



## CHAPTER II

### THEORY AND LITERATURE REVIEW

#### 2.1 Clay and Clay Mineral

Clay or layered silicate implies a natural, earthy, fine grained material which develops plasticity when mixed with a limited amount of water. The clay minerals defined particular kind of crystallographic structure, whose particle diameters were less than  $2\ \mu\text{m}$  [1]. They are hydrous silicates, which contain tetrahedral silicate sheet and octahedral aluminum or magnesium sheet.

Clays are called phyllosilicates. This name is given because in most cases their grain shape is that of a sheet, it is much thinner than it is wide or long. This aspect has a fundamental cause. The inner structure, the bonding direction of the constituent atoms, is such that the strong forces are essentially in a two dimensional array [2].

The crystalline clays are divided into chain and layer structures and that the layer structures are divided into 2:1 and 1:1 families, with the names triphormic and diphormic applied to these families [3].

##### (a) 1:1 type minerals

The 1:1 clay-mineral type consists of one tetrahedral sheet and one octahedral sheet. These two sheets are approximately  $7\ \text{\AA}$  thick.

##### (b) 2:1 type minerals

The three sheet or 2:1 layer lattice silicates consist of two silica tetrahedral sheets between which is an octahedral sheet. These three sheets form a layer approximately  $10\ \text{\AA}$  thick.

For example, the names kaolins for kaolinite, halloysite minerals and smectite for the montmorillonite minerals are shown in Table 2.1 [4].

**Table 2.1** Classification of phyllosilicates, example on clay minerals

Layer type	Group	Subgroup	Species
1:1	Serpentine-Kaolin (z~0)	Serpentines (Tr)	Chrysotile, antigorite, lizardite, berthierinc, odinite
		Kaolins (Di)	Kaolinite, dickite, nacrite, halloysite
2:1	Talc-pyrophyllite (z~0)	Talc (Tr)	
		Pyrophyllite (Dr)	
	Smectite (z~0.2-0.6)	Smectites (Tr)	Saponite, hectorite
		Smectites (Di)	Montmorillonite, beidellite, nontronite
	Vermiculite (z~0.6-0.9)	Vermiculite (Tr)	
		Vermiculite (Di)	
	Illite (0.6>z<0.9)	Illite (Tr)	
Illite (Di)		Illite, glauconite	
Mica (z~1.0)	Micas (Tr)	Biotite, phlogopite, lepidolite	
	Micas (Di)	Muscovite, paragonite	
Brittle mica (z~2.0)	Brittle micas	Margarite	
Chlorite (z variable)	Tr chlorites <sup>a</sup> (Tr)	Common name based on Fe <sup>2+</sup> , Mg <sup>2+</sup> , Mn <sup>2+</sup> , Ni <sup>2+</sup>	
	Di chlorites (Di)	Donbassite	
	Tr chlorites (Di)	Sudolite, cookeite (Li)	
	Di chlorites (Tr)	No known examples	
2:1	Sepiolite-palygorskite		Inverted ribbons (with z variable)

<sup>a</sup> 2:1 layer first in name of chlorite; Tr = trioctahedral and Di = dioctahedral; z = charge per formula unit.

### 2.1.1 Smectites Minerals

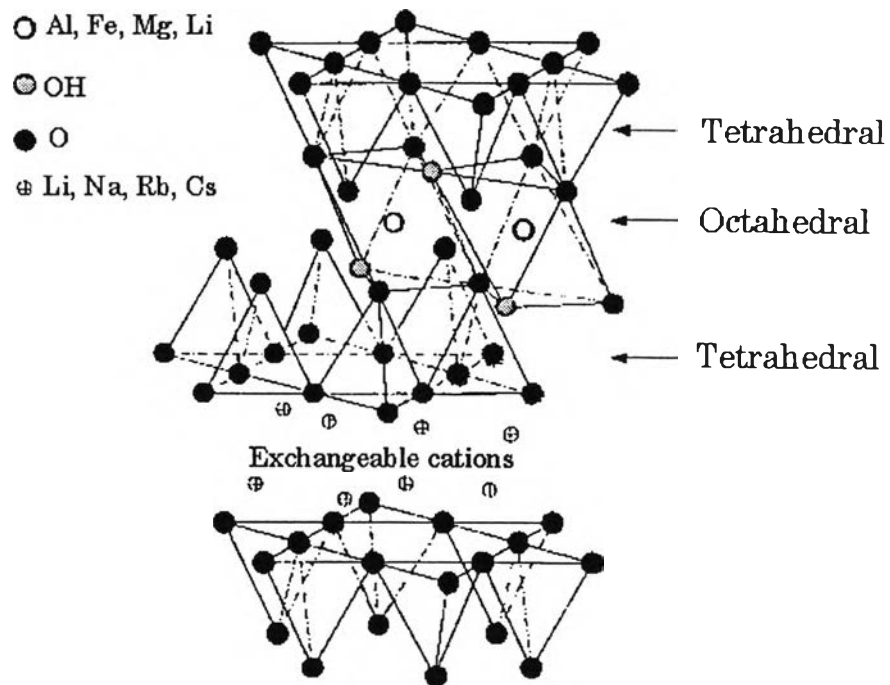
Smectites are a family of expandable 2:1 clay minerals having permanent layer charge because of the isomorphous substitution in either the octahedral sheet or the tetrahedral sheet. Although it is common for smectites to have both tetrahedral charge and octahedral charge, most of the charge originates from substitution in the octahedral layer, which means that the charge is relatively a long ways from the edge of the mineral. This has important implications for shrinking and swelling properties.

The principle smectite are montmorillonite, deidellite and nontronite, all of which are dioctahedral 2:1 layer, and saponite, hectorite and saconite, which are trioctahedral [5]. Their chemical composition are shown in Table 2.2.

**Table 2.2** Chemical formula of clay in 2:1 phyllosilicates types

Subgroup	Species	General formula
Dioctahedral smectictites	Montmorillonite	$M_{x/n}^{n+} \cdot yH_2O[Al_{4.0-x}Mg_x](Si_{8.0})O_{20}(OH)_4$
	Beidellite	$M_{x/n}^{n+} \cdot yH_2O[Al_{4.0}](Si_{8.0-x}Al_x)O_{20}(OH)_4$
	Nontronite	$M_{x/n}^{n+} \cdot yH_2O[Fe_{4.0}](Si_{8.0-x}Al_x)O_{20}(OH)_4$
Trioctahedral smectictites	Saponite	$M_{x/n}^{n+} \cdot yH_2O[Mg_{6.0}](Si_{8.0-x}Al_x)O_{20}(OH)_4$
	Hectorite	$M_{x/n}^{n+} \cdot yH_2O[Mg_{6.0-x}Li_x](Si_{8.0})O_{20}(OH,Fe)_4$

The net negative charges on the clay structure must be satisfied by the presence of charge-balancing alkali and alkaline earth cation situated inside the galleries. The interlayer is hydrated, which allows cation to move freely in and out of the structure. Because the interlayer is open and hydrated, cations may be present within the interlayer to balance negative charges on the sheets themselves. Cations between the layer are part of the cation exchange capacity of the soil. The total amount of cations adsorped in the clay interlayer, expressed in milliequivalents per hundred grams of dry clay, is called the cation exchange capacity (CEC). Figure 2.1 shows the structure of smectite clay [6]. Montmorillonite (MMT) is a smectite clay normally applied to polymer nanocomposites because it high cation exchange capacity, surface reactivity and adsorption properties.



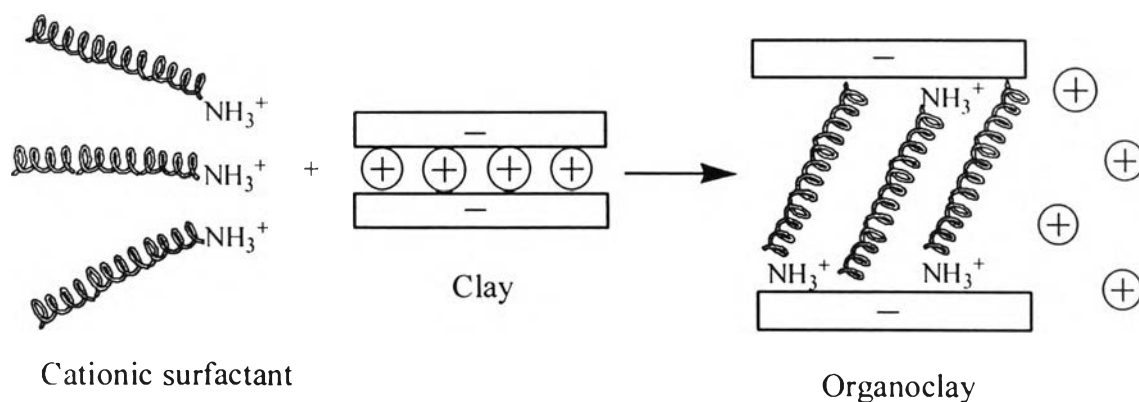
**Figure 2.1** Structure of smectite clay [6]

### 2.1.2 Montmorillonite (MMT)

A commercial name of MMT is bentonite. Practically all natural bentonites consist almost entirely of the crystalline clay-like minerals comprising the MMT family and small fragments of other minerals called “grit” such as feldspar, calcium carbonate, gypsum, quartz, etc. This grit may constitute from 5-10 percent of the prepared commercial bentonites.

MMT has a low thermal expansion coefficient and a high gas barrier property. Stacking of this structure leads to a regular weak dipolar or van der Waals interaction between the layers. Isomorphic substitution in each layer (for example,  $\text{Al}^{3+}$  replaced by  $\text{Mg}^{2+}$  or by  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$  replaced by  $\text{Li}^+$ ) generates negative charges that are counterbalanced by hydrated sodium or potassium ions residing in the interlayer spacing [6]. In this pristine state, MMT is too hydrophilic to disperse in a polymer matrix. To disperse layered silicates in a polymer matrix, one must convert the normally hydrophilic silicate surface to an organophilic clay or organoclay.

Generally, this can be done by ion-exchange reactions with cationic surfactants including primary, secondary, tertiary, and quaternary alkylammonium or alkylphosphonium cations as shown in Figure 2.2 [7].



**Figure 2.2** Exchangeable charge between surfactant and cations of clay

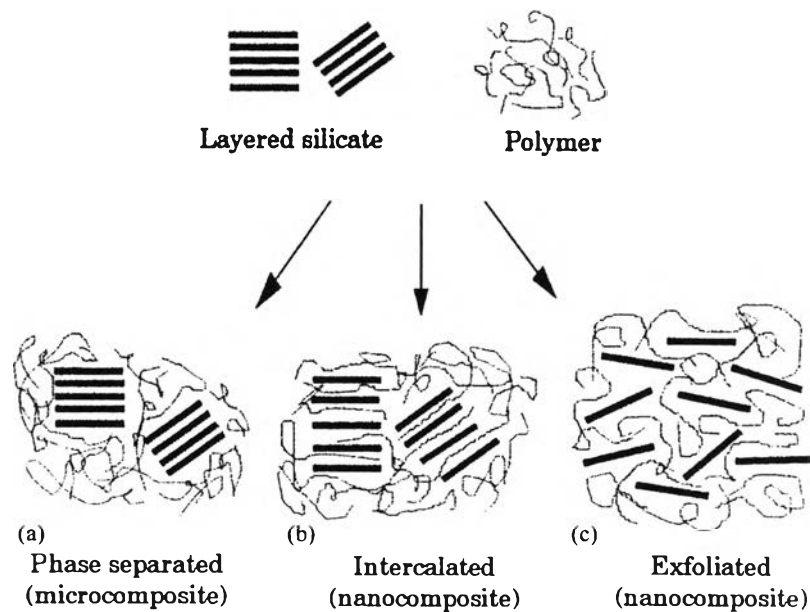
## 2.2 Polymer Nanocomposites

Nanocomposites are a combination of two or more phases containing different compositions or structures, where at least one of the phases is in the nanoscale regime. These materials exhibit behavior different from conventional composite materials with microscale structure, due to the small size of the structural unit and the high surface-to-volume ratio [8].

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 shows very well dispersed in the polymer matrix. For examples, Hsu and Chou [9] prepared a polyether-type polyurethane (PU) containing 0.043% gold nanoparticles ( $\sim 5$  nm) by mixing the waterborne PU with gold suspension.

Many nanocomposites use silicate layers for the preparation and can be divided into two types based on dispersion ability of silicate layers in the polymer matrix. The first one is called *intercalated structure*, which a single (and sometimes more than one) extended polymer chain is intercalated between the silicate layers resulting in a well ordered multilayer morphology built up with alternating polymeric

and inorganic layers. If the silicate layers are completely and uniformly dispersed in a continuous polymer matrix, it is called *exfoliated or delaminated* structure. If the polymer is unable to intercalate between the silicate sheet, a phase separated composite is obtained, whose properties stay in the same range as traditional microcomposites. Figure 2.3 shows the structure of conventional composite compared and the two types of nanocomposites [10].



**Figure 2.3** Scheme of different types of composite arising from the interaction of layered silicates and polymers: (a) phase-separated microcomposite; (b) intercalated nanocomposite and (c) exfoliated nanocomposite [10]

### 2.2.1 Preparation of Polymer Nanocomposites

Nanocomposites can be formed in one of three ways, *in-situ polymerization*, *solvent-based synthesis* and *melt blending synthesis* [6]. In the case of in-situ polymerization, the layered silicate is swollen within the monomer and therefore the polymer formation can occur in between the intercalated sheets. This method was initiated by the Toyota research team that studied the ability of MMT to be swollen by the  $\epsilon$ -caprolactam monomer at 100°C and subsequently to initiate its ring opening

polymerization to obtain nylon-6-based nanocomposites. A small amount of 6-aminocaproic acid was added as a polymerization accelerator when the relative amount of 12-mont (12-aminolauric acid modified MMT) used was smaller than 8 wt.% [11, 12]. Yeh et al. [13] used organically modified montmorillonite (MMT) clay platelets for preparation poly(methyl methacrylate)/clay nanocomposites through both *in situ* emulsion polymerization and solution dispersion. Wu et al. [14] prepared polyurethane (PU)/nanosilica composites which nanosilica particles were directly introduced into polyester resins through *in situ* polymerization and blending methods, then cured by isophorone diisocyanate trimers. Srihirin et al. [15] prepared polystyrene/clay nanocomposites and studied effect of the cation-exchange capacity on the formation of nanocomposites.

The solvent-based system in which the polymer or pre-polymer is soluble and the silicate layers are swellable. The layered silicate is first swollen in a solvent. When the polymer and layered silicate solutions are mixed, the polymer chains intercalate and displace the solvent within the interlayer of the silicate. Upon solvent removal, the intercalated structure remains, resulting in polymer/layer silicate nanocomposite. Aranda and Ruiz-Hitzky [16] reported the first preparation of polyethyleneoxide/montmorillonite nanocomposites by this method. Polyimide/clay hybrids can be prepared by dissolving clay in *N*-methyl-2-pyrrolidinone and mixing with precursor solution of polyimide, followed by removing the solvent [17]. Epoxy resin-layered silicate nanocomposites were successfully synthesized using pre-intercalated novolac resin-layered silicate nanocomposites (NR-LSN) by melt, melt-ultrasonic, solution, and solution-ultrasonic intercalation methods to prepare NR-LSN [18]. Shen et al. [19] synthesized different kinds of organophilic montmorillonite cotreated by cetyltrimethyl ammonium bromide (CATB) and aminoundecanoic acid (AUA) and applied to prepare polyurethane/montmorillonite nanocomposites. The organoclay was dispersed into dimethylformamide (DMF) before the addition of polyurethane then stirred until dissolved and then cast into mold. Martin et al. [20] prepared polyurethane/cloisite (organosilicate) nanocomposites via solvent casting and melt compounding. The tensile properties of the melt-compounded materials were lower than those of their solvent-cast counterparts because of thermal degradation. Chen-Yang et al. [21] studied thermal and anticorrosive of polyurethane/clay

nanocomposites and it was found that the nanocomposites showed better thermal stability, flame retardancy and exhibited better corrosion protection over the pure polyurethane.

The melt blending process involves mixing the layered silicate with the polymer while heating the mixture above the softening point of the polymer. During the annealing process, the polymer chains diffuse from the bulk polymer melt into the galleries between the silicate layers. This method is compatible with current industrial process, such as extrusion and injection molding. Polystyrene was the first polymer used for the preparation of nanocomposites with allylammonium cation modified MMT [22]. Ma et al. [23] developed a newly kind of layered clay, rectorite (REC), which has been used to yield intercalated or exfoliated thermoplastic polyurethane rubber nanocomposites by melt-processing intercalation.

### **2.2.2 Application of Polymer/Clay Nanocomposites**

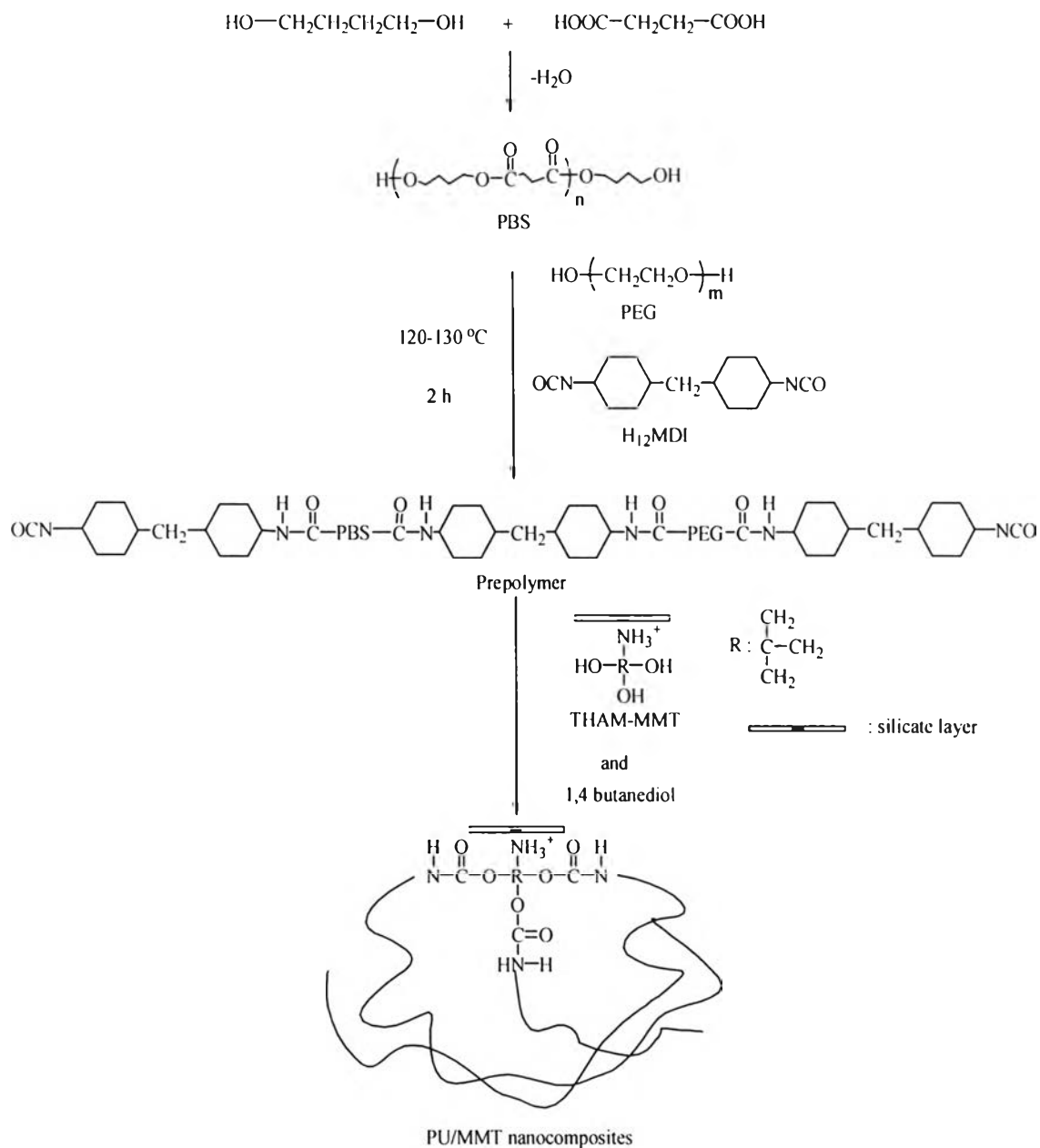
Polymer nanocomposites have emerged as a new class of materials and attracted considerable interest and investment in research and development worldwide in the past decade. Clay minerals are regarded as promising precursors for nanoparticles due to their unique layered structure, rich intercalation chemistry and low cost. The most critical issue in development and application of polymer nanocomposites is the surface modification of clays and the dispersion of clay platelets in the target polymer matrix. Polymer nanocomposites have recently attracted a great deal of attention because of the improvements in the physical, thermal, mechanical and barrier properties than those of conventional composites.

The various types of nanocomposites can be prepared from many types of polymer matrix. Furthermore, PU/clay nanocomposites have also been studied by several research groups [24-32]. PUs have a large variety of forms i. e. foams, adhesives, coating, elastomers etc. They are one of the most useful commercial polymer materials used in both industry and daily life.

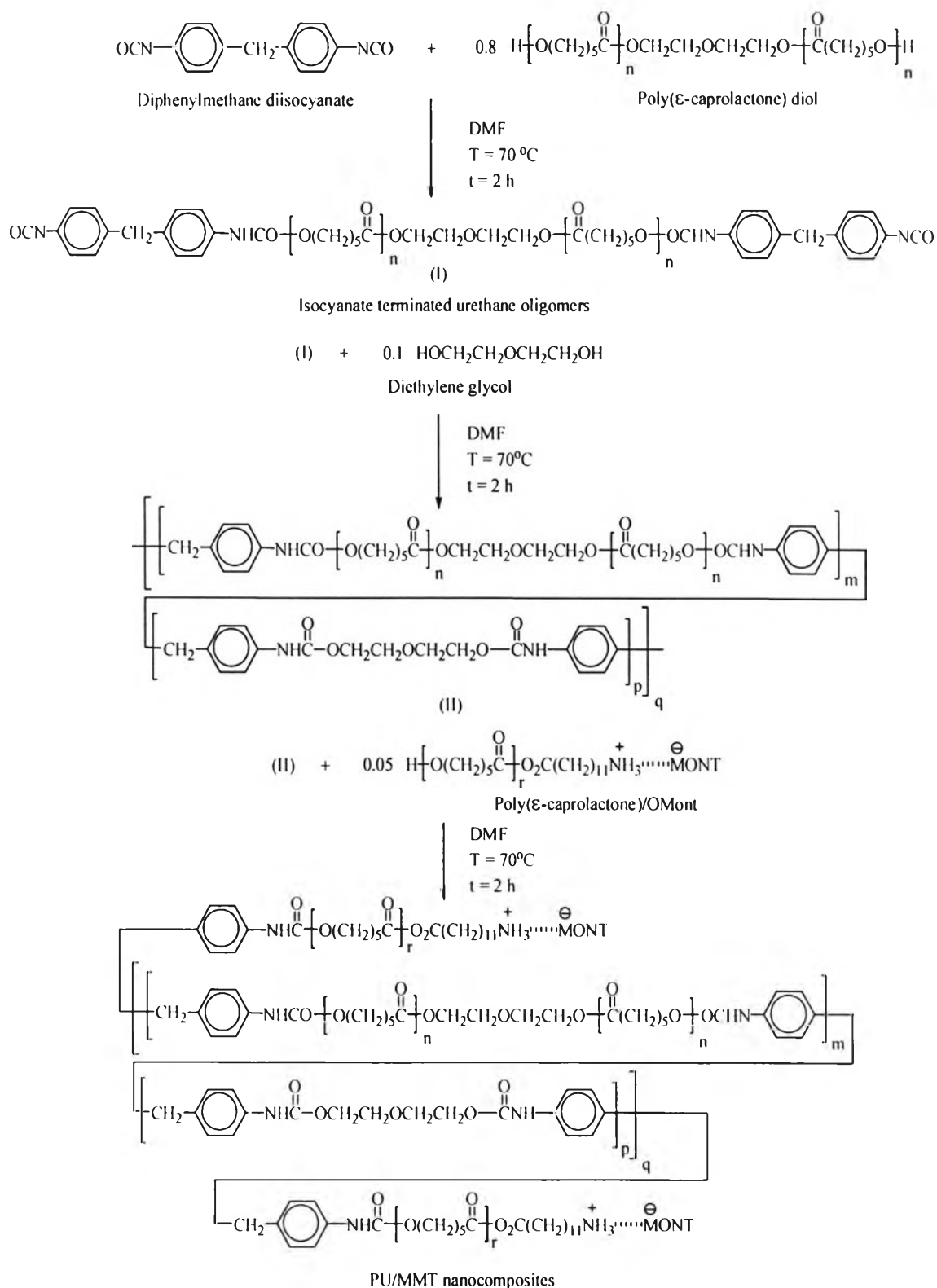
Most of modified clays used to prepare polyurethane nanocomposites contain hydroxyl functional groups which can be chemical bonded with the polymer matrix. The clay particles were allowed to react with prepolymer followed by chain extension



with butanediol [24-26] or the prepolymer and butanediol underwent chain extension reaction prior to mixing with clay particles [27-29]. In both methods, the polymer chains had –NCO end groups prior to mixing with organoclay. Lee et al. [24] prepared polyurethane (PU) /montmorillonite (MMT) nanocomposites via in situ polymerization. Highly crystalline poly(butylenes succinate) (PBS)/ poly(ethylene glycol) polyols (PEG) and 4,4'-dicyclohexylmethane diisocyanate ( $H_{12}$ MDI) were used to prepare the NCO-terminated prepolymer and then 1, 2 or 3 wt% of a tris(hydroxymethyl) aminomethane-MMT (THAM-MMT) hybrid was reacted with the NCO-terminated prepolymer, followed by the addition of 1,4-butanediol to obtain nanocomposites as shown in Scheme 2.1. Tortora et al. [27] prepared organically modified polyurethane (PU)/ montmorillonite (MMT) nanocomposites. They were obtained by a three step process using diphenylmethane diisocyanate, poly( $\epsilon$ -caprolactone), di(ethylene glycol) and poly( $\epsilon$ -caprolactone)-organically modified montmorillonite (OMont) nanocomposites. In the first step, an excess of diisocyanate was reacted with poly(1-caprolactone) diol to form isocyanate terminated urethane oligomers. In the second step, less than a stoichiometric amount of di(ethylene glycol) was used as a chain extender to produce PU. In the third step of the reaction, a fixed number of moles of previously prepared nanocomposites poly( $\epsilon$ -caprolactone)/OMont was added leading to the nanocomposites as shown in Scheme 2.2.

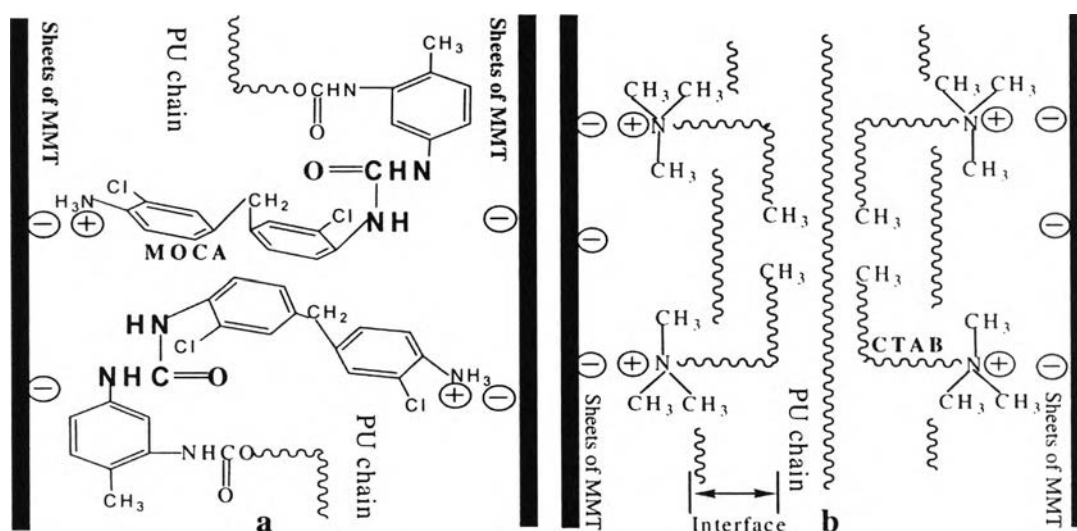


**Scheme 2.1** Preparation of PU/MMT nanocomposite through modified montmorillonite containing hydroxyl groups [24]



**Scheme 2.2** Preparation of PU/MMT nanocomposites containing poly( $\epsilon$ -caprolactone/OMont) [27]

However, some of the modified silicate layers are non-reactive clays which do not contain hydroxyl group. Hu et al. [30] prepared polyurethane/organoclay nanocomposites with intercalated morphology. Organoclay was prepared from montmorillonite (MMT) by ion exchange reaction with hexadecyl trimethyl ammonium chloride. The addition of organoclay improves the thermal and mechanical properties of nanocomposites. Zheng et al. [31] prepared PU/epoxy resin interpenetrating (IPNs) polymer networks nanocomposites. MMT was modified by octadecylammonium chloride to promote the compatibility and phase structure of the IPNs and improve the mechanical properties and waterborne resistance. Wang et al. [32] successfully prepared PU/MMT with a reactive modifier (methylene-bis-ortho-chloroaniline, MOCA) (PU/MO-MMT) which are connected with PU by covalent bond and a non reactive modifier (cetyltrimethyl ammonium bromide, CTAB) (PU/C<sub>16</sub>-MMT) which formed a thin interlayer in the PU nanocomposites (Figure 2.4). The moduli and the onset degradation temperature for the PU obviously increased by addition of MMT treated with MOCA (MO-MMT) and the mechanical strength dramatically increased by about 600% for the MO-MMT and only increased by about 450% for the CATB-MMT at the point of 5% organically modified MMT content.



**Figure 2.4** Structural models of intercalated PU/MMT nanocomposites: (a) PU/MO-MMT and (b) PU/C<sub>16</sub>-MMT [32].

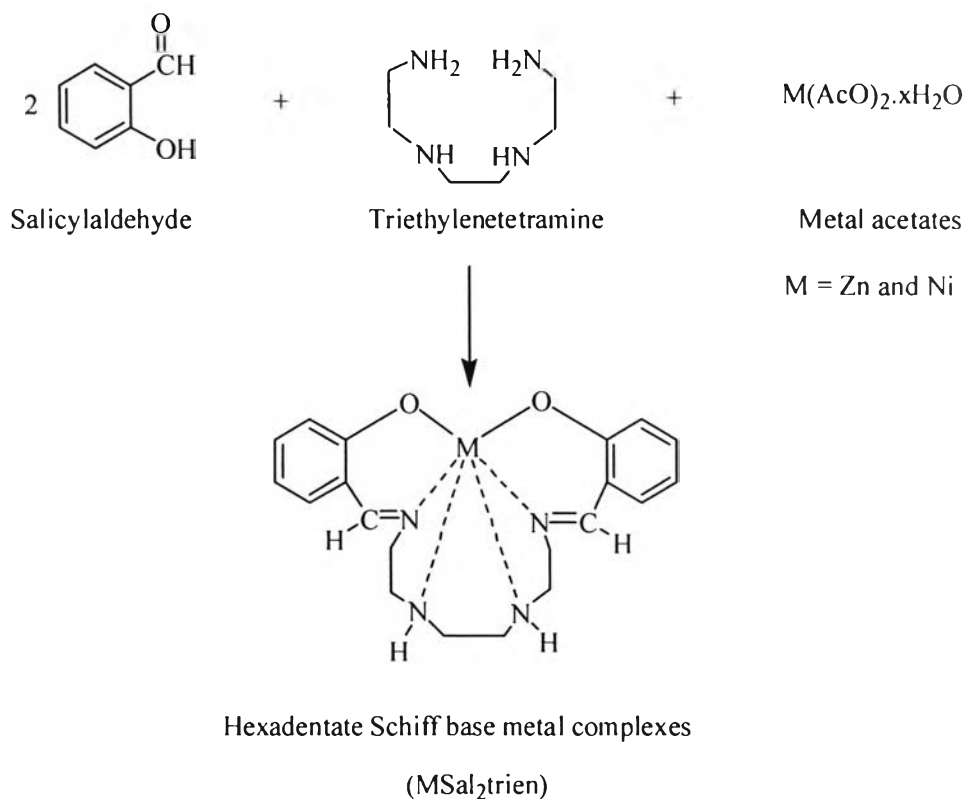
### 2.3 Metal-Containing Polyurethane

The polyurethanes with metal-complexes in the main chain are of great interest due to the numerous interesting properties and potential applications in many diverse fields. The incorporation of metal into urethane backbone results in a considerable increase in the decomposition temperature and the thermal properties of polymer is effected by the presence of metallic ions [33-36].

### 2.4 Objective and Scope of the Research

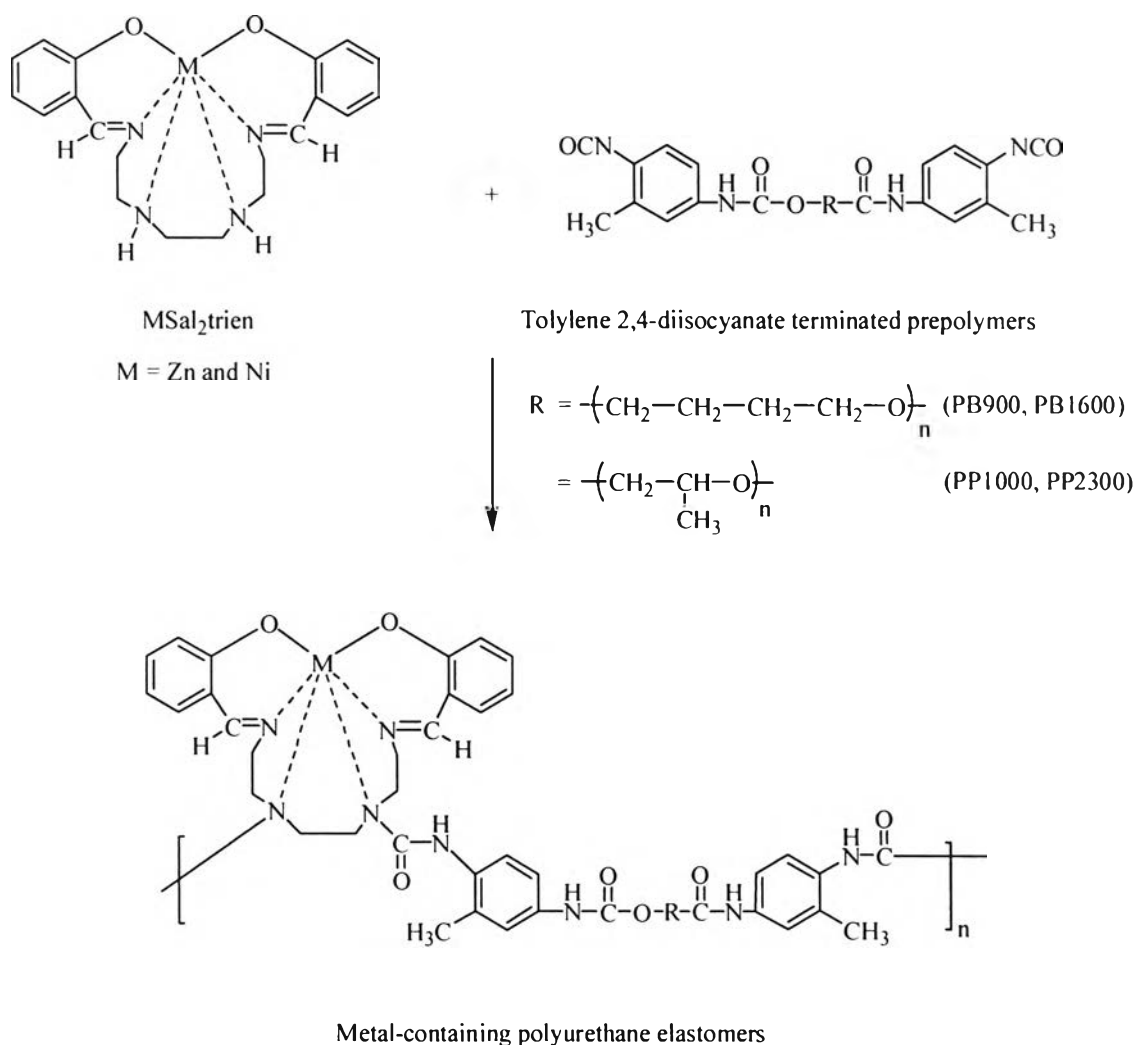
The target of this research is to synthesize metal-containing polyurethane/clay nanocomposites since it was known that the addition of clay into polymer chain could improve thermal properties of the polymer. Ngumnunjai [37] synthesized a non-reactive organoclay, of which bentonite H (BNH) was modified by oleylmethylbis(2-hydroxyethyl)ammonium chloride (OMH). Chantarasiri et al. synthesized hexadentate Schiff base zinc and nickel complexes [38] which were used in the synthesis of metal-containing polyurethanes [39]. In this work, these metal-containing polyurethanes and the organoclay described above were used in the synthesis of metal-containing polyurethane/clay nanocomposites.

In the first steps, hexadentate Schiff base zinc and nickel complexes were synthesized as shown in Scheme 2.3 [38].



**Scheme 2.3** Synthesis of Hexadentate Schiff base zinc and nickel complexes (ZnSal<sub>2</sub>trien and NiSal<sub>2</sub>trien) [38]

In the next step, metal-containing polyurethanes were synthesized from the reaction between metal complexes and tolylene 2,4-diisocyanate terminated poly(propylene glycol) prepolymers, molecular weight 1000 and 2300 (PP1000 and PP2300); tolylene 2,4-diisocyanate terminated poly(1,4-butanediol) prepolymers, molecular weight 900 and 1600 (PB900 and PP1600) as shown in Scheme 2.4 [39].



**Scheme 2.4** Synthesis of metal-containing polyurethane from MSal<sub>2</sub>triene and PB,PP prepolymers

Metal-containing polyurethane/clay nanocomposites were prepared from metal-containing polyurethane elastomers and organoclay by use of solvent method (Figure 2.5). The organoclay employed was prepared by solution intercalation of bentonite H by tallowtrimethyl ammonium chloride (TTM), oleylmethylbis(2-hydroxyethyl) ammonium chloride (OMH) and octadecylmethyl[ethoxylate(15)] ammonium chloride (ODMH) [37].

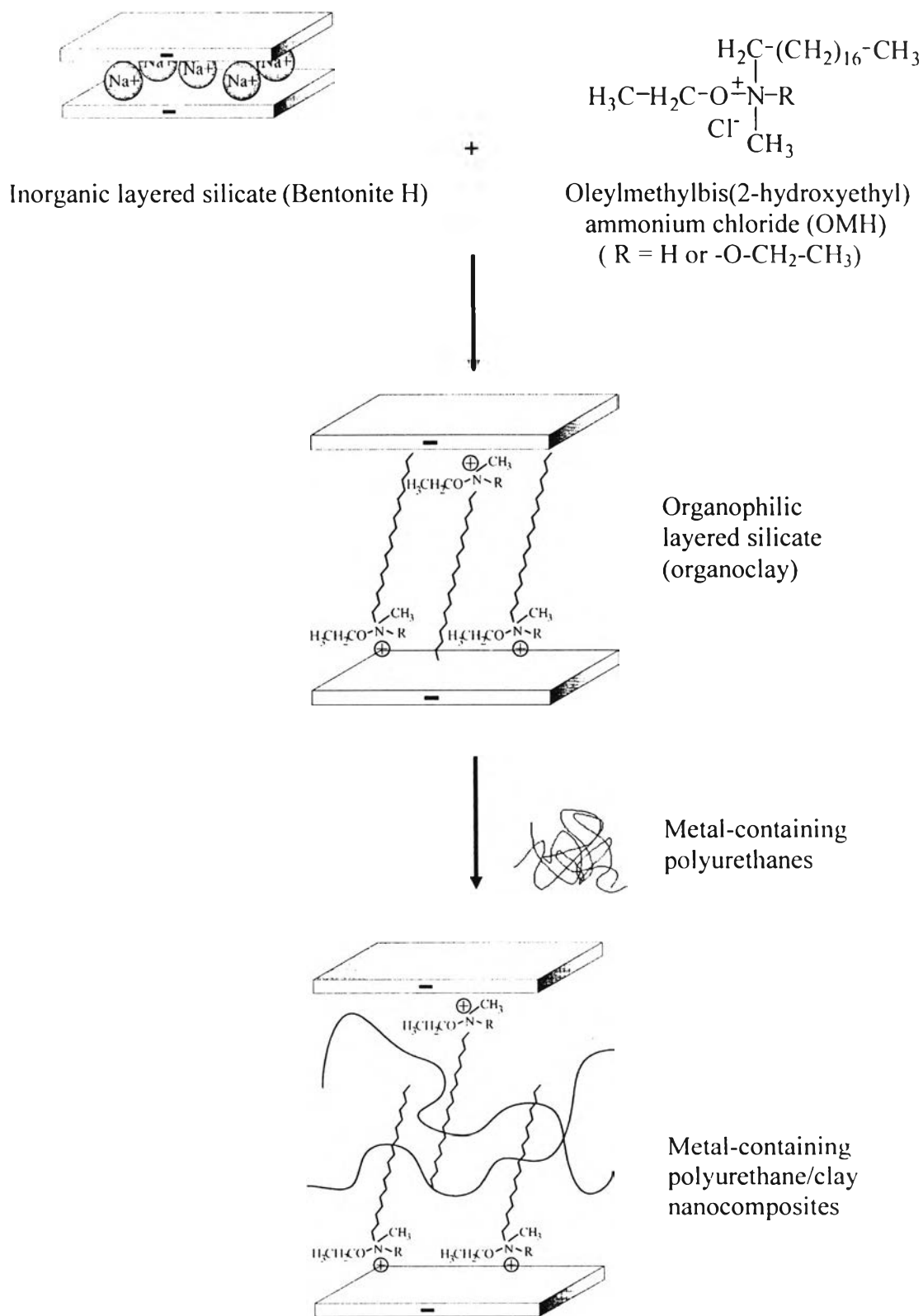


Figure 2.5 Preparation of metal-containing polyurethane/clay nanocomposite



Finally, the metal-containing polyurethane/clay nanocomposites were characterized by Fourier-transform infrared spectroscopy (FTIR) to study characteristic functional groups. Interlayer spacing in the structure of nanocomposites was investigated by X-ray diffraction (XRD). Transmission electron microscope was used to provide information on the morphology of nanocomposites. Thermal property of the nanocomposites was investigated by thermogravimetric analysis (TGA). Flammability of the nanocomposites was determined by measuring limiting oxygen index value (LOI).