POLYPROPYLENE/CLAY NANOCOMPOSITE
A STUDY OF MECHANICAL PROPERTIES

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ABSTRACT

Polymer nanocomposites (PNs) is a kind of polymer which fill with the composite with nano size and widely used especially in food packaging, labels, coatings and etc. The properties of Polypropylene can be adjusted by two approaches which is to change its molecule structure by modification of its three basic building blocks (polyether or polyester, diisocyanate, and chain extender) and then, to introduce the inorganic fillers into the polyprpylene matrix. In this project, pure PP will reinforced by adding the Cloisite® C20A at 1wt%,3wt% and 5wt% composites inside PP matrix by melt intercalation method using twin screw extruder, then molded using hot press to prepare samples. Attendance of C20A in polypropylene matrix can be detected by using FTIR at the peak 1580 cm^{-1}. Rockwell Brinell Hardness test was used to study the hardness and the result showed that the hardness increased up to 28%. Universal Mechanical test used to study the tensile of the samples and the result indicates that the strength of the PP with C20A had been improved up to 34%. The results show that, PP with additional of C20A was improved in their mechanical properties due to maximum intercalation and exfoliated between PP and C20A.

ABSTRAK

Polimer nanokomposit ialah polimer yang diisi dengan komposit bersaiz nano dan digunakan secara meluas terutamanya dalam pembungkusan makanan, pembalutan dan lain-lain. Sifat polipropailin boleh di ubah melalui dua cara iaitu dengan mengubah struktur asas molekulnya (poliether atau poliester, diisosianat, dan pemanjangan rantaian), dan seterusnya dengan memperkenalkan pengisi bukan organic ke dalam acuan polipropailin.. Di dalam projek ini, PP asli akan di perkuatkan dengan menambah Cloisite® C20A pada komposisi 1%, 3% dan 5% (peratusan berdasarkan berat) ke dalam acuan PP asli melalui kaedah pencairan interkalasi menggunakan penonjol skrew berkembar, kemudian, diacu menggunakan penekan panas untuk menyediakan sampel. Kewujudan C20 dalam acuan polipropailin boleh di kesan menggunakan FTIR pada puncak 1580 sm^{-1}. Penguji kekerasan Rockwell Brinell digunakan untuk mengkaji kekerasan polimer nanokomposit dan keputusan menunjukkan kekerasan meningkat sebanyak 28%. Penguji umum mekanikal pula digunakan untuk mengkaji regangan sampel, dan keputusan menunjukkan regangan PP dengan kewujudan C20A bertambah baik sebanyak 34%. Keputusan membuktikan bahawa acuan PP asli dengan C20A memperbaiki cirri-ciri mekanikal berdasarkan interkalasi dan eksfolasi maksimum di antara matrik PP dan C20A.

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LIST OF ABBREVIATION

PP	-	Polypropylene
CNT	-	Carbon nanotube
HDT	-	High heat distortion temperature
C20A	-	Cloisite C20A
PLS	-	Polymer layered-silicate
MMT	-	Montmorillonite
PLSN	-	Polymer layered-silicate nanocomposite
TSE	-	Twin-screw extruder
SSE	-	Single-screw extruder
TEM	-	Transmission electron microscop
XRD	-	X-ray diffraction
PPN	-	Polypropylene nanocomposite
Pf	-	Permeability of the filled and
Pu	-	Permeability of the unfilled polymer
Φp	-	Volume fraction of the polymer
Φf	-	Volume fraction of the filler
E	-	Modulus elasticity
FTIR	-	Fourier transform infrared spectroscopy
BHN	-	Brinell hardness number

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The field of nanotechnology is one of the most popular areas for current research and development in basically all technical disciplines. The investigations of nanotechnology cover a broad range of topics, but typically in polymer science and technology. Other areas include polymer-based biomaterials, nanoparticle drug delivery, miniemulsion particles, fuel cell electrode polymer bound catalysts, polymer blends and nanocomposites. There are diverse of topics to study on nanocomposites field including composite reinforcement, barrier properties, flame resistance, electro-optical properties, cosmetic applications, bactericidal and mechanical properties. Nanotechnology is not new to polymer science as prior studies before the age of nanotechnology involved nanoscale dimensions but were not specifically referred to as nanotechnology until recently (D.R Paul *et al.* 2008). Nanocomposites as a reinforced filler such as carbon black, colloidal silica and fiber has been investigated for decades. Almost lost in the present nanocomposite discussions are the organic–inorganic nanocomposites based on sol–gel chemistry which have been investigated for several decades (Wen J *et al.* 1996). The expended research's on Polymer Nanocomposites was started by Toyota Company when they created the first polymer clay nanocomposite in 1985 (Usuki et al. 1993, 1995). The momentum has steadily built to create reinforced engineering materials on the nanometer scale. Research and development has proceeded excitedly in efforts to incorporate the three primary nanoadditives to polymers clays, single-wall and multiwall Carbon Nanotubes (CNT), and metal or metal oxides, thereby improving performance of thermoplastics in various ways, from increasing polymer strength to enhancing inflammability or other properties.

Polypropylene (PP) is one of the fastest growing classes of thermoplastics. This growth is attributed to its attractive combination of low cost, low density, and high heat distortion temperature (HDT). However, there are still lacks in physical and chemical properties that can limit universal use of any given polymer resin. Pure PP is poor oxygen barriers and low in dimensional and thermal stability limits their scopes in food packaging and automotive applications. Most schemes to improve polypropylene gas barrier properties involve either addition of higher barrier plastics via a multilayer structure or surface coatings. Even this approach effective, but increasing on production cost enhance PP to be used in the first place economy. Currently, automotive and appliance applications employ glass or mineral-filled systems with loading levels ranging from 15 to 50 wt%. This approach improves most mechanical properties, but polypropylene's ease of processing is somewhat compromised. Furthermore, the need for higher filler loading leads to greater moulded part weight (Guoqiang Qian *et al*.2003).

When nanocomposites are formed, they exhibit significant characteristics improvements in physical, chemical, and mechanical properties. Usually at very low layered silicate loading, nanocomposites exhibit a greatly improved tensile strength, stiffness, hardness, better dimensional stability, decreased thermal expansion coefficient, and reduced gas barrier properties in comparison with pure polymer. In both academic and industrial locations, the study of polypropylene nanocomposites is an intense area of current interest and investigation (Guoqiang Qian *et al*.2003). The driving force for such efforts is attributed to huge commercial opportunities in both automotive and packaging applications. Material design at relatively low clay loading addresses the inherent weaknesses of pure polypropylene resin by itself and does so with favorable cost, processing, and reduced molded-part weight profiles.

1.2 Research Objectives

The objectives of this project is to study the effects of the introduction Cloisite® C20A in polypropylene matrix to its mechanical properties; by means of hardness and tensile strength properties.

1.3 Scope of study

Based on the objectives, the work carried out in this project are:

1. To study on the morphology and interference of the Cloisite® C20A in PP matrix.
2. To study the hardness properties of PP/Cloisite® C20A by mean of Rockwell/Brinell test.
3. To study the tensile strength of PP/Cloisite® C20A by mean of tensile test.

1.4 Main Contribution

Recent years, study and research on polymer nanoclay were well develop and ascend due to their performance and characteristics in many applications. In chemical engineering, polymer nanoclay is typically analyzed in terms of their properties changes. To understand about their properties changes, pure polymer was incorporated with a few percent of nanoclay (Cloisite C20A). In this work, C20A was added at 0%, 1%, 3% and 5% by weight into polymer matrix in case to study the optimum weight percent that PP/C20A can show their maximum changes in mechanical properties. Melt intercalation method was implemented in this work to carry out the best result.

CHAPTER 2

CHEMISTRY AND PHYSICAL PROPERTY OF POLYPROPYLENE NANOCOMPOSITES

2.1 Introduction

This chapter reviews the current development on polymer nanoclay. A crucial review on the increment of mechanical properties with the introduction of nanoclay (Closite C20A) is the main interest in this study. Besides that, a brief summary about the experimental measurement technique to determine the hardness and tensile strength was also discussed.

Layered silicates dispersed as reinforcing phase in an engineering polymer matrix are one of the most important forms of such ‘‘hybrid organic–inorganic nanocomposites’’. Although the high aspect ratio of silicate nanolayers is ideal for reinforcement, the nanolayers do not easily disperse in the most polymers due to their preferred face-to-face stacking in agglomerated tactoids. Dispersion of the tactoids into discrete monolayers is further hindered by the intrinsic incompatibility of hydrophilic-layered silicates and hydrophobic engineering plastics.

Work in polymer nanocomposites has exploded over the last few years. The prospect of a new materials technology that can function as a low-cost alternative to high-performance composites for applications ranging from automotive to food packaging to tissue engineering has became irresistible to researchers around the world.

The essence of nanotechnology is the ability to work at the molecular level to create large structures with fundamentally new molecular organization. Materials with features on the scale of nanometers often have properties different from their macro scale counterparts. Important among nanoscale materials are nanohybrids or nanocomposites, materials in which the constituents are mixed on a nanometer-length scale. They often exhibit properties superior to conventional composites, such as strength, stiffness, thermal and oxidative stability, barrier properties, as well as unique properties like self-extinguishing behavior and tunable biodegradability (Krishnamoorti, 2001).

Silicates are the most popular materials used in the synthesis of polymer nanocomposites. They are composed of layers that have one dimension in nano-scale. The most common nanofiller is sodium montmorillonite, i.e. a natural smectite clay (2:1 phyllosilicate) that consists of regular stacks of aluminosilicate layers with a high aspect ratio and a high surface area. Because of the hydrated sodium cations in the clay galleries, natural montmorillonite is hydrophilic, which is a major drawback to have it homogeneously dispersed in organic polymers. The penetration of polymer or monomer molecules into the silicate galleries in the nanocomposite system determines the homogeneity of the clay dispersion by breaking up the layered structure. The wetting of particle surfaces by organic polymers is very difficult due to this organophobic behavior of the natural clay. This may be overcome by the modification of clay with surfactants including onium ions. In this modification, a cation exchange reaction takes place between the metal cations in the galleries and the surfactant onium ions. The intercalation of interlayer spacing between silicate galleries occurs within organophilic clays due to the modification. This improves the diffusion of monomer and polymer molecules into the silicate galleries effectively during polymer/layered silicate nanocomposite synthesis.

2.2 Polypropylene

2.2.1 Synthesis of PP

An important concept in understanding the link between the structure of polypropylene and its properties is tacticity. The relative orientation of each methyl group (CH_3 in the figure 2.1) relative to the methyl groups in neighboring monomer units has a strong effect on the polymer's ability to form crystals.

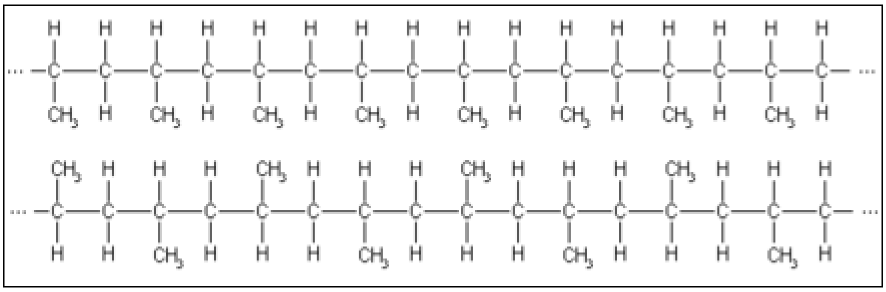
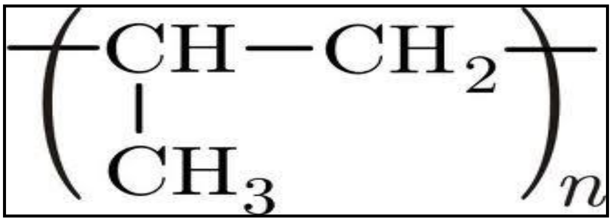


Figure 2,1: Short segments of polypropylene, showing examples of isotactic (above) and syndiotactic (below) tacticity.

A Ziegler-Natta catalyst is able to restrict linking of monomer molecules to a specific regular orientation, either isotactic, when all methyl groups are positioned at the same side with respect to the backbone of the polymer chain, or syndiotactic, when the positions of the methyl groups alternate. Commercially available isotactic polypropylene is made with two types of Ziegler-Natta catalysts. The first group of the catalysts encompases solid (mostly supported) catalysts and certain types of soluble metallocene catalysts. Such isotactic macromolecules coil into a helical shape; these helices then line up next to one another to form the crystals that give commercial isotactic polypropylene many of its desirable properties.

When the methyl groups in a polypropylene chain exhibit no preferred orientation, the polymers are called atactic. Atactic polypropylene is an amorphous rubbery material. It can be produced commercially either with a special type of supported Ziegler-Natta catalyst or with some metallocene catalysts.

Modern supported Ziegler-Natta catalysts developed for the polymerization of propylene and other 1-alkenes to isotactic polymers usually use TiCl4 as an active ingredient and MgCl2 as a support (Kissin, 2008, Severn and Jones, and Moore) The catalysts also contain organic modifiers, either aromatic acid esters and diesters or ethers. These catalysts are activated with special cocatalysts containing an organoaluminum compound such as Al(C2H5)3 and the second type of a modifier. The catalysts are differentiated depending on the procedure used for fashioning catalyst particles from MgCl2 and depending on the type of organic modifiers employed during catalyst preparation and use in polymerization reactions. Two most important technological characteristics of all the supported catalysts are high productivity and a high fraction of the crystalline isotactic polymer they produce at 70-80°C under standard polymerization conditions. Commercial synthesis of isotactic polypropylene is usually carried out either in the medium of liquid propylene or in gas-phase reactors.



$$\left(\underset{\displaystyle CH_3}{CH} - CH_2 \right)_n$$

Figure 2.2: Molecular structure of PP (Busico and Cipullo, 2001)

2.2.2 Physical Properties of PP

Another physical property of Polypropylene is a colourless, translucent to transparent solid with a glossy surface. Polypropylene does not present any risk to the skin. The polymer should not be exposed to flames as it gives off smoke on burning. Hence, PP is one of the most secure thermoplastics that can be use in most applications. Even Polypropylene has its own advantages in certain properties, but it still needed some modification to fulfill the current requirements from industries, automotives and etc. Table 2.1, 2.2, 2.3 shows the mechanical, thermal, physical, electrical and process properties for polypropylene.

Table 2.1: Mechanical properties for polypropylene.

Mechanical Properties	
Elastic Modulus (MPa)	7590 - 10350
Flexural Modulus (MPa)	6555 - 6900
Tensile Strength (MPa)	58 - 104
Compressive Strength (MPa)	61 - 68
at yield or break	
Flexural Strength (MPa)	72 - 15
at yield or break	
Elongation at break (%)	2 - 4
Hardness	102 - 111
Izod Impact (J/cm of notch)	0.7 - 1.1
1/8" thick specimen unless noted	

Table 2.2: Thermal properties for polypropylene.

Thermal Properties	
Coef of Thermal Expansion (10^{-6}/ºC)	27 - 32
Deflection Temperature (ºC)	166
	149 - 166
Thermal Conductivity (W/m-ºC)	0.351 - 0.368

Table 2.3: Processing properties for polypropylene

Processing Properties	
Melt Flow (gm/10 min)	1 - 20
Melting Temperature (ºC)	168
Processing Temperature (ºC)	232 - 288
Molding Pressure (MPa)	69 - 172
Linear Mold Shrinkage (cm/cm)	0.003 - 0.005

Table 2.4: Physical and Electrical properties for polypropylene

Physical & Electrical Properties	
Specific Gravity	1.22 - 1.23
Water Absorption (% weight increase)	0.09 - 0.1
	0.05 - 0.06
Dielectric Strength (V/mil);	500 - 510
1/8" thick specimen unless noted	

2.2.3 Application of PP

PP is widely used for many applications due to its low cost, low density, high thermal stability and resistance to corrosion and it is one of thermoplastic polymer, made by the chemical industry and used in a wide variety of applications, including food packaging, textiles, plastic parts and reusable containers of various types, basic euqipment for military, laboratory equipment, automotive components, and polymer banknotes (Michail Dolgovski *et al*.2003).

Many plastic items for medical or laboratory use can be made from polypropylene because it can withstand the heat in an autoclave. Its heat resistance also enables it to be used as the manufacturing material of consumer-grade kettles. Food containers made from it will not melt in the dishwasher, and do not melt during industrial hot filling processes. For this reason, most plastic tubs for dairy products are polypropylene sealed with aluminum foil (both heat-resistant materials).

Polypropylene is widely used in ropes, distinctive because they are light enough to float in water. For equal mass and construction, polypropylene rope is similar in strength to polyester rope. Polypropylene costs less than most other synthetic fibers.

Polypropylene is also used as an alternative to polyvinyl chloride (PVC) as insulation for electrical cables for LSZH cable in low-ventilation environments, primarily tunnels. This is because it emits less smoke and no toxic halogens, which may lead to production of acid in high-temperature conditions.

Polypropylene is also used in particular roofing membranes as the waterproofing top layer of single-ply systems as opposed to modified-bit systems. Polypropylene is most commonly used for plastic moldings, wherein it is injected into a mold while molten, forming complex shapes at relatively low cost and high volume; examples include bottle tops, bottles, and fittings.

2.3 Nanofiller

Fillers are defined as materials that are added to a polymer matrix formulation to lower the compound cost or to improve properties. Such materials can be in the form of solid, liquid or gas. By the appropriate selection of these materials, not only the economics but also the other properties such as processing and mechanical behavior can be improved. Although these fillers retain their inherent characteristics, very significant differences are often seen, depending on the molecular weight, compounding technique, and the presence of other additives in the formulation. In terms of nanocomposites, there are 3 commons nano filler that always used in polymerization which are clay, metal and carbon nanotube composites.

S. K. Samal *et al.* (2007) investigated that polymer clay nanocomposites have been the subject of many recent papers due to their excellent properties and industrial applications. While Patino-Soto *et al.* (2008) found that polymer-layered silicate nanocomposites enhanced the improvement of polymer properties, such as thermal and dimensional stability, lower gas permeability, better surface finish, improved biodegradability, and enhanced mechanical behavior.

Blending polypropylene with clays to form nanocomposites is a way to increase its utility by improving its mechanical properties. Compared to conventional composites, polymer layered-silicate (PLS) nanocomposites have maximized polymer-clay interactions since the clay is dispersed on a nanometer scale. This results in lighter materials with higher modulus and reduced linear thermal expansion making them desirable for some applications such as exterior automobile parts (Michail Dolgovski *et al*.2003).

2.3.1 Structure of Layered Silicate Organoclay

Layered silicates dispersed as a reinforcing phase in polymer matrix are one of the most important forms of hybrid organic-inorganic nanocomposites (Okada and Usuki, 1995). Their crystal structure consists of layers made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. The layer thickness is around 1 nm, and the lateral dimensions of these layers may vary from 30 nm to several microns or larger, depending on the particular layered silicate. Van der Waals forces stack the layers leading to a regular gap named as interlayer or gallery.

MMT, hectorite, and saponite are the most commonly used layered silicates. Layered silicates have two types of structure which are tetrahedral-substituted and octahedral substituted. In the case of tetrahedrally substituted layered silicates the negative charge is located on the surface of silicate layers, and hence, the polymer matrices can interact more readily with these than with octahedrally-substituted material. The structure and chemistry for these layered silicates are shown in Figure 2.3(Süd-Chemie, 2000) and Figure 2.4.

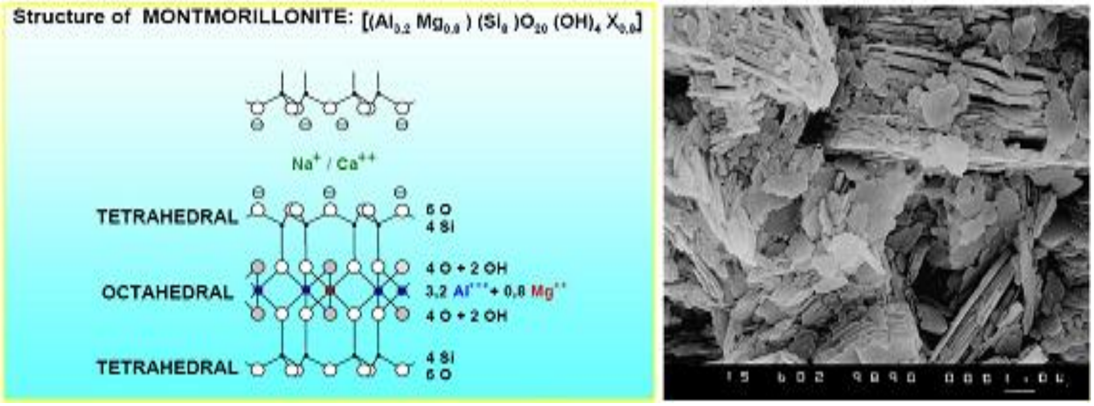


Figure 2.3: Schematic Illustration of 2:1 phyllosilicates structure and its SEM Image (Source: WEB_1 2000)

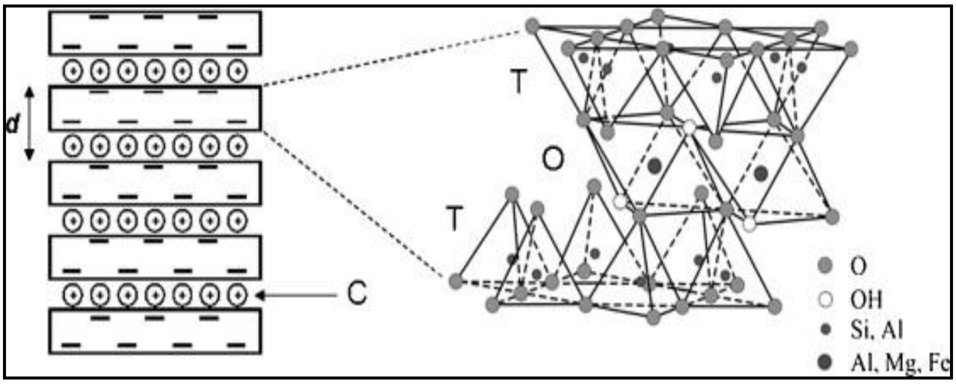


Figure 2.4: Layered silicate structure (T, tetrahedral sheet; O, octahedral sheet; C, intercalated cations; d, interlayer distance). Reproduced with permission from Lagaly copyright (1993) of Marcel Dekker.

There are two particular characteristics of layered silicates that are generally considered for polymer/layered silicate nanocomposites. The first is the ability of the silicate particles to disperse into separate layers. The second is the ability to modify their surface chemistry through ion exchange reactions with organic and inorganic cations. These two characteristics are related to each other since the degree of dispersion of layered silicate in a particular polymer matrix depends on the interlayer cation.

2.3.2 Organoclay Modified Layered Silicate

Nanocomposite synthesis may not be successful with a physical mixture of polymer and layered silicate. In immiscible systems, conventionally filled polymers, the poor physical interaction between the organic and the inorganic components leads to poor mechanical and thermal properties. In contrast, strong interactions between the polymer and the layered silicate in polymer/layered silicate nanocomposites lead to the organic and inorganic phases being dispersed at the nanometer level. As a result, nanocomposites exhibit unique properties not shared by their micro counterparts or conventionally filled polymers (Usuki *et al.* 1990, Biswas *et al.* 2001).

Pristine layered silicates usually contain hydrated Na+ or K+ ions (Brindly *et al.*1980). Obviously, in this pristine state, layered silicates are only miscible with hydrophilic polymers, such as poly(ethylene oxide) (PEO) (Aranda *et al.* 1992), or poly(vinyl alcohol) (PVA) (Greenland 1963). To render layered silicates miscible with other polymer matrices, one must normally convert the hydrophilic silicate surface to an organophilic one, making the intercalation of many engineering polymers possible.

Generally, this can be done by ion-exchange reactions with cationic surfactants including primary, secondary, tertiary, and quaternary alkylammonium or alkyl phosphonium cations. Alkyl ammonium or alkylphosphonium cations in the organosilicates lower the surface energy of the inorganic host and improve the wetting characteristics of the polymer matrix, and result in a larger interlayer spacing. Additionally, the alkylammonium or alkylphosphonium cations can provide functional groups that can react with the polymer matrix, or in some cases initiate the polymerization of monomers to improve the strength of the interface between the inorganic and the polymer matrix (Blumstein 1965, Krishnamoorti *et al.* 1996).

The replacement of inorganic exchange cations by organic onium ions on the gallery surfaces of smectite clays not only serves to match the clay surface polarity with the polarity of the polymer, but it also expands the clay galleries (Figure 2.5). This facilitates the penetration of the gallery space intercalation by either the polymer precursors or preformed polymer. Depending on the charge density of clay and the onium ion surfactant, different arrangements of the onium ions are possible. In general, the longer the surfactant chain length, and the higher the charge density of the clay, the further apart the clay layers will be forced. This is expected since both of these parameters contribute to increasing the volume occupied by the intra gallery surfactant. Depending on the charge density of the clay, the onium ions may lie parallel to the clay surface as a monolayer, a lateral bi-layer, a pseudo-tri-molecular layer, or an inclined paraffin structure. At very high charge densities, large surfactant ions can adopt lipid bi-layer orientations in the clay galleries.(Lagaly, 1986)

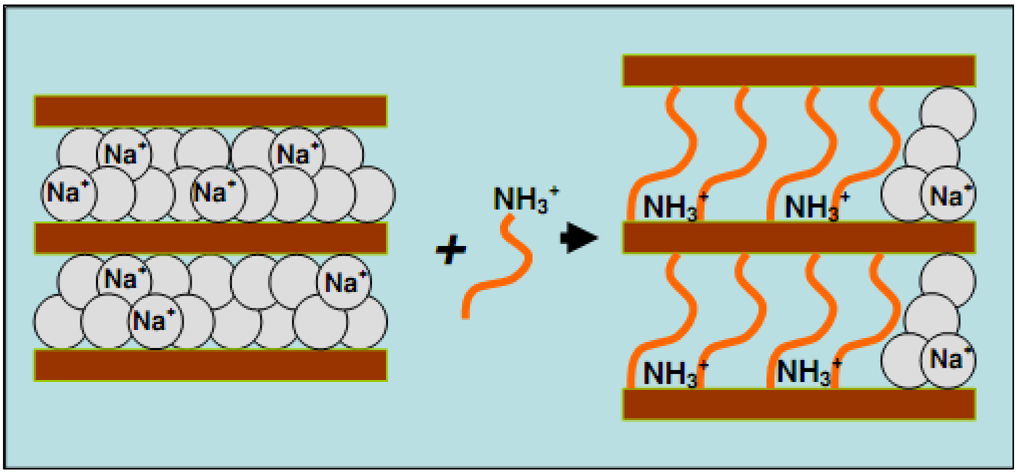


Figure 2.5: Ion Exchange Reaction between Na-MMT and Alkyl Ammonium Molecules (Lagaly, 1986).

Traditional structural characterization to determine the orientation and arrangement of the alkyl chain was performed using wide angle X-ray diffraction (WAXD). Depending on the packing density, temperature and alkyl chain length, the chains were thought to lie either parallel to the silicate layers forming mono or bi-layers, or radiate away from the silicate layers forming mono or bimolecular arrangements. (Lagaly,1986). The alkyl chains can vary from liquid-like to solid-like, with the liquid-like structure dominating as the interlayer density or chain length decreases (Figure 2.6), or as the temperature increases. There are three models for alkyl chain aggregation: (a) short chain lengths, the molecules are effectively isolated from each other, (b) medium lengths, quasi discrete layers form with various degree of in plane disorder and inter digitations between the layers and (c) long lengths, interlayer order increase leading to a liquid-crystalline polymer environment. This occurs because of the relatively small energy differences between the trans and gauche conformers; the idealized models described earlier assume all trans conformations. In addition, for longer chain length surfactants, the surfactants in