

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1. Polymer Matrix

Various kinds of thermoplastic polymers are reinforced with short fiber or other reinforcements. Thermoplastic polymers are commercially divided into two classes, commodity thermoplastic and engineering thermoplastic.

In general, properties of commodity plastic are intermediate and its product has many applications. These are, for examples, polyethylene, polypropylene, polystyrene, poly(vinyl chloride), poly(ethylene terephthalate), etc.

The engineering plastic is applied to material having a premium price, usually associated with low production volume. Their outstanding balance of properties allows them to compete successfully with other materials such as metals, ceramics, etc., for engineering application. They are strong, stiff, tough, abrasion-resistance, capable of withstanding wide ranges of temperatures, resistance to weather, chemicals, and other hostile conditions. The engineering plastics consist of acrylonitrile butadiene styrene terpolymer, polycarbonate, nylon, polyacetal, ultra high molecular weight polyethylene, etc.

2.1.1 High Impact Polystyrene

It is now, generally, known that hard, strong but brittle plastic can be modified by the addition of rubber to give impact-resistant materials with only minor sacrifices in hardness and strength. The widely used one is high impact polystyrene, known as HIPS.

Rubber is added to crystal polystyrene to increase its ability to absorb energy, that is to reduce its tendency to fracture when subjected to impact.

The initial charge usually consists of a solution of rubber in styrene, together with various optional additives such as catalyst, chain transfer agent, and mineral oil designed to produce an appropriate balance between production economics and desired end product properties. The rubber level used in HIPS is generally in the range of 2 to 10 %. The overall industry average is probably between 5 and 6 %.

2.1.1.1 Mechanism of Rubber Reinforcement

When high impact polystyrene is deformed, it begins to stress-whiten, an effect brought about by the formation within the polymer of large numbers of microcracks, or 'crazes', which consist of approximately 40 % voids and 60 % stress oriented polymer chains. The impact strength (toughness) of high impact polystyrene results from the absorption of large quantities of energy during the process of craze formation as shown in Figure 2.1. By acting as initiating sites for new crazes radiating from their surfaces, the rubber particles prevent the formation of macro-cracks which, in crystal polystyrene, grow rapidly to the point of rupture of the resin. If the new crazes do not absorb

enough of the energy imparted by the original stress, they encounter other rubber particles which, in turn, become the focus for sets of crazes.

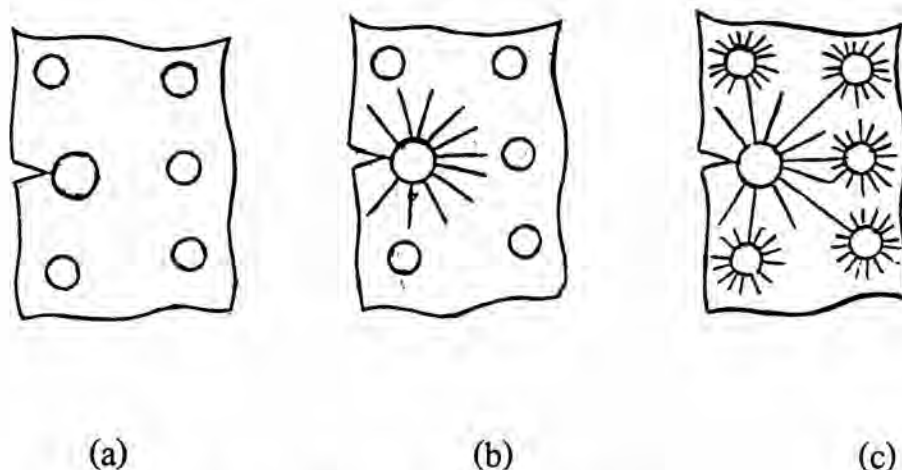


Figure 2.1 Craze formation of high impact polystyrene.

- a) Initial crack, b) New crazes formed absorbing energy,
- c) Remaining energy absorbed by formation of crazes at surface of neighbouring particles.

2.1.1.2 Effect of Rubber Level

The general effect of rubber on glassy polystyrene is to produce a softer, tougher, and more ductile polymer. As a result, the tensile strength of a HIPS resin is relatively low and its elongation relatively high. Toughness, as measured by impact resistance, increases significantly with increased rubber level.

The physical properties of HIPS resins are also related to such factors as the quantity of graft rubber and the molecular weight of the matrix polystyrene. For example, two resins with molecular weight (M_n) of 83,450 and 110,000

respectively, had impact strengths of 63.0 and 80.6 J/m (1.18 and 1.51 ft. lb/inch).

2.1.1.3 Rubber Particle Size

Most commercial polystyrene resins contain rubbery particles ranging in size from less than 1μ up to 10μ or more, with an average in the range of 1μ to 5μ . The function of rubber particles is to act as nuclei for craze propagation, the mechanism for improving the toughness of HIPS resins. If the particles are too small, they will not prevent the formation of large, linear crazes and the resin will rupture easily under impact. If the rubber particles are too big, they may break down during processing, thus giving rise to variations in physical properties.

In addition to its effect on physical properties, particle size is related to gloss and gel defects. Small particles produce good gloss: large particles give a non-glossy finish suitable for printing, and exceptionally large particles above 15 microns are visible to the naked eye as gel defects. When the average particle size is large, some particles are usually larger than 15 microns. It follows, therefore, that with the exception of specialty products requiring large particle size, it is desirable to keep the particles as small as possible within the acceptable range.

2.2 Principles of Glass Fiber Reinforcement

When high strength, high modulus glass fibers are added to a low modulus resin and are well dispersed, the plastic flow of the matrix under stress transfers the load to the fibers. This results in a high strength, high modulus composite. Besides high strength and high modulus, the fibers provide a large contact area, assuring good adhesion with the polymer matrix. Other innate characteristics of glass fibers that make them attractive for thermoplastic reinforcement are their elasticity, good thermal properties, dimensional stability, excellent chemical and moisture resistance, excellent electrical properties, and high performance at relatively low cost (28).

Fiber Fabrication

Glass fibers are fabricated from silica and other ingredients, primarily oxides, which are melted in a furnace at temperatures exceeding 1260 °C. The molten glass flows through spinnerettes and is stretched to a diameter of either 10 or 13 μm for most applications (Figure 2.2).

Immediately below the bushings, an organic coating, or sizing, is applied to the filaments. It contains agents to protect the fibers during processing and to promote binding to the polymer system. After the sizing is added, filaments are gathered into strands, generally containing 200 to 2000 filaments each. During further processing, a large number of strands may be wound together into a continuous “roving”. The strand may be cut to short lengths (chopped fiber).

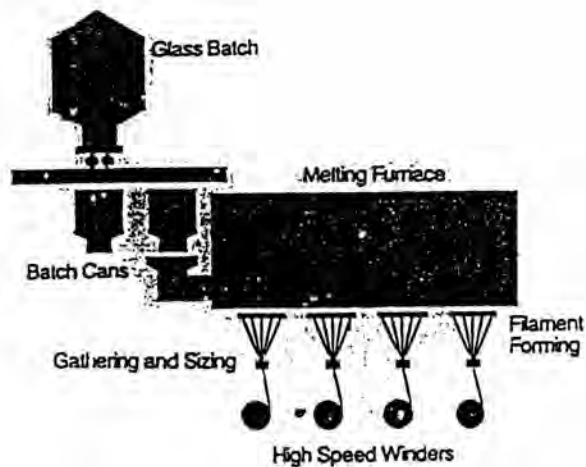


Figure 2.2 Direct melt continuous filament process.

Types of Glass

1. Continuous strand is composed of many continuous fine filament, from 51 to over 400, depending on the manufacture. A continuous filament can approach a length of several miles.

2. Mats (nonwoven) are made from strands evenly distributed in a random pattern. Their basic application is to insure maximum unforming in the finish laminated.

3. Chopped strands are produced by cutting continuous filament strands of spun strands. Chopped continuous filament strands are used when uniform standard lengths are desired from 1/4 inch to over 3 inch. Whereas chopped strands made from roving are not uniform in length and the lengths will range from 1/4 inch to 1/2 inch with the maximum length as the controlling specification.

4. Fabrics, tapes and woven roving are made by interfacing (weaving) of glass fiber yarns with various twist and ply constructions on conventional weaving looms. Fabrics and tapes offer exact control over thickness, weight, and strength.

Amount of Glass

The amount of glass used to reinforce a thermoplastic generally determines the extent to which composite properties are modified from those of the resin toward those of the fiber. The average loading of glass fibers used in thermoplastic compounds is about 25% by weight. While strength generally improves as the amount of glass in the composite increases, at about 30% loading, the curve begins to flatten. With higher glass content, the resin's flow rate is slowed and material processing becomes much more difficult. Thus, except in special circumstances where the need for greater strength overrides cost penalties in processing, maximum loading is usually about 30%. When strength requirements are low, less glass may be used to reduce material cost. On the other hand, flexural modulus increases linearly with the volume fraction loading to glass. Where this is the key property, high loadings might be considered.

Arrangement of Fibers

The way in which fibers are positioned or oriented in a thermoplastic component will determine the direction and level of strength. There are three types of orientation.

Unidirectional : All fibers are running in the same direction. This arrangement provides greatest strength in the direction of the fibers. With this orientation, up to 80% loading by weight is possible.

Bidirectional : Some fibers are positional at an angle to the rest, as with woven fabric. This provides different strength levels in each direction of fiber orientation. Up to 75% loading by weight can be obtained.

Multidirectional : Fibers are running in all directions with essentially equal strength in all directions. Used with chopped and mats fibers, from 10 to 50% loading by weight can be obtained.

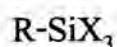
The relationship between the amount of glass reinforcement and the arrangement of the fibers is easily seen. The more directionally oriented the fibers, the greater the reinforcement loadings possible, and therefore, the greater the strength obtainable in the finished part in the direction of the fibers. The more random the arrangement, the lower the reinforcement loading and, therefore, the lower the resulting strength.

2.3 Silane Coupling Agents

The function of silane coupling agents is to provide a stable bond between two otherwise nonbonding surfaces. In reinforced and filled plastics, the improved bond between fibrous or particulate inorganic components and the organic matrix polymer results in greater composite strength and longer service life.

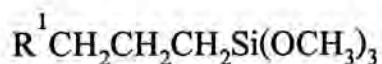
2.3.1 Silane Chemical Structure

Silane coupling agents are a family of organosilicon monomers which are characterized by the formula (5-6) :



In this formula. R is an organofunctional group attached to silicon in a hydrolytically stable manner, and X designates hydrolyzable groups which are converted to silanol groups on hydrolysis.

Most commonly, R is comprised of reactive group R¹ separated by a propylene group from silicon, and X is an alkoxy group (usually methoxy).



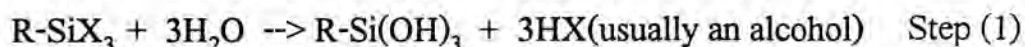
The group R¹ may be very simple, for example chlorine (Cl), or may contain several chemical functional groups.

Commercial silane coupling agents have been selected from innumerable possibilities, a very large number of which have been evaluated experimentally. A relative few possess a desired balance of reactivity with various polymers combined with hydrolyzability and useful secondary properties such as water solubility, surface activity, wetting control, and others.

2.3.2 Chemistry of The Interface

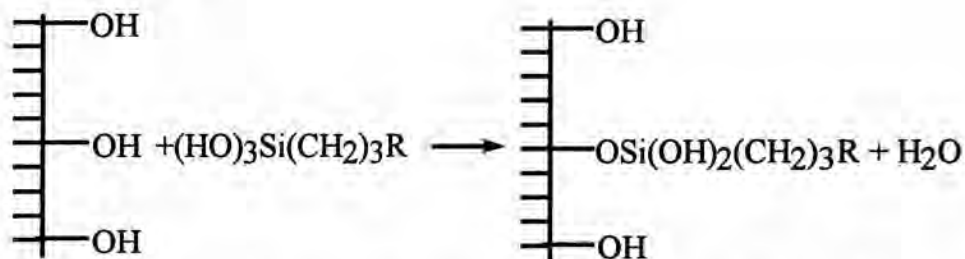
Silane coupling agents interact with “receptive” inorganic surfaces forming tenacious chemical bonds at the interface. Receptive inorganic surfaces are characterized by the presence of hydroxyl (OH) groups attached to certain specific elements, principally silicon and aluminum, in the form of hydrated oxides having adsorbed water of hydration as their outermost layer. The silanol (SiOH) groups present in such materials as glass and silica are particularly favorable for bonding with silanes. Hydrated alumina and aluminum (because of the always present oxide coating) have AlOH surface groups which are also receptive.

The coupling agent must first be converted to the reactive silanol form by hydrolysis:



Step (1) may occur on the surface which is being treated by reaction with water on the surface or in the resin, or it may be brought about in a previous step during preparation of the aqueous solution of the coupling agent. The reaction is rapid in the presence of slightly acidified water (pH 3-6).

The silanol form of the coupling agent now reacts with inorganic surface hydroxyl groups:



It is most important to note that the above reaction is reversible since dynamic equilibrium between bonding sites permits movement at the interface, thus allowing relief of internal stresses in composites which result from shrinkage during cure and differences in thermal expansion properties. The breaking and reforming of bonds also will allow stress relief under load via a degree of positional displacement of reinforcement relative to resin without permanent loss of interfacial adhesion. Water necessary for the equilibrium is presumed always present at the interface. Self-condensation of the silanol form of the coupling agent to form siloxane polymers (analogous to silicone resins)

is an important side reaction, particularly in aqueous pretreatment solutions and at a pH greater than 7.

2.4 Literature Reviews

There is a continued interest in the development of high performance composite materials consisting of high strength fibers, such as glass, embedded in a polymer matrix, i.e., fiber reinforced plastic (FRP) products. The properties of these materials depend on many factors like material properties of fibers, polymer matrix, additives, volume fraction of fiber, fiber aspect ratio, orientation of the fiber and polymer-fiber interface modification. In this literature survey, the works of fiber reinforced polymer are reviewed.

Jang, J. and Kim, S.H. (15) reported performance improvement of glass fiber-Poly (phenylene sulfide) (PPS) composite in which silane coupling agents were used to modify the glass fiber surface. RC-2 silane and styryl silane were applied to the surface of glass fiber with various concentrations from 0.1-0.5% wt. in solvent. The interlaminar shear strength (ILSS) and the flexural strength of the silane treated GF-PPS composite increased compared with the untreated one.

RC-2 silane was more efficient in enhancing the ILSS and the flexural strength of the GF-PPS composite. The optimum silane concentration for the improvement of the mechanical properties of the GF-PPS composite was 0.4 wt.% in both cases of RC-2 and styryl silane. Because the ILSS and the flexural strength of the GF-PPS composite changed in a similar fashion as a function of silane concentration, it could be concluded that improved interfacial adhesion of the composite played an important role in strengthening the

mechanical properties of the GF-PPS composite. From the SEM results, it was ascertained that the interfacial adhesion of the GF-PPS composite was efficiently improved when silane coupling agents were used.

Kinson, P.L. and Fober, E.M. (29) investigated a high temperature PVC resin blend which was made by blending from 60 to 85 parts PVC with no more than 40 parts of a copolymer of alpha-methyl styrene acrylonitrile, and less than 20 parts by wt. additives including stabilizers, antioxidants, lubricants, and procesing aids. In addition, an impact modifier was added. The blend with particularly sized glass fibers, was thermoformed at 160- 200°C and 1000 psi, to provide a reinforced composite in which the PVC was covalently bonded to the glass fiber. The composite had a substantially higher heat distortion temperature and equivalent tensile strength as listed data in Table 2.1

Table 2.1 Physical properties of the composites (29).

	Glass content of blend, % by wt.		
	This invention		
	10	20	30
Tensile strength, psi x 10 ³	10	11.1	12.2
Tensile modulus, psi x 10 ⁴	66	90	122.5
Elongation, %	3.3	2.4	1.5
Flexural strength, psi x 10 ⁴	65	96	120
Izod, notched, ft-lb/in	0.8	1	1
@ -40 °C.	0.8	1	1
Specific gravity	1.31	1.4	1.49
HDT (annealed) 264 psi, °F	185	185	185
Coeff of Therm Exp*,x 10 ⁻⁵	2.2	1.7	1.2
Relative Spiral Flow,in.	32	28	25

*in/in °F

A unique sequence of mixing the blend ingredients with glass fiber provides optimum properties in the composite. The sequence requires formation of a single phase of PVC and alpha-SAN copolymer before dispersing the glass fibers in the blend as in Table 2.2.

Table 2.2 Physical properties in each mixing (29).

Physical Property	Run 1	Run 2	Run 3
Tensile strength (psi)	10068	10829	8938
Tensile Modulus (psi)	730000	768000	657000
Elongation at yield (%)	2.5	2.4	2.5
Yield Work (ft-lbs/cu.in.)	14.2	14.1	12.6
Flexural Strength (psi)	16606	17436	14896
Flexural Modulus (psi)	644000	682000	598000
Notched Izod (ft-lb/in)	0.7	0.8	0.6
Unnotched Izod (ft-lb/in)	3.9	3.7	3.3
Annealed HDT ($^{\circ}$ C)	80	80	78
Spiral flow (in)	32.7	33.3	32.8

Run 1 :PVC and glass fibers are mixed before, then blended with copolymer.

Run 2 :PVC and copolymer are blended before mixing with glass fibers.

Run 3 :The copolymer and glass fibers were blended before adding PVC.

Peltonen, P., Paakkonen, E.J., Jarvela, P.K. and Tormala, P (23) investigated the influence of adhesion promoters on the properties of injection moulded long-glass-fiber polypropylene. Different grades of coupling agents were added to the polypropylene homopolymer matrix during melt impregnation of continuous glass fibers. All of the ingredients used in the experiments were commercial products, and the amounts of coupling agents added to the polypropylene were based on the recommendation of the manufacturer. The addition of coupling agents on the polypropylene matrix did

not decrease the degree of impregnation of manufactured prepreg. Melt impregnated PP/GF prepreg was pelletized to the length of 10 mm., injection molded and tested. In addition, two commercial long fiber materials and one commercial short fiber compound were injection molded and tested. All of the components included a glass fiber weight fraction of 40%. The addition to some coupling agents improved tensile and flexural properties remarkably compared to a non-coupled composite. As a typical result, impact strength values of the same specimens were decreased. Low temperature impact strength of long fiber composites was higher compared to impact strength obtained at room temperature. All long fiber composites showed superior impact properties compared to short fiber composites. The melting histories of the matrices were not affected by the addition of different grades of coupling agents, but the cooling run of the DSC analysis could cause differences in the crystallisation of the coupled matrices. Residual fiber lengths were analysed from the mouldings. The morphology of the interface of the composites, studied with scanning electron microscopy indicated a good relation with mechanical testing. The highest tensile and flexural strengths of the composites were obtained on the same materials that showed a partially cohesive fracture mechanism, by having matrix polymer on the fiber surface. An optical study of the fracture surfaces revealed a typical fiber pull-out phenomena in the weakest composites.

George, J., Bhagawan, S.S, Prabhakaran, N. and Thomas, S. (11) studied short pineapple-leaf-fiber (PALF) reinforced low-density polyethylene (LDPE) composites which were prepared by melt-mixing and solution-mixing methods. In the melt-mixing technique, a mixing time of 6 min, rotor speed of

60 rpm, and mixing temperature of 130 °C were found to be the optimum conditions. Tensile properties of melt-mixed and solution-mixed composites were compared. Solution-mixed composites had shown better properties than melt-mixed composites. The influence of fiber length, fiber loading, and orientation on the mechanical properties had also been evaluated. Fiber breakage and damage during processing were analyzed from fiber distribution curve and optical and scanning electron micrographs. Considering the overall mechanical properties and processability characteristics, fiber length of 6 mm was found to be the optimum length of pineapple-leaf-fiber for the reinforcement in LDPE. The mechanical properties were found to be enhanced and elongation at break reduced with increasing fiber loading. Longitudinally oriented composites shown better properties than randomly and transversely oriented composites. SEM indicated that fibers were well oriented during composite fabrication. Recyclability of the composite was found to be very good. A comparison of the properties of the PALF-reinforced LDPE composites with those of other cellulose-fiber-reinforced LDPE systems indicated superior performance of the PALF-LDPE composites.

Meer, R. and Zoom, B. (30) invented the polymer mixtures which comprises 20-40 parts by weight of a polyphenylene ether, 30-70 parts by weight of a rubber-modified polystyrene, 10-30 parts by weight of short, "pristine" (with a length from 3.1 to 25.4 mm, preferably of less than 6.35 mm), reinforcing fibers and 0.05-1.0 parts by weight of hydrogen siloxane compound. The mechanical properties such as thermal stability, impact strength of the polymer mixtures are improved by the addition of a hydrogen siloxane compound.