

CHAPTER I

INTRODUCTION

1.1 Background

At present, Polypropylene has been used in large quantities in numerous fields of application for many years. It has a number of favorable characteristics for using as a matrix material in high volume composite application. It is cheap, abundantly available in a variety of grades, very tough and easy to process. Because of those advantages, PP was used as polymeric matrix in this work to prepare the composite.

Filler morphology and interfacial characteristics are critical aspects of the engineering design of composite materials [Ishida, 1990]. Depending on the mechanism of material failure, different size filler particles and mechanical coupling are required to improve of the performance of polyolefins. PP are commonly used as pipes for natural gas lines. The reliability of these infrastructural materials is important for energy safety.

Because the toughness of these semicrystalline polymeric materials depends on the degree to which crystals are linked together, it is logical to increase the number and effectiveness of such linkages. To accomplish this design goal, polymer chains that can cocrystallize with the matrix will be grafted onto the particle surface. Moreover, interconnection between crystals will be multiplied if particles are extremely small and finely dispersed. In this research, nanocomposite material which is a type of composite containing particles, platelets, or fibers that have at least one dimension in the size range of nanometer will be developed by controlling filler morphology and interfacial

characteristic which are critical aspects for molecular engineering of composite materials. The method to prepare this nanocomposite is the utilization of intercalation reactions of clay minerals [Okada, 1995]. A clay mineral is a potential candidate for the filler of a molecular composite since it consists of layered silicates, 1 nm thick, and undergoes intercalation with organic molecules.

The lack of affinity between hydrophylic silicate and hydrophobic synthetic polymers causes agglomeration of the mineral in the polymer matrix. Swelling of each template of silicate with organic molecules is a matter of vital importance to produce this type of molecular composites. In this thesis research, we investigated whether PP could be inserted into clay gallery or a clay modified with silane coupling agent and MAPP. In this case, clays with grafted chain when co-crystallized with polymer matrix can act as an efficient link between crystals. Influence of molecular bridging between crystals on crack resistance is well known [Lustiger, 1983]. Tie chains are resistant to drawing in semicrystalline polymers. The break down of tie chains allow crack to grow slowly. Numerous tie chains can distribute the stress and cause the failure to be ductile. With tie chains, the composite is expected to have a higher resistance to slow crack growth. Slow crack growth is a serious concern for public safety as well as financial reasons. The slow crack growth failure occurs under a combination of a notch, low stress and high temperature. Slow crack growth period can be used to determine the life time of structure such as pipe or storage containers. In addition, the improvement of other mechanical properties such as the tensile and impact properties can be expected with an addition of tie chain.

1.2 Slow Crack Growth

Failures of polymeric materials and components often occur under long-term low-level loading conditions. One cause out of many reasons for this is due to a variety of environmental effects producing structural change. The slow crack growth (SCG) behavior of polyolefins can be explained by a structure consisting of a network of tie molecules and crystals. The SCG process consists of disentanglement of the tie molecules from the crystals. The density of the tie molecules is the primary factor that determines the rate of SCG; for a given applied stress, the average force on a tie molecules is inversely proportional to the density of tie molecules. The crystals are important because their strength determines the resistance to the disentanglement process and also the average distance between adjacent lamella influences the probability to form a tie molecule.

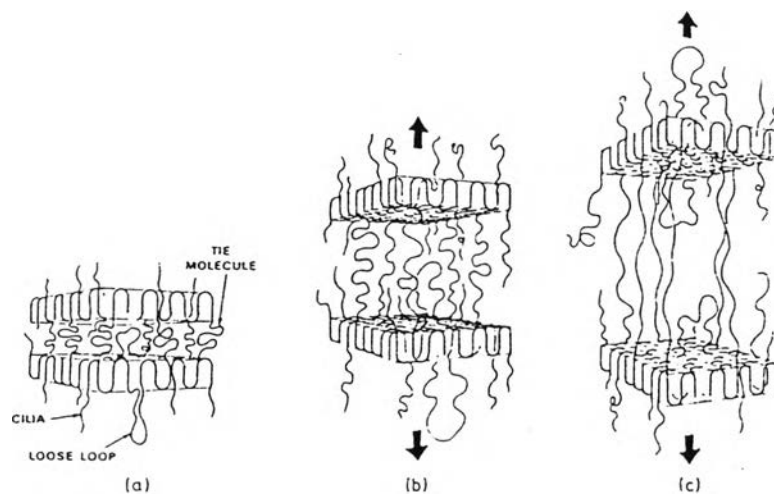


Figure 1.1 Picture of initial steps in the deformation of polyethylene.

Tie molecules can be viewed as the “ glue” that holds the crystalline regions together [Lustiger, 1983]. Separation between adjacent lamellae, either through disentanglement or rupture of the tie molecules, has been identified as the dominant molecular mechanism in the slow crack growth an environmental stress cracking [Lustiger, 1991]. Tie chains provide resistance to drawing in semicrystalline polymers. These load bearing points are attacked by various environmental agents. The breakdown of tie chains also allows cracks to propagate slowly, and with low fracture energy, by a brittle failure mechanism. Numerous tie chains distribute the stress and cause the failure to be ductile, thus improving the fracture energy and polymer lifetime.

It follows from the above discussion that polyolefins materials containing relatively few tie molecules are more susceptible to the various brittle modes of failure. Conversely, materials with relatively high concentrations of tie molecules are more resistant to these types of failures.

However, it should be added that if the proportion of tie molecules to crystalline molecules is too high, the material will display not only high ductility, but also very low stiffness. As in the case of polyethylene pipe, the material must have a certain stiffness to resist exterior mechanical deformation, a balance must be established.

Visualizing the mechanism of brittle failure in terms of the model can help identify molecular parameters of the slow crack growth. Some of these parameters are [Lustiger, 1983]:

- (1) Molecular weight of polymer. The higher the molecular weight, the longer the polymer chains, resulting in more tie molecules and more effective tie molecule entanglements.
- (2) Comonomer content between polymerization. Higher comonomer concentration and longer comonomer short-chain branches provides better brittle fracture resistance, because the portions of polymer chains with the

longer branches probably do not enter the tightly packed lamellar lattice and hence add to the intercrystalline tie molecule material.

- (3) Density/degree of crystallinity of polymer. More crystallinity, the fewer amorphous intercrystalline tie molecules are holding the crystalline phases and hence easier for the slow crack growth to initiate.
- (4) Lamellar orientation. If the lamellae are preferentially oriented perpendicular to the tensile stress direction, they would be more amenable to interlamellar failure than if they are parallel to the stress.

1.3 Clay (Kunipia F)

Clay is a hydrous aluminum silicate in which alkalines or alkaline earths are also present. Clay may be amorphous (allophane), crystalline (kaolinite, halloysite), montmorillonite, vermiculite, mixed-layer type (chlorite) or chain structured (attapulgite). These minerals, which are widely distributed geographically throughout the world, are the natural decomposition products of feldspar, and include kaolins (kaolinite, dickite, nacrite).

The clay used in this study was Kunipia F. It is highly refined montmorillonite whose purity is higher than 99%. Kunipia is composed of completely inorganic, colloidal particles with a large specific surface area as well as high cation exchange capacity and hydration power. Kunipia can easily swell and disperse in water and form a stable aqueous colloid.

Kunipia has a cation exchange capacity of 119 mequiv/100 g. It can intercalate various organic cations by ion exchange. The shape of the silicate sheets in montmorillonite is thin square plate and its dimension is about 2000Å° in length and 10Å° in thickness.

The chemical composition of montmorillonite is ideally:

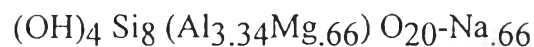


Figure 1.2 Molecular formula of Na^+ montmorillonite.

It is composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet as shown in Figure 3. All the tips of the tetrahedrons point in the same direction and toward the center of the unit. The tetrahedral and octahedral sheets are combined so that the tips of the tetrahedrons of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. The atoms common to both the tetrahedral and octahedral layer become O instead of OH. The layers are continuous in the a and b directions and are stacked one above the other in the c direction.

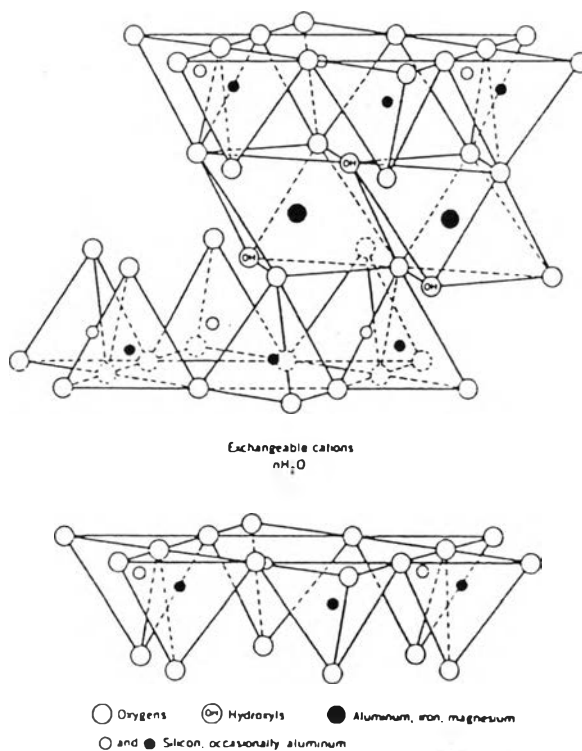


Figure 1.3 Picture of structure of clay.

In the stacking of the silica-alumina-silica units, O layers of each unit are adjacent to O layers of the neighboring units, with the consequence that there is a very weak bond and an excellent cleavage between them. The outstanding feature of the clay structure is that water and other polar molecules, such as certain organic molecules, can enter between the unit layers, causing the lattice to expand in the c direction. The presence of adsorbed intercalated organic molecules may usually be determined by X-ray diffraction techniques.

1.4 Silane Coupling Agent

The silane coupling agents are bifunctional molecules which can improve the bond between organic polymers and silicious fillers. Typical fillers are glass or minerals such as novaculite, kaolin clay, mica, wollastonite, and alumina trihydrate. The silanes have the highest consumption among the various groups of coupling agents. They are structurally similar compounds with the general formula $ZRSiX_3$. Z is a functional group reactive with the polymer components, R is a stable carbon linkage compatible with the resin, and X is a hydrolyzable group, frequently an alkoxy, which is displaced during reaction with the substrate (filler or reinforcer). The most common Z components are amines, methacrylates, epoxys, vinyls, alcoholic, acidic, and chlorinated groups. The R component is an alpha ($-CH_2-$), beta ($-CH_2CH_2-$), gamma ($-CH_2CH_2CH_2-$), or aromatic ($-CH_2C_6H_4-$) group. The gamma group is most heavily used for coupling agents because it provides adequate thermal stability and it is applicable to most resins. Aromatic groups gave thermal stabilities in excess of the gamma substituted silanes. The alkoxy or X group, generally a methoxy or ethoxy, hydrolyzes in aqueous solution to form the

reactive silanol group (Si(OH)_3). This then bonds to the substrate to provide the link between the resin and the filler.

Silane coupling agents are generally considered to be adhesion promoters between mineral fillers and organic matrix resins and they provide improved mechanical strength and chemical resistance to composites.

Silane modification of the organic-inorganic interface will also produce changes in other properties of the mixture that may, at times, be more important than the final adhesion across the interface. The interface, or interphase region, between polymer and filler involves a complex interplay of physical and chemical factors related to the composite performance.

The central area of adhesion determines the mechanical strength and the chemical resistance of a composite, assuming that all other factors are properly controlled. This is the area commonly associated with true coupling agents such as the chrome complexes and organofunctional silanes. The filler surface interacts with the polymer through catalytic activity, orientation of molecular segments, and other modification of polymer morphology. One important function of silane treatments on fillers is to reduce the inhibitory action of fillers on cure of thermosetting resins and to promote alignment of molecular segment of thermoplastic polymers.

Failure in a composite is often in a boundary layer of resin, rather than at the true interface. A silane at the interface may protect a mineral surface against fracture, or may strengthen the boundary layer of resin to have a positive effect on composite properties even if failure is not at the interface.

The heaviest use of silane coupling agents is in glass fiber reinforced plastic, although they have applications with other fillers containing surface hydroxyl groups such as wollastonite, clay, talc, mica, and alumina. The most efficient use of the silane is made by direct application to the filler in aqueous solution preceding processing; however, direct addition to the resin may be

used. The second method requires longer mixing times to assure migration of the coupling agent to the polymer-filler interface. The silanes basic function is to increase the strength of the resin; however, it may improve other properties as well. Silanes provide stable electrical properties including dielectric constant, dissipation factor, and volume resistivity. They increase the moisture of resins and control the rheology of the composite during processing.

1.5 Literature Survey

To date, there are no published reports concerning with the grafting of polypropylene onto these thin oxide silicate layers. But there are many papers in related fields.

Kato et al. [1997] had synthesized polypropylene (PP) oligomer-clay intercalation compounds by using three kinds of PP oligomers and organophylic clay. PP oligomers were two types of maleic-anhydride-modified PP oligomers containing different amounts of maleic anhydride groups and one type of hydroxy modified PP oligomer. Organophylic clay was sodium-ion-exchanged montmorillonite with octadecylammonium ion (C18-Mt). PP oligomer was mixed with C18-Mt at 200°C. Maleic-anhydride modified PP oligomer, which was of high acid value type, and hydroxy-modified PP oligomer were intercalated between silicate layers of clay; and PP oligomer-clay intercalation compounds were synthesized successfully. But maleic-anhydride-modified PP oligomer, which was of low acid value type, was not intercalated.

Kyu et al. [1996] had synthesized a novel in situ composite comprised of kaolin clay fillers and polyamide 6 (Nylon-6). It was prepared by colloidal approach by suspending kaolin particles in aqueous caprolactam and then

polymerizing the caprolactam under elevated temperature and pressure. This in situ polymerization technique was enable the deposition of nylon molecules directly onto the filler surface. It offered a much larger contact surface area for the nylon molecules to interact with the filler particles and enhanced filler/matrix interaction through polymer miscibility. The kaolin particles were shown to be uniformly dispersed in Nylon-6 matrix without appreciable agglomeration. In the highly clay-loaded composites such as the 50/50 kaolin/Nylon-6 in situ composite, the deposited nylon molecules probably formed a coated layer on the filler particles. This kind of nylon coated fillers may be applied as a reinforcing entity to commercial Nylon-6 or -66 by improving particle dispersion and melt processability. The 50/50 kaolin/Nylon-6 and Nylon-66 took advantage of their good properties and to reduce cost. Rheology and mechanical properties of the masterbatch/nylon composites had been investigated in comparison with those of the conventional melt-mixed composites. The improvement of rheological and mechanical properties of the in situ composites had been discussed in relation to the composite structure.

Lu et al. [1996] had studied the critical molecular weight for resisting slow crack growth in a polyethylene. In this study, an ethylene-hexene copolymer was fractionated into five fractions and the density of short-chain branches was measured for each fraction. The slow crack growth behavior was measured on each fraction by sandwiching the small amount of fractionated resin of about 0.2 g between polyethylene grips. The resistance to slow crack growth was negligible for the three fractions whose M_w was less than 1.5×10^5 . For the fourth fraction with MW greater than 1.5×10^5 , the resistance to slow crack growth was very high, being greater than that for the whole resin eventhough its density of short-chain branches was less than that of the whole resin. It could be concluded that a molecular weight greater than 1.5×10^5 was

required to create the number of tie molecules that was necessary to produce a high resistance to slow crack growth in this particular copolymer.

Jung et al. [1995] investigated the morphology of modified silicate filler in high density polyethylene and nitrile copolymer matrices. The hydrophilic clay was intercalated with dodecylamine by ion exchange reaction. X-ray diffraction and transmission electron microscopy showed that the modified silicate layers were dispersed in the polymeric matrices but most layers aggregated in thin stacks. When compared between HDPE and nitrile, XRD and TEM indicated that the modified silicate layers were more dispersed in the nitrile copolymer system than in the HDPE system. Due to their dispersion and morphology, the enhancement of barrier and mechanical properties for the nanocomposite system were expected.

Zhou et al. [1995] had measured the resistance to slow crack growth of the binary blends of high density polyethylene and ethylene-butene random copolymer. Results of this experiment showed that by an addition of the copolymer, time to failure under a constant stress intensity was increased. It was because the copolymer could crystallize and the effect was greater for the higher branch density.

Lemmon et al. [1995] had prepared and characterized nanocomposites of poly(ethylene oxide) with layered solids. Single-phase nanocomposites containing montmorillonite, MoS_2 , MoO_3 or TiS_2 with poly(ethylene oxide) were obtained by the exfoliation of the layered solid, adsorption of polymer, and subsequent precipitation of solid product. Aqueous solutions could be employed for all syntheses except PEO/ TiS_2 , which was prepared from LiTiS_2 in an N-methyl formamide (NMF) solution. X-ray diffraction indicated that the resulting solids increased in basal-plane repeated by approximately 4 or 8 Å, consistent with the incorporation of single or double layers of polymer between sheets. Reaction stoichiometry and elemental analysis provided compositions

for the single-phase products, and thermal and electrical properties were examined.

Okada et al. [1995] prepared several polymer-clay hybrids, in which polymers were nylon 6, nitrile rubber and others. These hybrids were prepared by the utilization of intercalation reactions of clay minerals. They, when molded, had excellent mechanical, thermal and chemical properties compared with unfilled polymers and/or conventional composites. Syntheses, structures and application of the hybrids were presented. In the hybrids negatively charged silicate (clay mineral) and positively charged polymer-ends were directly connected through ionic bonding.

Phillip et al. [1995] synthesized a new polymer-ceramic nanocomposite which consisted of well-dispersed, two-dimensional layers of an organically modified mica-type silicate (MTS) within a degradable poly(ϵ -caprolactone) matrix. A protonated amino acid derivative of MTS was used to promote delamination/dispersion of the host layers and initiate ring-opening polymerization of ϵ -caprolactone monomer, resulting in poly(ϵ -caprolactone) chains that were ionically bound to the silicate layers. The polymer chains could be released from the silicate surface by a reverse ion-exchange reaction and were shown to be spectroscopically similar to pure poly(ϵ -caprolactone). Thick films of the polymer nanocomposite exhibited a significant reduction in water vapor permeability that showed a linear dependence on silicate content. The permeability of nanocomposite containing as low as 4.8% silicate by volume was reduced by nearly an order of magnitude compared to pure poly(ϵ -caprolactone).

Kojima et al. [1993] reported the synthesis of composites of nylon 6 and silicate layer of montmorillonite and saponite, NCH and NCHP, by changing the type and the amount of clay minerals. From the experiment, NCH had excellent mechanical properties when compared with pure nylon 6; strength,

modulus and heat distortion temperature were higher than nylon 6. NCHP had a smaller effect on the increase of these mechanical properties. Higher crystallinity or a higher filler amount gave a higher elastic modulus, strength and heat resistance.

Khunova et al. [1993] studied on the effect of reactive polypropylene on the properties of filled polypropylene composites. They showed that mechanical properties of polypropylene composites based on inorganic fillers could be significantly improved if a small part of the added polypropylene was chemically modified by maleic anhydride. The effect of addition of maleic anhydride modified polypropylene in calcium carbonate as well as in zeolite-filled polypropylene composites was to increase tensile strength and impact resistance. The ultimate properties of the composites, however, were determined by both filler and modifier concentrations. This paper reported the design and execution of a planned experiment using a statistical method to study the complex dependence of product composition on the ultimate composite properties. While the effect of modifier concentration on tensile strength of all composites was unique and positive, the impact strength of zeolite-filled polypropylene composite showed a more complex dependence on the modifier and filler concentrations. Thus, appropriate selection of a surface diagram involving composition and properties helped in the design of polypropylene composites with a wide range of properties.

Kojima et al. [1993] synthesized nylon 6-clay hybrid which is a molecular composite of nylon 6 and uniformly dispersed silicate layers of montmorillonite. One-pot synthesis of the hybrid was carried out by the following procedures. Montmorillonite was dispersed in water, and then ϵ -caprolactam, acid (phosphoric acid, hydrochloric acid, benzenesulfonic acid, isophthalic acid, trichloroacetic acid, or acetic), and 6-aminocaproic acid were added to the dispersion. The mixtures were reacted at 260°C for 6 hours,

yielding the nylon 6-clay hybrids (1potNCHs). X-ray diffraction revealed that the silicate layers of 1potNCH by phosphoric acid were uniformly dispersed in the nylon 6 matrix. The 1potNCH had excellent mechanical properties. The strength and the modulus of the hybrid increased when compared with previously reported nylon 6-clay hybrid (NCH) synthesized by montmorillonite intercalated with 12-aminolauric acid. The heat distortion temperature (HDT) of the 1potNCHs, montmorillonite had a smaller effect on the increase of those properties, and interlayer spacing of montmorillonite was observed at 20 \AA .

Chiang et al. [1988] prepared the PP/mica composites. To improve adhesion between polypropylene (PP) and mica in PP composites, acrylic acid (AA) was grafted-copolymerized on to PP by a melt-mixing method. At the same time, applying a silane coupling agent to treat the surface of organic filler enhanced the mechanical, thermal, and electrical properties, as well as decreased mold shrinkage and color difference of the composites.

Lustiger et al. [1983] studied the slow crack fracture in polyethylene pipe used for natural gas distribution. Constant tensile load testing of polyethylene pipe sections indicated a link between this mode of failure and environmental stress cracking. Interlamellar fracture could occur in both the presence and absence of an acceleration environment. The fiber deformation process was reviewed, describing the role of amorphous entangled tie molecules in preventing slow crack-type fracture. Relative resistance to slow crack brittle failure was explained in terms of the model for various materials tested.

1.6 Objectives

The objectives of this work are to prepare and characterize the nanofiller and PP/clay nanocomposites. The nanofiller was developed by grafting MAPP and silane coupling agent onto the silicate clay. The effect of tie molecules and dispersability of these filler particles in PP matrix were expected to increase the mechanical properties. The tensile, impact properties and the resistance to slow crack growth were investigated.