CHAPTER II
LITERATURE SURVEY

Jaynes and Boyd (1991) summarized previous research papers on alkylammonium expansion of expansible clay minerals. They concluded that the alkyl chain length might form monolayers (13.7 Å), bilayers (17.7 Å), pseudotrimolecular layers (21.7 Å), or paraffin complexes (>22 Å), and alkyltrimethylammonium salts of comparable alkyl chain length produced slightly greater expansions.

Cationic surfactants with longer chain lengths may be packed more closely in a monolayer (Connor and Ottewill, 1971) and are more likely to adsorb in multiple layers (Greenland and Quirk, 1962). Yan *et al.* (1998) studied the adsorption of cetyltrimethylammonium bromide (CTMA) and dodecyltrimethylammonium bromide (DTMA). The results show that the process of adsorption is exothermic and that the type of clay and the alkyl chain length of surfactant affect the amount of adsorption and the enthalpy of adsorption significantly. The magnitudes of adsorption amount and adsorption enthalpy the order Na-montmorillonite>Fe-montmorillonite, CTMA>DTMA. The d_{001} spacing of Na-montmorillonite (14.8 Å) is larger than that of Fe-montmorillonite (13.2 Å), which means that the attractive forces between silicate sheets and Fe^{3+} are stronger. The basal spacing values of Na-montmorillonite and Fe-montmorillonite when adsorbing CTMA at saturation are 19.0 and 18.2 Å, respectively, suggesting densely packed bilayers in the interlayers of Na-montmorillonite and Fe-montmorillonite (Figure 3b). Basal spacings of DTMA–Na-montmorillonite and DTMA–Fe-montmorillonite are 16.5 and 14.5 Å, respectively. DTMA may pack as bilayers in the interlayers of Na-montmorillonite at saturation adsorption but as monolayer in the interlayers of Fe-montmorillonite (Figure 3a). One of the main reasons may be the arrangement of cationic surfactant between interlayers of Fe-montmorillonite.

Figure 2.1 Alkyl chain aggregation in layered silicates: a) lateral monolayer; b) lateral bilayer (Vaia *et al.*, 1994).

Thaijaroen W. (2000) found in case of primary-alkylamine modified montmorillonites (MMTs), the degree of basal spacing expansion was 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.

Lee J.Y. and Lee H.K. (2004) modified montmorillonite-rich clay with 99% purity was fractionated from bentonite mined from Kampo area in Korea, and it was modified with many cationic organic surfactants, 1-hexadecylamine (HDA), 1-octadecylamine (ODA), cetyltrimethylammonium bromide (CTMA), and octadecyltrimethylammonium bromide (ODTMA). The chemical and physical characteristics of them were investigated, and epoxy nanocomposites were also studied. As the molecular weight of the organic surfactants increased, the exchanged weight content of them increased. However, if the weight unit converted into molar unit, the exchanged content decreased with the increment of molecular weight of the organic surfactants. For the same main chain carbon number of the surfactants, the exchanged contents in mole of the primary types were higher than those of the quaternary types due to the smaller molecular weight. The interlayer distance (d-space) of MMT-III, HDA–MMT-III, ODA–MMT-III, CTMA–MMT-III and ODTMA–MMT were 1.21, 1.53, 1.57, 2.04, and 2.07 nm, respectively. As the amount of exchanged organic surfactant increased, d-space increased, which was due to the organophilic surfactant of the interlayer repulsed the hydrophilic surface of clay mineral, and the effect increased with the increasing the molecular weight of the organic surfactant.

Xi *et al.* (2004) synthesized surfactant–clay hybrids. The montmorillonites (the cation exchange capacity (CEC): 76.4 meq/100 g) were modified with

octadecyltrimethylammonium bromide (ODTMA. The concentrations of ODTMA$^+$ used are 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 3.0, and 4.0 CEC of the montmorillonite, respectively. They have proposed a model based upon the changes in the d_{001} spacings as a function of surfactant concentration. The basal spacing obtained from X-ray diffraction give details of arrangement of surfactant in the organoclays. For OMMT-0.2CEC and OMMT-0.4CEC (OMMT: octadecyltrimethylammonium montmorillonite), there is a lateral-monolayer arrangement of ODTMA$^+$ in the interlayer space of montmorillonite. For OMMT-0.6CEC and OMMT-0.8CEC, the surfactant takes a lateral-bilayer arrangement. When 1.5 CEC of surfactant is used, the basal spacing reaches a plateau of 20.1 Å. From 1.5CEC to 4.0CEC, the basal spacings only increase slightly. The maximum value at 4.0 CEC is 20.3 Å. OMMT-1.5CEC to OMMT-4.0CEC, the basal spacings reach >20 Å, which reflects a pseudotrimolecular layer arrangement with excess surfactant adsorbed onto the clay surface. As for OMMT-1.0CEC, the arrangement of surfactant is in between a lateral-bilayer and pseudotrimolecular layer structure.

Pérez-Santano *et al.* (2005), montmorillonite has been intercalated with octadecylamine, varying the amine/clay and the HCl/amine ratios in the reaction medium. The efficiency of intercalation depends on the amine/clay ratio, good results being obtained in the range 1–3 mmol/g , when it is lower than 1, the amount fixed is not enough to efficiently swell the clay. The HCl/amine also influences the process, a certain amount of HCl is necessary to protonate the amine and thus to permit the cation exchange reaction, higher amounts favor the solubility of the amine. It may be considered that the ratio HCl/amine is in all synthesis clearly higher than the amount necessary to protonate the amine, which is 1:1.

Usuki *et al.* (1997) prepared a PP-clay hybrid by using a functional oligomer. PP mixed with montmorillonites were intercalated by using distearyldimethylammonium ion (DSDM-Mt) and a polyolefin oligomer with polar telechelic OH groups (PO-OH) as a compatibilizer. In this process, at the first stage, the PO-OH oligomer intercalates between the layers of the clay through the strong hydrogen bonding between the OH groups of the PO-OH and the oxygen groups of the silicates. The interlayer spacing of the clay increases, and as a result, the interaction of the layers should be weakened. By mixing the DSDM-Mt/PO-OH

composite with PP, the hybrid with improved dispersion of the silicate clay layers was obtained. However, some aggregates of the clay minerals were still observed in it.

Kawasumi *et al.* (1997) prepared Polypropylene (PP)-clay hybrids by simple melt-mixing of three components, i.e., PP, maleic anhydride modified PP oligomers (PP-MA), and clays intercalated with stearylammonium. The dispersibility of 10-Å-thick silicate layers of the clays in the hybrids was investigated by using a transmission electron microscope and X-ray diffractometer. It is found that there are two important factors to achieve the exfoliated and homogeneous dispersion of the silicate clay layers in the hybrids. Firstly, the oligomers should include a certain amount of polar groups to be intercalated between silicate layers through hydrogen bonding. Secondly, 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.
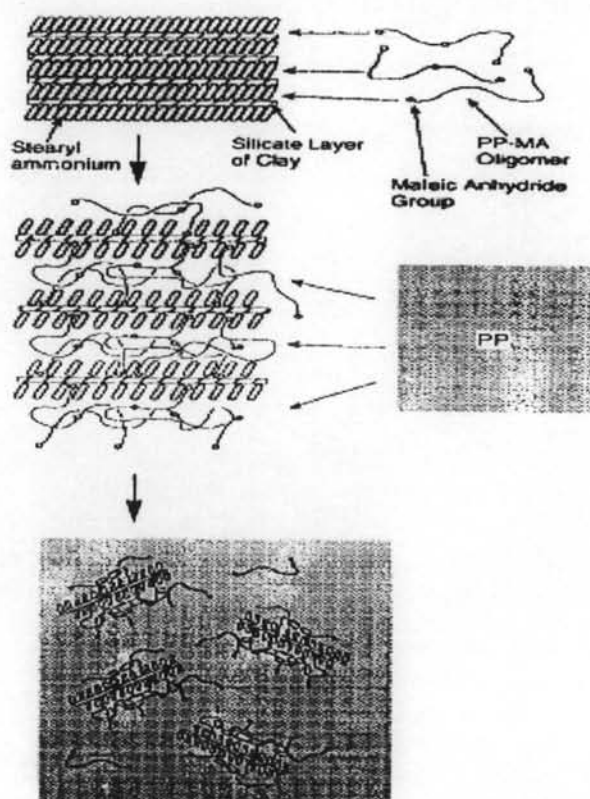

Figure 2.2 Schematic representation of the dispersion process of the organized clay in the PP matrix with the aid of PPMAs.

The driving force of the intercalation originates 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 (Figure 2.2).

On the other hand, if the miscibility is not good enough, the phase separation occurs with no exfoliation. Therefore, it is quite reasonable to say not only the intercalation ability of the oligomers but also the miscibility should be a very important factor to achieve the exfoliated homogeneous dispersion of the clays in their work using PP-MA as a compatibilizer containing different amounts of maleic anhydride groups (PP-MA-1001, acid value = 26 mmol of KOH/g, PP-MA-1010, acid value = 52 mmol of KOH/g). The miscibility between PP and PP-MA-1001 is much better than that between PP and PP-MA-1010. The results are quite reasonable since the maleic anhydride is a polar group and should decrease the miscibility with PP by increasing its content in the oligomers. Therefore, the silicate clay layers in the PP-clay hybrids with PP-MA-1001 should be more exfoliated and dispersed compared to those in the PP-clay hybrids with PP-MA-1010.

However, PP/clay nanocomposites used PP-g-MA as compatibilizer have mechanical properties lower than the native polypropylene, due to chain scission during grafting. Therefore, the addition of PP-g-MA can result in lower mechanical properties of the final composite. Hence, there is a new way to prepare nanocomposites by using a co-intercalation agent, reducing PP-g-MA content in the nanocomposites and enhancing the properties of the nanocomposites.

Liu X. and Wu Q. (2001) prepared PP/clay nanocomposites via grafting-melt compounding by using a new kind of co-intercalation organophilic clay. Modified organoclay with epoxypropyl methacrylate had a larger interlayer spacing than organophilic clay modified by alkyl ammonium. One of the co-intercalation monomer was unsaturated so it could tether on the PP backbone by a grafting reaction. The larger interlayer spacing and strong interaction caused by grafting

could improve the dispersion effect of silicate layers in the PP matrix. The incorporation of silicate layers also gave rise to a considerable increase of the storage modulus (stiffness), demonstrating the reinforcing effect of clay on the PP matrix. The addition of clay did not change the crystal structure of PP, however silicate layers acted as nucleating agents for the crystallization of PP.

Zhang Y.-Q. *et al.* (2004), Polypropylene–clay nanocomposites (PPCN) were prepared by in situ grafting-intercalating in melt. The organoclay was first modified with maleic anhydride (MA) in solution with a small quantity of a co-swelling agent and an initiator. It was then blended with PP in melt to obtain PP/clay grafting-intercalating composites (GIC). Finally, the GIC were blended with PP in melt to obtain PPCN. The XRD patterns show that the basal distance in the MA-modified organoclay was 30 nm, which was larger than that of the original organoclay (19.6 nm). The XRD and TEM results for GIC and PPCN demonstrate that the layers of clay were partially exfoliated in the GIC and fully exfoliated in the PPCN. The introduction of clay into the PP matrix showed good thermal stability and increased the storage modulus (stiffness) of PP indicates that the clay has a reinforcing effect in the PP matrix.

García-López *et al.* (2003) studied PP/clay nanocomposities by using two different clays, a commercial montmorillonite (Nanomer I30.TC) and a sodium bentonite purified and modified with octadecylammonium ions have also been used. The commercial clay of montmorillonite has very high purity, being very homogeneous. The clay modified by them, is a low purity bentonite, which has many inhomogeneous aggregates, due to calcium content, and siliceous impurities. Although many of the impurities are eliminated during modification process, some micrometric impurities can be found, which act as stress concentrators, allowing crack initiation and propagation, decreasing consequently the mechanical performance of the nanocomposite.