

CHAPTER II

LITERATURE SURVEY

2.1 Poly (Ethylene Terephthalate)

2.1.1 General

Poly (ethylene terephthalate), or PET, is a thermoplastic polyester resin that has been widespread commercial product because of its high crystalline melting temperature (270-280°C) and stiff polymer chains.[23] PET has good mechanical strength, toughness, and fatigue resistance up to 150-175°C as well as good chemical, hydrolytic, and solvent resistance. In film applications, PET has outstanding crease resistance and good abrasion resistance. Moreover, the outstanding barrier properties of PET has led to a rapid growth in the use of blow molded bottles for soft drinks, beers, spirits, and other food products. PET also finds use as an engineering plastic where it replaces steel, aluminum, and other metals in the manufacture of precision moldings for electrical and electronic devices, domestic and office appliances, and automobile parts. [24]

2.1.2 Synthesis [24-27]

Poly (ethylene terephthalate) is synthesized from dimethyl terephthalate (DMT) and ethylene glycol (EG) by a two-stage ester interchange process. The first stage involves an ester interchange reaction of DMT, with EG, forming a so-called prepolymer which contains the monomer bis-(2-hydroxyethyl) terephthalate (BHET) and short-chain oligomers. The reactions are heated at temperatures increasing from 150°C to 210 °C and the methanol by-product is continuously distilled off. The second-stage, as the solid polymerization, is further heating to 270-280 °C under vacuum with the catalyst conversion of bis-(2-hydroxyethyl) terephthalate to poly (ethylene terephthalate) and, oddly, ethylene glycol as a by product. The catalyst can be antimony oxide (Sb_2O_3). The schematic of PET synthesis is shown in Figure 2.1

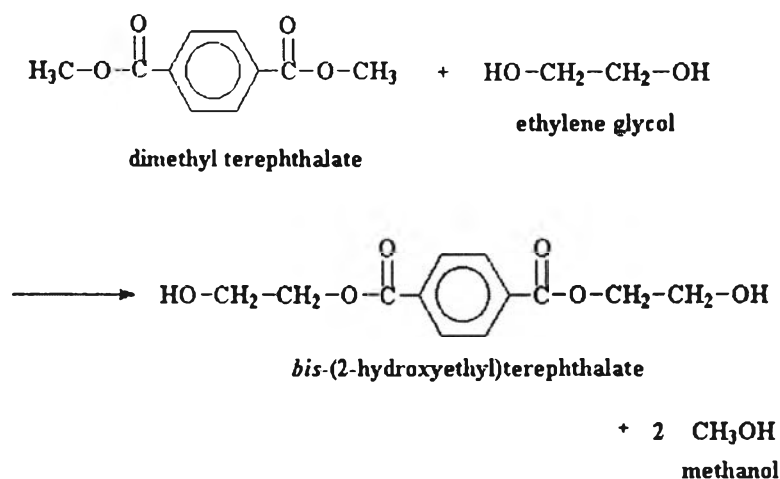
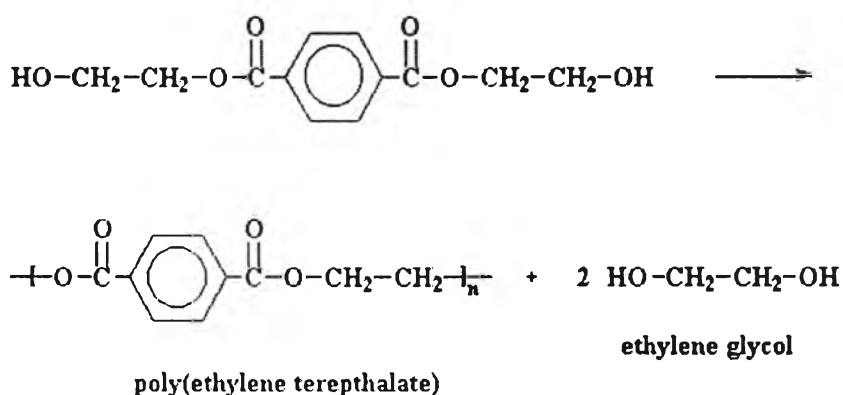
Stage 1**Stage 2**

Figure 2.1 The schematics of two-stage synthesis of Poly(Ethylene Terephthalate) from Dimethyl Terephthalate (DMT) and Ethylene Glycol (EG) [24]

Solid-phase polymerization in the melt temperature range also reduces the formation of extractable oligomers, resulting in a purer higher molecular weight (MW) weight polymer, and the final intrinsic viscosity (IV) can be determined in this phase. IV is another distinguishing characteristic between fiber-, film-, and bottle-grade PET resins. IV, a measure of molecular weight differences, ranging from 0.62 to 1.04 for clear PET resins. [20] The PET resin may be classified as low-viscosity or high-viscosity resins. Low-viscosity PET typically has an intrinsic viscosity of less than 0.75, while high-viscosity PET typically has an intrinsic viscosity of 0.9 or higher. Low-viscosity resins, which are sometimes referred to as "staple" PET (used in textile applications), are used in a wide variety of products, such as apparel fiber, bottles, and photographic film.

High-viscosity resins, sometimes referred to as "industrial" or "heavy denier" PET, are used in tire cord, seat belts, and the like. [24]

2.1.3 Properties

Within the group of engineering thermoplastics, the polyesters have some unique properties that lead to use in applications which are not readily filled by other engineering thermoplastics.

The thermal property measurements have shown that virgin PET has a melting temperature at 280°C, but for commercial PET, it is between 255 and 265°C. This reduction is due to the chemical impurities during production. The impurity, usually a by-product, resulted from diethylene glycol, which acts as a co-monomer in further stages of polymerization. [25] The specific gravity is 1.33 for normal and 1.39 for highly oriented crystalline PET. The average molecular weight (MW) of injection-mold PET is around 80,000, which is higher than the range for fiber production. High-molecular-weight PET improves the mechanical properties, especially the impact strength. Other physical properties are shown in Table 2.1. For the chemical properties, PET is one of the thermoplastic polymers that are highly resistant to a wide range of organic solvents, such as alcohol, water, ketones, etc. Table 2.2 is listed the chemical resistance of Poly (ethylene terephthalate).

Table 2.1 Summary of properties of PET [20]

Property	Value
Specific gravity	1.37
Melting temperature (°C)	
Equilibrium	280 (310)
Commercial PET	255-265
Glass transition temperature (°C)	67-140
Heat deflection temperature (°C)	
At 0.46 MPa	115
At 1.82 MPa	85
Water absorption at 23°C (%)	
After 24 h	0.08
At equilibrium	0.60
Tensile strength (MPa)	53
Tensile elongation (%)	300
Flexural strength (MPa)	114
Compressive strength (MPa)	8
Shear strength (MPa)	55
Izod impact strength (notched) J/m ²	43
Izod impact strength (unnotched) J/m ²	No break
Rockwell hardness	M106

Table 2.2 Summary of properties of PET (Chemical resistance) [28]

Reagent	Value
Acid- Concentrated	Good
Acid- Diluted	Good
Alcohol	Good
Alkali	Poor
Aromatic Hydrocarbon	Fair
Greases and Oil	Good
Halogen	Good
Ketone	Good

2.1.4 Applications

PET has been used widespread in commercial application in the packaging industry due to its low cost, clarity, and good barrier properties. [24] When biaxially oriented, it is suitable for various applications, including blow-molded containers. In addition PET also used in the packaging industry application that requires high levels of rigidity and dimensional stability, particularly at elevated temperatures.

This resin has been used extensively in three major product types [21] —fibers, films, and molding resins. The fibers have been used for textile applications, where the polyester gives wrinkle resistance, permanent pleat capability, and staining resistance to the fabric. Fibers made from polyester are also used as reinforcements in tires, conveyor belts, and hoses, especially where hot water is likely to be present making nylon inappropriate.

PET films are used extensively because of their ruggedness and clarity. The films are used as magnetic tapes, substrates for photographic films, release films, drawing foils, and sterilizable packaging for medical, because of the high operating temperature capability of PET, and other applications. A copolymer of PET with a modified glycol is available as a film that is completely amorphous and has improved processing. This copolymer is called PETG.

To use as blow molding application, PET made for soft drink bottles requires that the resin be tough (so that it can withstand a drop), inexpensive, and have a low permeability to carbon dioxide. PET is a reasonable compromise and has performed well in this application. The use of PET for soft drink bottles has increased its use in other bottle applications, some where permeability is not a major issue. The clarity and durability of PET, along with the excellent odor resistance have led to many of these applications.

2.2 Nanoscale Filler: Montmorillonite

2.2.1 General [29-32]

Mineralogists use the term "clay minerals" for a group of hydrous layered magnesium- or aluminosilicate (phyllosilicate). Each magnesium- or aluminosilicate is essentially composed of two types of sheets, octahedral and tetrahedral, designated O and T, respectively. Each sheet is composed of planes of atoms, arranged one above the other, a plane of hydroxyls and/or oxygens above a plane of aluminums and/or magnesiums or silicons, the latter above another plane of hydroxyls and/or oxygens, and so on. Variations among clay minerals and the differences in their physical and chemical properties arise from the various combinations of octahedral and tetrahedral sheets and the electrostatic effects that chemical substitutions have on the units. [29]

Silicate clay minerals are called aluminosilicates, which have a layered structure, and consist of silicon tetrahedral bonded to aluminium octahedral sheet in a variety of ways. They are classified into "layer types", differentiated by the number of tetrahedral and octahedral sheets that have combined.

(1) The 1:1 layer type consists of one tetrahedral sheet fused to an octahedral sheet. It is represented in Figure 2.2(a) by the kaolinite group. Kaolinite is the most common of this group and has the chemical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$.

(2) The 2:1 layer type has two tetrahedral sheets fused to an octahedral sheet. Four clay mineral groups having this structure are Pyrophyllite, Illite, Vermiculite, and Smectite. It is represented in Figure 2.2(b)

The majority of the interest presently centered on the phyllosilicate mineral, principally the smectite group.

Mineral in the smectite group (sometimes known as a montmorillonite group) is characterized by its expandable properties. Unlike the other clays, only smectite can absorb toxins. This qualifies its structural uniqueness and sets it apart from all other clays. For this reason, smectite has become a favorite clay for industrial and dietary use.

The most familiar species of smectite is montmorillonite, with a general chemical formula is $(\frac{1}{2}\text{Ca},\text{Na})(\text{Al},\text{Mg},\text{Fe})_4(\text{Si},\text{Al})_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ [32]

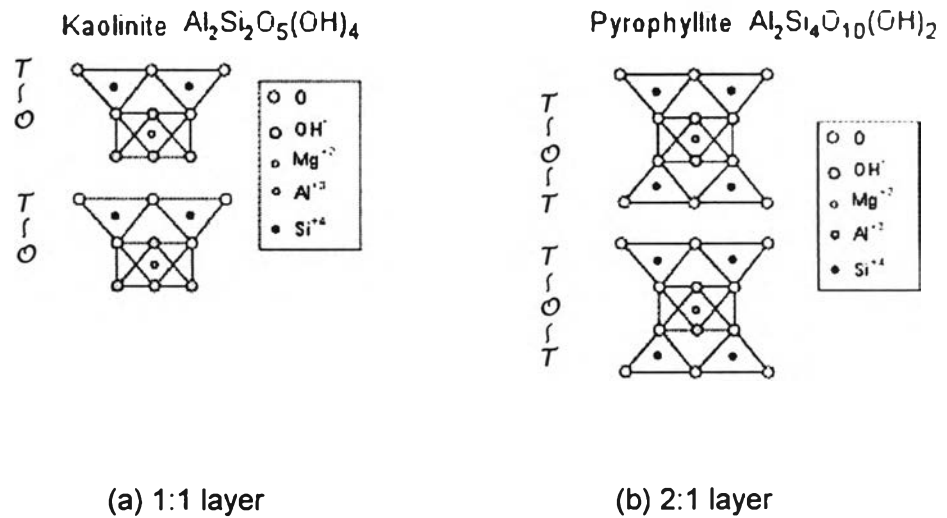


Figure 2.2 Crystal structure of (a)1:1 and (b)2:1 layer type clay minerals [30]

2.2.2 Montmorillonite

Montmorillonite has a 2:1 layer structure (TOT). All tetrahedral in the sheets contain Si^{4+} ions. Aluminium is the normal ion in the central sheet, but about one-eighth of the octahedral contain Mg^{2+} as a substituting ion for Al^{3+} . Parallel TOT layers are packed one above the other and the exchangeable hydrated cations are located between the layers. The diagrammatic sketch of the structure of montmorillonite is shown in Figure 2.3.

However, the force of bonding between cations and the sheets is not very strong and depends on the amount of water present. In dry montmorillonites the bonding force is relatively strong. When wet conditions occur, water is drawn into the interlayer space between sheets and causes the clay to swell dramatically (expanding clay).

The thickness of the silicate unit is approximately 10 \AA .[30] In addition to its already unique structure, montmorillonite has a particularly large surface area when properly hydrated in water, which further boosts its adsorptive and absorptive properties. Montmorillonite is more complicated clay and has a higher exchange

capacity than the simpler species of clay, such as kaolinite. Its ability to adsorb and absorb is greater than that of the clays in the other groups.

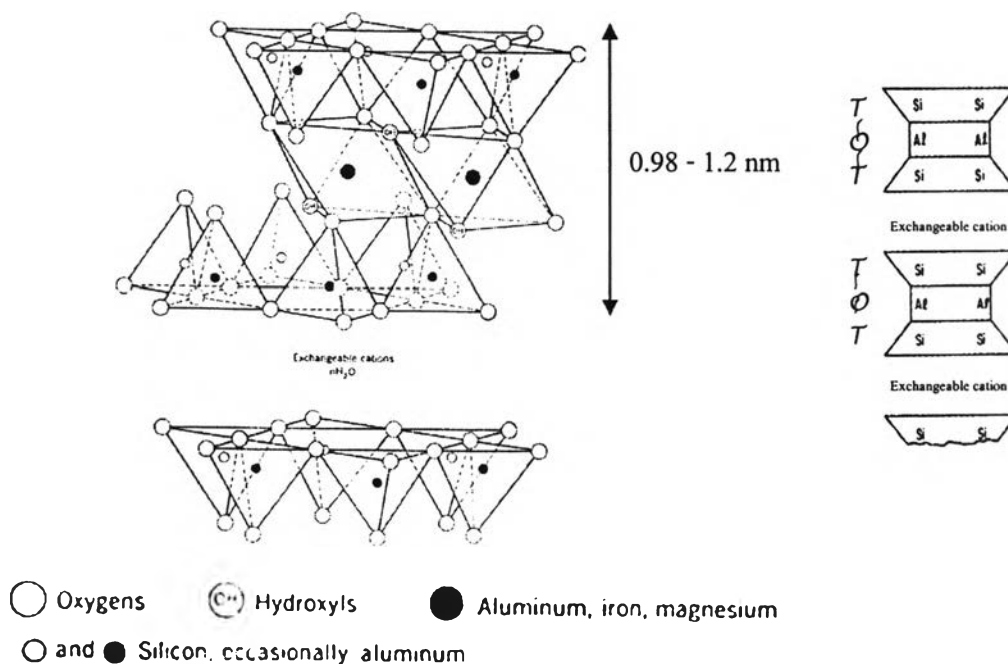


Figure 2.3 Schematic representation of typical montmorillonite structure [31,34]

Water and polar organic molecules are attracted by the exchangeable cations and may intercalate between the layers, causing the structure to expand in the direction perpendicular to the layers. The interlayer space between the TOT layers, obtained as a result of the expansion of the clay, has special chemical properties.[29] The swelling of this space depends on several factors, such as the type of exchangeable interlayer cation present, the concentration of ions in the surrounding solution, and amount of water present in the soil. [34] The basal spacing may vary from 1000 pm (for dry smectites) to more than 2000 pm.

The common property of montmorillonite is that there are hydrophilic and the stacking of the clay platelets is held tightly together by electrostatic force. As shown in the Figure 2.3. The exchangeable counterions, aluminium sodium or magnesium ion, are attracted to the net negative charge within the clay platelets. Because polymer is

generally organophilic, unmodified clay disperses in polymers with great difficulty. That would be essential to improve the dispersibility of clay in polymer matrix. Due to the unique characteristic, montmorillonite can be swelling or dispersing in water or organic molecule via "ion- exchange reaction" by the interlayer cation. In the case of exchange with organic molecule the final product is called "Organo-clay".

2.2.3 Clay Modification

The method to modify clay is called ion exchange reaction. From the unique characteristic of clay, the varieties exchangeable cations can be held around the outside of the silica-alumina clay mineral structural units. And the exchange reaction generally does not affect the structure of the silica-alumina packet [31]. However, the exchangeable cations have difference ability to exchange with other cations because of the cation exchange capacity properties (CEC) of clay itself. The property of CEC is the maximum amount of any one cation that can be taken up [3] because cations retained electrostatically are easily exchangeable with other cations in the soil solution and are thus readily available for plant uptake. Thus, CEC is important for maintaining adequate quantities of plant available calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^+) in soils. Other cations include Al^{3+} (when $\text{pH} < 5.5$), Na^+ , and H^+ .

Cation Exchange Capacity can be expressed two ways:

- The number of cation adsorption sites per unit weight of soil or,
- The sum total of exchangeable cations that a soil can adsorb.

Soil CEC is normally expressed in units of charge per weight of soil. Two different, but numerically equivalent sets of units are used: meq/100 g (milliequivalents of element per 100 g of dry soil) or cmole/kg (centimoles of charge per kilogram of dry soil).[35]

The unit of milliequivalents (meq) per 100 g of oven dry soil is used to better reflect that it is the *charge* in the soil that determines how many cations can be attracted. The range of the cation-exchange capacity of the clay minerals is given in Table 2.2.

Table 2.3 Cation-exchange capacity of the clay minerals [31]

Clay mineral	cation-exchange capacity (in mqv per 100 grams)
Kaolinite	3-15
Halloysite. 2H ₂ O	5-10
Halloysite. 4H ₂ O	10-40
Montmorillonite	80-150
Illite	10-40
Vermiculite	100-150
Chlorite	10-40
Sepiollite-Attapilgite	20-30

2.2.3.1 Cation exchange reactions with organic ions [35]

Clay mineral-organic complexes can be formed by ion-exchange reactions. Basic organic compounds that ionise in aqueous solution may also replace other cations on clay surfaces. Amines, for example, may react with calcium clays:



In the above equation, R stands for an alkyl or aryl group. Whatever the nature of the original counterions, replacement of the original counterions by an amine invariably results, in aqueous suspensions, in the clay being strongly flocculated, possibly because the amine is strongly attracted to the stern layer. Another explanation may be that since the amine is adsorbed with the NH₃⁺ group close to the surface, the alkyl or aryl group R projecting outwards, the surface presented to the suspending medium is effectively an 'organic' surface and is therefore hydrophobic; thus, they may be polymerized with a variety of organic compounds. In addition, the organic cation may contain various function groups that can react with the polymer matrix to improve the interaction between two phases. The most popular surface treatment is to ion exchange the clay with organic ammonium cations, which not only render its surface more hydrophobic, but also expand the spaces between the silicate layers.[9] The

schematic of ion-exchange reaction of montmorillonite with quaternary ammonium cations is shown in Figure 2.4 and the evidence that presents the difference in the d spacing of modified montmorillonite with increasing the length of the alkylammonium chain using the XRD is shown in the Figure 2.5 below.

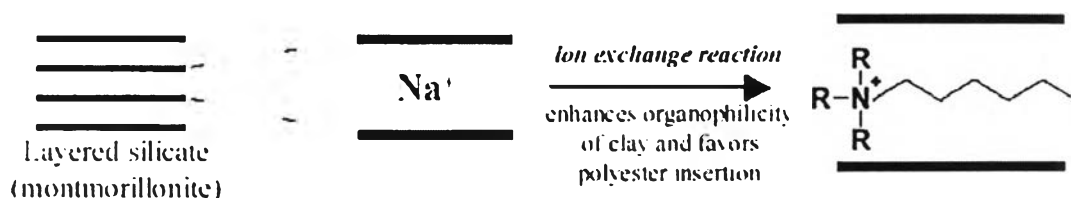


Figure 2.4 The schematic of ion-exchange reaction of montmorillonite with quaternary ammonium cations [19]

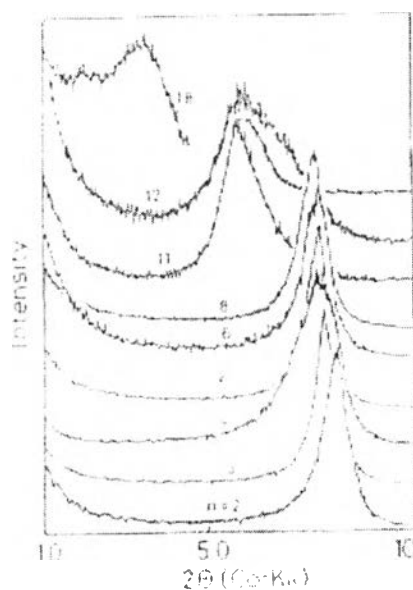


Figure 2.5 X-ray diffraction patterns of n-montmorillonite as the length of the alkylammonium chain length increases.[19]

Most of the studies are devoted to the modification and characterization of organophilic-clay as used in the function of nanofiller for polymer nanocomposites. In the early stage, organic compound of bentonite (clay) was prepared by Jordan in 1949 [6]. The expansion of silicate layer depended on the length of hydrocarbon. The expansion of layer was multiple of 4 Å, which was about the thickness of one

hydrocarbon chain. Moreover, the swelling ability of organic bentonite in various organic solvents was studied. Binary solvents showed better achievement to swell the organic compound of bentonite than monosolvent systems.

Several years later, in 1997, Jin-Ho Choy *et al.* [7] reported the dispersion 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 of the modifying agent and type of solvents.

Recently, in 2003, D.Merinska *et al.* [4] presented the good result of montmorillonite (MMT) modification with octadecylamine (ODA) and stearic acid (STA) as co-intercalation. The result of co-intercalation process is increasing of d spacing from approximately 0.9 nm of unmodified MMT to 4.8 nm and the suitable MMT: ODA: STA ratio is 1:0.5:0.5 which gives the highest level of exfoliation.

Later in 2004, A. Sánchez-Solis *et al.* [8] discussed about the influence of intercalation agent on the structure of MMT. The Wide Angle X-ray Diffraction (WAXD) patterns showed the basal spacing of MMT with various intercalation agents. The basal spacing of MMT was increased by the organo-modification. For a certain type of intercalation agent, the basal spacing of organo-modified MMT increased with the length of the alkyl group in an intercalation agent.

2.3 Polymer-Clay Nanocomposite

2.3.1 Composites [37-39]

A composite in engineering sense is any materials that have been physically assembled to form one single bulk without chemical blending to form a homogeneous material. The resulting material would still have components identifiable as the constituent of the different materials. One of the advantages of composite is that two or more materials could be combined to take advantage of the good characteristics of each of the materials.

Usually, composite materials will consist of two separate components, the matrix and the filler. The matrix is the component that holds the filler together to form the bulk of the material. The various matrix materials have been used either commercially or in research such as thermoplastic, thermoset, metallic and ceramic. Metallic and ceramic matrices are considered primary for high-temperature application. [3] The filler is the material that has been impregnated in the matrix to lend its advantage (usually strength) to the composite which added primarily to increase the strength and stiffness of the matrix.[38]The fillers can be of any material such as carbon fiber, glass bead, sand, or ceramic.

The main advantage of most composites materials are in the weight savings. A quick way to illustrate this advantage is in the strength to weight ratio. Different materials have different strength that is each material can take different of amount of load for the same volume (cross sectional area) of the material. For a given design, the material used must be strong enough to withstand the load that is to be applied. If a material selected is not strong enough, the part must be enlarged to increase the load bearing capacity. But doing so increases the bulk and weight of the part. Another option is to change material to one that has high enough strength to begin with.

The advantages extend not only to aircraft but to everyday activities also, such as longer drives with a graphite-shafted golf club (because more of the mass is concentrated in the club head) and less fatigue and pain because a graphite composite tennis racquet has inherent damping. Generally the advantages accrue for any fiber composite combination, whereas the disadvantages are more obvious with certain combinations. Proper design and material selection can avoid many of the disadvantages.

The major classes of the structural composites can be categorized as follow [38-39]

- Polymer Matrix Composites (PMCs); also known as FRP: Fibre Reinforced Polymers (or Plastics). PMCs are the most developed class of composite materials in that they have found widespread application, can be fabricated into large,

complex shapes, and have been accepted in a variety of aerospace and commercial applications. They are constructed of components such as glass, carbon, aramid or boron fibers bound together by an organic polymer matrix.

- Metal Matrix Composites (MMCs); These composites consist of metal alloys reinforced with continuous fibers such as silicon carbide, whiskers (a version of short fibers that are in the form of single crystals), or particulates (fine particles, as distinct from fibers). Because of their use of metals as matrix materials such as aluminium, they have a higher temperature resistance than PMCs but in general are heavier. They are not as widely used as PMCs but are finding increasing application in the automotive industry.

- Ceramic Matrix Composites (CMCs); CMCs used in very high temperature environments because the monolithic ceramic materials have a natural high-temperature resistance but also have fundamental limitations in structural applications owing to their propensity for brittle fracture. The incorporation of reinforcement, for example, ceramic fiber reinforcement, into the ceramic matrix can improve the forgivability of the material by allowing cracking to be retarded by the fiber-matrix interfaces. CMCs are a class of structural materials with reinforcements such as SiC fibers embedded in a ceramic matrix such as Al_2O_3 , Si_3N_4 , or SiC. The reinforcements can be continuous fibers, chopped fibers, small discontinuous whisker platelets, or particulates. They have the potential for high-temperature application above 1649°C .

- Carbon-carbon composites (CCCs); CCCs consist of carbon fiber reinforcements embedded in a carbonaceous matrix. Preliminary processing is very much like that for PMCs, but the organic matrix is subsequently heated up to the point where it is converted to carbon. Carbon-carbon is a superior structural material for applications where resistance to very high temperatures and thermal shock is required. No other material has higher specific strength properties (strength-to-density ratio) at temperatures in excess of 1371°C .

- Intermetallic composites (IMCs); IMCs are currently of extreme interest for use in future high-temperature, high-efficiency, high-performance gas turbine

engines for both civil and military applications. Both of the reinforcement and the matrix are metal, for example, regarding the SiC fiber in aluminide matrices or SCS-6 fiber-Ti₃Al + Nb matrix system for more complicity IMCs. By going the composite route, the low density of the intermetallic compounds can be utilized to good advantage, and if low-density, high-strength fibers are available, the low strength of intermetallic matrices becomes less of an issue. Although, one of the major problems facing the successful development of IMCs is the compatibility between fiber and matrix both from chemical viewpoint and from the mismatch in CTE.

- Hybrid composites materials (HCMs); Hybrid composite materials represent the newest of the various composite materials currently under development. HCM is defined as a composite material system derived from the integrating of dissimilar materials at least one of which is a basic composite material. The hybrid composite category covers both the hybridizing of a composite material with other materials (either other composites or base unreinforced materials) and composites using multiple reinforcements. An existing example of a hybrid composite is an aramid-reinforced aluminum laminate (ARALL), which consists of high-strength aluminum alloy sheets interleaved with layers of aramid fiber-reinforced adhesive as illustrated in Figure 2.6. A second example of a hybrid composite is a Carbon-Carbon Composite (CCC) with a single side application of the refractory metal rhenium; carbon-carbon-rhenium material which being developed for thermal management heat pipes on space-based radiator systems. Other examples include interpenetrating polymer networks (IPNs), which are hybrid resin matrices consisting of thermoset and thermoplastic resin combinations. Other HCMs include new composite materials such as nanocomposites, functionally gradient materials (FGMs), hybrid materials (hymats), interpenetrating polymer networks (IPNs), microinfiltrated macrolaminated composites (MIMLCs), and liquid crystal polymers (LCPs).

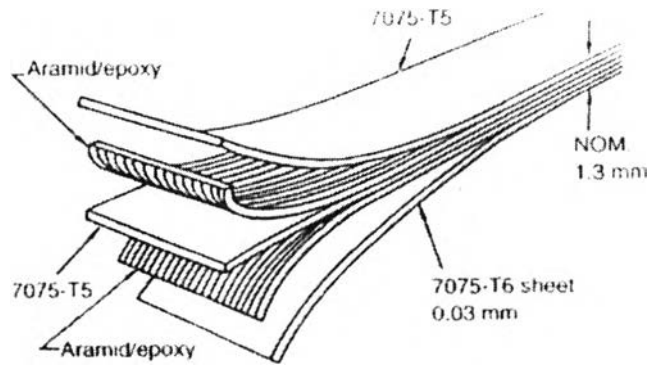


Figure 2.6 ARALL is an example of a hybrid composite material.[39]

Many different materials have been used to reinforce composites. The most popular are the fibers. Flake and particulate materials have also been used to reinforce polymer matrices. A fairly new area of composites has merged in which the reinforcing material has dimensions of less than or equal to one billionth of a meter, or one nanometer. Such a composite is called a nanocomposite. Very few nanocomposites have actually been developed to the point of commercial application, but their potential has produced a frenzy of research. [40]

2.3.2 Nanocomposites[41-43]

A polymer-clay nanocomposite is a polymer that contains nanometer sized clay particles. Such a nanocomposite can have favorable properties, like high stiffness and barrier resistance. The best properties are obtained if the clay is fully exfoliated into single clay layers with a thickness of about one nanometer and a diameter of 20-500 nanometers.

During exfoliation, the clay particles do not only become much smaller but simultaneously their shape changes from cubical blocks to flat platelets. The shape of clay platelets is usually expressed in its aspect ratio. This is the ratio between the diameter and the thickness of a platelet.

Because of their small dimensions, the clay platelets have a large specific surface area of about $700 \text{ m}^2/\text{g}$. Their small size also results in small inter platelet distances in a polymer-clay nanocomposite. At a loading of one weight percent of clay

these distances are about 250 nanometers while they are merely 10 nanometers at a loading of 20 weight percent.[41]

These nanocomposites possess a unique combination of properties with relatively high strength and stiffness, high barrier resistance, good flame retardancy and processibility similar to unfilled polymers with much lower filler contents than used in conventional polymer compounds [19]. Nanocomposites also offer extra benefits like low density, transparency, good flow, better surface properties, improved dimensional stability and recyclability. [42]

In the areas of application, such mechanical property improvements have resulted in major interest in nanocomposite materials in numerous automotive and general/industrial applications. These include potential for utilization as mirror housings on various vehicle types, door handles, engine covers and intake manifolds and timing belt covers. More general applications currently being considered include usage as impellers and blades for vacuum cleaners, power tool housings, mower hoods, and covers for portable electronic equipment such as mobile phones, pagers etc.[43]

2.3.3 Types of Polymer-Clay Nanocomposites[44]

There are several types of polymer-clay nanocomposites that can be classified, from a structural point of view, polymer-clay composites can be generally classified into 'conventional composites' and 'nanocomposites'. In a conventional composite the registry of the clay nanolayers is retained when mixed with the polymer, but there is no intercalation of the polymer into the clay structure as seen in Figure 2.7 (a).

The resulting polymer-clay nanocomposites can have several structures, as shown in Figure 2.7. The first possible structure is an intercalated nanocomposite that means a regular insertion of the polymer chain between the clay layers; (Figure 2.7 (B)) .The structure of an intercalated nanocomposite is a tactoid with expanded interlayer spacing, however, the clay galleries have a fixed interlayer spacing. Another possible structure is an exfoliated nanocomposite which is formed when the individual clay layers

break off the tactoid and are either randomly dispersed in the polymer (an ordered nanocomposite) (Figure 2.7 (C)) or left in a disordered array (Figure 2.7 (D)).

The exfoliated or delaminated structure maximizes the polymer-clay interactions, dramatically changing the properties of the final nanocomposite.[9-10] Because the properties of nanocomposite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics. [45-46]

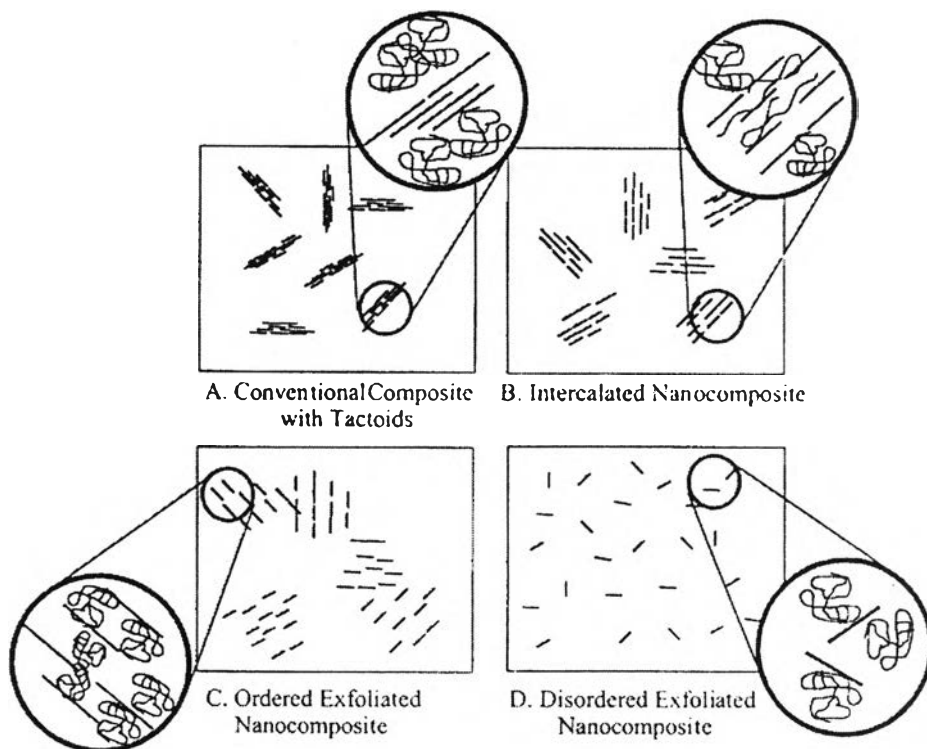


Figure 2.7 Schematic of microstructures that can develop in clay-filled polymer composites: (A) a conventional composite with tactoids, (B) an intercalated nanocomposite, (C) an order exfoliated nanocomposite, (D) a disordered exfoliated nanocomposite [19]

2.3.4 Processing[19,45]

The objective of polymer-clay nanocomposites fabrication is to uniformly disperse and distribute the inorganic (initially comprised of aggregates of the nanoparticles) within the polymer. The final polymer-clay nanocomposites structure

results from the transformation of an initially microscopically heterogeneous system to a nanoscopically homogenous system. In general, the organically modified clay can be intercalated with polymer by several routes;

1. Solution processing involves dispersion of both the organically modified clay and the polymer in a common solution. Variations on this process include emulsion or suspension polymerization. Highly polar polymers such as Nylon and polyimides [12] are more easily intercalated than nonpolar polymers such as polypropylene, because polar polymers have a higher affinity for the polar clay galleries. Especially the alkyl-ammonium ion treated nanoclays have the capability to swell very well in organic solvents, so that the incorporation of the nanoclay into the solvent is very easy even at room temperature.

2. In situ polymerization intercalates monomer directly into the organically modified clay galleries, and the monomer can either adsorb onto the layer surface or be anchored by free radical techniques. [9] This is the conventional process used to synthesize thermoset-clay nanocomposites. The nanoclay is first swollen in the monomer, after that the reaction can be initiated either with a curing agent or simply increasing the temperature depending on the system. In this way the monomer diffuses between the nanoclay layers, and when polymerization starts the polymer chains grow, dividing the nanoclay platelets and realizing the nanocomposite. Polymer-clay nanocomposites based on epoxy, unsaturated polyester, polyurethanes and polyethylene terephthalate have been synthesised by this method.

3. Melt intercalation involves mixing the clay and a polymer melt, with or without shear. The success of melt intercalation is surprising, given that the gallery spacing is only about 2 nm and the radius of gyration of the polymer is significantly larger than this. Even more surprising is that the speed of melt intercalation is faster than that of self diffusion of polymers and scales with the inverse of the molecular weight.

The schematic of the basic three steps in processing clay-filled polymer (nano) composite is shown in figure 2.8

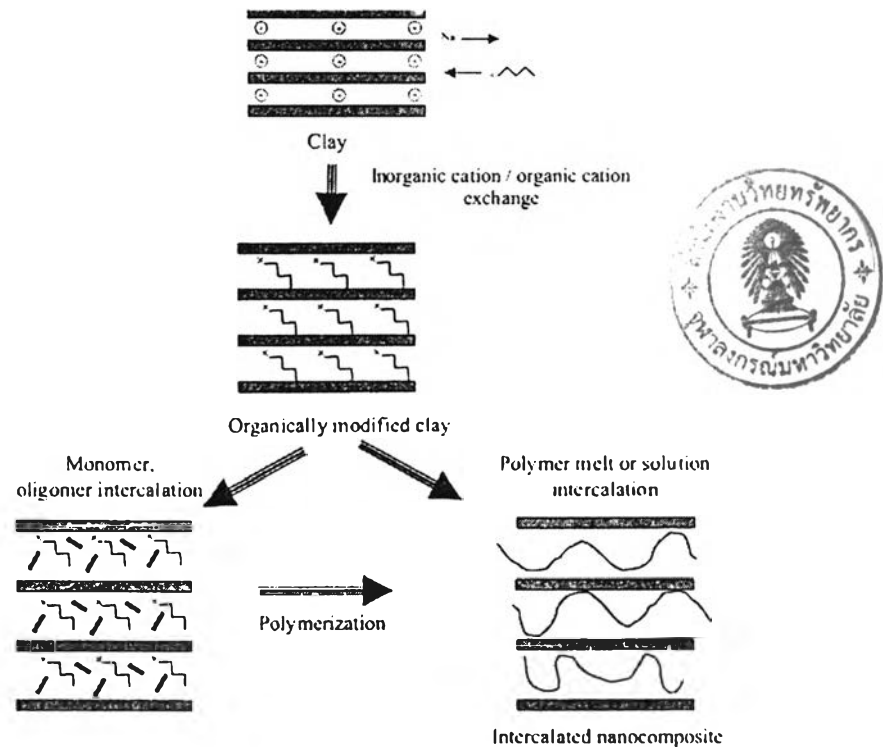


Figure 2.8 The schematic of the basic step in processing clay-filled polymer[19]

2.3.5 Properties of nanomposites [19,48-49]

Many researchers have found that polymer composites containing small amounts of nanosize clay articles (silicates, e.g. montmorillonite) possess unusual mechanical properties relative to their parent materials. In addition, these hybrid materials were found in many cases to tolerate higher temperatures than traditional polymer/particle composites. Nanoparticle reinforcement increases the polymer-particle interfacial surface area by orders of magnitude relative to conventional reinforcing particle sizes. The increased surface area increases the volume fraction of polymer that may have decreased segmental motion due to surface pinning (formation of a constrained layer). It has been hypothesized that the polymer close to the particle surface has an effective shift in the polymer's glass transition temperature, leading to lower permeability and altered thermomechanical properties.

The incorporation of nanoscale clays into polymeric matrices has been shown to yield improve barrier properties, increased mechanical properties, and better fire

resistance properties, relative to the unfilled polymer. However, these materials typically require chemical treatments of the clays to provide the exfoliated dispersions that are critical to achieve the noted improved properties. Development of successful surface treatment of silicate nanoparticles is non-trivial, and must be specifically tailored to each polymer type.

- Mechanical properties

Plate-like fillers can also increase the modulus of a polymer significantly. A comparison of the upper bound modulus prediction (assuming incompressibility) shows that the modulus for well-aligned platelets can be three times that for well-aligned fibers. In addition, there is direct evidence that nanoclay carries load; for example, as the aspect ratio of the clay layers increases, the modulus increases. Some indirect evidence also shows that the stiffness of the clay layers affects the modulus (e.g., a stiffer filler leads to a higher composite modulus). Neither of these observations is surprising if the clay platelets are carrying load. Other studies, however, suggest that the modulus increase is not entirely due to the load-carrying ability of the platelets, but is caused by the volume of polymer constrained by the platelets. This suggests that, to optimize the increase in modulus, the degree of dispersion must be optimized to maximize the degree of matrix/filler interaction.

The addition of rigid micrometer-scale fillers to a polymer often increases its strength, but decreases the toughness. This tradeoff is a significant technical problem for commercial applications of filled polymers. The reason for the decrease in ductility is straightforward: the fillers or agglomerates act as stress concentrators, and the defects initiated at the filler quickly become larger than the critical crack size that causes failure.

Well-dispersed nanoparticles are much smaller than the critical crack size for polymers and need not initiate failure. Thus, they provide an avenue for simultaneously toughening and strengthening polymers.

- Glass Transition and Relaxation Behavior

As know that the interfacial region is extremely large in nanocomposites. The interaction of the polymer with the nanoparticles gives significant opportunity for changing the polymer mobility and relaxation dynamics. For example, polystyrene chains intercalated between the layers of a smectic clay have more mobility locally than in the bulk polymer. This greater mobility may be due to an ordering that occurs between the layers, which creates low- and high-density regions, thus providing the opportunity for mobility in the low-density regions. If, however, the polymer is tethered to the clay, the relaxation spectra broaden to include slower relaxation times, suggesting that the clay can reduce the mobility locally. Recent work on silica/polyvinylacetate nanocomposites indicates that, for equi-axed particles, the overall effect of the filler is to create a weak network structure that contains both physical entanglements in the matrix phase and 'trapped' entanglements arising from temporary bonds to the filler particles. This suggests a greater far-field effect of altering chain dynamics than simply a local immobilization of the polymer chain. Another example of altered mobility was found for gold particles dispersed in poly(tert-butylacrylate). For particle sizes <10 nm, the viscosity of the low molecular weight polymer at 30 vol. % filler increased by a factor of 4 [315]. The authors claim this result is due to bridging of the polymer chains between the particles. The bridges have relatively long lifetimes and decrease segmental motion at the interface compared to the bulk.

Although the specific mechanics of chain dynamics are not yet completely understood, it is very clear that the rheology/glass transition temperature of a polymer can be controlled by changing the polymer mobility with nanocomposite interfaces. For example, the glass transition temperature can be eliminated for clay nanocomposites with intercalated polymer chains. This indicates a limited ability for cooperative chain motion when the polymers are confined between the layers. If the clays are exfoliated, and thus the polymer is not confined between layers, the T_g does not change significantly.

Without the help of confinement, the T_g can be increased if the polymer is tightly bound to the nanofiller. Increases of 10° have been observed for clay-filled Nylon, PMMA, and PS, as well as for polyimide composites. The behavior is not limited to clays.

The T_g can decrease if the interaction between the filler and the matrix is weak. This decrease in T_g was recently given more attention in nanoalumina/PMMA composites, where it was found that the T_g did not decrease until a critical volume fraction was reached. Furthermore, changing the particle surface and making it compatible with the matrix eliminated the T_g depression.

- Abrasion and Wear Resistance

Although it is well known that the abrasion resistance of filled polymers depends on particle size, the incorporation of nanoscale fillers has led to unexpected results. For filler particles that are larger than the abrasive particles, most of the filler particles are stable and increase the abrasion resistance of the composite. This does not happen on the nanoscale. In addition, nanoparticles can simultaneously improve wear resistance and decrease the coefficient of friction.

- Permeability

Platelet particles enhance barrier (reduce gas permeability) of polymers according to a tortuous path model, developed by Nelson, in which the platelets obstruct the passage of gases and other permeates through the matrix polymer. The barrier improvement is predicted by this model to be a function of the volume fraction of platelets (ϕ) and a function of the aspect ratio of the platelets (α) with higher aspect ratios providing greater barrier improvement according to the following equation for permeability:

$$P_{\text{nanocomposite}} = \frac{(1 - \phi) P_{\text{polymer}}}{1 + \alpha\phi/2}$$

or total path of a diffusing gas

$$d' = d + \frac{d\phi}{2\alpha}$$

Where $P_{\text{nanocomposite}}$ represents the permeability of the resulting nanocomposite, P_{polymer} represents the permeability of the matrix polymer, d represents thickness and d' represents the tortuosity path of diffusing gas. An illustration of the tortuous path model for barrier enhancement is presented in Figure 2.9

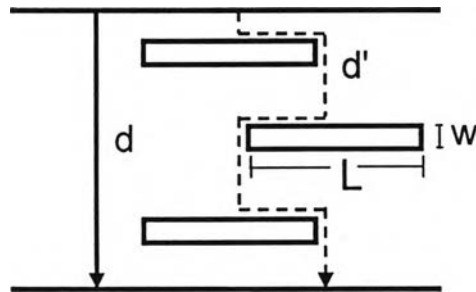


Figure 2.9 Illustration of Neilson's tortuous path model for barrier enhancement of nanocomposites. P_{matrix} represents the permeability of the matrix polymer in the absence of the platelets, and $P_{\text{nanocomposite}}$ represents the tortuous path created by the platelets. [44]

Figure 2.9 shows schematically how the tortuous pathways through an exfoliated polymer/clay nanocomposite can improve barrier properties, chemical resistance, and reduce solvent permeability because of the hindered diffusion. Figure 2.9 concerns the case of an oriented, exfoliated polymer/clay nanocomposite system. Orientation of plates along a plane normally occurs due to processing conditions. However, one also can envision a case where the plates are randomly oriented, and in this latter system, the tortuous path is even greater. As study on Nylon 6 nanocomposites the Oxygen Transmission Rate was reduced 80% with 8 wt.% modified-montmorillonite [47].

- Thermal Stability and Flammability

The dispersion of the clays is critical to increasing the degradation temperature. Exfoliated composites have significantly higher degradation temperatures than intercalated nanocomposites or traditional clay composites [14]. Some speculate

that this increase in stability is due to the improved barrier properties of the composites. If oxygen cannot penetrate, then it cannot cause oxidation of the resin. In addition, the inorganic phase can act as a radical sink to prevent polymer chains from decomposing. The improved thermal stability of some composites may be limited by the lower thermal stability of alkylammonium ions.

- Optical Clarity

A limitation in the development of optical composites or transparent nanocomposites with improved mechanical or electrical performance is minimizing light scattering due to the presence of the particles. The scattering power for light propagation through a collection of scattering particles can be predicted by Rayleigh scattering:

$$P_{\text{scat}} = 24 \pi^4 P_0 \rho ((n' - n)/n^2)^2 (V^2 / \lambda^4)$$

Where P_0 is the incident power, ρ is the concentration of particles, n' is the refractive index of the particles, n is the refractive index of the matrix, V is the volume of a single particle, and λ is the wavelength of light. Therefore, to minimize scattering, the particles must be as small as possible with an index of refraction as close as possible to that of the matrix material. This equation assumes, however, that the particles are much smaller than the wavelength of light. Relatively good optical clarity has been obtained in many nanocomposites, particularly at low volume fractions. Studies on PMMA modified with n-dodecylmethacrylate during polymerization were shown to maintain optical clarity up to 10 wt. % of bentonite. [44] In addition, when exfoliation was achieved in polyimide matrix composites, the 2 wt. % hybrid were relatively transparent [8] compared to nonexfoliated clay.

The best performances are commonly observed for the exfoliated nanocomposites which the individual clay layers break off the tactoid and are either randomly dispersed in the polymer. However, this is very difficult to attain by simple mixing method. So, the development of methods to attach polymer to nanoparticles has

progressed significantly. For example, separation of the nanoparticles from their aggregates is required. This separation can be achieved by "ion-exchange reaction" with organic molecule such as quaternary ammonium salt with or without the aid of a compatibilizer or swelling agent, choosing an appropriate synthesis method and /or using high intensity ultrasound to achieve effective breakup of the clay agglomerates and exfoliated of the silicate layer to yield useful various polymer-clay nanocomposites[5].

There are many researches studied the preparation of polymer-clay nanocomposite, especially regarding to the problem of the incompatible of polymer matrix and the nanoparticles. And from these researches it was found that there are many ways to improve compatibility of two components to receive the enhance performance of final product. For example;

In 1996, E.P.Giannelis [18] prepared poly (ethylene oxide)-clay nanocomposite by direct polymer melt intercalation. This process involves mixing the layer silicate with the polymer and heating the mixture above the softening point of the polymer. The results from differential scanning calorimetry (DSC) shown that the intercalation reaction progresses and more poly (ethylene oxide) chains were intercalated. Moreover the area of endotherm corresponding to crystalline PEO was reduced. This result agreed with XRD patterns, which demonstrated the increment of intensity of the PEO-intercalated silicate peak. In addition to XRD, the nanocomposite was characterized by TEM. Well-dispersed individual silicate layers of thickness 10 Å were embedded in the epoxy matrix. This nanocomposite showed improvement in the mechanical properties, barrier properties, heat resistance and thermal stability. The conductivity of the melt-intercalated hybrid was much higher and more isotropic than that of pure matrix.

Two years later, D.C.Lee and L.W.Jang [15] prepared epoxy-clay hybrid nanocomposite by emulsion polymerization without any kind of ion-exchange reaction or aryl onium ions or by employing special coupling agents. The structural characterizations by FTIR and XRD of the extracted product gave strong evidence that an overwhelming fraction of MMT was intercalated with the epoxy polymer. The

enhancement of thermal stability of those post cured product was confirmed by TGA and DSC analysis.

Later on in 1999, N.Hasegawa *et al* [17] reported the results of preparation and mechanical properties of polystyrene-clay hybrid by melt-blending. It was found that silicate layers of clay were delaminated and uniformly disperse to the nanometer level. The strong moduli of the hybrid materials were higher than those of matrix polymer at all temperatures.

Similarly, within the same year, L.Lie *et al* [15] prepared nylon 6-clay nanocomposite by melt-intercalation process. X-ray diffraction and DSC results showed that the crystal structure and crystallization behaviors of the nanocomposites were different from those of nylon 6. Mechanical and thermal testing showed that the properties of nanocomposites were superior to nylon 6 in terms of heat-distortion temperature, strength, and modulus without sacrificing their impact strength. This is due to the nanoscale effects and the strong interaction between the nylon 6 matrix and the clay interface, as revealed by X-ray diffraction and transmission electron microscope.

In 2000, A.Gu *et al* [12] synthesized polyimide/clay hybrid with cetylpyridium chloride modified MMT by solution method. From the results, they found that tensile, thermal, dielectric, and water-absorption properties of hybrids depend on the clay type (organophilic or not), clay concentration and the method to synthesize hybrids. The organo-MMT concentration of 3 wt % in the hybrid results in the optimum properties in tensile strength, modulus, elongation, coefficient of thermal expansion (CTE), and water-absorption.

Later on in 2002, J.H.Chang *et al* [14] synthesized thermotropic liquid crystalline polyester (TLCP) nanocomposites with modified MMT by the melting intercalation method above the melt transition temperature (T_m) of the TLCP. Liquid crystallinity, morphology, and thermo-mechanical behaviors were enhanced with increasing organoclay content from 0 to 6%. Moreover, tensile properties; ultimate strength and initial modulus of the TLCP hybrids increased with increasing clay content and the

maximum values of the mechanical properties were obtained from the hybrid containing 6% of the organoclay.

Next, in 2003, J.H.Chang *et al* [11] synthesized poly (lactic acid) /clay nanocomposite film by using the solution intercalation method at different organoclay contents. This study was to clarify that the intercalation of polymer chains to organoclays and to improve the thermo-mechanical properties. The maximum ultimate tensile strength was observed for blends containing 4 wt% and the initial modulus increased with increasing organoclay content up to 4 wt% for C₁₆-MMT. When the C₁₆-MMT content was greater than this critical wt%, the modulus of the hybrids started to decrease. The optical translucency was not affected by the organoclay content up to 6 wt%; however, the films containing 8 wt% organoclays were slightly cloudier.

Also, within this year G.Liang *et al* [10] used PE-g-MAH as a compatibilizer in the preparation PE/ PE-g-MAH/Org-MMT nanocomposites. They were found that the intercalation effect of PE/PE-g-MAH /Org-MMT could be enhanced by increasing the content of PE-g-MMT. The PE-g-MAH was used as the function of matrix modification which increases the polarity of PE matrix to enhance its miscibility with inorganic clay. The results clearly showed that Org-MMT and PE-g-MAH had a heterogeneous nucleation effect on crystallization of PE from the melt. The tensile strength initially increased and then decreased with increasing contents of PE-g-MAH. The maximum value was achieved when the concentration of PE-g-MAH was 6 wt %. The impact strength increased concomitantly with the content of PE-g-MAH.

Recently, in year 2004, Y.Q.Zhang *et al* [9] prepared polypropylene /clay nanocomposites (PPCN) using melt blending method. The clay was treated with a swelling agent (maleic anhydride, MAH) and a co-swelling agent in solution. Then, it was melt blended with PP-g-MAH to generate a pre-intercalated composite (PIC). With the aid of swelling agents, the organic clay treated with MAH had a larger basal space than in the original, demonstrating the strong intercalating effect of MAH. Moreover, the nanocomposites prepared with the aid of swelling agents contained some PP-g-MAH showed good dispersion of the clay layers resulting in the PPCN with greater thermal stability and enhanced storage modulus.

Similarly, J.G.Ryu *et al* [5] compared the preparation of polypropylene/styrene-clay nanocomposites by ultrasonically assisted polymerization and melt mixing processes. The sonication process using power ultrasonic wave was employed to enhance nano-scale dispersion during melt mixing of monomer, polymer and organically modified clay. Using the unique mode of power ultrasound wave, the enhancement breakup of layer silicate bundle and further reduction in the size of dispersed phase with better homogeneity compared to the in situ polymerization. Also, the clay aggregates in the ultrasonically processed nanocomposites are more finely dispersed than in the simple mixing methods. Moreover, it is related to the degree of the compatibilization between the polymer matrix and the clay. In addition to the exfoliated structure, it is important to notice that the overall homogeneity of the composite was also superior to those formed by typical compounding processes which greatly affect the performance of the nanocomposites.

With in the same year, A.Pegoretti *et al* [13] prepared nanocomposite between recycled poly (ethylene terephthalate) (rPET) and non-modified and modified MMT by a melt intercalation process. The results show that the modified MMT are much better dispersed in the rPET matrix than those of non-modified MMT. Moreover, uniaxial tensile tests show that both clays increase the modulus of the rPET composites; but nanocomposites with modified MMT give more effective of those properties than non-modified MMT up to 30% increase at loading of 5 wt % modified MMT. Both clays have beneficial effect on the dimensional stability of the composites since, in contrast to the neat rPET, the creep rate does not rise at long creep periods.