

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Clay and clay mineral

Clays and clay minerals are two terms which are easily confused. A natural clay is not composed of one clay mineral only but composed of clay minerals and non-clay minerals. Impurities such as calcite, quartz, feldspars, iron oxides and humic acids are the most common components in addition to the pure clay mineral. Calcite, iron oxides and humic acids can be removed by chemical treatments. Quartz and feldspars can be removed by sedimentation if the particle size is bigger than that of the clay minerals but traces of quartz are often found in the purified samples [Ammann, 2003; Moore and Reynolds, 1997].

Type of clay can be identifying by mainly chemical composition of clay mineral. Clay minerals are hydrous silicates which contain tetrahedral silicate sheet and octahedral aluminum or magnesium sheet. There are four important clay mineral groups, including kaolinites, illites, smectites and vermiculites which have different structure and composition.

The clay mineral usually classifies by layer type and position of cations which replace in octahedral sheet [Deer et al., 1996]. (Display in Table 2.1)

1) Kaolinites is 1:1 type of layer silicate, clay minerals in this group are kaolinite, dickite, nacrite and halloysite

2) Illites is 2:1 type of layer silicate which has potassium ion compensate charge in interlayer, including illite, hydrous mica, phengite, brammallite, glauconite and celadonite

3) Smectites is 2:1 type of layer silicate, including montmorillonite, beidellite, nontronite, hectorite, saponite, and saunonite

4) Vermiculites is 2:1 type of layer silicate which has magnesium ion compensate charge in interlayer

Table 2.1 Type of clay minerals

	Kaolinites	Illites	Smectites	Vermiculites
Structure type	1:1	2:1	2:1	2:1
Octahedral component	di-octahedral	Mostly di-octahedral	di- or tri-octahedral	Mostly tri-octahedral
Principal interlayer cations	nil	K	Ca, Na	Mg
Interlayer water	Only in halloysite (one layer)	Some in hydromuscovite	Ca two layers; Na one layer	Two layer
Basal spacing	7.1 Å (10 Å in halloysite)	10 Å	Variable, most~15 Å (for Ca)	Variable, 14.4 Å when fully hydrated
Glycol	Taken up by halloysite only	No effect	Takes two layers glycol, 17 Å	Takes one layers glycol, 14 Å
Chemical formula	$Al_4Si_4O_{10}(OH)_8$	$K_{1.0-1.5}Al_4(Si,Al)_8O_{20}(OH)_4$	$M^{+}_{0.7}(Y^{3+}, Y^{2+})_{4-6}(Si,Al)_8O_{20}(OH)_4 nH_2O$	$M^{2+}_{0.66}(Y^{2+}, Y^{3+})_6(Si,Al)_8O_{20}(OH)_4 8H_2O$
Paragenesis	Alterlation of acid rocks, feldspars, etc. Acidic condition	Alterlation of micas, feldspars, etc. Alkaline condition	Alterlation of basic rocks, or volcanic material. Alkaline condition	Alterlation of biotite flakes or volcanic material, chlorites, hornblende, etc.

2.1.1 Smectite clay

Smectite clay is the name for group of clay mineral which can be expanded and attracted crystal structure when immerse in water or some organic solvent. The clay minerals in this group are montmorillonite, beidellite, nontronite, hectorite, saponite, and sauconite with the main difference in chemical composition.

The clay mineral type 2:1 structural units including one octahedral sheet of aluminium oxide, called alumina sheet, sandwiched between two tetrahedral sheets of silicon oxide, called silica sheet, one unit layer is adjacent to another tetrahedral sheet of another layer as showing in the Figure 2.1. The unit layers are stacked together face-to-face to form the crystal lattice. The distance between the plane in one layer and the corresponding plane in the next layer is called the *basal spacing* or *c-spacing*. The sheets in the unit layer are tied together by covalent bonds; therefore, the unit layer is stable. The layers in the lattice layer are held together only by Van der Waals forces and secondary valences between juxtaposed atoms. Therefore, the lattice cleaves along the basal surfaces. The repulsive potential on the surface of the layers is depending on an isomorphous substitution. These two factors contribute to the increase of the *c-spacing* between the layers due to the penetration of water. Thus smectites have an expanding lattice, where all the layer surfaces are available for hydration and cation exchange. Interlayer surface and cation hydration between smectite structural units is a unique property of smectite clays. The crystal structure of smectite clay can be detected by X-ray diffraction. The unit cell are $a \sim 5.2 \text{ \AA}$, $b \sim 9.1-9.2 \text{ \AA}$ and the *c* axis is commonly 10-15 \AA , depending on the water content [Deer et al., 1996].

Montmorillonite is the best known member of the smectite group. The montmorillonite structure is classified as dioctahedral, having two thirds of the octahedral sites occupied by trivalent cations. Dioctahedral montmorillonite has its structural charge originating from the substitution of Mg^{2+} for Al^{3+} in the octahedral sheet. The idealized structural formula of montmorillonite is $\text{M}_y^+ \text{nH}_2\text{O}(\text{Al}_{2y}\text{Mg}_y)\text{Si}_4\text{O}_{10}(\text{OH})_2$. The negative charge at surface of clay layers are balanced by cations intercalated between the structural units and these cations may be alkaline earth ions or the alkali metal such as Ca^{2+} , Mg^{2+} and Na^+ . When Na^+ cations are exclusively in exchange with the montmorillonite surface, the clay is known as Na-montmorillonite is otherwise known as *Bentonite* especially in drilling fluid literature. The expanding lattice may provide the clay with a specific area of as high as $760 \text{ m}^2/\text{g}$. The chemical formula for Na-montmorillonite is $\text{Na}_{0.33}[(\text{Al}_{1.67}\text{Mg}_{0.33})(\text{O}(\text{OH}))_2(\text{SiO}_2)_4]$ [Paul, 1999].

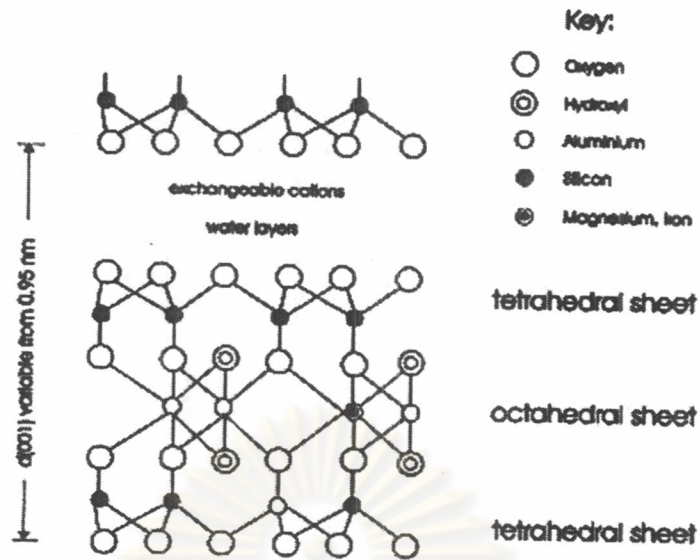
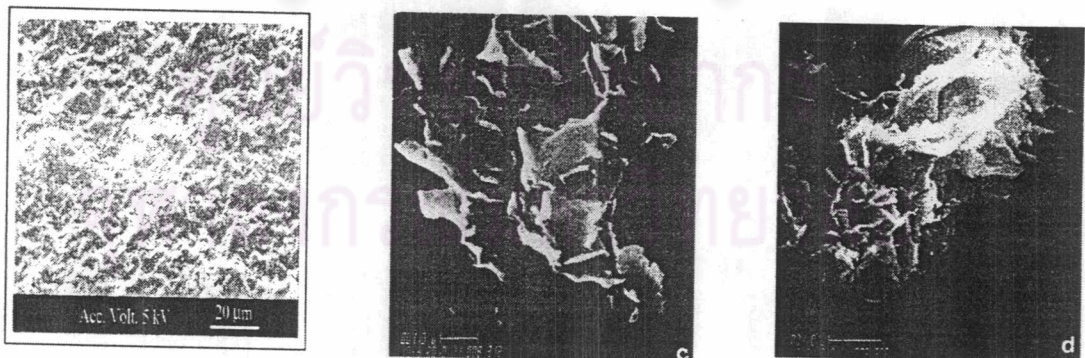


Figure 2.1 The layer structure of smectite clay

The microstructure of montmorillonite is difficult to indicate the shape, the micrograph has been investigated by scanning electron microscope in several papers shown in platy forms and very crumpled layer [Grim, 1968; Welton, 1984]. (See Figure 2.2)



(a) at 5 kV.

(b) at 20 kV.

(c) at 20 kV.

Figure 2.2 Micrograph of bentonite by SEM at various magnifications

In commercial, smectite clay can be removed from nonclay particles by sieve and sedimentation method as shown in Figure 2.3 [Grim, 1968] In water, the clay particle can be separated to individual platelet which acts as a colloid particle (particles less than 2 μm).

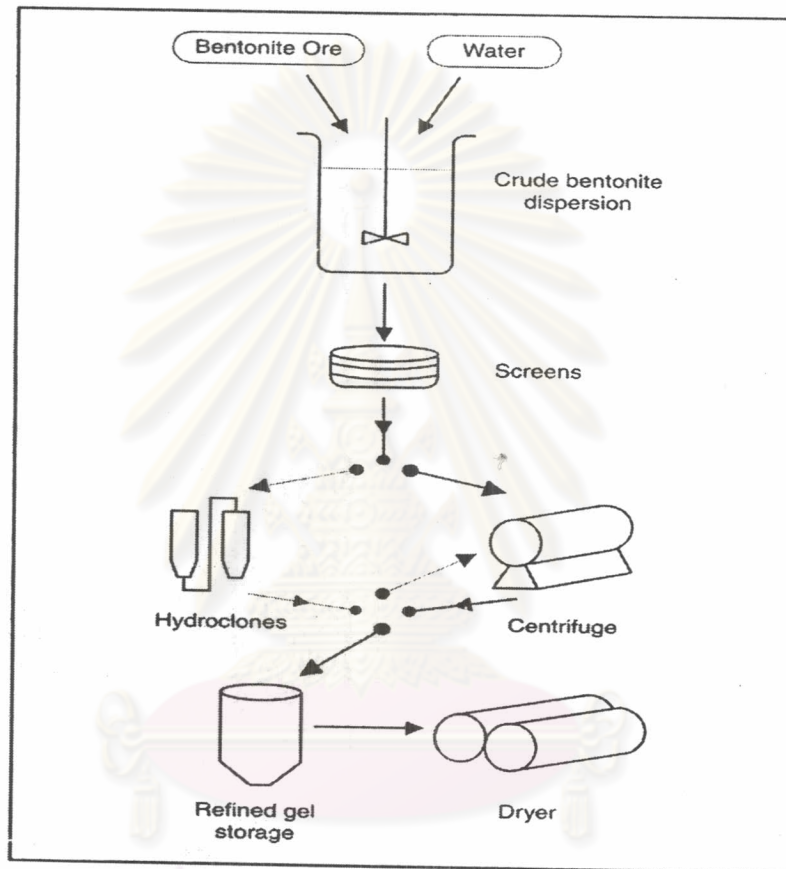


Figure 2.3 Flow chart of bentonite preparation [Grim, 1968].

2.1.2 Properties of smectite clay

2.1.2.1 Specific surface area

The specific surface area is an intrinsic property of smectite clay. From the crystal structure and microstructure, they indicate that the smectite clay particle possess a thin plate shape with a high aspect ratio, about 100 – 200 [Akelah, 1994]

The maximum specific surface area can be calculated from crystallographic data. The basal plane surface of montmorillonite covers a specific surface area of $760 \text{ m}^2/\text{g}$. Depending on the particle size the edges contribute $40 - 50 \text{ m}^2/\text{g}$, thus the resulting total surface area is about $800 - 810 \text{ m}^2/\text{g}$ [Ammann, 2003]. However, this value is valid only for a pure clay mineral whereas natural samples always contain some impurities. Gas adsorption technique can be used to determine the surface area from the relationship between applied pressure and volume of gas forced into the specimen as describe by The Brunauer, Emmett, and Teller (BET) gas adsorption theory [Shaw, 1980]. Another technique is the absorption of molecules solution onto a solid surface, in particular, dyes such as methylene blue. Additionally, specific surface values can be inferred from known thermodynamic properties, the rate of dissolution of soluble materials, microscopy, and the diffusiveness of X-ray diffraction patterns. Details of these measurement techniques can be found in Adamson (1990) and Chen et al. (1999). The gas adsorption and methylene blue absorption techniques involve the sorption of an adsorbate onto the clay surface. The methylene blue technique involves high bonding energy (ionic Coulombian attraction – chemisorption) and it is generally limited to a monolayer. In the gas absorption method, gas molecules are attracted to the surface by van der Waals forces (physisorption), and multiple layers may form. Multilayer adsorption is considered in the BET theory when it is used to analyze the experimental results. Chan et al. (1999) reported the specific surface of montmorillonite comparison between N_2 and methylene blue adsorption method in Table 2.2. Methylene blue adsorption method get higher values than N_2 adsorption method, as a result of clay layer delaminated under a wet condition. Heating and degassing the specimen of gas adsorption procedure attains a dry condition. Bentonite suffers a similar fate and causes a reduction in specific surface [Zerwer and Santamarina, 1994]. The specific surface values of clay mineral especially montmorillonite is depending on the particle size, measurement method and procedure. The methylene blue technique is a simple and reliable technique for the determination of the specific surface of soils, including swelling clays [Santamarina, 2002]

Table 2.2 A comparison specific surface of montmorillonite between N₂ adsorption and MB absorption techniques

Soil type	S _s (m ² /g)	
	MB adsorption	N ₂ adsorption
Na-montmorillonite	700	31
Al-montmorillonite	509	37
Fe-montmorillonite	410	47

Methylene blue (MB) dye has been used to determine the surface area of clay minerals for several decades. The chemical formula is C₁₆H₁₈N₃SCl, with a corresponding molecular weight of 319.87 g/mol. Methylene blue in aqueous solution is a cationic dye, C₁₆H₁₈N₃S⁺, which absorbs to negatively charged clay surfaces [Hang and Brindley 1970; Chen et al. 1999]. Hence, the specific surface of particles can be determined by the amount of absorbed methylene blue. The surface area covered by one methylene blue molecule is typically assumed to be 130 Å². It is important to highlight that the technique is done in water suspensions, thus expansive minerals can expose all available surface area.

The specific surface area from the spot test, as explain by Santamarina (2002), can relate to amount of MB required reaching the end point is

$$S_s = \frac{1}{319.87} \times \frac{1}{200} [0.5N][A_v A_{MB}] \times \frac{1}{10} \quad [1]$$

where N is the number of MB increments added to the soil suspension solution,

A_v is Avogadro's number (6.02 x 10²³ /mol), and

A_{MB} is the area covered by one MB molecule (typically assumed to be 130 Å²)

The methylene blue molecule has a rectangular shape with The methylene blue molecule has a rectangular shape with dimensions of approximately 17 Å x 7.6 Å x 3.25 Å This molecule may attach to the mineral surface in various orientations, the

most common assumption is that the molecule lies flat on the mineral surface on its largest face, so the area covered by one methylene blue molecule may be about 130 \AA^2 per molecule [Hang and Brindley, 1970; Santamarina, 2002].

The amount of absorption increases with surface area and surface charge density, which is affected by pH and ionic concentration. Furthermore, absorption involves ion replacement, which depends on the valence, size, and relative concentration of ions [Mitchell, 1993]. The accuracy of this method is limited by the size of adsorbates. The size and the shape of particles strongly affected to determine the specific surface.

Additional, Lagaly (1994) explained the relative of CEC and specific surface in equation [2]

$$S_s = 2 \times 6.02 \times 75 \times f \times \text{CEC} \quad [\text{m}^2/\text{g}] \quad [2]$$

When CEC units is meq/g, f is 0.8
and equivalent areas of montmorillonite is $75 \text{ \AA} / \text{charge}$

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย




Geometry	Equation	Example
sphere or cube 	$S_s = \frac{6}{b\rho_w G_s}$	Amorphous clay minerals Allophane, hollow spherules $b = 50 \text{ \AA}$, $G_s = 2.65$ $S_s = 453 \text{ m}^2/\text{g}$ (extreme case: $b = 9.6 \text{ \AA}$, then $S_s = 2250 \text{ m}^2/\text{g}$)
thinplate  $l \gg t ; b \gg t$	$S_s = \frac{2}{t\rho_w G_s}$	Sheet structure clay minerals Montmorillonite (extreme case: fully swollen) $t = 9.6 \text{ \AA}$, $G_s = 2.65$ $S_s = 786 \text{ m}^2/\text{g}$
prism and rod  $l \gg b$	$S_s = \frac{4}{b\rho_w G_s}$	Chain structure clay minerals Palygorskite, thread $b = 100 \text{ \AA}$, $G_s = 2.65$ $S_s = 151 \text{ m}^2/\text{g}$

Figure 2.4 Illustrated the relative of particle shape and specific surface area

The Figure 2.4 shows the relationship between specific surface and the size of a grain. The specific surface of a soil made of spherical or cubical particles, with a cumulative grain-size distribution represented by

$$S_s = \frac{3(C_u + 7)}{4\rho_w G_s D_{50}} \quad [3]$$

where C_u is the coefficient of uniformity,

ρ_w is the mass density of water,

G_s is the specific gravity of the minerals, and

D_{50} is the particle diameter corresponding to 50% passing.

The straight-line distribution assumption enforces the coefficient of curvature to be $C_c = C_u^{-0.2}$. The coefficient of uniformity increases, a wider range of particle sizes is present and the contribution of the smaller particles to the total surface of the soil increases.

Expressions in Figure 2.4 show that specific surface is determined by the smallest particle dimension. Equation [3] can be extended to platy particles (dimensions $b \times b \times t$, where b is the length and width of the particle and t is the particle thickness), assuming that particles in the given specimen have the mean slenderness $\beta = b/t$:

$$S_s = \frac{(C_u + 7)}{4\rho_w G_s D_{50}} (\beta + 2) \quad [4]$$

This equation permits computing the mean slenderness from the measured specific surface and grain-size distribution.

2.1.2.2 Cations exchange capacity (CEC)

In natural, the crystals structure of smectite clay usually has an isomorphous substitution of certain atoms in their structure with others ions which has lower valence such as the tetrahedral sheet, Si^{4+} may be replaced by trivalent cations Al^{3+} or Fe^{3+} , or divalent cations Mg^{2+} or Fe^{2+} may replace Al^{3+} in the octahedral sheet. As a result of clay surface arise negative charge. The negative potential is compensated by the adsorption of cations on the surface. Additional, cations and anions are also held at the crystal edges when the crystal is broken. In aqueous suspension, both sets of ions may exchange with ions in the bulk solution. They are known as exchangeable cations. The total amount of cations adsorbed on the clay, expressed in miliequivalents per hundred grams of dry clay (meq/100 g of clay), is called the cation exchange capacity CEC. It is an important characteristic of clay mineral. The cation exchange capacity is high for sodium montmorillonite, comparing it to the other clay minerals.

There are many ways to investigate the CEC values. The principle method suggest by Rhoades (1982) is displacement of saturating index cation and then displacement the saturating index cation after washing free from saturating salt. The last step, detect the saturating index cation by many technique such as titration, atomic emission spectroscopy depending on the type of index.

Methylene blue index is the simple method to detect the CEC values. There is contain in the ASTM C 337-99 for characterize property of clays.

2.1.2.3 Particle association in clay suspensions

Clay particles in suspension involve the interparticle double layer repulsion and Van der Waals attractive forces interacting on clay particles. The double layer is made up of the negative surface charge and the balancing cation charge in Figure 2.5. The negative charge at surface is a consequence of imperfections within the interior of the crystal lattice.

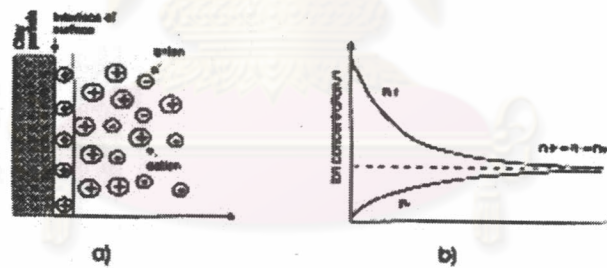


Figure 2.5 a) structure of a diffuse electrical double layer at the surface of a clay particle; b) distribution of the concentration of cations n^+ and anions n^- with distance from the surface for a symmetrical electrolyte with a bulk concentration of n_0 . [Paul, 1999],

The opposite charges, called counter-ions, are electrostatically attracted to the surface of clay particle. Therefore, the concentration of the counter-ions near the particle surface is high, and it decreases with increasing distance from the surface. As two particles approach each other in suspension due to Brownian motion, their diffuse double layers begin to interfere, leading to increase of the free energy of the system. The amount of work required to carry out those changes and to bring the particles from infinite separation to a given distance is the repulsive energy or repulsive potential. The repulsive potential V_R between two clay platelets can be computed from the diffuse double layer theory as:

$$V_R = \frac{64\rho k_B T}{\chi} \left(\tanh \frac{ze\Psi_s}{4k_B T} \right)^2 e^{-kH} \quad [5]$$

where ρ is the counterion density, k the Boltzmann constant, T the absolute temperature, Ψ the Stern layer potential, H the distance between the centre of two particles, e the electron charge and χ the reciprocal Debye length.

$$\kappa = \sqrt{\frac{2e^2 \rho z^2}{\epsilon_0 k_B T}} \quad [6]$$

The repulsive potential decrease exponentially with an increasing particle separation and the range of repulsion is considerably reduced with an electrolyte concentration. The DLVO theory assumes that the dispersed particles are not hydrated and hence do not have an additional repulsive force when two particles approach one another in aqueous solution. It appears that for Na^+ -montmorillonite, the total interaction between the charged platelet surfaces should involve both short range repulsion forces, due to partially bound hydrated cations and longer range repulsion due to hydrated counter-ions in the double layer.

Van der Waals attractive forces, there are three types of intermolecular attraction that are recognized: dipole-dipole interaction; induced dipole-dipole interaction and attractive forces between non-polar molecules London dispersion forces. The London dispersion forces, which are due to the polarization of one molecule by fluctuations in the charge distribution in the second molecule, account for nearly all of the Van der Waals attraction in colloidal systems. The attractive energy between two semi-infinite flat plates may be expressed by the following equation:

$$V_A = -\frac{A}{12\pi} \left(\frac{1}{H^2} + \frac{1}{(H+2t)^2} - \frac{1}{(H+t)^2} \right) \quad [7]$$

where A is the Hamaker constant and H is the distance between the surfaces of the plates, and t is the thickness of the clay platelet.

Total interaction energy, V_T is the sum of the repulsive potential V_R and attractive potential V_A

The Na^+ ions of the montmorillonite particles form diffuse ionic layers surrounding them and create an electrostatic repulsion between the particles. The addition of electrolytes in the system or an increase in temperature will reduce the maximum energy and so the clay particles will come into contact with one another and agglomerate. The aggregation of particles is known as *coagulation* or *flocculation*. The extent to which the particles become flocculated depends on the degree of compression of the double layer, which is dominated by the concentration and valence of counter-ions.

If the concentration of clay is high enough, gel structures will build up under the influence of Brownian motion, the concentration for Na-montmorillonite is usually above 3% w/w. In suspension, plate-like clay particles associate three different modes of particle: face to face FF, edge to face EF and edge to edge EE. The various modes of particle association are illustrated in Figure 2.6. FF association leads

to thicker and larger flakes, and EF and EE association lead to build gel structure, called house-of-cards structures.



Figure 2.6 Different modes of clay particle association in suspension:
 (a) dispersed; (b) face-to-face FF; (c) edge-to-face EF; and
 (d) edge-to-edge EE.

2.1.3 Rheological behavior of clay suspensions

Rheological behavior of colloidal dispersion depends on the four factors

- 1) Viscosity of dispersion medium,
- 2) Particles concentrations,
- 3) particles size and shape and
- 4) particle-particle and particle-dispersion medium (Shaw 1980).

The rheological behavior of any system is described in terms of the relationship between the shear stress τ and the shear rate $\dot{\gamma}$. The shear rate is defined as the change of shear strain per unit time, and the shear stress as the tangential force applied per unit area. The ratio of shear stress t to shear rate $\dot{\gamma}$ is called viscosity η :

$$\eta = \frac{\tau}{\dot{\gamma}}$$

[8]

Viscosity is a measure of the resistance to flow of the fluid. The plot of the shear stress vs. the shear rate is called a consistency curve. Four different types of flow may be distinguished: Newtonian, pseudoplastic, Bingham plastic, and dilatant, as illustrated in Figure 2.7. When the shear stress is directly proportional to the shear rate, the fluid is Newtonian and exhibits a constant viscosity. In the other types of flow behavior, the viscosity varies with the shear rate and these are called non-Newtonian fluids.

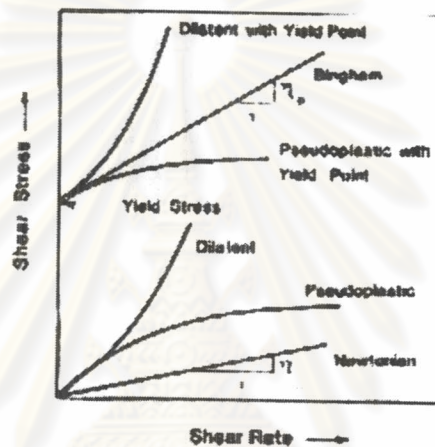


Figure 2.7 Consistency curves for four different types of flow [Reed, 1987].

Aqueous clay suspensions that possess a relatively high particle concentration have been described traditionally in accordance to the Bingham theory of plastic. The Bingham model postulates that a finite stress must be applied to initiate flow and at greater stresses the flow will be Newtonian as shown in Figure 2.7. The resistance of the suspension to flow can therefore be considered as consisting of two parts: a Newtonian part in which the shear stress is proportional to the shear rate and a non-Newtonian part in which the shear stress is constant irrespective of the shear rate. The equation for the Bingham model is:

$$\tau = \tau_B + \eta_{pl} \dot{\gamma} \quad [9]$$

where η_{pl} is the plastic viscosity, defined as the slope of the curve, and τ_B is the Bingham yield stress normally taken as the intercept of the flow curve at high shear rates.

Very dilute clay suspensions or drilling fluids that contain polymers behave as pseudoplastic fluids, which may be described by the power-law equation:

$$\tau = K\dot{\gamma}^n \quad [10]$$

where K is a measure of the consistency of the fluid; and n the flow-behavior index, which is a measure of the decrease of effective viscosity with shear rate. Other models have been considered in describing the rheological behavior of clay suspensions, such as the Casson equation:

$$\tau^{1/2} = k_0 + k_1\dot{\gamma}^{1/2} \quad [11]$$

and the Herschel-Bulkley equation

$$\tau = \tau_y + k\dot{\gamma}^n \quad [12]$$

Both equations 11 and 12 have been used to describe the consistency curves of drilling fluids, with the Herschel-Bulkley equation being the most suitable. In both cases, the suspension has an initial yield stress at low shear rates, and afterwards presents pseudoplastic or 'shear-thinning' type behavior at higher shear rates. In the last case, the viscosity decreases with shear rate. The parameters of the above equations may be divided between two groups. The first group, the Bingham yield stress, consistency coefficient and Casson yield stress are affected by changes in the low shear properties. In the second group, the plastic viscosity, flow-behaviour index and the Casson viscosity, reflect the high shear rate behavior of the fluid.

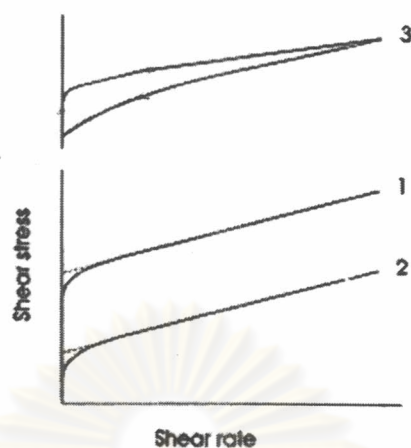


Figure 2.8 Typical flow curves of clay suspensions; 1) initial flow curve; 2) flow curve after mixing; and 3) thixotropic loop.

Clay suspensions frequently show time dependent flow behavior, known as thixotropy. After mixing the suspension, the yield stress and plastic viscosity decrease as illustrated in Figure 2.8, but will recover with time if left standing. Curve 1 represents the original flow behavior and after mixing the suspension displays a flow behavior represented by Curve 2. After a period of rest, the initial Curve 1 will be obtained. Concentrated clay suspensions are very sensitive to shear and their rheological properties will vary during the determination of the rheogram (shear stress vs. shear rate). If the shear rate is ramped-up and then immediately ramped-down, the stresses recorded for each rate of shear will be lower and a 'hysteresis loop' is obtained (Curve 3). This occurs because the fragments of the network which are broken under shear, need time to be linked again to a three-dimensional network. In addition, when the clay system is subjected to a constant rate of shear, the viscosity decreases with time as the gel structure is broken down, until an equilibrium viscosity is reached. In view of their shear and time dependency, the clay suspensions require the same preparation, handling and measurement conditions if comparisons are to be made between the rheological properties of different samples.

Various factors affect the flow behavior of clay suspensions. Naturally, the clay concentration will bring about an increase of all rheological properties. Due to the negative particle charge and double-layer structure, the yield stress and viscosity change with variations of the pH of the suspension and electrolyte concentration. Also, differences in the rheological properties are observed depending on the type of electrolyte in solution and on the nature of the exchangeable ions. A rise of the temperature increases the interparticle attractive forces, which in turn, leads to enhanced particle-particle interactions affecting the yield stress and suspension viscosity.

The suspension viscosity also depends to a great extent on the viscosity of the medium, which is also a function of temperature. Pressure effects may also alter the flow properties on clay suspensions, due to the exponential increase of liquid viscosity with pressure and the differential compression of clays and liquids.

In 1964 Van Olphen has indicated that rheological behavior of concentrated Na^+ montmorillonite suspensions behaved according to the Bingham model. A very low amount of NaCl led to a decrease of the yield stress and viscosity, while higher amounts increased both of these values gradually. The results were explained in terms of the charges on the clay platelets, which were assumed to be positive on the edges and negative on the faces. Initially, edge-to-face EF type association occurs owing to the opposite charge attraction, which results in 'internal mutual flocculation'. Upon the addition of small amounts of salt, the double layers are compressed and the effective charge determining the electrostatic attraction between edges and faces is reduced. This results in the network breaking down, accompanied by the lowering of the rheological properties. However, further compression of the double layers by increasing the salt concentration restores the edge-to-face attraction, which is now greater than the face-to-face repulsion. In this region the rheological properties were found to increase. At very high salt concentrations the yield stress of the suspensions tended to decrease, as a result of association transition from EF to FF association, the formation of thicker particles by which the number of links within the clay structure is reduced.

2.1.4 Surface modification of clay mineral

Clay and clay mineral involved in material science studies and parent of organic-inorganic hybrid materials from the swelling behavior, adsorption properties colloidal and rheology phenomena. There are many methods to modify smectite clay minerals including (1) adsorption (2) ion exchange with inorganic cations and cationic complexes (3) ion exchange with organic cations (4) binding of inorganic and organic anions, mainly at the edges, (5) grafting of organic compounds (6) reaction with acids (7) pillaring by different types of poly (hydroxo metal) cations (8) interlamellar or intraparticle and interparticle polymerization (9) dehydroxylation and calcination (10) delamination and reaggregation of smectitic clay minerals and (11) physical treatments such as lyophilisation, ultrasound and plasma [Bergaya, 2001].

Ion exchange with inorganic cations and cationic complexes is the principle reaction to convert clay mineral to organophilic clay. The natural smectite clay usually has an impurity phase such as quartz, cristobalite, feldspar, calcite then they should be purify before ion exchange process.

2.2 Organophilic clay

Organophilic clay or organoclay was introduced in 1941 by Dr. Jhon W. Jordan, father of organoclay technology. His research was sponsored by NL Industry. He tries to develop the high value added product from bentonite. Normally, bentonite use as a gallant for water system but not simplify for organic system. Organoclay was exchange the inorganic cations in the interlayer with organic cations to convert the clay into organophilic compound as show in Figure 2.9 which suitable for use in organic system.[Clarke 1989]

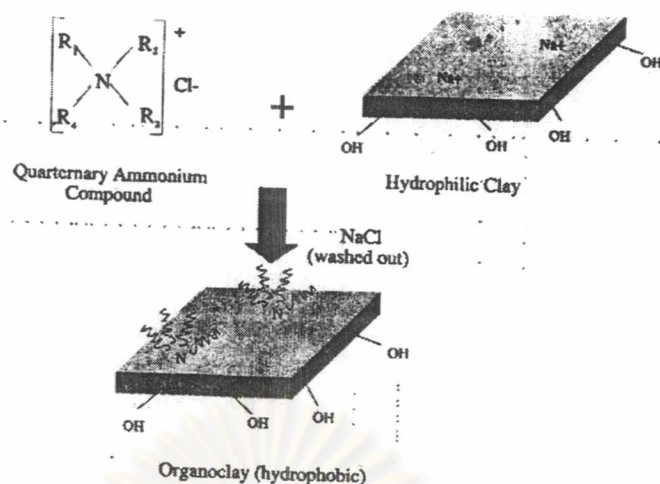


Figure 2.9 Scheme of clay mineral reacted with organic compound

Since 1941 the numerous researches in organophilic clay, such as the preparation technique, characterization technique, thermal property, has been report. How ever, the parameters to control the intercalation process and rheological property in organic system are inadequate.

2.2.1 Preparation and characterization of organophilic clay

The adsorption of cationic surfactants on clay at the solid–liquid interface is of great technological interest and fundamental importance and has been investigated by several experimental techniques [Cases, 1992]. The adsorption of surfactants on clay surface involves the electrostatic interactions between the surfactant head group and the surface, the interaction between the tails, and the electrostatic repulsion between the head groups. Usually a “two-step” adsorption isotherm of cationic surfactants was found for smectite surfaces [Xu, 1995]. At low surface coverage, first stage surfactant cations adsorb on the negatively charged surface sites, the cations exchange with protons or other counterions depending on the properties of the solid–water interface and the type of surfactant. When the surface charge has been compensated, the “electrostatic” driving force for surfactant

adsorption is annihilated and the adsorption will only increase if the affinity of hydrophobic part of the surfactant is low.

The replacement of inorganic exchange cations by surfactant on the interlayer surfaces of smectite clays not only converts to match the clay surface polarity with the polarity of organic system, but it also expands the spacing of clay interlayer. The interlayer space by organic ions intercalation is depending on the charge density of clay and the onium ions size. In general, the longer chain length surfactant, and the higher the charge density of the clay are a mainly force. These parameters contribute to increasing the volume occupied by the surfactant. Three type of surfactant arrangement in interlayer; a monolayer, a lateral bilayer, a pseudo-trimolecular layer, or an inclined paraffin structure as illustrated in Figure 2.10. At very high charge densities, large surfactant ions can adopt lipid bilayer orientations in the clay interlayer. The orientations of surfactant chains in organoclay were deduced based on infrared and XRD measurements [Lagaly, 1986]. More recent molecular dynamics (MD) simulations were used to study molecular properties such as density profiles, normal forces, chain configurations and trans-gauche conformer ratios. For the mono-, bi- and psuedo-trilayers with respective d -spacings of 13.2, 18.0 and 22.7 Å, a disordered liquid-like arrangement of chains was preferred in the gallery. In this disordered arrangement the chains do not remain flat, but instead, overlap and co-mingle with onium ions in opposing layers within the galleries. However, for the trilayer arrangement, the methylene groups are primarily found within a span of two layers and only occasionally do they continue into the layer opposite to the positive head group. As anticipated, the onium head group is also noted to reside nearer the silicate surface relative to the aliphatic portion of the surfactant. The highest preference conformer is trans over gauche for the maximum surfactant chain length just before the system progresses to the next highest layering pattern. This is expected since the alkyl chains must be optimally packed under such dense surfactant concentrations. The MD simulation experiments have agreed well with experimental XRD data and FTIR spectroscopy for the stacked interlayer alkyl chains. However, the inclined paraffin association is not addressed for $< C_{15}$ surfactants with clays of CEC less than 1.2 meq/g.

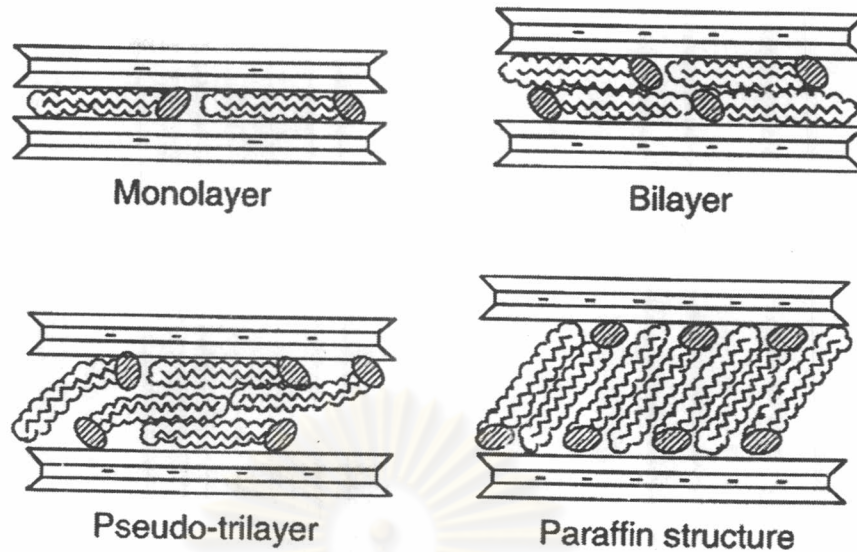


Figure 2.10 Orientation of alkylammonium ions in the interlayer silicate with different layer charge densities [Lagary 1986].

Lee (2002) study the reaction of smectite with hexadecyl trimethyl ammonium cations at 0.01-3.0 times of CEC, show that a heterogeneous increase of interlayer spacings as HDTMA loading increases, the chance of delaminated layers being developed increases locally in the low-charge interlayer regions by the sufficient adsorption of organic surfactants beyond the CEC value due to the tendency of alkyl chain interaction.

2.2.2 Application

The applications of organoclay or organophillic clay were depending on the grades which there are many different types on the market as shown in Figure 2.11. It usually use as a gallant or viscosifying agent in paint, printing ink, grease and cosmetic industry [Gerry, 1989].

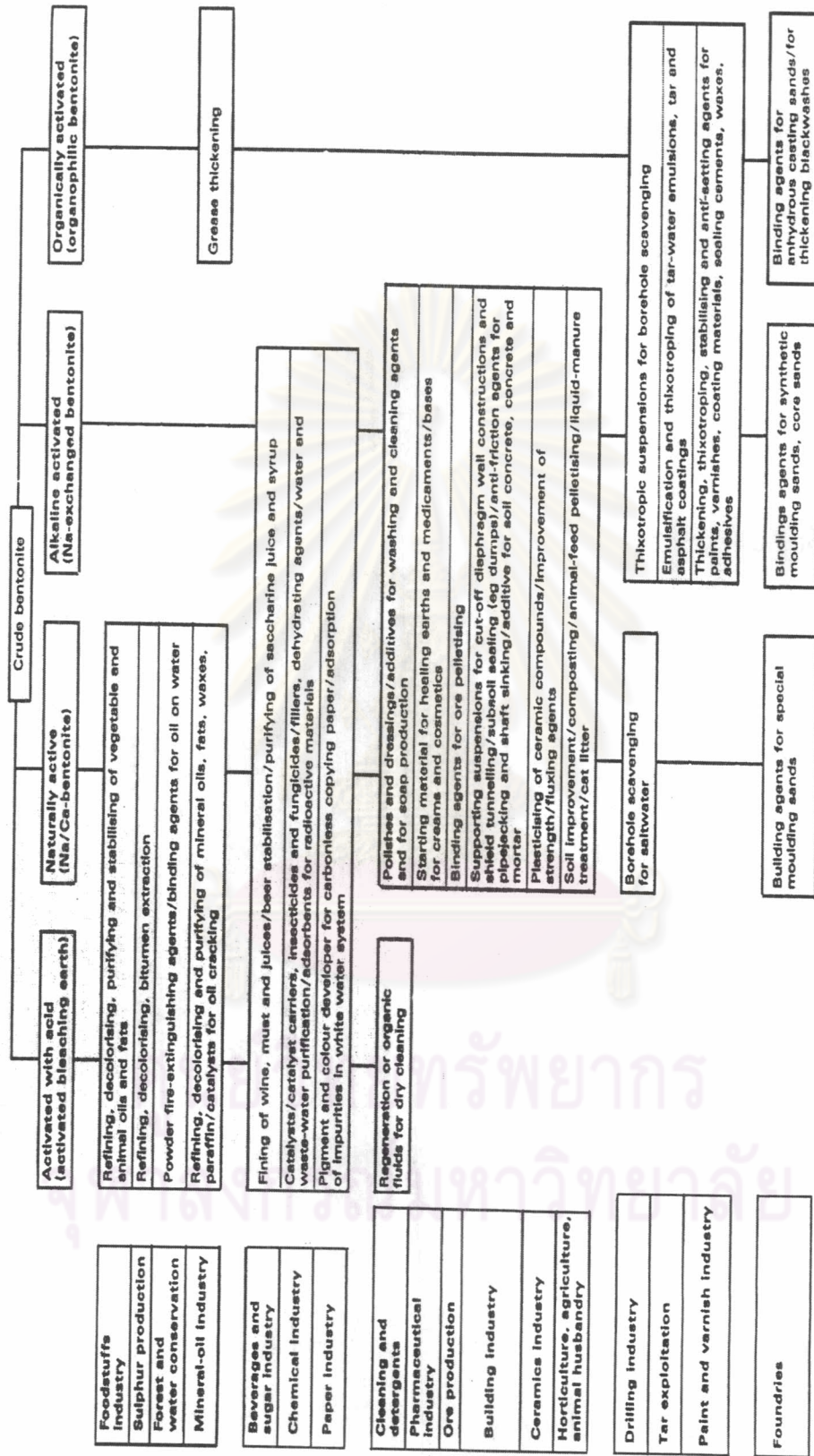


Figure 2.11 Application of bentonite and organophilic bentonite in industries.

2.3 Polymer-clay nanocomposite

The term “nanocomposite” describes a material which combining two or more phase where at least one of the phases is dispersed in the other one on a nanometer (10^{-9} m) level. The behavior of these materials exhibits different from conventional composite materials, due to the high surface-to-volume ratio. This term is commonly used in ceramics and polymers. However, we will only consider nanocomposites based on polymers. The polymer nanocomposites has attracted attention to achieve the enhance polymer and extending their utility by using nanoscale reinforcements. The polymer nanocomposites is based on polymer matrices reinforced by nanofillers such as precipitated silica and silicatitania oxides synthesised by the sol-gel process, silica beads, cellulose whiskers, zeolites as well as colloidal dispersion of rigid polymers and many others. Clay mineral has used as filler in conventional composite for long times ago. Since 1987 Toyota research group discovered new materials based on polyamide 6 and organophilic montmorillonite, known as “hybrid organic–inorganic nanocomposites”, showed dramatic improvements of mechanical properties, barrier properties and thermal resistance as compared with the pristine matrix and this at low clay content around 4 wt% [Fukushima,1987]. Since then, polymer-clay composites are divided into three general types: conventional composite where the clay acts as a conventional filler, intercalated nanocomposite consisting of a regular insertion of the polymer in between the clay layers and delaminated nanocomposite where 1 nm-thick layers are dispersed in the matrix forming a monolithic structure on the microscale as show in Figure 2.12. The latter configuration is of particular interest because it maximises the polymer-clay interactions, making the entire surface of the layers available for the polymer. This should lead to most dramatic changes in mechanical and physical properties.

The nanolayers are not easily dispersed in most polymers due to their preferred face-to-face stacking in agglomerated tactoids. Dispersion of the tactoids into discrete monolayers is further hindered by the intrinsic incompatibility of hydrophilic layered silicates and hydrophobic engineering plastics.

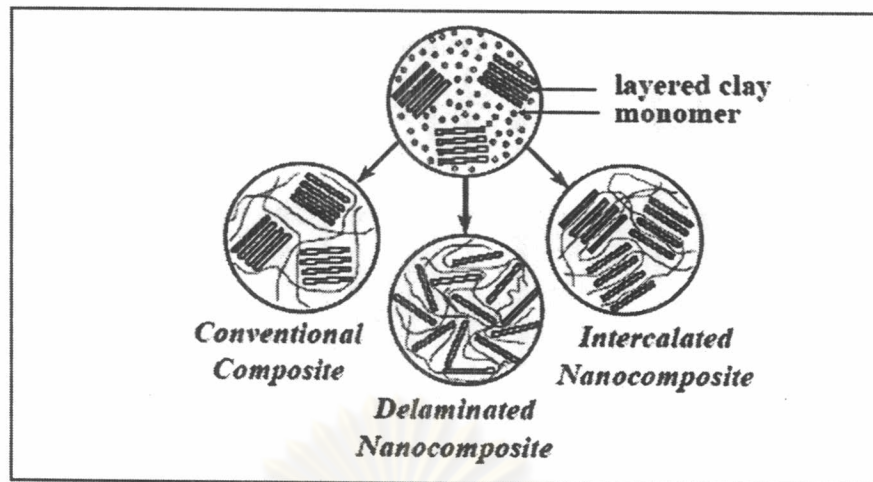


Figure 2.12 The three idealised structures of polymer-clay composites.

In 1993, at loading of only 4.2 wt.% clay, the modulus doubled, the strength increased more than 50%, and the heat distortion temperature increased by 80 °C compared to the pristine polymer. They also demonstrated that organoclays exfoliated in a nylon 6 polymer matrix greatly improved the dimensional stability, the barrier properties and even the flame retardant properties [Kojima et al., 1993a,b; Gilman et al., 1997].

The use of organoclays as precursors to nanocomposite formation has been extended into various polymer systems including epoxys, polyurethanes, polyimides, nitrile rubber, polyesters, polypropylene, polystyrene and polysiloxanes,

In recent years, there has been extensive study of the factors which control whether a particular organo-clay hybrid can be synthesized as an intercalated or exfoliated structure. These factors include the exchange capacity of the clay, the polarity of the reaction medium and the chemical nature of the interlayer cations. By modifying the surface polarity of the clay, onium ions allow thermodynamically favourable penetration of polymer precursors into the interlayer region. The ability of the onium ion to assist in delamination of the clay depends on its chemical nature such as its polarity. The loading of the onium ion on the clay is also crucial for success and it should be borne in mind that a commercial organoclay may not have

the optimum loading for a particular application. For positively charged clays such as hydrotalcite, the onium salt modification is replaced by use of a cheaper anionic surfactant. Other types of clay modification can be used depending on the choice of polymer, including ion-dipole interactions, use of silane coupling agents and use of block copolymers. An example of ion-dipole interactions is the intercalation of a small molecule such as dodecylpyrrolidone into the clay. Entropically-driven displacement of the small molecules then provides a route to introducing polymer molecules. Unfavourable interactions of clay edges with polymers can be overcome by use of silane coupling agents to modify the edges [LeBaron et al., 1999]. The enhance properties of polymer-clay nanocomposite depending on the structure of composites

2.3.1 Preparation

There are 3 methods to synthesis of polymer-clay nanocomposite including in situ polymerization, solution and melt intercalation.

2.3.1.1 In situ polymerisation

In situ polymerization is the first method to synthesis polymer-clay nanocomposite in 1987 by toyota research group [Fukushima, 1987]. The organoclay is swollen in the monomer, then the reaction is initiate by catalytic or increases temperature.

2.3.1.2 Solution intercalation

Solution intercalation is the simple method to synthesis polymer-clay nanocomposite but it's has an impact to environment because of the large amount of solvent were used in this process. First step, the organoclay and polymer have to dissolve in the solvent before mixing together. And the last step polymer-clay composite is formed after evaporating the solvent.

2.3.1.3 Melt intercalation

Melt intercalation is a new method to produce the polymer-clay nanocomposite, which introduce by Vaia [1993]. The strategy consists in blending a molten thermoplastic with an organoclay in order to optimise the polymer-clay

interactions. The mixture is then annealed at a temperature above the glass transition temperature of the polymer and forms a nanocomposite the polymer chains experience a dramatic loss of conformational entropy during the intercalation. The proposed driving force for this mechanism is the important enthalpic contribution of the polymer/organoclay interactions during the blending and annealing steps.

The melt intercalation process has become increasingly popular because of its great potential for application in industry. Indeed, polymer-clay nanocomposites have been successfully produced by extrusion. A wide range of thermoplastics, from strongly polar polyamide 6 to styrene have been intercalated between clay layers. However, polyolefins, which represent the biggest volume of polymers produced, have so far only been successfully intercalated to a limited extent [Kormann, 2003].

2.3.2 Characterization

There are mainly two methods to characterize the structure of polymer-clay nanocomposites. The most straightforward is X-ray diffraction because it is a good way to evaluate the spacing between the clay layers. The sample preparation is relatively easy and the X-ray analysis can be performed within a few hours. However, one needs to be very careful with the interpretation of the results. Lack of sensitivity of the analysis and limits of the equipment can lead to wrong conclusions about the nanocomposite structure. Therefore, transmission electron microscopy is a necessary complement to X-ray diffraction. TEM gives a direct measure of the spatial distribution of the layers but it requires substantial skills in specimen preparation and analysis.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย