# CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Poly(Methyl Methacrylate)

Poly(methyl methacrylate) is polymerized by methyl metharcrylate monomer, MMA. Physical and thermodynamic properties of methacrylate monomer are shown in Table 2.1.

Table 2.1 Physical and thermodynamic properties of commercially methyl methacrylate monomer

Physical properties	
Molecular weight	100.11
Melting point, ^oC	-48
Boiling point, ^oC	100-101
Refractive index, n_D^{25}	1.4120
Density, d_5^{25} g/cm^3	0.939
Flash point, ^oC, TOC	13
Typical inhibitor, ppm	10 MEHQ
Thermodynamic Properties	
Heat of vaporization, kJ/g	0.36
Heat capacity, $J/(g \cdot K)$	1.9
Heat of polymerization, kJ/mol	57.7

Poly(methyl methacrylate)(PMMA) is one the most important member of an acrylic based polymers.[1-2] At room temperature, PMMA is a hard, stiff, and brittle thermoplastic. Like other amorphous thermoplastics, it softens and loses its strength above the glass-transition temperature.

(a)   **(b)**
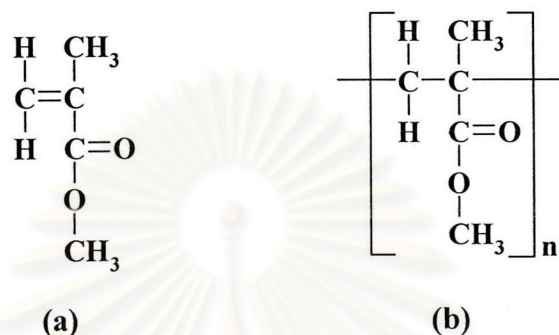
Scheme 2.1   Structure of (a) MMA monomer and (b) PMMA

2.1.1 Polymerization of PMMA

PMMA is usually produced by a free-radical polymerization. Peroxide or azo is usually used as an initiator. The polymerization can be carried out in bulk, solution, or emulsion. The temperatures range is often keep in a range of 50 to 170°C, depending on the process being used and the desired properties of the polymer.[1]

At constant temperature, the initial rate of the bulk or solution radical polymerization of acrylic monomers is first order with respect to monomer concentration, and one-half order with respect to the initiator concentration. Rate data for polymerization of several common methyl methacrylate monomers initiated with 2,2′-azobisisobutyronitrile (AIBN) have been determined (Table 2.2).

Table 2.2 Polymerization data for methyl methacrylate monomer

|	K_{sp}, 44.1 ^{o}C	Heat, kJ/mol	Vol.% shrinkage
Methyl methacrylate	27	57.7	21.0

The polymerization of methyl methacrylate is related with amount of heat and a substantial decrease in volume. These factors significantly influence most of the manufacturing processes. Firstly, because the reaction of polymerization is exothermic polymerization, excess heat has to avoid uncontrolled. The heat transfer (q) between the polymerization medium and the air circulation around the molds can be expressed by the following Equation 1

$$q = \frac{T_1 - T_2}{\dfrac{1}{\alpha} + \dfrac{d_2}{K_1} + \dfrac{d_2}{K_2}} \tag{1}$$

Where q is heat transfer (W); T_1 is prepolymer temperature (^{o}C); T_2 is circulating air temperature (^{o}C); α is heat transfer coefficient; K_1 is silicate glass thermal conductivity (W/m ^{o}C); K_2 is PMMA thermal conductivity (W/m ^{o}C); d_1 is silicate glass thickness (mm); and d_2 is PMMA sheet thickness (mm). The value of α depends on air speed, which has to be greater than 7 m/s.
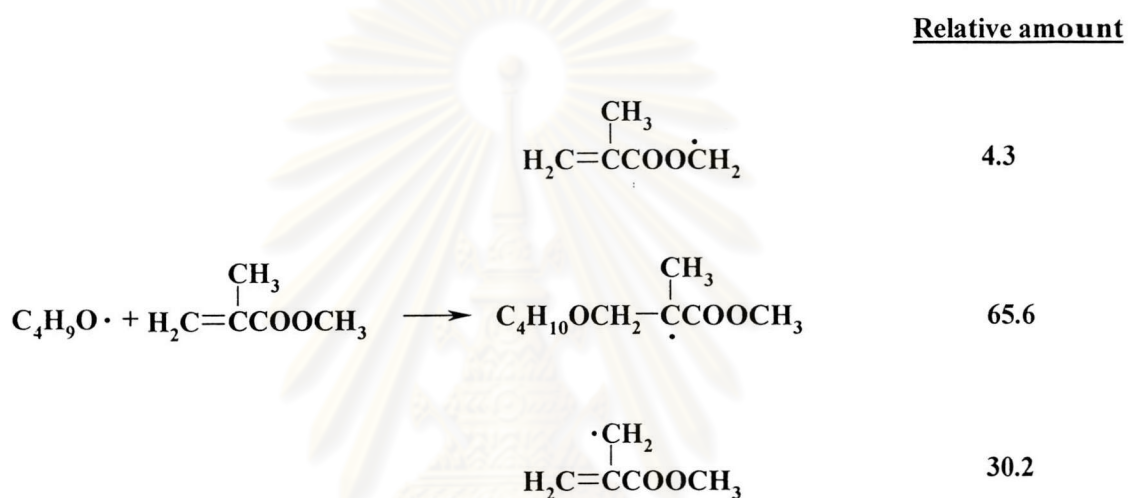
Secondly, volume changes are particularly important in sheet-casting processes. Mold should compensate for the decrease volume.

The free radical polymerization of methyl methacrylate monomers follows a classics chain mechanism in which the chain propagation step entails the head-to-tail growth of the polymeric free radical by attack on the double bond of the monomer shown in Scheme 2.2.
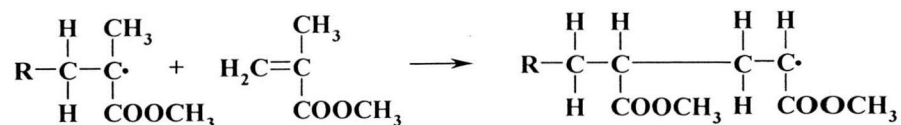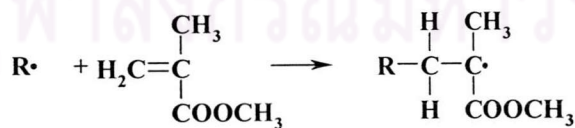
Scheme 2.2 Chain propagation step for PMMA polymerization

Chain termination can occur by either combination or disproportionation depending on the conditions of the process. Some details of the chain-initiation step have been elucidated. With an oxygen radical-initiator such as the t-butoxyl radical, both double bond addition and hydrogen abstraction are observed. Hydrogen abstraction is observed at both the α-methyl and the ester alkyl group of methyl methacrylate. The relative proportions are shown in Scheme 2.3.

Relative amount

$$CH_3$$
$$H_2C=C\overset{\cdot}{C}OOCH_2$$
4.3

$$C_4H_9O\cdot + H_2C=C\overset{CH_3}{\underset{|}{C}}OOCH_3 \longrightarrow C_4H_{10}OCH_2-\overset{CH_3}{\underset{\cdot}{C}}COOCH_3$$
65.6

$$\overset{\cdot CH_2}{\underset{|}{H_2C=CCOOCH_3}}$$
30.2

Scheme 2.3 Relative proportion of the free radical PMMA

The reaction shown in Scheme 2.2 can be inhibited by oxygen; therefore, the air has to be excluded during polymerization. This inhibitory effect has been caused by copolymerization of oxygen with monomer forming an alternating copolymer, shown in Scheme 2.4.
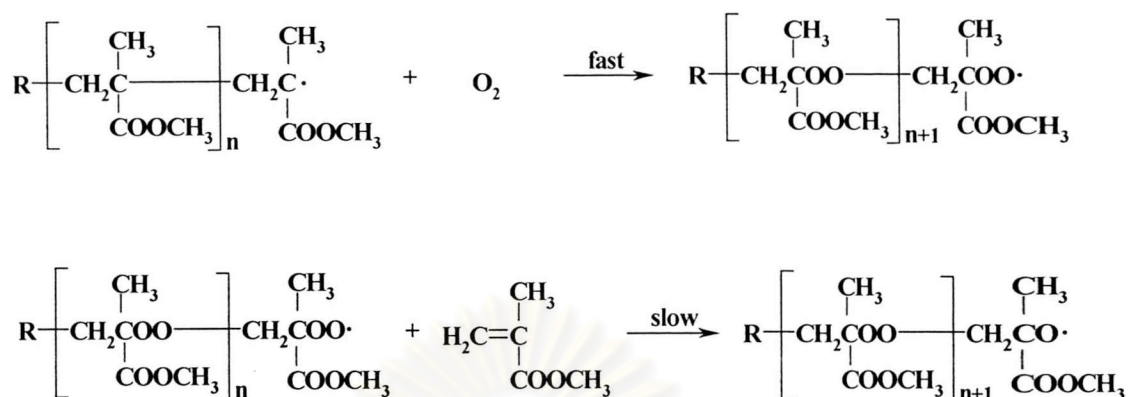
Scheme 2.4 Inhibitory reaction of PMMA by oxygen

2.1.2 Properties and Application

General Properties

The molecular weight of the polymer was used in molding and extrusion averages between 100,000 and 200,000 g/mol. The molecular weight of cast material is much higher (3×10^5 to 6×10^6). This variation accounts for many of the differences between articles made of cast acrylic and those made from molding or extrusion compound. Among different molding compounds, there is also a significant difference in the molecular weight and the comonomer content, and thus certain properties. Such things as pellet size and residual monomer or solvent content can affect properties.

Glass-Transition Temperature (T_g)

The T_g is influenced primarily by the nature of alcohol group, which is raw material while preparation of monomers, but also to lesser extent, by the stereoregularity of a polymeric backbone. Poly(methyl methacrylate) has a glass transition temperature at 105 $^{\circ}$C for atactic, 160 $^{\circ}$C for syndiotactic, and 43 $^{\circ}$C for isotactic configuration. Below the T_g polymers are stiff, hard, brittle, and glasslike; above the T_g, the polymers are high mobility and if the molecular weight is high enough, they are relatively soft, limp, stretchable, and can be somewhat elastic. At even higher temperatures, they flow and are tacky.

Molecular Weight

The mechanical properties of polymer depend on the molecular weight. For PMMA, high molecular weight of polymer is stiffness property more than low molecular weight and at the low molecular weight, they can generate a problem, which is cracking on the surface because of the residual monomers. Furthermore, the relationship of molecular weight and T_g can be shown in equation 2

$$T_g = T_g - k/\overline{M}_m \qquad (2)$$

where T_g is glass-transition temperature at infinite molecular weight and $\overline{M}_n$ is the number-average molecular weight. The value of k for PMMA is about $2x10^{-5}$.

Mechanical Properties

At room temperature, PMMA is a hard, fairly rigid material, which can be sawed, carved, or worded on a lathe. When heated above its T_g, PMMA is a tough, pliable, extensible material that is easily bent or formed into complex shapes, and can be molded or extruded.

Solution Properties

Viscosity of polymer solution depends on the concentration of the solvent, the molecular weight of the polymer, the polymer composition, the solvent composition, and the temperature. Solubility occurs when the free energy of mixing is negative. In solution, there is more movement of polymer chains: therefore, entropy increases as a polymer dissolves.

Optical and Other Electromagnetic Spectral Properties

In fact, the wavelength of visible light is approximately between 400-700 nm. PMMA almost perfectly transmit light in the range of 360-1000 nm but at a thickness of 2.54 cm or less, PMMA absorbs virtually no visible light, essentially all infrared radiation is absorbed. Commercially, PMMA usually contain UV radiation absorbers, which can block the wavelength of 290-350 nm. Moreover, PMMA sheets

are opaque to α–particles, and for thickness above 6.35 nm, the polymer is essentially opaque to β–radiation that it is used as a transparent neutron stopper.

Electrical Properties

The electrical properties of PMMA can be shown in Table 2.3. PMMA can be used for high voltage application because it has high electrical resistance and nontracking characteristics, and also it has excellent weather resistance, which promotes the use of PMMA for outdoor electrical application.

Table 2.3 Electrical properties of 6.35 mm thick PMMA sheet

Property	Typical values	ASTM
Dielectric strength		
Short-term test, Vμ	>16.9-20.9	D 149
Dielectric constant, V/min		*D 150*
At 60 Hz	142-154	
At 1,000 Hz	130-134	
Power factor, V/cm		*D 150*
At 60 Hz	20-24	
At 1,000 Hz	16-20	
At 1,000,000 Hz	8-12	
Los factor, V/cm		D 150
At 60 Hz	75-87	
At 1,000 Hz	51-59	
At 1,000,000 Hz	24-31	
Arc resistivity	no tracking	D 495
Volume resistivity, $\Omega \cdot cm$	1×10^{14}-6×10^{17}	D 257
Surface resistivity, Ω/square	1×10^{17}-2×10^{18}	D 257

Hydrolytic Stability

Conversional and syndiotactic polymer can be hydrolyzed relatively slow when compared to the isotactic polymer. The configuration of the polymer is unchanged by hydrolysis. Complete hydrolysis of nearly pure syndiotactic PMMA under drastic conditions with desertification with diazomethane yields a polymer syndiotactic configuration present in conversional PMMA contributes to its high degree of chemical inertness, which is summarized in Table 2.4.

Table 2.4 Chemical resistance of PMMA

Not affected by	Attacked by
Animal oils	
Mineral oils	
Most inorganic solutions	High concentrations of alkalines and oxidizing agent
Low concentrations of	High concentrations of alcohols, e.g. methanol
Alcohols	
Paraffins	
Olefins	
Amine	
Alkyl monohalides	Alkyl polyhalides, e.g. methylene dichloride
Aliphatic hydrocarbon	Aromatic hydrocabons, e.g. BTX
Higher esters, >10	Lower ester, e.g. ethyl acetate, isopropyl acetate
carbon atom	phenol, and aliphatic acid

Advantages/Disadvantages

PMMA is most often used because of its superior clarity, transparency, and weatherability. It is rigid strong, hard and tough. PMMA is commercially available in a wide range of colors and opacities, nearly 100 grades. Some of the disadvantages of PMMA are the lack of abrasion resistance (compare with glass), limited stress crack resistance, flammability, vulnerability to attack by some

chemicals, limited long-term load-bearing characteristics, a service temperature limited to 93 °C or lower for a load-bearing part, and notch sensitivity.

2.1.3 PMMA Sheet and Manufacturing

PMMA sheet is manufactured in a wide variety of grades, which include clear and colored transparence, clear and colored translucence, and colored semiopaque. However, grades of PMMA are depended on the properties, shown in Table 2.5.

Table 2.5 Typical properties of commercial PMMA sheet

Property	Value	ASTM
Specific gravity	1.19	D 792 66
Refractive indexs (1965)	1.49	D 542 50
Tensile strength		D 638 64T
Maximum, mPa	72.4	
Rupture, mPa	72.4	
Elongation, rupture,%	4.9	
Modulus of elasticity, mPa	4.9	
Flexrul strenght		D 790 66
Maximum, mPa	110.3	
Rupture, mPa	110.3	
Deflection, max, cm	1.52	
Deflection, rupture, cm	1.52	
Modulus of elasticity, mPa	3103	
Compressive strength		
Maximum, mPa	124.1	
Modulus of elasticity, mPa	3103	

Table 2.5 Typical Properties of Commercial PMMA Sheet (continued)

Property	Value	ASTM
Compressive deformation under load		
14 mPa at 50 ^{o}C, 24 h, %	0.2	
28 mPa at 50 ^{o}C, 24 h, %	0.5	
shear strength, mPa	62.1	
impact strength		
Charpy unnotched, ^{o}C	2.94	
Rockwell hardness	M-93	
Hot forming temperature, ^{o}C	144-182	
Heat distortion temperature		
2 ^{o}C/min, 1.8 mPa, ^{o}C	96	
2 ^{o}C/min, 0.46 mPa, ^{o}C	107	
Maximum recommended continuous service		
temperature, ^{o}C	82-94	
Coefficient of thermal expansion, cm/cm/^{o}C x10^{-5}		
-40 ^{o}C	5.0	
-18 ^{o}C	5.6	
5 ^{o}C	6.5	
27 ^{o}C	7.6	
38 ^{o}C	8.3	
Coefficient of thermal conductivity, kw/(m·K)	0.00344	
Specific heat, 25 ^{o}C, kJ/(kg· ^{o}C)	0.452	

PMMA sheet is produced by bulk polymerization in a *casting* process. The typical production of PMMA sheets is mainly produced as three processes, which are batch cell, continuous process, and extrusion process. The batch cell processes are the most common method because it is inherently simple and easily adapted for manufacturing a wide variety of grades, colors, and sizes. The continuous process is

more economical method, and is used primarily to manufacture the widely used grades of thinner gauge sheet. Sheets are also produced by extruding PMMA. For gauges below 0.3 cm and for certain specialty applications, extruded sheets are economically preferred.

Preparation of Prepolymer (Syrup)

In batch cell process, the MMA monomers are prepared as syrup, which is prepolymer before take to the next steps, shown in Figure 2.1.
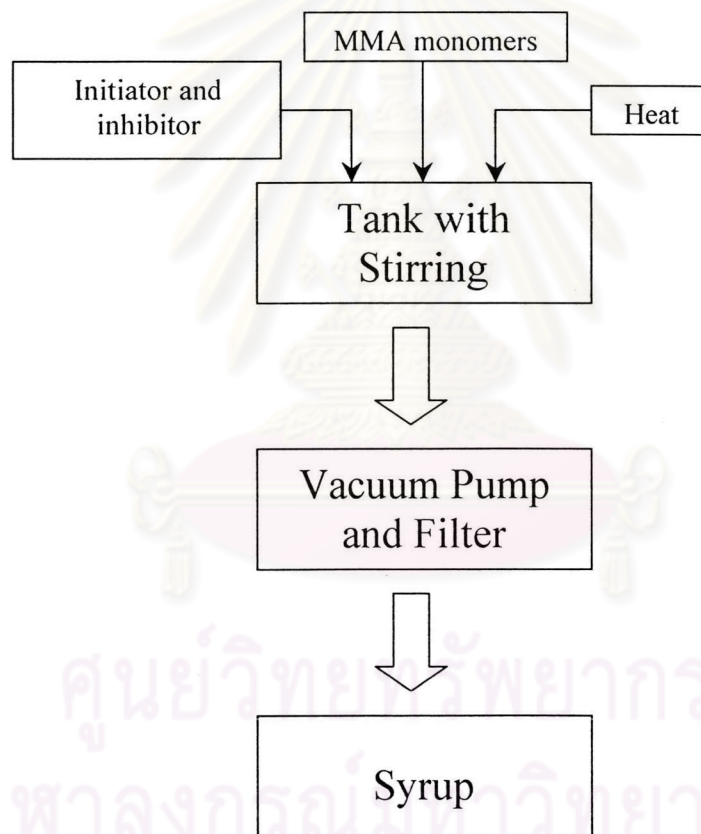
Scheme 2.5 Preparation of prepolymer

Additives of PMMA

The additives are often added in order to improve the properties of PMMA. For example, copolymer of PS with PMMA is used to control the transparence of light. UV absorber is added to MMA as antioxidant. Optical brightener (OB) is added as a substance to improve its fluorescence property. Releasing agents are used to improve the mold release property. Plastisizer can generate a high soft PMMA and easy for molding.

Mold Preparation

Molds are prepared by two silicate glasses and attached them by clamp. The molds, which have a defect, can generate a defect on PMMA sheets. Therefore, they must be precisely calculated because it may cause the defect in the sample.

Pouring

While the monomers are poured in mold, air bubble can be generated. These must be highly looked after finishing and the quantity of monomer must be calculated too because it is also a defect on PMMA sheets.

Air Expulsion

When PVC gaskets seal the molds and monomers, air bubble is generated. Therefore, it must be eliminated to protect a hole on PMMA sheets.

Polymerization

The polymerization of PMMA can generate at suitable temperature because it is exothermic reaction. The reaction is then needed to be careful taking care of.

Annealing

The PMMA sheets that finished polymerization are taken to a hot oven. This was done in order to increase the molecular weight. After this process, the PMMA sheets are high mechanical properties.

2.2 Clay and Clay Mineral

Clay or layered silicate is a natural, earthy, fine-grained material composed largely of a limited group of crystalline minerals known as the clay minerals. Generally, it can be classified into many types according to differences in its structure and composition. The clay minerals are hydrous silicates, which contain tetrahedral silicate sheet and octahedral aluminum or magnesium sheet. The clay minerals were classified by used layer type 1:1 or 2:1, as the main criterion for establishing divisions (Table 2.6).[3]

Clay minerals find almost innumerable applications, and the diversity of uses is still increasing. The reason is the large variety of clays and clay minerals and the ease with which these materials are modified. Swelling behavior, adsorption properties, colloidal and rheological phenomena can be optimized and adjusted to the intended used.[4] In addition to applications well known for a long time, new uses are found and new types of materials are created. Clay minerals and clays are more and more involved in material science studies and are parent materials of organic-inorganic composite. Among several types of clays, the smectite is usually used as additive in polymer composites. The layered silicates are the most attractive because it can intercalate organic molecule.

Table 2.6 Classification of phyllosilicates, emphasis on clay minerals

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

[a] 2:1 layer first in name of chlorite; Tr = trioctahedral and Di = duictagedrak; z = charge per formula unit.

2.2.1 Smectites

Smectites are a group of clay minerals, which process expandability, taking up water or organic molecules between their structural layers, and also marked cation exchange properties. The structure can be either dioctahedral or trioctahedral depending upon a type of substituted center cationic atom. Dioctahedral means two of octahedrons are filled with trivalent cation such as Al^{3+} or Fe^{3+}. Trioctahedral means all their octahedrons were filled with divalent Mg^{2+} or Fe^{2+}.

Table 2.7 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 principal smectite are montmorillnite, beidellite and nontronite, all of which are dioctahedral 2:1 layer silicate, and saponite, hectorite and sanconite, which are trioctahereal.[5] Its structure illustrate in Table 2.7.

The smectite clay minerals consist of many layers of octahedral aluminates sheets sandwiched between tetrahedral silicate layers. Oxygen atoms reveal the layer edge of tetrahedral site and octahedral site. Illustration in Figure 2.1 is structure of smectite clay.[6]
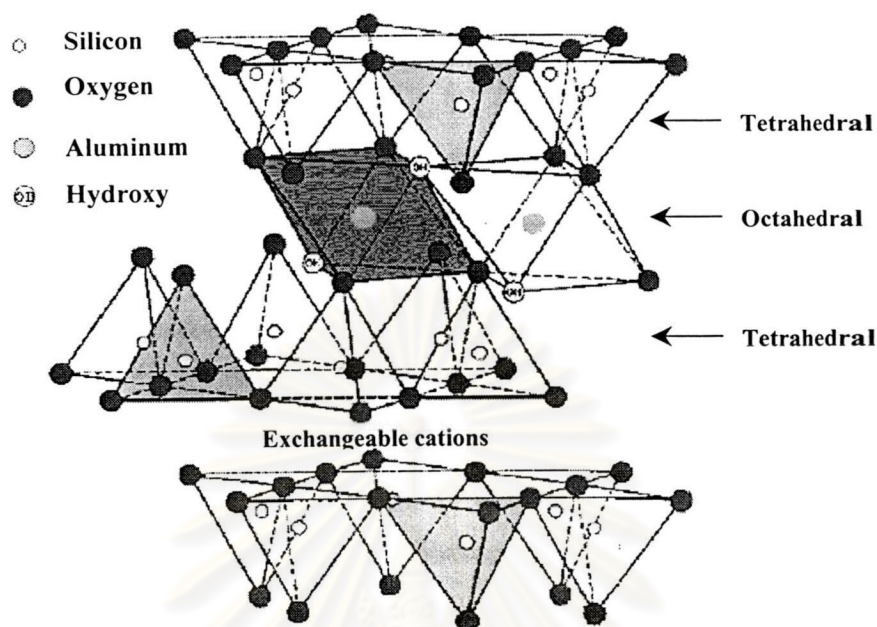
Figure 2.1 Structure of 2:1 phyllosilicates

The 2:1 type layers of smectites have various cation substitutions in both the tetrahedral and octahedral positions. Substitutions of ions of the same valence, notably Mg-Fe(II) and Al-Fe(III) substitutions, are common in octahedral positions. Coupled substitutions also occur such as $Fe^{3+} + O^{2-}$ replacing $Fe^{2+} + (OH)^-$ which is equivalent to a combined oxidation-dehydration process. Anion substitutions, particularly F^- for $(OH)^-$, are not common in natural smectites but it is utilized in synthetic materials.

The isomorphic substitutions within metal oxide sheets with the lower valency species give the silicate layer slightly negative charges, and it is counterbalanced by interlay cations namely Na^+ and K^+. As the forces that hold the stacks together are relatively weak, the intercalation of small molecules between the layers is easy.[7]

Montmorillonite(MMT) is classified smectite group normally applied to polymer nanocomposites because of its have suitable layer charge density.

2.2.2 Montmorillonite

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 generates negative charges that are counterbalanced by hydrated sodium or potassium ions residing in the interlayer spacing.[8] In aqueous suspension, cations in interlayer may exchange with ions in the bulk solution. They are known as *exchangeable cations*. The total amount of cations adsorbed in the clay interlayer, expressed in miliequivalents per hundred grams of dry clay, is called the cation exchange capacity (CEC). It is an important characteristic of clay mineral. The cation exchange capacity is high for sodium montmorillonite, comparing it to the other clay minerals.

There are many ways to investigate the CEC values. The principle method suggest by Rhoades in 1982 is displacement of saturating index cation and then displacement the saturating index cation after washing free from saturating salt. The last step, detect the saturating index cation by many technique such as titration, atomic emission spectroscopy depending on the type of index. Methylene blue index is the simple method to detect the CEC values.[9] There is contain in the ASTM C 337-99 for characterize property of clays.

On a larger scale of MMT, each layer can be seen as a high aspect ratio lamella about 100-200 nm in diameter and 1 nm in thickness (Figure 2.2).
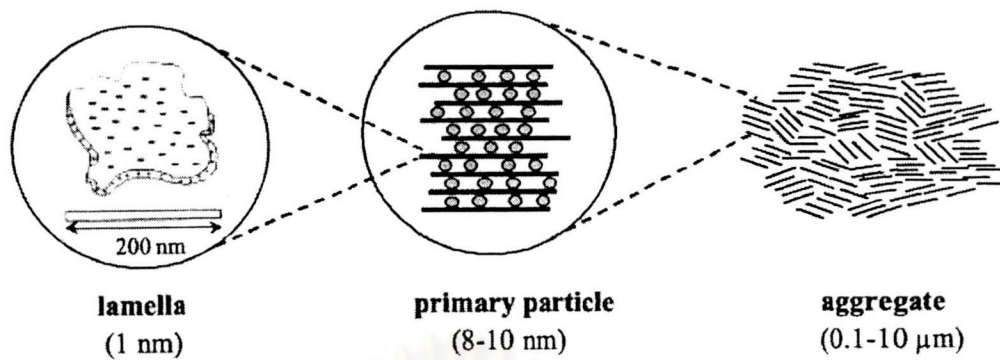
Figure 2.2 Microstructure of montmorillinte

Five to ten lamellae are associated by interlayer ions in primary particles (8-10 nm in the "transverse" direction which, in turn, form larger irregular aggregates (0.1 – 10 μm in diameter) giving to the clay its turbostatic structure. Due to this special characteristic, MMT can be easily dispersed in water resulting in a stable colloid. Typically, the natural MMT is too hydrophilic to disperse in an organic matrix. Its dispersibility can be improved to make it useful by several ways[4]; (1) adsorption, (2) ion exchange with inorganic cations and cationic complexes, (3) ion exchange with organic cations, (4) binding of inorganic and organic anions, mainly at the edges, (5) grafting of organic compounds, (6) reaction with acids, (7) pillaring by different types of poly(hydroxo metal) cations, (8) interlamellar or intraparticle and interparticle polymerization, (9) dehydroxylation and calcinations, (10) delamination and reaggregation of smectitic clay minerals, and (11) physical treatment such as lyophilication, ultrasound, and plasma. Ion Exchange with organic cations is the principle reaction to convert clay mineral to organophillic clay or organoclay.

2.3 Organoclay

It has long been known that the clay's surface property can be modified from hydrophilic to organophilic. The modification can be done by (a) an adsorption of the organic molecule into an interlayer, (b) a covalently bonding of the surfactant to a free hydroxyl group on the clay surface and (c) an exchanging of an interlayer cation with a cation surfactant. This is resulting in a more compatible between organic molecule and the clay. The adsorption of the organic molecule often occurs via a complex

formation between the organic molecule and the interlayer cation. The amount of the adsorbed molecule changes as a vapor pressure or temperature changes. The covalent bonded organoclay can be prepared by a condensation of a functionalized organo siloxane. Replacing an exchangeable interlayer cation by the cationic surfactant can carry out the exchange reaction.

The intercalation causes an increased in the height of the clay's gallery. Several models were proposed in order to explain the packing of the alkylammonium salt within the clay layer.

Dr. John W. Jordan, father of organoclay technology, introduced Organophillic clay or organoclay in 1941. NL Industry sponsored his research. He tries to develop the high value added product from bentonite. Normally, bentonite uses as a gallant for water system but not simplify for organic system. Organoclay was exchange the inorganic cations in the interlayer with organic cations to convert the clay into organophilic compound as show in Figure 2.3 which suitable for use in organic system.[10]
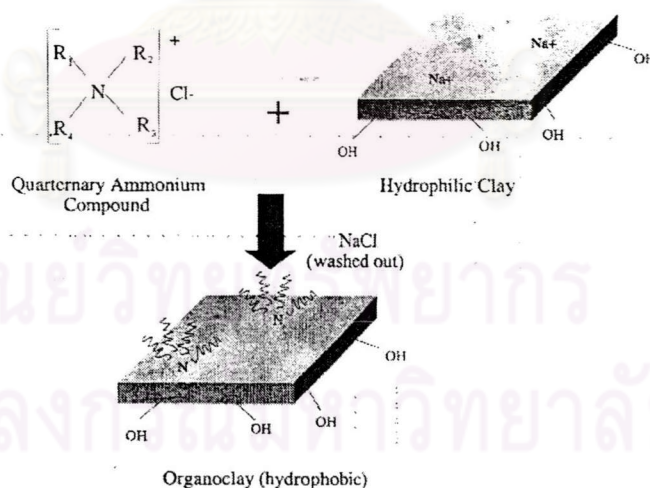
Scheme 2.3 The reaction between clay and organic cation

Since 1941 the numerous researches in organophillic clay, such as the preparation technique, characterization technique, thermal property, has been report.

There still a lack of an understanding in controlling the intercalation process and rheological property in organic system.

2.3.1 Preparation and characterization of Organophilic Clay

The most widely used method in preparation of the organoclay is ion exchange with organic onium ions. The adsorption of cationic surfactants on clay at the solid–liquid interface is of great technological interest and fundamental importance. It has been investigated by several experimental techniques.[11] The adsorption of surfactants on clay surface involves the electrostatic interactions between the surfactant head group and the surface, the interaction between the tails, and the electrostatic repulsion between the head groups. Usually a "two-step" adsorption isotherm of cationic surfactants was found for smectite surfaces.[12] At low surface coverage, first stage surfactant cations adsorb on the negatively charged surface sites, the cations exchange with protons or other counterions depending on the properties of the solid–water interface and the type of surfactant. When the surface charge has been compensated, the "electrostatic" driving force for surfactant adsorption is annihilated and the adsorption will only increase if the affinity of hydrophobic part of the surfactant is low.

The replacement of inorganic exchange cations by surfactant on the clay surface not only neutralized the clay surface, but also expanded the interlayer spacing. Three type of surfactant arrangement in interlayer; a monolayer, a lateral bilayer and a pseudo-trimolecular layer, or an inclined paraffin structure as illustrated in Figures 2.4. At very high charge densities, large surfactant can adopt lipid bilayer orientations in the clay interlayer. The orientations of surfactant chains in organoclay were deduced based on infrared and XRD measurements.[13] More recent molecular dynamics (MD) simulations were used to study molecular properties such as density profiles, normal forces, chain configurations and trans-gauche conformer ratios. For the mono-, bi- and psuedo-trilayers with respective d-spacings of 13.2, 18.0 and 22.7 Å, a disordered liquid-like arrangement of chains was preferred in the gallery. In this disordered arrangement the chains do not remain flat, but instead, overlap and co-single with onium ions in opposing layers within the galleries. However, for the

trilayer arrangement, the methylene groups are primarily found within a span of two layers and only occasionally do they continue into the layer opposite to the positive head group. As anticipated, the onium head group is also noted to reside near the silicate surface relative to the aliphatic portion of the surfactant. The highest preference conformation is trans over gauche for the maximum surfactant chain length just before the system progresses to the next highest layering pattern. This is expected since the alkyl chains must be optimally packed under such dense surfactant concentrations. The MD simulation experiments have agreed well with experimental XRD data and FTIR spectroscopy for the stacked interlayer alkyl chains. However, the inclined paraffin association is not addressed for $< C_{15}$ surfactants with clays of CEC less than 1.2 meq/g.
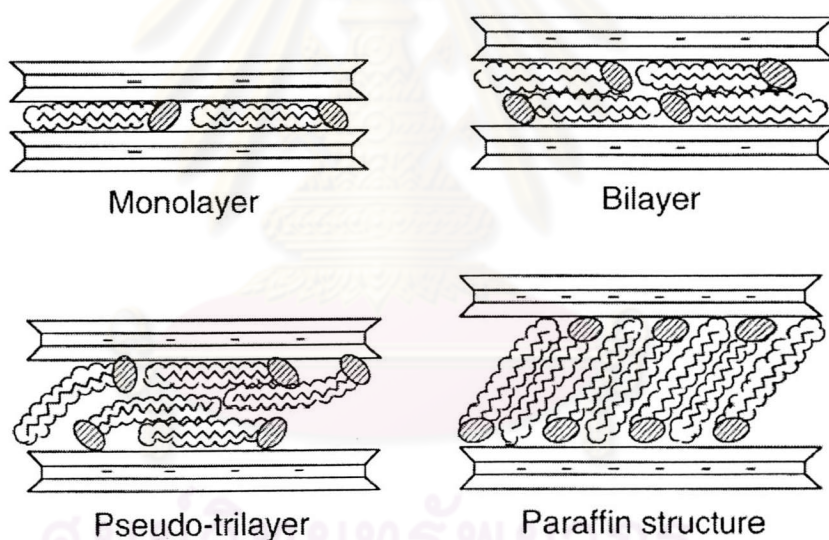

Monolayer

Bilayer

Pseudo-trilayer

Paraffin structure

Figure 2.4 Orientation of alkylammonium ions in the interlayer silicate with different layer charge densities

Seung Yeop Lee (2002) study the reaction of smectite with hexadecyltrimethylammonium cations at 0.01-3.0 times of CEC, show that a heterogeneous increase of interlayer spacing as HDTMA loading increases, the chance of delaminated layers being developed increases locally in the low-charge interlayer regions by the sufficient adsorption of organic surfactants beyond the CEC due to the tendency of alkyl chain interaction.[14]

2.3.2 Application

The application of organoclay depending on the grades, which there are many different type on the market. It usually use as a gallant or viscosifying agent in paint, printing ink, grease and cosmetic industry.[10]

2.4 Polymer Nanocomposite

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.[15] The properties of composite materials are greatly influenced by the degree of mixing between the two phases. In conventionally filled polymers, the constituents are immiscible. This is resulting in a coarsely blended macrocomposite with chemically distinct phases which causes a poor physical attraction between the organic and inorganic components and lead to an agglomeration of the inorganic phase. Thus weaken the materials. In addition, the micrometer size particles act as stress concentrators. In nanocomposites, chemically dissimilar components are combined at the nanometer scale and are too small to act as a stress concentrator. Stronger interactions between the polymer and silicate clay often leads to an improvement in the mechanical properties. The structure of the composite depends on the extent to which the organic and inorganic components is being made.[16]

Depending on the nature of the components used (layered silicate, organic cation and polymer matrix) and the method of preparation, three main types of composite maybe obtained when layered clay is associated with a polymer (Scheme 2.7).[17]
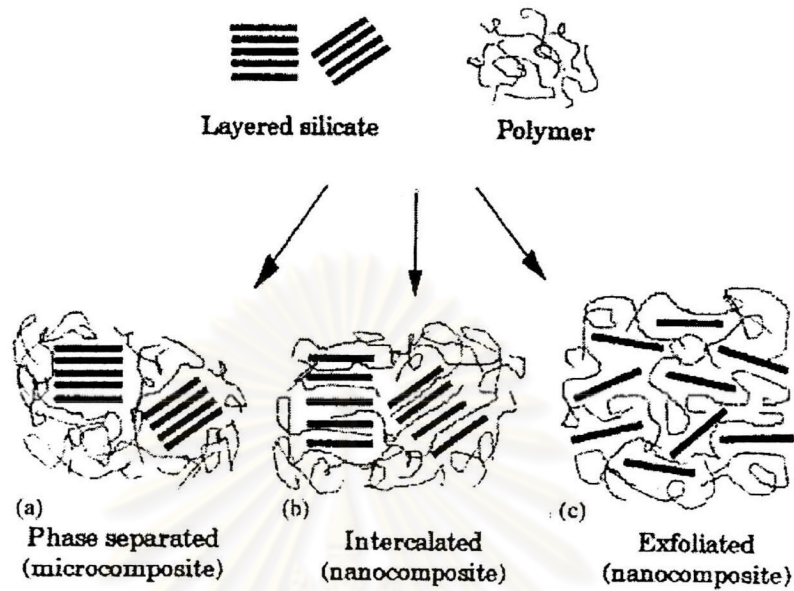
Scheme 2.7 The different types of composite arising from the interaction of layered silicates and polymer:

> (a) phase separated microcomposite;
>
> (b) intercalated nanocomposite and
>
> (c) exfoliated nanocomposite.

Phase Separated Microcomposite

Phase separated microcomposite where the clay acts as conventional filler. When the polymer is unable to intercalate between the silicate sheets, is obtained, whose properties stay in the same range as traditional microcomposites.

Intercalated Nanocomposite

Intercalated structure in which a single (and sometimes more than one) extended polymer chain in intercalated between the silicate layers resulting in a well dormered multiplayer morphology built up with alternation polymeric and inorganic layers.

Exfoliated Nanocomposite

Exfoliated or delaminated structure is obtained when the silicate layers are completely and uniformly dispersed in a continuous polymer matrix.

2.4.1 Nanocomposite Preparation

Synthesis of Polymer/clay nanocomposite can be carried out by the four methods which are exfoliation-adsorption (solution method),[18] in *situ* polymerization,[19-24] melt intercalation[16, 25-28] and template synthesis.[29,30]

Exfoliation-Adsorption

The layered silicate is exfoliated into single layers using a solvent in which the polymer (or a prepolymer in case of insoluble polymers such as polyimide) is soluble. It is well known that such layered silicates, owing to the weak forces that stack the layers together, can be easily dispersed in an adequate solvent. The polymer then adsorbs onto the delaminated sheets and when the solvent is evaporated (or the mixture precipitated), the sheets reassemble, sandwiching the polymer to form, in the best case, an ordered multiplayer structure. Under this process are also gathered the nanocomosites obtained through emulsion polymerization where the layered silicate is dispersed in the aqueous phase.

In situ Polymerization

In situ polymerization was the first method used to synthesize polymer-clay nanocomposites based on polyamide 6 in 1987 by Toyota research group. In this technique, the layered silicate is swollen within the liquid monomer (or a monomer solution) so as the polymer formation can occur in 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 cationic exchange inside the interlayer before the swelling step be the monomer.

Melt Intercalation

The melt intercalation process was first reported by Vaia et al. in 1993.[25] This method, the layered silicate is mixed with the polymer matrix in the molten state. Under these conditions and if the layer surfaces are sufficiently compatible with the chosen polymer, the polymer can crawl into the interlayer space and either an intercalated or an exfoliated nanocomposite. In this technique, no solvent is required.

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

Template Synthesis

This technique, where the silicates are formed in *situ* in an aqueous solution containing the polymer and the silicate building blocks has been widely used for the synthesis of double-layer hydroxide-based nanocomposites but is far less developed for layered silicates. In this technique, based on self-assembly forces, the polymer aids the nucleation and growth of the inorganic host crystals and gets trapped within the layers as they grow.

2.4.2 Characterization of Polymer-Clay Nanocomposites

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

X-Ray Diffraction

XRD is used to identify intercalated structures. In such nanocomposites, the repetitive multilayer structure is well preserved, allowing the interlayer spacing to be determined. The intercalation of the polymer chains usually increases the interlayer spacing, in comparison with the spacing of the organoclay used, leading to a shift of the diffraction peak towards lower angle values.

Angle and layer spacing values being related through the Bragg's relation:

$$\lambda = 2d \sin \theta$$

where λ corresponds to the wave length of the X-ray radiation used in the diffraction experiment, d the spacing between diffractional lattice planes and θ is the measured diffraction angle or glancing angle.

As far as exfoliated structure is concerned, no more diffraction peaks are visible in the XRD diffractograms either because of a much too large spacing between the layers (i.e. exceeding 8 nm in the case of ordered exfoliated structure) or because the nanocomposite losses its order structure.

Transmission Electron Spectroscopy

Transmission electron spectroscopy (TEM) is used to characterize the nanocomposite morphology. Besides these two well-defined structures, other intermediate organizations can exist presenting both intercalation and exfoliation. In this case, a broadening of the diffraction peak is often observed and one must rely on TEM observation to define the overall structure.

2.4.3 Properties of Polymer-Clay Nanocomposite

Layered silicate nanofillers have proved to trigger a tremendous properties improvement of the polymers in which they are dispersed. Amongst those properties, unexpected large increase in moduli (tensile or Young's modulus and flexural modulus) of nanocomposites at filler contents sometimes as low as 1 wt.% has drawn a lot of attention. Thermal stability and fire retardancy through char

formation are other interesting and widely searched properties displayed by nanocomposites. Those new materials have also been studied and applied for their superior barrier properties against gas and vapor transmission. Finally, depending on the type of polymeric materials, they can also display interesting properties in the frame of ionic conductivity or thermal expansion control.

Mechanical Properties
- Tensile Properties

The dramatic improvements of tensile strength and tensile modulus given by the delaminated nanocomposite structure on polyamide 6-clay hybrids were first reported by the Toyota researchers.[31] The tensile strength of polyamide 6 was increased by 55% and the modulus by 90% with the addition of only 4 wt.% of delaminatd clay. Later, Lan et al.[19] reported more than a ten-fold increase in strength and modulus in a rubbery epoxy matrix with only 15 wt.% of delaminated organoclay. At last, the modulus of an intercalated PMMA-clay nanocomposite with 20 wt.% of clay was reported to be superior by 60% to the pristine polymer.[32]

This short review of the tensile properties of polymer-clay nanocomposite suggests that the performance of nanocomposites is related to the degree of delamination of the clay in the polymer matrix that increases the interaction between the clay layers and the polymer.

- Impact Properties

Impact properties have been measured for nylon-6 nanocomposites prepared either by in *situ* intercalative polymerization of ε-caprolactam using protonated aminododecanoic acid-exchanged montmorillonite[33] or by melt intercalation of nylon-6 in octadecylammonium-exchanged montmorillonite.[34] Both methods lead to exfoliated nanocomposites especially when the filler content does not exceed 10 wt.% (at higher filler level, melt-intercalation provides partially-exfoliated-partially-intercalated materials). The formation of nylon-6-based nanocomposites does not reduce too much the impact properties, whatever the exfoliation process used. In the case of in situ intercalative polymerization, the Izod impact strength is reduced from 20.6 to 18.1 J/m^2 when 4.7 wt.% of nanoclay is incorporated. Charpy

impact testing shows similar reduction in the impact strength with a drop from 6.21 kJ/m^2 for the filler-free matrix down to 6.06 kJ/m^2 for the 4.7 wt.% nanocomposite.

Barrier Properties

- *Permeability*

The substantial decrease of permeability brought by nanocomposite structure is also a major advantage of polymer-clay nanocomposite. It was first reported by the Toyota researchers[31] that their polyamide 6-clay hybrid had a rate of water absorption reduced by 40% as compared with the pristine polymer. Later, Messersmith et al.[35] observed a dramatic decrease of water permeability with their poy(ε-capolactone) layered silicate nanocompostie, up to 80% with only 5 vol% of clay. The gas permeability in rubber-clay hybrid was also reduced by 30% with 4 vol.% of delaminated clay.[36]

- *Solven Resistance*

The better barrier properties of polymer-clay nanocomposites also increase solvent resistance. A recent study performed on epoxy-clay nanocomposites demonstrates that nanocomposites offer a better resistance to organic solvents (alcohol's, toluene, and chloroform), particularly when the solvent molecules are small enough to penetrate into the polymer network and large enough so that once they are absorbed, they cause molecular damage to the epoxy matrix, as with propanol or toluene.

Thermal Properties

- *Thermal Stability*

The thermal stability of a material is usually assessed by thermogravimetric analysis (TGA) where the sample mass loss due to volatilization of degraded by-products is monitored in function of a temperature ramp. When the heating is operated under an inert gas flow (nitrogen, helium, *etc.*), a non-oxidative degradation occurs while the use of air or oxygen allows following the oxidative degradation of the sample.

The first indication of thermal stability improvement in nanocomposites appears in the seminal work by Blumstein[37] who studied the thermal stability of PMMA intercalated within montmorillonite. He also found that the thermal stability of the PMMA extracted from the montmorillonite was higher than for a PMMA conventionally produced in solution. The higher stability of PMMA synthesized by in situ intercalative polymerization is more likely due to a decrease in the relative amount of PMMA endcapped by carbon-carbon double bond, as a result of reduced propensity to disproportionation reactions.

- *Flame Retardacy*

The flame retardant properties of nanocomposites have been very recently reviewed in detail by Gilman.[38] The main bench-scale method used to measure important parameters in the flame retardant behavior of a material (heat release rate, peak of heat release rate, heat of combustion, *etc.*) is Cone calorimetry. In a typical experiment, the sample is exposed to a given heat flux (often taken as 35 kW/m^2) and the heat release rate (HRR) as well as the mass loss rate are recorded as a function of time. It is worth noting that reduction of the peak HRR is the most clear-cut evidence for the efficiency of a flame retardant. Moreover, gas and soot production are also measured.

Cone calorimetry experiments have been carried out on other nanocomposites such as exfoliated nylon-12 (2 wt.% organoclay), exfoliated poly(methylmethacrylate-co-dodecylmethacrylate),[39] intercalated PS (3 wt.%) or intercalated PP (2 wt.%) and for each material, a significant decrease in the peak HRR is recorded while the heat of combustion, smoke and the carbon monoxide yields (other important properties in flammability concern) are usually not increased.

Optical Properties

Traditional composites tend to be largely opaque because of light scattering by the particles or fibres embedded with in the continuous phase. In nanocomposites, the domain sizes are reduced to a level such that true "molecular composites" are formed. As a result of this intimate mixing, these hybrids are often highly transparent, a property which renders them amenable to applications outside

the boundaries of traditional composites. Wang et al.[40] demonstrated that magadiite-nanocomposites baned on an epoxy matrix were much more transparent than corresponding smictite-nanocomposites at the same loading. They attributed ths phenomenon to the possibility that the refraction index of magadiite matched more nearly that of the organic matrix or that the magadiite was more fully delaminated than smectite. Later, they reported the high transparency of smectite-nanocomposites based on a polyurethane matrix.[41]