ$ , but in (b) both chains mix in the hydrophobic part of the interlamellar space and the orientation of the head group changes so that the chains are at an angle of  $35^\circ$ .

Tang *et al.* (2003) studied the influence factors on the thermal stability of PP/montmorillonite nanocomposites. They used two different methods to prepared PPCNs. One was from pristine montmorillonite and a reactive compatibilizer hexadecyl trimethyl ammonium bromide (C16); the other is from different organophilic montmorillonites (OMT). The nanocomposite structure was demonstrated by XRD and TEM. The thermal stability of PPCNs was investigated by TGA. It is shown that different methods and OMT influence the morphology and thermal stability of PPCNs.

García-López *et al.* (2003), Polypropylene/ clay nanocomposites were obtained and studied by using two different clays, a commercial montmorillonite (Nanomer I30.TC) and a sodium bentonite purified and modified with

octadecylammonium ions. Small angle X-ray diffraction patterns of modified montmorillonite and bentonite clays showed that the  $d_{001}$  peak shift to lower angles, corresponding to an increase on the basal spacing of the clays by exchange of interlayer sodium with onium cations. However, this modified bentonite showed a much broader peak compared with the commercial sample. This is due to the inhomogeneous distribution of the surfactant between the layers of the clay, presenting a broader range of interlayer distances depending on the extent of ion exchange. In the nanocomposite, the two different clays also show differences in mechanical properties and TEM images. Modified bentonite, improves mechanical performance in a lower extent than the commercial modified montmorillonite, due to the lower extent of modification and low homogeneity.

Bentonite is the one type of clay that used as a nanofiller in polymer nanocomposite. In 2004, Lee Y. J. and Lee K. H. prepared 99% purity montmorillonite-rich clay from Ca-bentonite that mined from Kampo area in Korea. They found that the physical properties such as cation exchange capacity, specific surface area, swelling power, etc. were similar to those of Kunifia-F (Tokyo, Japan). It was found that the exchange weight contents of the organo-surfactants increased with the increasing molecular weight of them. For the same main chain carbon number of surfactants, the exchange contents in mole of primary types were higher than those of the tertiary types. The interlayer distance for MMT-III, organobentonites treated with 1-hexadecylamine (HAD-M), 1-octadecylamine (ODA-M), cetyltrimethylammonium bromide (CTMA-M) and octadecyltriethylammonium bromide (ODTMA-M) were 1.21, 1.53, 1.57, 2.04, and 2.07 nm. All organobentonites were delaminated in the epoxy matrix forming the epoxy/organobentonite nanocomposites. Tensile strength and Young's modulus increased with the treatment of organo-surfactants and with the increasing clay loading content.

A year later, Ding *et al.* (2004) studied the effect of the OMMT on the structure and properties of PP. PP/ organo-montmorillonite (OMMT) nanocomposites were prepared by using a highly effective PP solid-phase graft (TMPP) as compatibilizer. As a very low amount of PP graft was used. A typical intercalated structure was formed in the composites. The incorporation of silicate layers and

TMPP gave rise to a considerable increase in impact strength and flexural modulus compared with the neat PP. The crystallization peak temperature of nanocomposites was about 10 °C higher than that of PP. The T<sub>g</sub> of PP was lowered by the incorporation of the OMMT. The changes of the properties could be correlated with the formation of the PP/OMMT nanocomposites.

Fornes *et al.* (2004), Investigated the effect of the number of alkyl groups attached to the nitrogen of the organic modifier on the level of organoclay exfoliation and prepared Nylon-6-organoclay nanocomposites by melt processing via twin-screw extrusion. Wide-angle X-ray scattering and transmission electron microscopy techniques were employed to assess the morphology developed in each type of nanocomposite, while stress-strain diagrams were used to evaluate mechanical property performance. Nanocomposites derived from an organoclay having no alkyl tails in the quaternary cation result in an immiscible morphology, consisting primarily of unexfoliated clay particles, whereas those derived from an organoclay having one alkyl tail in the quaternary cation lead to a well-exfoliated morphology. Increasing the number of alkyl tails to two produced a mixed structure comprised of a large fraction of clay stacks intercalated with polymer as well as a fraction of dispersed clay platelets. The extent of mechanical reinforcement parallels the degree of exfoliation. Overall, the results may be explained by the competition between the effects of platelet-platelet interactions and the interaction of the polymer with the organoclay platelet.

In the same year, Hotta and Paul (2004) prepared polyethylene-clay nanocomposites by melt compounding various combinations of a maleic anhydride grafted linear low density polyethylene (LLDPE-g-MA), a linear low density polyethylene (LLDPE), and two organoclays. The two types of organoclay were selected to show the effect of the number of alkyl groups attached to the nitrogen of the organic modifier on exfoliation and improvement of mechanical properties. Nanocomposites derived from the organoclay having two alkyl tails, M<sub>2</sub>(HT)<sub>2</sub>, exhibited better dispersion and improvement of mechanical properties than nanocomposites based on the organoclay having one alkyl tail M<sub>3</sub>(HT)<sub>1</sub>. This result is the opposite of what is observed for nylon-6 nanocomposites. In addition, the rheological properties and gas permeability of the nanocomposites derived from the

organoclay having two alkyl tails,  $M_2(HT)_2$  were investigated. Both melt viscosity and melt tension (melt strength) increased with increased content of clay (MMT) and LLDPE-g-MA. Gas permeability was decreased by the addition of MMT.

Parija *et al.* (2004) studied on physico-mechanical properties of the virgin PP and nanocomposites with different nanomer loadings. Thermal characteristics of polypropylene/ layered silicate nanocomposites were also compared with those of the virgin polymer. Polypropylene/layered silicate nanocomposites were prepared from base polymer (10 MFI) and octadecylamine modified montmorillonite (1.30P nanomer), melt compounded with compatibilizer and without compatibilizer, i.e., maleic anhydride grafted polypropylene (Epolene-G3015). TEM analysis of the nanocomposites was carried out to study the dispersion of nanomer in the resulting hybrids. The experimental findings revealed a consistent improvement in the mechanical properties of the polypropylene/ layered silicate nanocomposite for a relatively lower nanomer loading (3%) due to the reinforcing and toughening effect of nanoparticles. Addition of compatibilizer further enhanced the mechanical properties of nanocomposites because of the compatibilization of the clay and host polymer interface.

Recently, structure–property relationships for nanocomposites formed by melt processing from a series of organoclays and poly (ethylene-co-methacrylic acid) ionomers were studied by Shah *et al.* (2005). The chemical structure of the alkyl ammonium surfactants was systematically varied to determine how specific groups might affect the mechanical properties and morphology of these composites. Four distinct surfactant structural effects have been identified that lead to improved levels of exfoliation and higher stiffness for these nanocomposites: (1) higher number of alkyl tails on the amine rather than one, (2) longer alkyl tails instead of shorter ones, (3) 2-hydroxy-ethyl groups as opposed to methyl groups on the ammonium ion, and (4) excess amount of the amine surfactant on the clay instead of an equivalent amount. Most of these trends are opposite to what has been observed in nylon 6 based. It seems nylon 6 has a higher affinity for the silicate surface than does the poly(ethylene-co-methacrylic acid) ionomer while the latter is less repelled by the alkyl tails than the polyamide. Hence, surfactant structural aspects that lead to more shielding of the silicate surface or increased alkyl material leads to improved

exfoliation in the ionomer. These observations are similar to those seen with LDPE and LLDPE based nanocomposites. It should also be noted that, although some organoclays were exfoliated better than others, none of the ionomer-based nanocomposites exhibited exfoliation levels as great as those seen in nylon 6 nanocomposites. Nevertheless, nanocomposites prepared from such ionomers offer promising improvements in performance and may be particularly suitable for barrier applications.

The effect of an organophilic bentonite on the thermal degradation of polypropylene was evaluated by Ramos Filho *et al.* (2005). A polycationic bentonite clay (PB) was organically modified with a quaternary organic salt (cetyl trimethyl ammonium bromide) and added to isotactic polypropylene (PP). The compounds were prepared by melt intercalation using a twin extruder. The results showed that the modified clay had higher thermal stability in the solid state than the natural clay. This may be connected to a higher dispersion of clay particles, reducing oxygen diffusion through the sample.

In same year, Lertwimolnun and Vergnes (2005) characterized the influence of processing conditions on clay dispersion. Polypropylene/ organoclay nanocomposites were prepared via direct melt intercalation in an internal mixer. Maleic anhydride grafted polypropylene (PP-g-MA) was used as a compatibilizer to improve the dispersability of the clay. The structures of nanocomposites were characterized by X-ray diffraction and transmission electron microscopy. Wide angle X-ray diffraction showed that the interlayer spacing was not significantly influenced by processing conditions.