

## **CHAPTER I**

### **INTRODUCTION**

#### **1.1 Background**

Polypropylene has been used in large quantities in numerous fields of application for many years. It has a number of favorable characteristics for use as matrix material in high volume composite applications. It is cheap, abundantly available in a variety of grades, very tough and easy to process. Its properties are determined by its crystalline structure, the relative amount of amorphous and crystalline phases and crystal modification of PP products [Samuel, 1974].

In the case of ethylene - alpha olefin copolymers, which are being used increasingly in transoceanic fiberoptic cable, as well as for piping for natural gas distribution and in - ground liners for solid waste disposal, cracks initiate at a point of stress concentration such as void, notch or dirt particle and grow under low stresses that occur during service. This type of failure, slow crack growth, is a serious concern for public safety and financial reasons. The slow crack growth failure occurs under a combination of a notch, low stress and plane strain condition [Lustiger, 1991]. This property will be investigated because they are very sensitive to the change in the molecular and morphological structure and the lifetime of structures such as pipe or storage containers are determined by their resistance to the slow crack growth. A good understanding of this type of failure process in semicrystalline polymers can be realized by developing a good understanding of the amorphous

of the amorphous region. Particularly important is the role of tie molecules - the amorphous chain that bridge adjacent lamellae. The influence of molecular bridging between crystals such as tie chains constitute a “glue” that holds the crystalline regions together. The separation between adjacent lamellar, either through disentanglement or rupture of the tie molecules, has been identified as the dominant molecular mechanism in the slow crack growth type of failure found in polyolefins. Large number of ties chain are critical for resistance to environmental effects. The breakdown of tie chains also allows cracks to grow slowly with low fracture energy. Numerous tie chains distribute the stress and cause the failure to be ductile, therefore improving the fracture energy and polymer lifetime [Lustiger and Ishikawa, 1991].

In this research a nanocomposite, which is the physical arrangement of the different phase on a scale of less than 100 nm [Roy, et al., 1986], will be developed by taking the knowledge of filler morphology and interfacial characteristics as critical aspects of the engineering design for composite materials. Changes in interfacial interactions can modify the mechanism of micromechanical deformations, failure behavior and the overall performance of composites. The obvious route to change properties and prepare tailor-made composites is the modification of interactions. Depending on the mechanism of material failure, different size filler particles and mechanical coupling are required. In this study a novel ceramic oxide filler for the modification of polypropylene was developed for the purpose of increasing the resistance to slow crack growth and mechanical properties.

## 1.2 Slow Crack Growth

Failure of polymeric materials and components occurs often at relatively insignificant stress levels, far below the tensile strength. One cause of many reasons for this is due to a variety of environmental effects producing structural changes: penetration of liquid and vapour condensates into the material, irradiation from sun or other light sources, nuclear radiation and so on. The second category of causes is related to the presence of flaws, inclusions and other stress concentration factors in the material, typically introduced during processing, which in service can grow and results in shear bands, crazes and cracks [Brostow, et al., 1991].

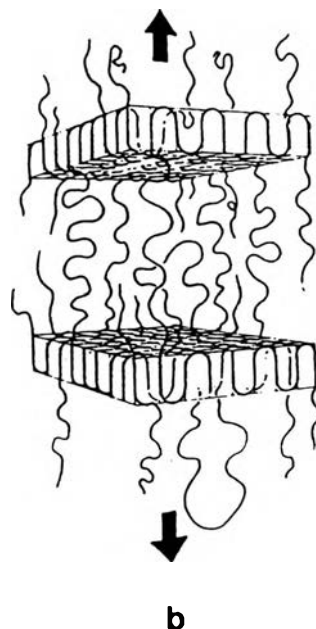


Figure 1.1 Tie chains.

When a stress is applied to the structures shown in fig. 1.1, the morphology suggests that the fundamental resistance to the disentanglement process is produced by the crystals. The structure comes apart as the tie

molecules disengage from the crystals. The disentanglement process may involve the pulling of tie molecule through the crystal or a shredding of the crystals as the tie molecules pull them. Based on this model it is expected that the time to failure would be influenced mostly by the concentration of tie molecules since the load transmitted between a tie molecule and the crystal is inversely proportional to the concentration of tie molecules [Zhou and Brown, 1994].

Lustiger and Markham [1983] visualized the mechanism of failure in terms of the model which can help identify molecular parameters of importance in optimizing piping materials for resistance to slow crack growth. Some of these parameters are:

- 1) Molecular weight. The higher the molecular weight, the longer the polymer chains, resulting in more tie molecules and more effective tie molecule entanglements.

- 2) Comonomer content. The short chain branches tend to inhibit crystallinity. Higher comonomer concentration and longer comonomer short chain branches provide 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. Another possible effect of short chain branching is the increased effectiveness of tie molecule entanglements because the chain in effect contains protrusions thereby inhibiting the ability of the tie molecules to slip past one another.

- 3) Density / degree of crystallinity. It would be expected that the more crystalline the material, the fewer amorphous intercrystalline tie molecules are available to hold crystalline domain together.

- 4) Lamellar orientation. If the lamellar 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 Montmorillonite (Kunipia F)

The clay used in this study was Montmorillonite, a natural hydrous alumino silicate, also known as the principal component of bentonite.

Kunipia 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 / 100g. It can intercalate various organic cations by ion exchange. Its structure consists of stacking of silicate sheets whose dimensions is 200 nm in length, 200 nm in width and 1 nm in thickness.

The montmorillonite possess large amounts of highly reactive surfaces. Berger [1941] first detected the presence of OH groups in the montmorillonite surfaces by esterification with diazomethane. Two general types of organic montmorillonite derivatives had been studied in the past. They are 1) clay salts with organic cations on the exchange positions and 2) complexes in which the organic group is attached to the clay through a covalent bond. The organic cation clay complex has been studied more extensively and systematically than the latter type of complex. Giesecking [1939] studied the mechanism of exchange reactions in the montmorillonite - type clays and demonstrated that the organic cations tend to be attracted onto the surfaces of the mineral plates. Deuel [1950] succeeded in preparing some organic montmorillonite derivatives with a covalent ether or ester - type linkage. He found that approximately 60 meq of OH groups per 100g. of clay were esterified. Giesecking [1949] observed that montmorillonite, when treated with acetyl chloride, lost its hydrophilic properties.

### The nature of the OH groups in montmorillonite

Martin and Kipping [1959] found that the silicols were chlorinated by acetyl chloride but did not react with acetic anhydride. The acetylation of montmorillonite by both acetyl chloride and acetic anhydride indicates that the involved OH groups are more acidic than the OH groups of the silicols.

The presence of OH groups in the montmorillonite structure can be explained by either the Edelman structure or by the substitution of OH for O in the tetrahedral layer adjacent to the site of substitution of Al for Si as postulated by Mc Connell [1950] in his modification of the Hofmann structure. This proximity of OH groups to the Al ions in the crystal lattices could well explain the acidic character of the OH groups in montmorillonite as a result of the strong electrostatic attraction between the Al ions and the O ions of the OH groups.

Water hydrolysis of montmorillonite, acetylated with acetic anhydride, releases approximately 20 % of the total acetyl groups and increases the cation exchange capacity of the derivative an equivalent amount. Hendricks [1940] found that 20% of the cation exchange capacity of montmorillonite resides on the edges of the plate like crystals, it would seem that the acetylated edges of the montmorillonite crystals are less stable toward water hydrolysis than the acetylated flat surfaces of the crystals.

Okawa, et al. [1990] had formed organoammonim montmorillonites from dehydrated sodium montmorillonite and organoammonium halides by solid - solid reactions. The formation depends on the sizes and counter anions of the ammonium ions used. The behavior is different from that observed in a conventional solution method.

#### **1.4 Silane Coupling Agents**

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 [Plueddemann, 1982].

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 segments of thermoplastic polymers.

Failure in a composite is often in a boundary layer of filler or 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.

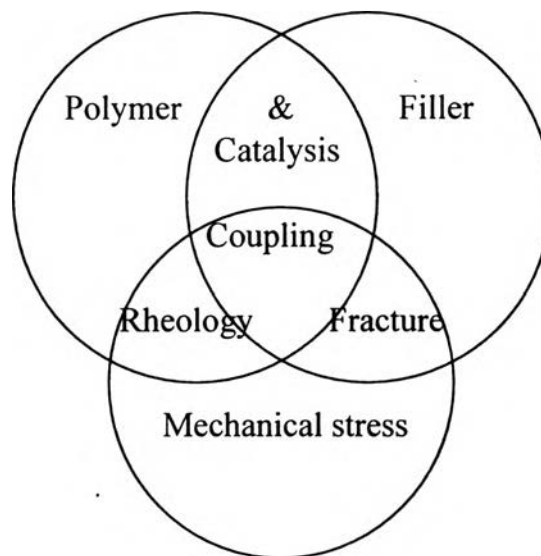


Figure 1.2 Interrelationships of polymer, filler and mechanical stress in composites.

Surface modification of fillers also affects the rheology of the polymer mixed by changing wet - out, dispersion of particles, viscosity, thixotropy and flow during plastic fabrication. Surface - active additives have been used with pigments and fillers to control rheology of paints but very little has been published about such materials in filled plastics [Plueddemann, 1982].



## 1.5 Literature Survey

To date, there are no published reports concerning with the grafting of polypropylene onto these thin oxide silicate layers. But these ceramics are being studied for a variety of polymers.

Kojima, et al. [1993] had reported that when this silicate was intercalated by 12 - aminododecanoic acid. It was dispersed at the molecular level into the Nylon 6 matrix. The degree of orientation of Nylon - 6 crystallites increased with content of montmorillonite and was assumed to be accelerated in the presence of anisotropic silicate layers dispersed in the dimension of molecules. Nylon - 6 clay hybrid has a high strength, a high modulus and a high heat distortion temperature in comparison with ordinary Nylon - 6.

Yano, et al. [1991] had synthesized the polyimide - clay hybrid where montmorillonite was dispersed at the molecular level. It was found that when specific ammonium ions are chosen as intercalating reagents, it dispersed homogeneously in dimethylacetamide (DMAC) which is a solvent for preparation of polyimides. The montmorillonite dispersion was mixed with precursor solution of polyimide, yielding a polyimide clay hybrid which showed an excellent gas barrier property and a lower thermal expansion property.

Wang and Pinnavaia [1994] had prepared a new type of clay - polymer nanocomposite by the spontaneous self polymerization of an epoxy resin, the diglycidyl ether of bisphenol A (DEEBA), and the concomitant delamination of acidic forms of montmorillonite at elevated temperatures. Evidence for nanocomposite formation was provided in part by a dramatic liquid to powder transformation of the clay - epoxide mixture upon formation of the polyether.

It also had been reported in the patent literature that dispersed montmorillonite particles improved several mechanical properties of an amine

- cured epoxy resin [  $\text{H}_3\text{N}(\text{CH}_2)_{11}\text{COOH}$  ]<sup>+</sup> - montmorillonite enhanced the impact resistance and the heat distortion temperature of epoxy resin Epicoat - 828 cured by p, p' - diaminophenylsulfone (DDS).

## 1.6 Objectives

The objective of this work is to develop a novel ceramic oxide filler for modification of polypropylene for an increase resistance to the slow crack growth and mechanical properties. By grafting of these oxide filler with maleic anhydride modified polypropylene, we will enhance the dispersibility of the filler particles in organic polypropylene matrices. We will prepare nanocomposite of polypropylene and measure their mechanical properties including a resistance to the slow crack growth.