

CHAPTER II

LITERATURE REVIEW

2.1 Clay Minerals

Clay minerals, or phyllosilicate, consist of sheets of silica tetrahedral and alumina octahedral which are held together by only weak interatomic forces between the layers. Owing to their chemical composition and crystal structure, they are divided into four main groups which are illite, smectite, vermiculite and kaolinite. Among these, the one that is found to be useful in the field of polymer composites is a group of expandable clay known as smectite clay.

Smectite clay is a phyllosilicates or layer silicates having a layer lattice structure in which two-dimensional oxoanions are separated by hydrated cations (Klopprogge et al., 1998). Montmorillonite, which is the main constituent of bentonites, is a mainly species of smectite clay. The structure of MMT is made of several stacked layers, with a layer thickness around 0.96 nm and a lateral dimension of 100-200 nm (Lertwimolnum and Vergnes, 2005). Its crystal lattice consists of a central octahedral sheet of alumina fused between two external silica tetrahedral sheets (in such a way that the oxygens from the octahedral sheet also belong to the silica tetrahedral), as shown in Fig. 2.1. These layers organize themselves in a parallel fashion to form stacks with a regular gap between them, called interlayer or gallery (Manias *et al.*, 2001).

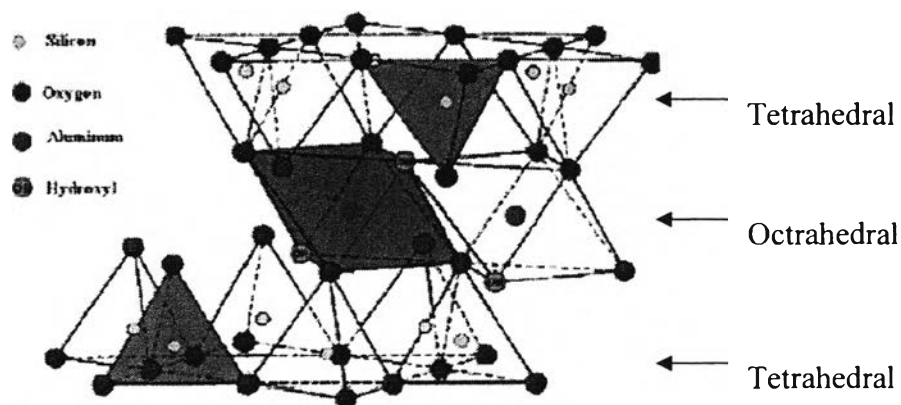


Figure 2.1 Structure of montmorillonite (Morlat *et al.*, 2004).

Isomorphous substitution within the layers (for example, Al^{3+} replaced by Mg^{2+} or Fe^{2+} , or Mg^{2+} replaced by Li^{1+}) generates negative charges that are counter-balanced by alkali and alkaline earth cations situated inside the galleries. This type of layered silicate is characterized by a moderate surface charge known as the cation exchange capacity (CEC), and generally expressed as mequiv/100 gm. This charge is not locally constant, but varies from layer to layer, and must be considered as an average value over the whole crystal (Manias *et al.*, 2001; Sinha Ray Okamoto., 2003).

In the present work, bentonite is a clay mineral used for the preparation of polymer-clay nanocomposites. Bentonite is a clay minerals derived from the alteration of volcanic ash, comprising predominantly of montmorillonite. Depending on their sources, bentonite contains a small portion of accessory minerals and metal oxides in addition to montmorillonite. The presence of these compounds can impact the industrial value of bentonite. It has unique water absorbing and swelling characteristics. These characteristics make bentonite to be a very desirable industrial mineral. The adsorption and ion exchange properties of clay minerals depend on many parameters. In addition to electrolyte concentration, pH of solution (H^+ ion) controls the swelling behavior of expandable clay minerals.

In 1999, Altin *et al.* determined surface area, pore volume distribution, and porosity of montmorillonite after being exposed to aqueous solutions with various pH values. For the pH-adjusted montmorillonite, the results demonstrated that the micropore and mesopore surface areas were greatly increased by increasing pH due to increasing pH creates a more porous structure, since the interlayer repulsive force become dominant. Then pore volume distributions showed that lowering pH of montmorillonite reduced the mesoporous and microporous.

2.2 Porous Clay Heterostructure (PCH)

A variety of ordered mesoporous materials have been synthesized by surfactant-templated methods. Porous clay heterostructure (PCH) is a recent class of solid porous materials formed by the intercalation of surfactant within the intragalleries of clays. Various types of expandable clay could be employed such as hectorite, vermiculite, synthetic saponite and montmorillonite for the synthesized of these highly

porous clays.

Polverejan *et al.* (2000) prepared porous clay heterostructures within the galleries of synthetic saponite clays with targeted layer charge densities in the range $x = 1.2-1.7 e^-$ units per $Q^+_x[Mg_6](Si_{8-x}Al_x)O_{20}(OH)_4$ unit cell. The CEC value increase in proportional to the aluminum content of the clays. All three saponites were used to assemble porous clay heterostructures that were denoted SAP1.2-, SAP1.5-, and SAP1.7-PCH, respectively. The removal of the intragallery mixture of neutral alkylamine and quaternary ammonium ion surfactant (Q+) by calcination afforded PCH intercalates with basal spacings of 33-35 Å. The BET specific surface areas progressively decreased with increasing aluminum loading from 921 to 797 m² g⁻¹ and the framework pore volumes decreased from 0.44 to 0.37 cm³ g⁻¹. Moreover, these materials exhibited the framework pore sizes were in the supermicropore to small mesopore region 15-23 Å as can be seen in TEM image (Fig. 2.2.). In 2000, they synthesized acid-functionalized porous clay heterostructure from synthetic saponite through postsynthesis grafting reactions using AlCl₃ and NaAlO₂ as alumination agents under acid and basic condition, respectively. The amount of tetrahedral aluminum incorporated into the saponite gallery structure is correlated with the concentration of aluminum in the grafting solution. However, some loss of gallery mesostructure occurred at higher aluminum loadings (e.g., Si/Al = 5) with sodium aluminate. Depending on the choice of aluminum reagent (AlCl₃ or NaAlO₂), the Al-SAP/PCH derivatives exhibited basal spacings of 32-34.8 Å, BET surface areas of 623-906 m²/g, pore volumes of 0.32-0.45 cm³/g, and pore sizes in the large micropore to small mesopore range (14-25 Å).

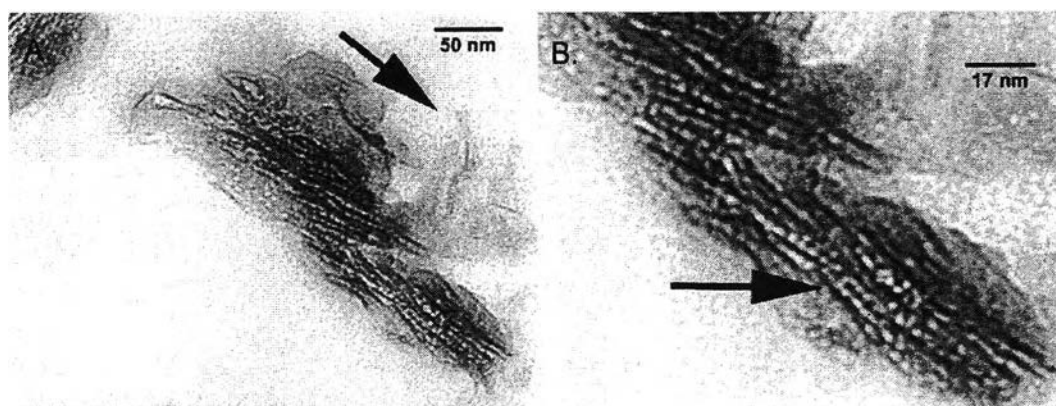


Figure 2.2 TEM images of saponite heterostructures (Polverejan *et al.*, 2000).

Benjelloun *et al.* (2001) studied the cationic exchange capacities (CECs) of two porous clay heterostructures (PCHs), derived from natural montmorillonite (PMH) and synthetic saponite (PSH). Three methods for the formation of NH_4^+ -exchanged PCH forms are describe and evaluated: (1) adsorption of ammonia under a gas flow on calcined and extracted PCHs in acidified methanol; (2) direct exchange in NH_4Cl solutions; (3) solvent extraction with $\text{NH}_4\text{Ac}/\text{EtOH}/\text{H}_2\text{O}$. The obtained ammonium containing materials are subsequently exchanged for K^+ cations in aqueous solution in order to determine the CEC of the PCH solids. Several extraction media were tested for their efficiency in extracting the hexadecyltrimethylammonium surfactant from the PCH precursor. The best results were obtained with methanol:water mixture with 9:1 vol%. The resulting extracted materials had a higher specific surface area and porosity and even a slightly narrower pore size distribution than the calcined ones with maxima of $997 \text{ m}^2/\text{g}$. and $0.76 \text{ cm}^3/\text{g}$ for montmorillonite PCH (PMH) and $1118 \text{ m}^2/\text{g}$ and $0.97 \text{ cm}^3/\text{g}$ for saponite PCH (PSH).

2.3 Hybrid Organic-Inorganic PCH

The interesting way to modify the physical and chemical properties of mesoporous silicates is the incorporation of organic components, either on the silicate surface or within the walls. Organic modification of the silicates permits precise control over the surface properties and pore size of the mesoporous materials for spe-

cific applications.

Surface modified mesoporous silicas via covalent bonding of organic molecules can be achieved by using two general strategies which are post-synthesis modification (also called "grafting method") and co-condensation reaction (also called "one-pot synthesis") (Stein *et al.*, 2000; Sayari and Hamoudi, 2001).

1) *Post-synthesis modification*. In this approach, it refer to direct grafting of a mesoporous support by attachment of functional molecules to the surface of mesoporous, usually after surfactant removal either by calcination or solvent extraction. In this method, mesoporous silicates posses surface silanol (Si-OH) groups that can be present in high concentration and act as anchoring points for organic functionalization. Surface modification with organic groups is most commonly carried out by silylation with a suitable organosilane reagent.

2) *Co-condensation reaction*. In this method, it refer to co-condensation of tetraalkoxysilane and one or more organosilane precursors via sol-gel technique to produce organic functionalized mesoporous silicates. In this approach, the organic moieties are covalently linked via a nonhydrolyzable Si-C bonds to a silaxane species, which hydrolyzes to form a silica network.

In 2004, Wei *et al.* incorporated phenyl groups into the porous clay heterostructures within the galleries of montmorillonite via co-condensation reaction of tetraethxysilane and phenylethoxysilane in the presence of surfactant templates (dodecylamine and cetyltrimethylammonium ion), as shown in Fig. 2.3. The surfactant templates were removed from the pores by solvent-extraction (C₂H₅OH/HCL). Depending on the loading of phenyl groups, the hybrid porous clay heterostructures had BET surface areas of 390-771 m²g⁻¹, pore volumes of 0.3-0.59 cm³g⁻¹, and the framework pore sizes in the supermicropore to small mesopore range (1.2-2.6 nm).

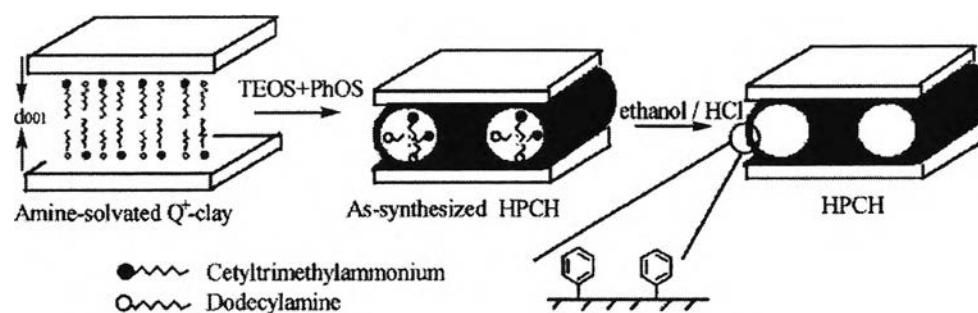


Figure 2.3 Schematic illustration of mechanism for formation of hybrid porous clay heterostructure (HPCH) through surfactant-directed assembly of organosilica in the galleries of clay (Wei *et al.*, 2004).

Nakatsuji *et al.* (2004) synthesized a microporous clay minerals with organic-inorganic pillared by using C_2H_5OH/HCl extraction method after intercalation of tetraethoxysilane (TEOS) or TEOS/methyltriethoxysilane (MTS) into the cetyltrimethylammonium ion (CTA)-exchanged vermiculite. The BET surface areas increase to above $500\text{ m}^2\text{g}^{-1}$ with an increase of the HCl concentration to 0.4 mol dm^{-3} . A water adsorption study showed that the product treated with a TEOS/MTS mixture had a hydrophobic surface as a result of the successful incorporation of methyl groups at the surface of the pillars.

Ishii *et al.* (2005) synthesized highly porous silica nanocomposites from a clay mineral by a new approach using a pillaring method combined with a selective leaching method. Preparation was conducted by applying an HCl/ethanol treatment after intercalation and condensation of tetraethoxysilane (TEOS) and/or methyltriethoxysilane (MTS) into cetyltrimethylammonium (CTA) ion-exchanged vermiculite. The products are porous nanocomposites consisting of TEOS and/or MTS-derived polysiloxane and hydrated silica, resulting from the selective leaching process of the inorganic constituents and the extraction of CTA ions from CTA-exchanged vermiculite after the intercalation of TEOS and/or MTS. N_2 adsorption isotherms revealed that the products had high porosity with $1205\text{--}715\text{ m}^2\text{g}^{-1}$ of BET surface area, owing to the multiple pore formations in and between the silicate layers.

2.4 Polypropylene-Clay Nanocomposites

Polymer-clay nanocomposites exhibit outstanding properties that are synergistically derived from the organic and inorganic components. They exhibit superior mechanical properties, reduced gas permeability, improved solvent resistance and enhance ionic conductivity (Galgali *et al.*, 2001).

Several strategies have been considered to prepare polymer-clay nanocomposites. The preparative methods are divided into three main groups according to the starting materials and processing techniques (Sinha and Okamoto., 2003).

- *Intercalation of polymer or pre-polymer from solution:* This is based on a solvent 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, such as water, chloroform, or toluene. 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/layered silicate nanocomposite.

- *In situ intercalative polymerization method:* In this method, the layered silicate is swollen within the liquid monomer or a monomer solution so the polymer formation can occur between the intercalated sheets. Polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator, or by an organic initiator or catalyst fixed through cation exchange inside the interlayer before the swelling step.

- *Melt intercalation method:* This method involves annealing, statically or under shear, a mixture of the polymer and organically modified layered silicate above the softening point of the polymer. This method has great advantages over either in situ intercalative polymerization or polymer solution intercalation. First, this method is environmentally benign due to the absence of organic solvents. Second, it is compatible with current industrial processes, such as extrusion and injection molding. The melt intercalation method allows the use of polymers which were previously not suitable for in situ polymerization or solution intercalation.

Depending on the strength of interfacial interactions between the polymer matrix and layered silicate (modified or not), three different types of polymer layer silicates (PLS) nanocomposites are thermodynamically achievable, as shown in Fig. 2.4. (Sinha and Okamoto, 2003).

- *Intercalated nanocomposites*: in intercalated nanocomposites, the insertion of a polymer matrix into the layered silicate structure occurs in a crystallographically regular fashion, regardless of the clay to polymer ratio. Intercalated nanocomposites are normally interlayer by a few molecular layers of polymer.

- *Flocculated nanocomposites*: conceptually this is same as intercalated nanocomposites. However, silicate layers are some times flocculated due to hydroxylated edge–edge interaction of the silicate layers.

- *Exfoliated nanocomposites*: in an exfoliated nanocomposite, the individual clay layers are separated in a continuous polymer matrix by an average distances that depends on clay loading. Usually, the clay content of an exfoliated nanocomposite is much lower than that of an intercalated nanocomposite.

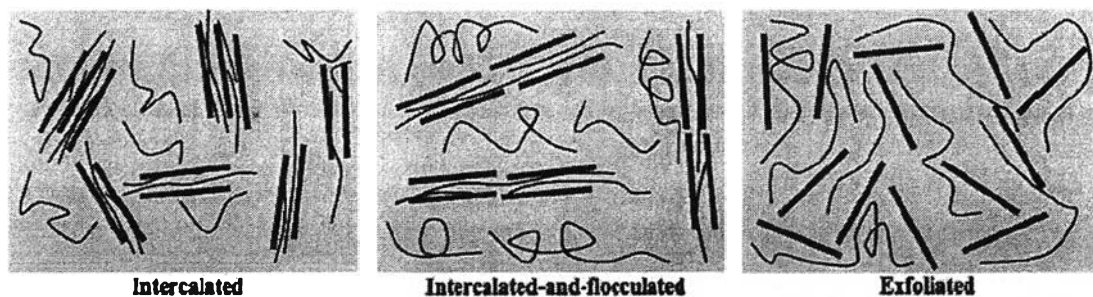


Figure 2.4 Schematically illustration of three different types of thermodynamically achievable polymer/layered silicate nanocomposites (Sinha and Okamoto, 2003).

Polypropylene (PP) is one of the most widely used plastics in large volume which is a fast growing thermoplastic that dominated the industrial applications due to it is relatively inexpensive, easily modified to meet a wide range of thermal and mechanical requirements and suitable for virtually all kinds of processing equipment. However, there are many disadvantages such as low toughness and low service temperature (Ding et al., 2005). Many research efforts focus on the preparation of poly-

propylene-clay nanocomposites. But PP does not include polar groups in its backbone, it was thought that the homogeneous dispersion of the silicate layers in PP would not be realized. Hence, it is frequently necessary to use a compatibilizer such as maleic anhydride modified polypropylene (PP-g-MA). There are two important factors to achieve the exfoliation of the clay layer silicates: (1) the compatibilizer should be miscible with the polypropylene matrix, and (2) it should include a certain amount of polar functional groups in a molecule. Generally, the polypropylenes modified with maleic anhydride (MA) fulfill the two requirements and are frequently used as compatibilizer for polypropylene nanocomposites. However, they have mechanical properties lower than the native polypropylene, due to chain scission during grafting (Lertwimolnum and Vergnes., 2005).

Surlyn is a commercial thermoplastic ionomer resin used in the packaging industry. It is excellent for packaging applications due to its sealing performance, formability, clarity, oil-grease resistance and high hot draw strength. Good hot draw strength allows faster packaging line speeds and reduces packaging failures. Structure-property relationships for nanocomposites formed by melt processing from a series of organoclays and poly(ethylene-co-methacrylic acid) ionomers are studied (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 synthetic routes and materials properties of polypropylene/ montmorillonite nanocomposites are reviewed (Manias et al., 2001). The nanocomposite formation is achieved in two ways: either by using functionalized polypropylenes and common organo-montmorillonites, or by using neat/unmodified polypropylene and a semi-fluorinated organic modification for the silicates. All the hybrids can be formed by solventless melt-intercalation or extrusion, and the resulting polymer/inorganic structures are characterized by a coexistence of intercalated and exfoliated montmorillonite layers. Small additions typically less than 6 wt % of these nanoscale inorganic fillers promote concurrently several of the polypropylene materials properties, including improved tensile characteristics, higher heat deflection temperature, retained optical clarity, high barrier properties, better scratch resistance, and increased flame retardancy.

2.5 Applications of Mesoporous Clay in Adsorbent Materials

The first major challenge for the adsorption field is to select the most promising types of sorbent form and extremely large readily available materials. The usage of natural mineral adsorbents is increasing because of their abundance and low price. Due to the ability to form mesoporous materials with closely reproducible pore size of the PCHs and the ability to control surface properties of the hybrid organic-inorganic PCHs, adsorption properties of these materials obtained from the intercalation of clays attracted the interest. The most extensive work dealt with the adsorption of heavy metals.

Mercier and Pinnavaia (1998) demonstrated the first potential environmental application of a porous clay heterostructure. A heavy metal ion adsorbent that bind Hg^{2+} ions was prepared by grafting 3-mercaptopropyltrimethoxysilane to the intragallery framework walls of a porous fluorohectorite clay heterostructure (PCH) as illustrated in Fig. 2.5. The results revealed that the immobilized thiol groups (up to

67%) were accessible for Hg^{2+} trapping.

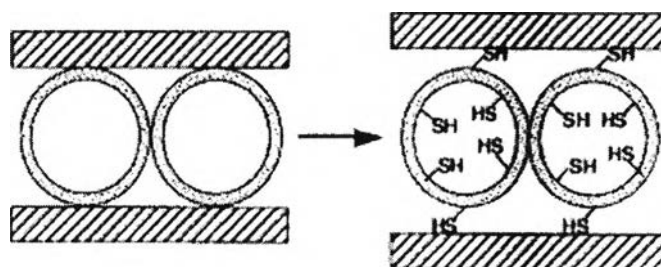


Figure 2.5 Grafting of mercaptopropylsilane groups to the inner and outer walls of mesostructural silica intercalated in smectite clay (Mercier and Pinnavaia, 1998).

The adsorption properties of PCHs have been considered in a number of studies, particularly when considering adsorption process as the recovery of volatile organic compounds or the enrichment of the more valuable fractions of natural or land fill gas. In 2004, Pires *et al.* prepared porous materials from a natural smectite by the gallery templated approach, using a quaternary ammonium cation (CTAB) and neutral amines with different chain length (octylamine and decylamine). The materials prepared in this work, after calcination at 650 °C, had A_{BET} values in the range of 600–700 $\text{m}^2 \text{g}^{-1}$ and micropore volumes near 0.3 $\text{cm}^3 \text{g}^{-1}$. Furthermore, the samples presented pores with widths in the transition between micro to mesopores. The possibility of using such materials as adsorbents of volatile organic compounds, due to their textural and hydrophobic characteristics, was studied by the adsorption of ethanol and methyl ethyl ketone and water for comparison. The data from the adsorption showed that particularly one sample were decylamine was used in the synthesis, has interesting properties regarding the adsorption of VOCs.

Pinto *et al.* (2005) prepared composite adsorbent material supporting pillared clay in a polyurethane foam for application in air filtering systems combining the ability of retaining noxious volatile organic compounds (VOC). The pillared clay was obtained from a natural montmorillonite by pillaring with aluminium oxide pillars. Adsorption isotherms of nitrogen and toluene were determined to evaluate the adsorption capacity of the adsorbent material before and after being support in the polyurethane. The result indicated that the pillared clay presented a decrease of about

97% in nitrogen adsorption capacity and also pronounced decrease in the toluene adsorption capacity. In 2006, they also studied the thermal regeneration of the composite material and the recycling of the adsorbents. The results showed a decrease in the adsorption capacity about 60% after regeneration process. However, the recycling of the adsorbent materials was possible since the adsorption capacity of the recycled material was in fact similar to the initial material before being support in the polyurethane.

2.6 Development of the Ethylene Scavenging System

The quality of food products may deteriorate biologically, chemically and/or physically during distribution and sale. Therefore, the packaging requirements for foodstuffs are more diverse and complex than those for other products. Active packaging, one of the innovative food packaging concepts that has been introduced as a response to the continuous changes in current consumer demands and market trends, can be defined as a type of packaging that changes the condition of the packaging to extend shelf-life or improve safety or sensory properties while maintaining the quality of food (Hong, 2002). It can be classified into active scavenging systems (absorbers) and active-releasing systems (emitter) (Kruigf *et al.*, 2002).

One of the most important active packaging concept as ethylene scavenging is a great interest. Ethylene (C_2H_4) has been recognized as a plant hormone controlling ripening and senescence in fruit and vegetable. If ethylene produced by fresh fruits accumulates in the packaging, it will speed up the respiration rates, reducing product storage life. Because of this, many packaging strategies for fresh fruits sensitive to ethylene seek to avoid ethylene accumulation inside the package, thereby limiting fruit senescence (Paz *et al.*, 2005). A lot of ethylene adsorbing substances are applied. Most of these are supplied as sachets or integrated into films.

There are diversified ethylene scavenging systems. Many supplier offer ethylene scavengers based on potassium permanganate, which oxidizing ethylene to acetate and ethanol. This substance is not integrated directly into food contact materials because of its toxicity. In addition, metal catalyst (e.g. palladium) on activates carbon can effectively remove ethylene. Other scavenging materials are base on in-

clusion of finely dispersed minerals such as zeolites and clays into packaging film. Unfortunately, these packaging films are not capable of adsorbing ethylene sufficiently, although the incorporated minerals may adsorb ethylene (Vermeiren *et al.*, 1999).

In 2005, Kim *et al.*, studied binary adsorption of very low concentration ethylene and water vapor on mordenites (MORs), both in sodium type (NaMOR) and proton type (HMOR). In the binary adsorption, all MOR showed linear adsorption for ethylene in very low concentration range and the amount of ethylene decreased as compared with the adsorption of single component. In case of the single component adsorption, the adsorption isotherm of ethylene on HMOR implied two kind of adsorption sites. The one, such as Bronsted acid site, has strong acidic property and strong interaction with ethylene. Conversely, the another like Si-O-Si and silanol group interact weakly with ethylene.

In the present research work, ethylene adsorbing capacity of packaging films will be enhanced owing to the present of mesoporous structures within the clay layer and this will be also incorporated with organic moiety improving organophilicity of this ethylene scavenger.