

## CHAPTER II

### LITERATURE SURVEY

#### 2.1 Structure, Properties and Application of Clay

Clay or layered silicate is ubiquitous mineral that is component of soil. These kinds of materials were widely used as filler in polymer to improve some physical properties and for economy reasons. Clay can be divided into groups according to their structure and layer charge such as talc, micas and smectites clay.

The structure of smectite clay minerals is composed of layer lattice structure of oxyanions and hydrated cation layer which oxygen atoms reveal the layer edge of tetrahedral site and octahedral site. Illustration in figure 2.1 is structure of smectite clay.

This figure shows 2:1 relationship of tetrahedral site with octahedral site that combined into one layer of structure. Therefore, the smectite clay was

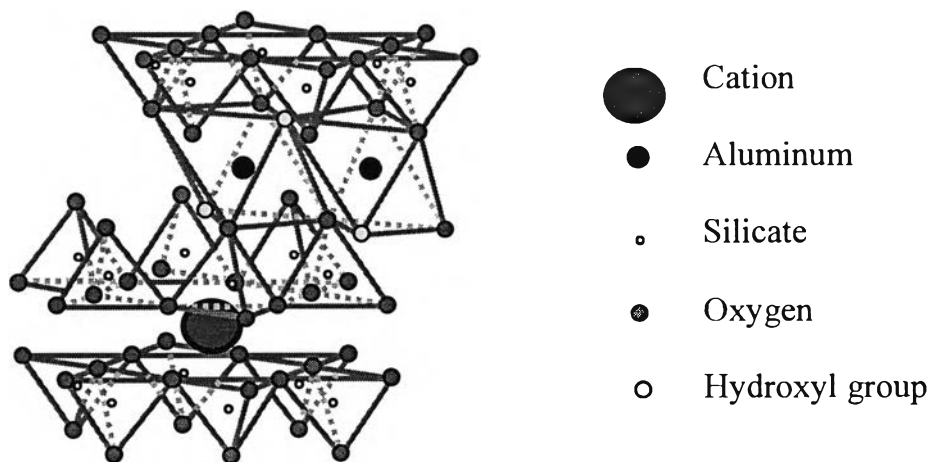


Figure 2.1 Idealized structure of 2:1 layered silicate.

**Table 2.1 Idealized formula of dioctahedral and trioctahedral of 2:1 phyllosilicate.**

Mineral group	Dioctahedral	Trioctahedral
Pyrophyllite-talc	Pyrophyllite: $[Al_{4.0}](Si_{8.0})O_{20}(OH)_4$	Talc: $[Mg_{6.0}](Si_{8.0})O_{20}(OH)_4$
Smectites	Montmorillonite: $M_{x/n}^{n+} \cdot yH_2O [Al_{4.0-x}Mg_x](Si_{8.0})O_{20}(OH)_4$	Hectorite: $M_{x/n}^{n+} \cdot yH_2O [Mg_{6.0-x}Li_x](Si_{8.0})O_{20}(OH,F)_4$
	Beidellite: $M_{x/n}^{n+} \cdot yH_2O [Al_{4.0}](Si_{8.0-x}Al_x)O_{20}(OH)_4$	Saponite: $M_{x/n}^{n+} \cdot yH_2O [Mg_{6.0}](Si_{8.0-x}Al_x)O_{20}(OH)_4$
	Nontronite: $M_{x/n}^{n+} \cdot yH_2O [Fe_{4.0}](Si_{8.0-x}Al_x)O_{20}(OH)_4$	
Micas	Muscovite: $K_2[Al_{4.0}](Si_{6.0}Al_{2.0})O_{20}(OH)_4$	Phlogopite: $K_2[Mg_{4.0}](Si_{6.0}Al_{2.0})O_{20}(OH)_4$

classified as 2:1 phyllosilicates. A unit cell of this structure composes of twenty oxygen and four hydroxyl groups which show eight tetrahedral site and six octahedral site. The members of smectite clay are classified by type and location of cations in oxygen framework. The mineral is classified as dioctahedral 2:1 phyllosilicate when two-thirds of octahedral site are occupied by cation. When all of octahedral site are filled by cation, it is called trioctahedral 2:1 phyllosilicate. Table 2.1 shows ideal formula for dioctahedral and trioctahedral smectite clay compares with micas, pyrophyllite and talc (Pinnavaia, 1983). All of mineral in table 2.1 has the same 2:1 phyllosilicate oxygen framework like smectite. Pyrophyllite and talc are electro-neutral clay. However some kind of silicate layer contains negative charge in their layers. The negative charge of silicate layer originates from the substitution of cation in octahedral or tetrahedral with lower positive charge cation such as micas

type silicate. The negative charges of mica result from the substitution of  $\text{Si}^{4+}$  with  $\text{Al}^{3+}$  in tetrahedral position and are counterbalanced with gallery cation between silicate layers. This mineral clay has higher negative charges than smectite clay; however it has lower exchangeability. Because of the negative charges of silicate layer are generated at the tetrahedral layer, so ionic bonding between silicate layer and gallery cation is very strong and difficult to exchange with other type of organic cation. Montmorillonite, applied for this work, is the most familiar and common member of smectite group, which has  $\text{Al}^{3+}$  occupying the two-third of octahedral site, but some of  $\text{Al}^{3+}$  are substituted by  $\text{Mg}^{2+}$ . These negative layer charges was counter-balanced with alkali and alkali earth which occupy between silicate layers and present in the hydration form. The negative charges of smectite clay in octahedral is distributed over all in oxygen framework. So, this smectite clay tends to be aligned in plane orientation. These types of materials show very high exchangeability because of the weak ionic bonding between negative charges in the octahedral and gallery cation. Moreover this smectite clay has unique properties; for example cation exchange, intercalation and swelling. These fundamental properties are different from micas and pyrophyllite-talc groups, which have little or no ion exchange capacity. Those are reasons of smectites clay becoming interested and used in this work.

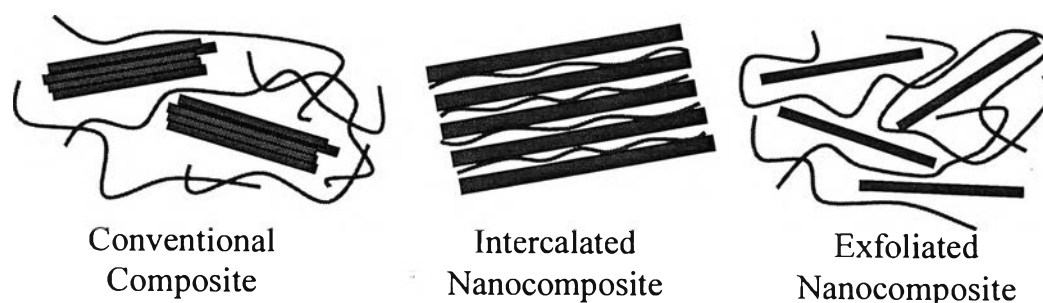
This type of materials is used as filler in the polymer matrix. However its structure is inorganic material while most of polymer is organic material. That is reason why organically modified silicate layers were become interest to apply in polymer. Generally, ions between silicate layers are exchanged with protonated form of amine group. Many kind of amine has been studied in the modified silicate layers by intercalation into the space between silicate layers. Jin-Ho Choy et al (1997) studied on the dispersibility of quaternary alkylammonium modified montmorillonite in polar and nonpolar solvents. It was showed that the dispersibility of modified montmorillonite depended on

compatibility between functional group on the modifying agent and type of solvent. Jordan (1948,1949) had prepared organic compounds of bentonite and studied on effect of organic chain length. They showed the expansion of silicate layer, which was dependent on length of hydrocarbon chain. The expansion of layer is multiple of 4 Å, which is about the thickness of one hydrocarbon chain. Moreover, he had studied on swelling of organic bentonite in many organic solvents; not only study on monosolvent system but also in the binary solvent system. Binary solvent showed good achievement to swell the organic compounds of bentonite. Granquist and McAtee (1963) had studied binary solvent system. They had shown some of alcohol presented in binary solvent could increase dispersity of silicate layer in organic liquid. These agreed with Kemnetz et al. (1989) who revealed dispersion of silicate layer with some polar activator such as methanol.

Alignment of intercalated compound had been studied with molecular dynamic simulation (Hackett, 1998) and showed relationship between inplane alignment of hydrocarbon and number of carbon atom.

## **2.2 Nanocomposite of the Polymer Matrix**

The composite material is used to describe macroscopic combination of two or more material. However some kind of composite can be prepared with ultra fine phase in the range of nanometer that is called nanocomposite. Most of nanocomposite are prepared with clay or silicate layers reinforced in polymer matrix, however some type of nanocomposite was prepared with other type of filler that can form shape in the range of nanometer size and show very well dispersed in the polymer matrix. Ray and coworker (1998) had prepared modified silicate powder embedded in poly (N-vinylcarbazole) and it was a kind of nanocomposite. Moreover, nanocomposite of non-layered silicate can



**Figure 2.2 Schematic illustrations of the three possible types of polymer-clay composite.**

achieved by sol-gel method (Wen, 1996) that polymeric/oligomeric can be chemically bonded with inorganic component to produce organic/inorganic hybrid network material.

However, lots of nanocomposites use silicate layers for preparation the nanocomposite, and can be divided into two types of nanocomposite based on ability to disperse silicate layers. The first one called intercalated nanocomposite. Silicate layers are expanded to allow penetration and polymerization of polymer or monomer molecule in the gallery pathway. If the silicate layers is fully expanded and embedded individually in the polymer matrix, it is called exfoliated nanocomposite. Figure 2.2 shows the structure of conventional composite compared with the two kinds of nanocomposites.

Nanocomposite of silicate layers can be achieved with modified and non-modified silicate layers. Lemmon and coworker (1995) had prepared nanocomposite containing poly (ethylene oxide) with layer solid of Na-Montmorillonite without any modified silicate layers, but layers of silicate could be expanded  $\sim 4\text{-}8 \text{ \AA}$ . Not only poly (ethylene oxide) was used to prepare composite with non-modified clay but also poly(ethylenimine) whose nanocomposite was prepared by Oriakhi and coworker (1996). Silicate layers exhibit lattice expansion along stacking direction  $3.9\text{-}4.7 \text{ \AA}$ . Moreover, some kind of monomer can function as modifying agent for silicate layer because the monomer have amine at one end of molecule such as amine-terminated

butadiene acrylonitrile. This material was butadiene acrylonitrile/montmorillonite nanocomposite (Akelah, 1994).

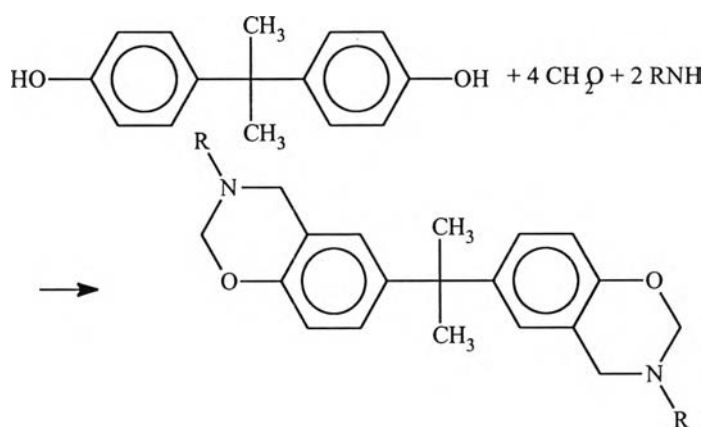
Most of modified clay used to prepare nanocomposite is protonated organic compound containing amine functional group. This kind of modified silicate layer is preferable to prepare nanocomposite because the nature of silicate layers is inorganic while most of polymer is organic. So it is sensible to use modified silicate layers for preparation of nanocomposite. Messersmith and coworker (1995) used organically modified silicate layers with 12-aminododecanoic acid for preparation of nanocomposite of caprolactone. Content of silicate in the polymer matrix directly affected to molecular weight and size of crystalline of poly(caprolactone). The barrier properties to prevent water vapor transmission of poly(caprolactone) nanocomposite was dramatically increased with small content of silicate layers. The various types of modified silicate layers were used with numerous kinds of polymers such as nylon 6 (Watari and coworker, 1997), polyimide (Yano and coworker, 1993), poly(l-lactide) (Ogata and coworker, 1997), poly(dimethylsiloxane) (Burnside and coworker, 1995), polypropylene (Kurokawa, 1996) and epoxy (Pinnavaia, 1996).

However, some of modified silicate layer is not modified with organic compound containing amine functional group.  $\text{CuSO}_4$  was used as modifying agent of silicate layers for preparation nanocomposite of styrene with in-situ polymerization process. This technique, the organic monomers were intercalated into the interlayer regions of the hosts where subsequent polymerization might then occur (Porter et al, 1998).

The various types of nanocomposites can be prepared from many types of polymer matrices. However, the polybenzoxazine-clay nanocomposite is no one try to prepare that is the interest of this work.

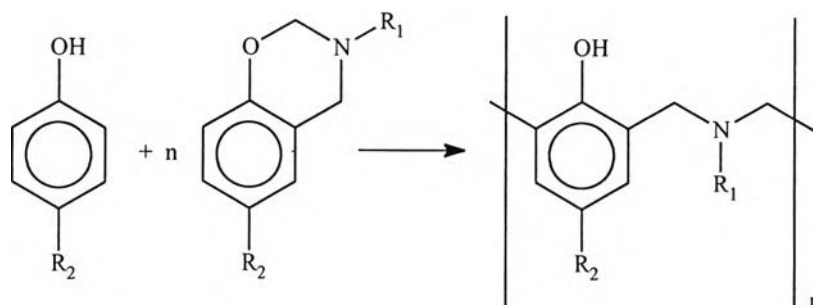
### 2.3 Structure, Properties and Application of Polybenzoxazine

Polybenzoxazine is a kind of phenolic resins from reaction of phenol and formaldehyde. Phenolic resin can be derived into 2 types. The first is novolacs that have linear structure because it has ratio of formaldehyde lower than phenol. Moreover this reaction occur in acid condition while another type of phenolic resin, resoles, the reaction occur in basic condition, and it has network structure (Odien, 1991). Both types of phenolic resins release water during polymerization that is a disadvantage of phenolic resin. It had been studied about the fire retardant properties of phenolic resin by Brown (1996). However, polybenzoxazine is prepared by ring opening polymerization of oxazine ring (Ning, 1994), which is prepared from reaction of phenol, formaldehyde and primary amine compound as shown in figure 2.3.



**Figure 2.3 Schematic of reaction for preparation of benzoxazine monomer with bisphenol-A, formaldehyde and primary amine.**

This polybenzoxazine polymerization does not produce any by-product and therefore good mechanical properties and risen glass transition temperature are usually obtained. Figure 2.4 illustrates the curing reaction of benzoxazine monomer. The kinetic of curing polybenzoxazine can be studied by differential scanning calorimetry (Ishida and Rodriguez, 1995). The polybenzoxazine



**Figure 2.4 Illustration of the curing reaction of benzoxazine monomer.**

precursor is an autocatalyzed reaction (Ishida et al., 1995). Moreover, the various types of catalyst were used to determine its influence on curing kinetics. The presence of the phenol structures with free ortho positions in the as-synthesized precursor have a catalytic effect on the curing reaction. Expansion and shrinkage of polybenzoxazine was studied by Ishida et al. (1997). It was found that this type of polybenzoxazine could be either expanded or shrunk. This phenomenon depended on kind of primary amine which was used for preparation monomer. The amine had effect to hydrogen bonding between monomers. The further studying on physical and mechanical properties of polybenzoxazine found that it had near zero shrinkage (Ishida et al., 1996). This polybenzoxazine overcomes many disadvantages of conventional novolaks and resoles while retaining their benefits. The dynamic mechanical analysis showed that these candidates for composite applications possess high moduli and glass transition temperatures, but low crosslink densities. The results of the dielectric analysis on polybenzoxazine demonstrated that it was suitable for electrical application. Moreover the effect of molecular structure on mechanical and dynamic mechanical properties was studied (Ning et al., 1994). The effect of molecular structure on the glass transition temperature determined the different performance on heat resistance. There is a great potential for developing this thermosetting material according



to its low-cost, and high performance with good handling ability for material processing and composite manufacturing.