



CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Glass fiber

Fiberglass is material made from extremely fine fibers of glass. It is used as a reinforcing agent for many plastic products. The resulting composite materials, known as glass-reinforced plastic (GRP) or glass-fiber reinforced epoxy (GRE), is called “fiberglass” in popular usage.

The basis of textile grade glass fibers is silica, SiO_2 . In its pure form, it exists in polymeric form $(\text{SiO}_2)_n$. It has no true melting point but softens up to 200°C , where it starts to degrade. At 1713°C , most of the molecules can move freely. Upon quick cooling, they are unable to form an ordered structure. In the polymeric form, it forms SiO_4 groups which are configured as a tetrahedron with the silicon atom at the center, and four oxygen atoms at the corners, in which its structure is shown in Figure 2.1. These atoms then form a network bonded at the corners by sharing the oxygen atoms [19-20].

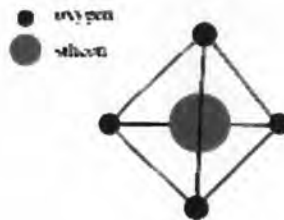


Figure 2.1 Molecular structure of glass fiber [19].

Glass fibers are useful because of their high ratio of surface area to weight. However, the increased surface makes them much more susceptible to chemical attack. Humidity is an important factor in the tensile strength. Moisture is easily adsorbed, and can worsen microscopic cracks and surface defects, and lessen tenacity. End uses for regular fiber glass are mats, insulation, reinforcement, heat resistant fabrics, corrosion resistant fabrics and high strength fabrics [21-30].

2.2 Clay

Clay minerals are a group of hydrous layered magnesium or aluminosilicates (phyllosilicates). Each magnesium-phyllosilicate or alumino-phyllosilicate is essentially composed of two types of sheet, octahedral and tetrahedral sheet. The tetrahedral sheet is a continuous linkage of SiO_4 tetrahedrons, in which its structure is shown in Figure 2.2 through sharing of three oxygen atoms with three adjacent tetrahedral that produces a sheet with a planar network in the form of hexagonal network [14].



Figure 2.2 Silicon-oxygen tetrahedron, SiO_4 [18].

The other one is an octahedral sheet, which is obtained through condensation of single $\text{Mg}(\text{OH})_6^{4-}$ or $\text{Al}(\text{OH})_6^{3-}$ octahedral as shown in Figure 2.3. Each oxygen atom is shared by three octahedra, but two octahedra can share only two neighboring O atoms that are arranged to form a hexagonal network [14].



Figure 2.3 Aluminum octahedron, $\text{Al}(\text{OH})_6^{3-}$ [18].

The most well known layered silicate is smectite. Smectite clays or phyllosilicates have relatively weak bonding between the layers which are small flakes. Each layer consists of two sheets of silica tetrahedral sandwiched octahedral sheet of either alumina (aluminosilicates) or magnesia (magnesium silicates). Due to isomorphous substitution of alumina into the silicate layers (Al^{3+} for Si^{4+}) or magnesium for aluminum (Mg^{2+} for Al^{3+}),

each unit cell has a negative charge. The layers are held together with a layer of charge-compensating cations such as Li^+ , Na^+ , K^+ and Ca^{2+} . These charge-compensating cations provide a route to the rich intercalation chemistry and surface modification required to disperse clays at the nanoscale into polymers.

Montmorillonite is one of smectite group which structure stacked leads to a regular weak dipolar or van der waals interaction between the layers. Isomorphous substitution in each layer generates negative charges that are counterbalanced by hydrated sodium or calcium ions residing in the interlayer spaces [18]. The general structure of montmorillonite is shown in Figure 2.4.

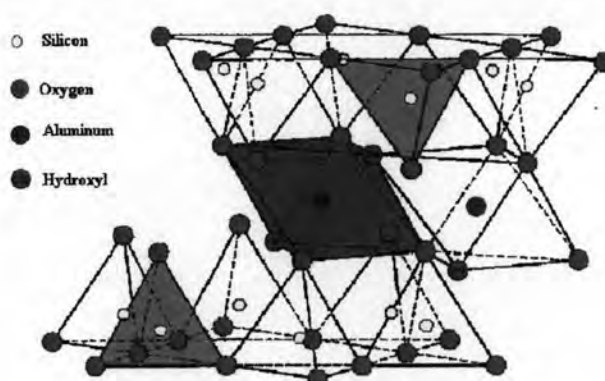


Figure 2.4 Structural scheme of montmorillonite [18].

2.2.1 Clay modification

Typically, the natural clay minerals are hydrophilic inorganic material while the most of polymers are organic material. Therefore organically modified silicate layers can be applied in a wide range of polymer types such as polyethylene and polypropylene. For successful formation of polymer/clay nanocomposites, alteration of clay polarity to make the clay 'organophilic' can be produced by ion exchange reactions between metallic cation of clay minerals (such as sodium ion, calcium ion) and organic cation or surfactant such as an alkylammonium ion. The organic cation may contain various functional groups that can interact with polymer molecules to improve adhesion strength between inorganic phase of clay minerals and the polymer matrix [18].

2.3 Polymer/clay nanocomposites

Composite materials are formed when at least two materials are mixed. Conventional composites are called when phase mixing occurs in a macroscopic (μm) length scale while nanocomposites occur on a nanometer length scale. In addition, nanocomposites can improve several properties such as mechanical, barrier and thermal properties because of their unique phase morphology and improved interfacial properties.

2.3.1 Type of polymer/clay nanocomposites

The dispersion of clay minerals in polymer matrix can be characterized in three general types of composite materials which are shown in Figure 2.5. The conventional composite contains clay tactoids in aggregated state with unintercalated polymer along the silicate layers. The clay tactoids are simply dispersed as a segregated phase. The intercalated nanocomposite is formed by the insertion of one or more molecular chains of polymer between clay galleries, resulting in an expanded interlayer distance. The exfoliated nanocomposite is formed when silicate nanolayers are individually dispersed in polymer.

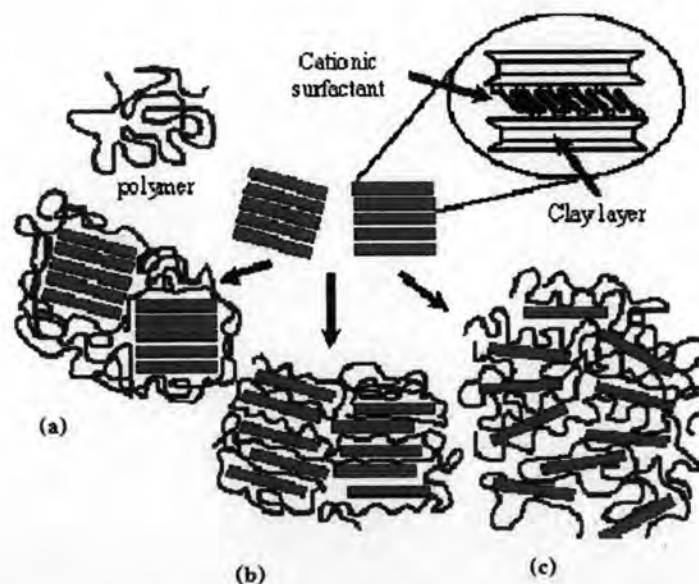


Figure 2.5 Illustration of the three possible types of polymer/clay nanocomposites: (a) conventional composites, (b) intercalated nanocomposite, (c) exfoliated nanocomposite [18].

More importantly, each nanolayer in an exfoliated nanocomposite contributes fully to interfacial interactions with polymer matrix. This structural distinction is the primary reason why the exfoliated clay state is especially effective in improving the reinforcement and other performance properties of clay composite materials [14, 18].

2.3.2 Preparation methods

The polymer/clay nanocomposites may be obtained mainly by three methods which are solution methods, *in situ* polymerization methods and melt processing. In the solution methods, nanocomposite is formed by dissolving the soluble polymer into an organic solvent. The clay is then dispersed in the obtained solution. Therefore, this technique allows modification of the particle surface without drying, which reduces particle agglomeration problem. After that the nanoparticle/polymer solution can be cast and dried. The nanoparticle/polymer can be isolated from solution by solvent evaporation or precipitation. Unlike the solution method, nanoscale particles are dispersed in monomer and the result mixture is polymerized in *in situ* polymerization. Thus, polymer chains are grown and push layered silicate to be apart from each other. On the other hand, melt processing method, the silicates layers are directly dispersed into the polymers while polymers are in a melted state. In order to use this method, layered silicates need to be previously surface treated through the organo-modification like previously mentioned. Among these techniques, melt processing method is the most attractive way because of its low cost, high productivity and compatibility with current polymer processing techniques [16-17].

2.4 Extrusion process

Extrusion, is the process where a solid plastic, usually in the form of beads or pellets, is converted into a particular form with different shape. A cold plastic material is carried by the action of the screw of an extruder (Figure 2.6), which consists of three sections, and heated in order to change into the molten state. During the process, it creates a pressure on material before the molten plastic enters the die. A pressure which creates on the materials forced through into the die. The screen pack, which composes of a number of coarse meshes and is placed between the screw and the die, can help filter out dirt from polymer matrix. After that the molten plastic is extruded through the die with different shape and cooled at below melting temperature or glass transition [16].

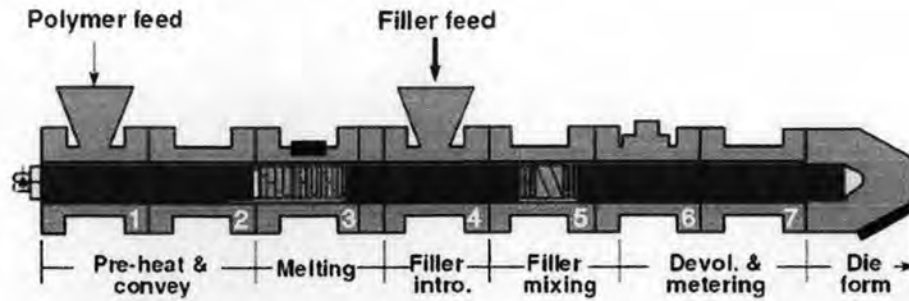


Figure 2.6 Scheme for a typical single-screw extruder [16].

2.5 Literature review

In the recent years, glass fiber (GF), glass ball, calcium carbonate, talc, and montmorillonite reinforced composites have been widely studied and developed rapidly, which provide an alternation to increase the stiffness of polymer composites

Numerous studies have investigated the effect of injection temperature and fiber content on the properties of PP/GF composites [21]. The XRD patterns of neat PP and the two composites having two different fiber contents as shown in Figure 2.7. Also, peaks of PP20%GF are higher and sharper than PP30%GF. It was also found that injection temperature did not show a significant effect on the diffraction patterns. However, tensile strength of composite increased with the fiber content. This indicated that glass fiber reinforcement is a relatively more important factor to increase stiffness of polymer.

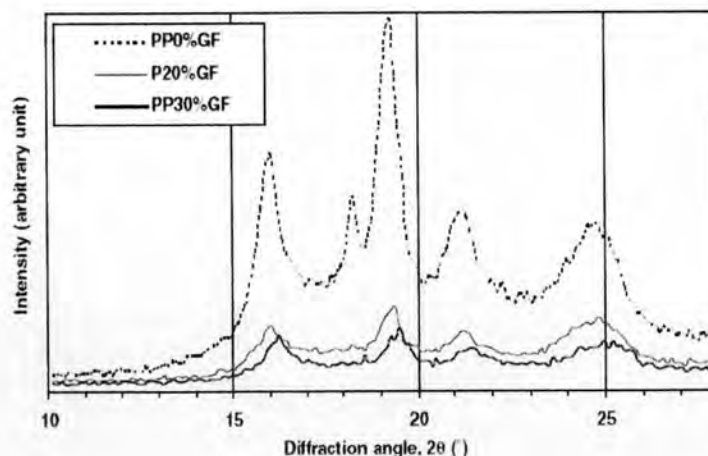


Figure 2.7 WAXS patterns for neat PP, PP20%GF and PP30%GF [21].

Furthermore, glass fibers have been the root cause of the greenhouse effect and extension the world's climatic changes [22]. The disadvantages of glass fiber have indicated in Table 2.1. Therefore, many researches attempted to use natural fiber in place of glass fiber, for example, cellulose-based fibers as reinforcing fillers for plastics.

Table 2.1 Comparison of properties between natural fibers and glass fibers [22].

	Natural fibres	Glass fibres
Density	Low	Twice that of natural fibres
Cost	Low	Low, but higher than NF
Renewability	Yes	No
Recyclability	Yes	No
Energy consumption	Low	High
Distribution	Wide	wide
CO ₂ neutral	Yes	No
Abrasion to machines	No	Yes
Health risk when inhaled	No	Yes
Disposal	Biodegradable	Not biodegradable

The mechanical properties of the natural fiber/PP composites tested were found to be comparable with the corresponding properties of glass fiber/PP composites. The specific properties of the natural fiber/PP composites were in some cases better than those of the glass fiber/PP composite as shown in Figure 2.8. This suggests that natural fibers have a potential to replace glass fiber in many applications that do not require very high load bearing capabilities.

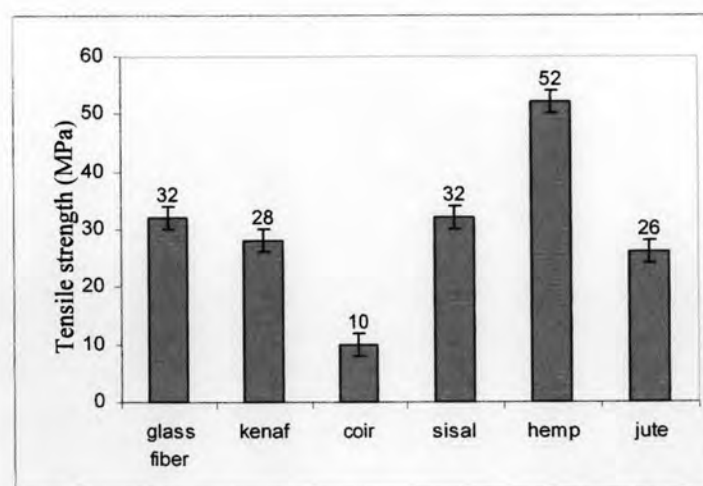


Figure 2.8 Tensile strength of fiber reinforced polypropylene composites [22].

Other researchers have studied polymer/clay nanocomposites because they enhance various properties at low clay loading [3-12]. However, clays are hydrophilic and naturally incompatible with a wide range of polymer types, especially polyolefins. Therefore, hydrophilic clay must be treated with organic cation such as an alkyl ammonium ion by ion exchange reaction [9]. By modifying the surface polarity of hydrophilic clay, organic cation is essential to ensure thermodynamically favorable penetration of polymer chains into layered silicates [18].

However, the dispersion of layered silicates in polymer matrix affects strongly on the final properties of polymer/clay nanocomposites. Especially, exfoliated structure of polymer/clay nanocomposite is favorable in enhancing several properties as compared with neat polymer such as mechanical, thermal properties because of the high aspect ratio of layered silicates and high surface area of clay in which the interfacial interaction between polymer matrix and surface of clay would also be high [13-14].

In case of polypropylene, it is necessary to use a compatibilizer, such as maleic anhydride-grafted polypropylene (PP-g-MA) that should be miscible with the polypropylene matrix and include a certain amount of polar functional groups in a molecule [12].

Many researches have studied the effect of compatibilizer of the organoclay [4], process condition [5] and molecular weight [11] on dispersion of layered silicates which affects on the final properties of polymer/clay nanocomposites, such as tensile modulus, yield strength, elongation at break and thermal properties.

Polymer/clay nanocomposites can be formed by different methods i.e. *in situ* polymerization, solution method and melt processing technique [3, 15-16]. Melt processing technique is the most attractive way due to its low cost, high productivity and compatibility with current polymer processing techniques [16]. By melt processing technique of polypropylene/clay nanocomposites preparation, maleic anhydride-grafted polypropylene (PP-g-MA) used as a compatibilizer with lower molecular weight and higher MA content led to the good clay dispersion or nearly exfoliated structure that were shown in Figure 2.9.

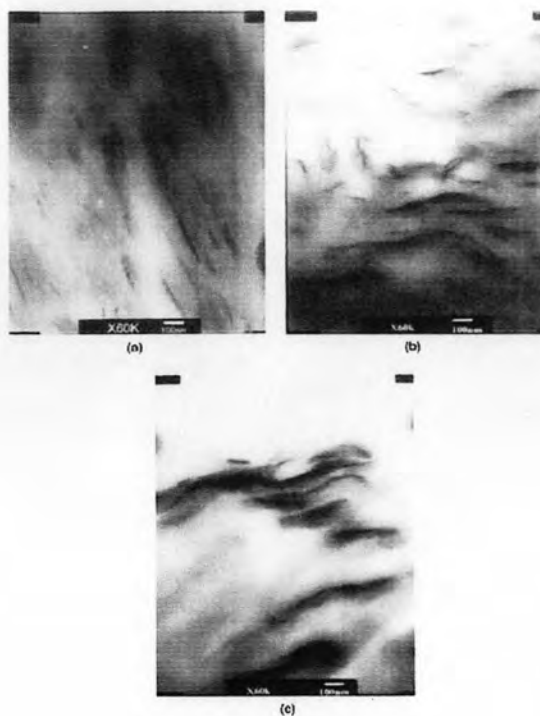
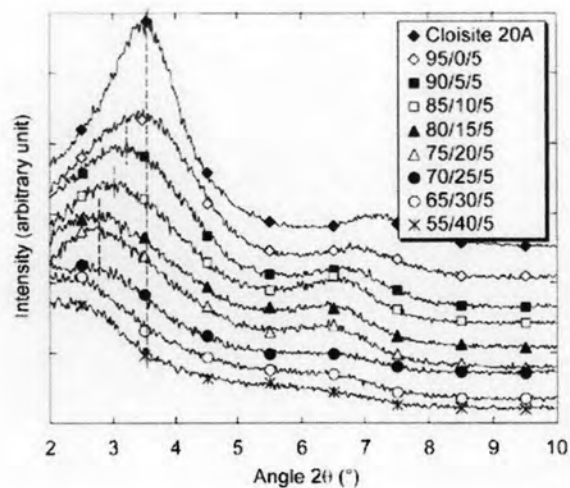


Figure 2.9 TEM micrographs of lower molecular weight and high content of compatibilizer based on (a) PB3150 ($M_w = 330,000$ and 1.5 wt% of MA content), (b) PB3000 ($M_w = 120,000$ and 2.5 wt% of MA content) and (c) E43 ($M_w = 22,880$ and 3.0 wt% of MA content) [16].

For XRD patterns, uncompatibilized system exhibits no significant increase in interlayer spacing. This indicates that the polymer does not intercalate into the interlayer. In contrast, for compatibilized systems, X-ray diffraction peaks are shifted to lower angles, indicating the increase in interlayer spacing by the intercalation of polymer as shown in Figure 2.10 [12].



Formulation (PP/PP-g-MA/Cloisite®20A)	<i>d</i> spacing (nm)
Cloisite®20A	2.51
95/0/5	2.56
90/5/5	2.83
85/10/5	3.04
80/15/5	3.11
75/20/5	3.18
70/25/5	3.11
65/30/5	NA*
55/40/5	NA*

NA*: peak location is difficult to determine due to peak's broadness.

Figure 2.10 XRD patterns of composites prepared with different ratios of PP-g-MA [12]

Interestingly, processing conditions also affected the dispersion of silicate platelets [5]. Figure 2.11 shows TEM micrographs of PP/clay nanocomposites at different temperature profile and screw speed. This indicates that the shear stress exerted clay platelets are slide apart from each other and separation increased by the diffusion of polymer chains into the clay galleries at higher screw speed and lower temperature

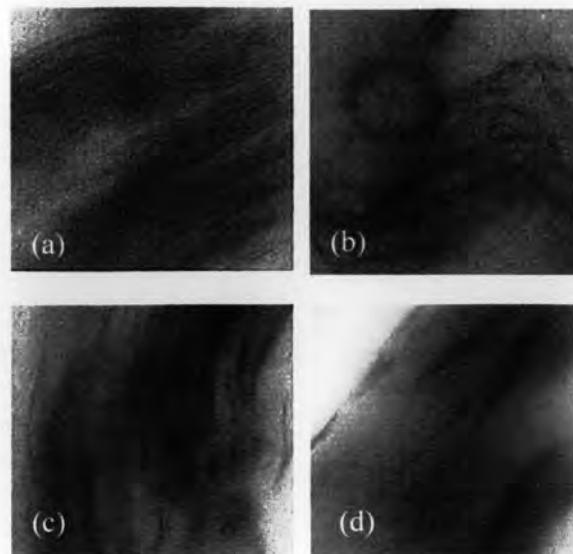


Figure 2.11 TEM micrographs of PP/clay nanocomposites at different temperature profile and screw speed : (a) high temperature (200°C) and lower screw speed (250), (b) low temperature (180°C) and lower screw speed (250) (c) high temperature (200°C) and higher screw speed (350) and (d) low temperature (180°C) and higher screw speed (350). [5].

It is well known that the degree of clay dispersion (intercalation and exfoliation) strongly affects the properties of polymer/clay nanocomposites. Exfoliated nanocomposite contributes fully to interfacial interactions with polymer matrix. This structural distinction is the primary reason why the exfoliated clay state is especially effective to improve various properties such as mechanical, optical, thermal properties due to the incorporation of clay platelets with polymer matrix. Figure 2.12-2.13 shows the effect of clay loading on mechanical properties of PP/clay nanocomposite. Tensile modulus and flexural modulus apparently increase with increasing clay loading. In other word, the addition of organoclay leads to substantial improvement in stiffness because layered silicates serve as a reinforcement agent.

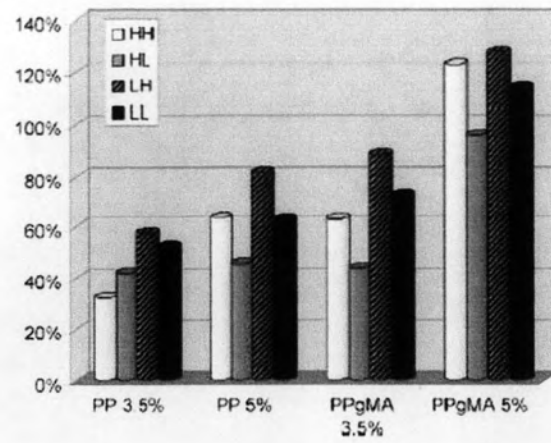


Figure 2.12 Tensile modulus of PP/clay nanocomposite with various clay loading [5].

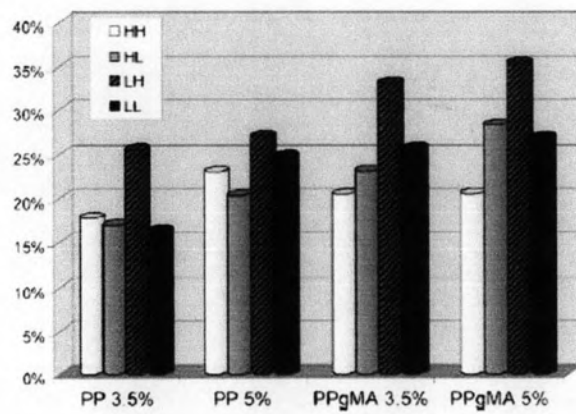


Figure 2.13 Flexural modulus of PP/clay nanocomposite with various clay loading [5].