

## CHAPTER II

### THEORY AND LITERATURE REVIEW

#### 2.1 Composite Materials

Composite materials may be defined as materials made up of two or more components and consisting of two or more phases. Such materials must be heterogeneous at least on a microscopic scale. Many commercial polymeric materials are composites. There are many reasons for using composite materials rather than the simpler homogeneous polymers. Some of these reasons are:

- 1) Increased stiffness, strength, and dimensional stability
- 2) Increased heat distortion temperature
- 3) Increased toughness or impact strength
- 4) Increased mechanical damping
- 5) Reduced permeability to gases and liquids
- 6) Modified electrical properties
- 7) Reduced cost.

Not all of these desirable features are found in any single composite. The advantages that composite materials have to offer must be balanced against their undesirable properties. The properties of composite materials are ascertained by the properties of the components, by the shape of the filler phase, by the morphology of the system, and by the nature of the interface between the phases. Thus a great variety of properties can be obtained with composites just by alteration of one of

these items. An important property of the interface that can greatly affect mechanical behavior is the strength of the adhesive bond between the phases.

### 2.1.1 Classification of Composite Materials

Composite materials may be divided into three general classes[4,5].

#### Particulate Composites

A composite having particle reinforcement is called a particulate composite. A particle, by definition, is nonfibrous and generally has no long dimension with the exception of platelets. The dimension of the reinforcement ascertains the capability of contributing its properties to the composite. The reinforcement having long dimension will discourage the growth of incipient cracks. However, it might lead to failure, particularly with brittle matrices. Therefore, fibers are more effective in improving the fracture resistance of the matrix. In general, particles are not so effective in improving fracture resistance. Other types of particle, such as ceramic, metal, or inorganic particles, provide reinforcing effect to metallic matrices with different strengthening mechanisms. The particles in a particulate composite give constraints to plastic deformation of the matrix because of their inherent hardness relative to the matrix. The particles also share the loss, but much smaller extent than the fiber in fibrous composites that lie parallel to direction of the load. Thus the particles are effective in enhancing stiffness of the composites but do not have much potential for strengthening. The particles and matrix material in a particulate composite can be any combination of metallic and nonmetallic materials. Choice of a particular combination depends on the desired end properties.



### Fibrous Composites

Most of the materials traditionally considered as composites have used fibers as the filler phase. It is well known that the measured strengths of most materials are found to be much smaller than their theoretical strengths. The strength discrepancy is believed to be due to the presence of imperfections or strength enhancement of inherent flaws. Flaws in the form of cracks that lie perpendicular to the direction of applied loads are particularly detrimental to the strength.

Therefore, comparing with the strength of bulk material, man-made filaments or fibers of nonpolymeric materials exhibit much higher strength along their lengths since large flaws, sometimes present in the bulk material, are minimized due to small cross-sectional dimension of the fiber. In the case of polymeric materials, orientation of molecular structure is responsible for high strength and stiffness. Properties of some common fibers as well as some conventional materials are given in Table 2.1, which clearly shows the importance of fiber in achieving higher strengths. The most important reinforcement fiber is E-glass because of its relative low cost. However, boron, graphite, and aramid fibers (Kevlar 49 ) are most exceptional because of their high stiffness values. Graphite fibers offer the greatest variety because of the ability to control their structure.

Fibers, are not directly usable for engineering applications because of their small cross-sectional dimensions. They are, therefore, embedded in matrix materials to form fibrous composites. The matrix serves to bind the fibers together, transfer loads to the fiber, and protect them against environmental attack and damage due to handling. In discontinuous fiber-reinforced composites, the load-transfer function of the matrix is more critical than in continuous fiber composites. The fibrous composites have become the most important class of composite materials because of their capability of achieving high strengths.

Table 2.1 Selected properties of fibers and conventional bulk metals[1].

Material	Tensile strength $10^3$ psi (MPa)	Tensile modulus $10^6$ psi (GPa)	Density lb/in <sup>3</sup> (g/cm <sup>3</sup> )
Bulk 6016T6 Aluminum	45.0(310)	10.0(69)	0.098(2.71)
Bulk SAE 4340 Steel	150.0(1034)	29.0(200)	0.283(7.83)
E-glass fiber	500.0(3448)	10.5(72)	0.092(2.54)
S-glass fiber	650.0(4482)	12.5(86)	0.090(2.49)
Graphite fibers (PAN precursor)			
AS-4 (Hercules)	580.0(4000)	33.0(228)	0.065(1.80)
IM-7 (Hercules)	785.0(5413)	40.0(276)	0.064(1.77)
T-300 (Amoco)	530.0(3654)	33.5(231)	0.064(1.77)
T-650/42 (Amoco)	730.0(5033)	42.0(290)	0.064(1.77)
Graphite fibers (pitch precursor)			
P-55 (Amoco)	250.0(1724)	55.0(379)	0.072(1.99)
P-75 (Amoco)	300.0(2068)	75.0(517)	0.072(1.99)
P-100(Amoco)	325.0(2241)	100.0(690)	0.078(2.16)
Aramid fibers			
Kevlar 29 (Dupont)	550.0(3792)	9.0(62)	0.052(1.44)
Boron fibers			
0.004" diameter	510.0(3516)	58.0(400)	0.093(2.57)
0.0056" diameter	510.0(3516)	58.0(400)	0.090(2.49)
Silicon carbide fiber			
0.0056" diameter	500.0(3448)	62.0(427)	0.110(3.04)

Fibrous composites can be broadly classified on the basis of theoretical and experimental properties into single-layer and multilayer (angle-ply) composites. "Single-layer" composites may actually be made from several distinct layers, each layer has the same orientation and properties. The entire laminate may be considered as a "single-layer" composite. In the case of molded composites made from discontinuous fibers, although the planar fiber orientation may not be uniform through the thickness, there is no distinct layer, thus they can be classified as single-layer composites. In the case of composites fabricated from nonwoven mats, the random orientation is constant in each layer, and the resulting composite would be considered as a single-layer composite even though a resin-rich layer might be found between each reinforcement layer on microscopic examination. Most composites used in structural applications are multilayered, i.e., they consist of several layers of fibrous composites. Each layer or lamina is a single-layer composite, and this orientation is varied according to the design. Each layer of the composite is usually very thin, typically 0.1 mm in thickness, and hence cannot be directly used. Several identical or different layers are bonded together to form a multilayered composite usable for engineering applications. When the constituent materials in each layer are the same, they are called simply as laminates. Hybrid laminates refer to multilayered composites consisting of layers made up of different constituent materials. For example, one layer of a hybrid laminate may be a glass fiber reinforced epoxy, whereas another layer may be graphite-fiber reinforced epoxy. It is possible, but not as common, to find hybrid composites having a mixture of fibers within a single layer. A single layer of a composite, therefore, represents basic building block for their structure applications.

Reinforcing fiber in a single-layer composite may be shorter or longer than its overall dimensions. Composites with long fiber are called continuous-fiber-reinforced

composites and those with short fibers are called discontinuous-fiber-reinforced composites.

Short fiber-reinforced composites are not as strong or as stiff as continuous fiber-reinforced composites and are not likely to be used in critical structural applications such as aircraft primary structures. However, short fiber composites do have several attractive characteristics that make them worthy of consideration for other applications. For example, in components having complex geometrical contours, continuous fibers may not be practical because they may not conform to the desired shape without being damaged or distorted from the desired pattern. On the other hand, short fibers can be easily mixed with the liquid matrix resin, and the resin/fiber mixture can be injection or compression molded to produce parts having complex shapes. Such processing methods are also fast and inexpensive, which makes them very attractive for high-volume applications. Composites having randomly oriented short fiber reinforcement are nearly isotropic, whereas unidirectional continuous fiber composites are highly anisotropic. In many applications the advantages of low cost, ease of fabricating complex parts, and isotropic behavior are enough to make the short fiber composites material of choice.

Short fiber composites with three types of fiber reinforcement will be considered here, as shown in Fig. 2.1 : aligned discontinuous fibers, off-axis aligned discontinuous fibers, and randomly oriented discontinuous fibers. The randomly oriented short fiber composites are the most widely used of the three types.

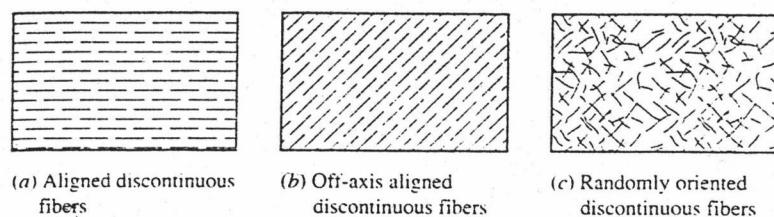


Figure 2.1 Types of discontinuous fiber reinforcement [1].

The orientation of short fibers cannot be easily controlled in a composite material. In most case the fibers are assumed to be randomly oriented in the composite. Short fibers, sometimes referred as chopped fibers, may be sprayed simultaneously with a liquid resin towards a mold to build up a reinforced plastic structure. In this process the chopped fibers are randomly oriented in planes generally parallel to the mold surface. Therefore, the properties of a discontinuous fiber reinforced composite can be isotropic; that is, they do not change with direction within the plane of sheet.

Composite materials consist of a continuous matrix phase that surrounds the reinforcing phase structures. The relative role of the matrix and reinforcement generally fall into the following categories:

1. The reinforcement has high strength and stiffness, and the matrix serves to transfer stress from one fiber to the next and to produce a fully dense structure.

2. The matrix has many desirable, intrinsic physical, chemical, or processing characteristics, and the reinforcement serves to improve other certain important engineering properties, such as tensile strength, creep resistance, or tear resistance.

3. Emphasis is placed on enhancing the economic attractiveness of the matrix, e.g., by mixing or diluting it with materials that will improve its appearance, processability, or cost advantage while maintaining adequate performance.

The first category constitutes the high performance composites. High strength fibers are used with high volume fractions, having orientations controlled and tailored for optimum performance. Considerations of such a system performance benefits often ascertain the range of applications of this class of composites.

In the remaining two categories, cost is the more immediate consideration. The second category emphasises the improvement of engineering properties, extending the range of usefulness and marketability of a given matrix. Moderate

concentrations of fibers, often as discontinuous random fibers, flake or certain particulate reinforcements are used. The reinforced plastics fall in this class.

In the third category, the emphasis is somewhat the inverse, i.e., how to make other attractive materials with lower cost per se, or how to process the material at lower cost without unacceptable degradation properties through the use of particulate, flake or fibers, fillers and colorants. This category largely consists of the filled polymers.

A composite material, though it is made up of more than one material, can be considered to be a new material having characteristic properties derived from its constituents, its processing, and its microstructure.

#### Interpenetrating Network Composites

Interlocking or interpenetrating networks (IPNs) have not been studied as intensively as fiber or particulate composites or as simple block copolymers or blends, which the polymer-polymer IPN systems resemble. One reason for this lack of data on rigid filler IPNs is the difficulty of fabricating such composites. Examples of interlocking network composites are (1) open-celled foams of one material filled with another material; (2) wire mats that have been sintered together at crossover points and are impregnated with a polymer or other matrix material; (3) polymer-polymer blends in the concentration range in which phase inversion occurs; and (4) a crosslinked polymer swollen in a monomer, which is subsequently polymerized and cross-linked[3].

#### 2.1.2 Fabrication Process

A large number of methods are presently available for manufacturing both short and long fiber composites. The cost of finished components depends not only

on the price of the raw materials but also on labor costs and energy requirements. The selection of a fabrication process obviously depends on the constituent materials in the composite, with the matrix material being the key[1].

A summary of fabrication processes used for polymer composites with various types of fiber reinforcement is given in Table 2.2. The open mold process with hand

Table 2.2 Fabrication processes for polymer matrix composites[1].

Process	Type of fiber reinforcement			
	Continuous	Chopped	Woven	Hybrid
Open mold				
Hand lay-up		x	x	
Spray-up		x		
Autoclave	x		x	
Compression molding	x	x	x	x
Filament winding	x			
Pultrusion	x		x	
Reinforced reaction injection molding (RRIM)		x		
Thermoplastic molding	x	x	x	x
Resin transfer molding (RTM)	x	x	x	x
Structural reaction injection molding (SRIM)	x	x	x	x

lay-up of woven fiber mat (Figure 2.2) or chopped strand mat or spray-up of chopped fibers (Figure 2.3) is used for development work, prototype fabrication, and production of large components and relatively small quantities. A mold having the desired shape

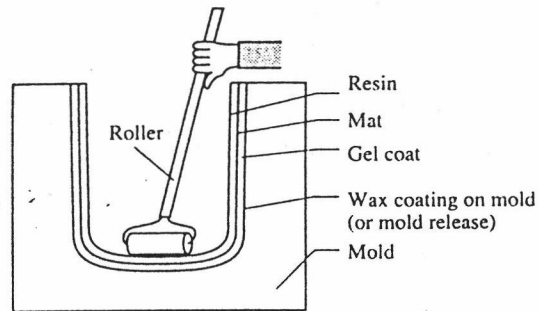


Figure 2.2 Open mold, hand lay-up composite fabrication[1].

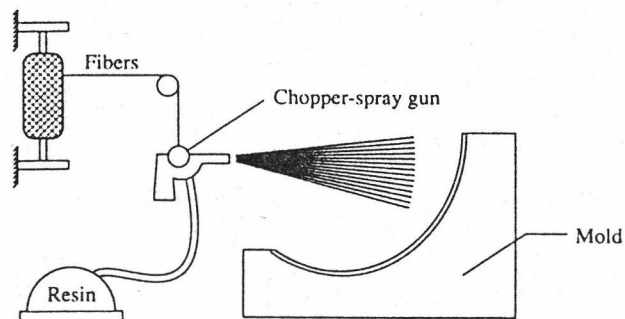


Figure 2.3 Open mold, spray-up composite fabrication[1].

is first coated with a mold release which prevents bonding of the resin matrix material to the mold. If a smooth surface on the part is desired, a gel coat is then applied to the mold, followed by a thermosetting polymer resin and the fibers. A roller may then



be used for consolidation, followed by curing of the polymer resin at the required temperature.

Autoclave molding (Figure 2.4) is the standard aerospace industry process for fabrication with prepreg tapes. The autoclave is simply a heated pressure vessel into which the mold (with lay-up) is placed and subjected to the required temperature and pressure for curing. The mold and lay-up are often covered with a release fabric, a bleeder cloth, and a vacuum bag. A vacuum line is then attached to the mold for evacuation of volatile gases during the cure process.

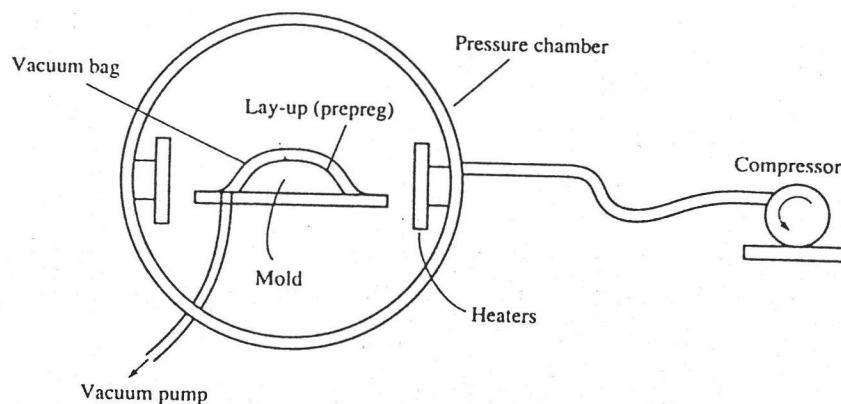


Figure 2.4 Autoclave molding[1].

Sheet-molding compound (SMC) is an important innovation in composite manufacturing which is used extensively in the automobile industry. SMC is similar to prepreg tape in that the fibers and the resin are “prepackaged” in a form that is more easily used by fabrication. SMC consists of a relatively thick, chopped fiber-reinforced resin sheet, whereas prepreg usually has continuous fibers in a thin tape. A machine for producing SMC is shown schematically in Figure 2.5.

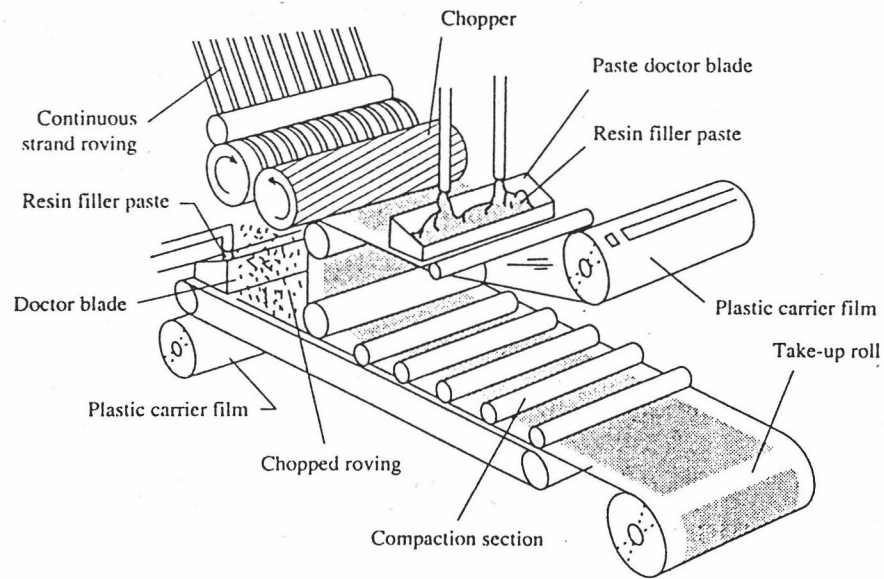


Figure 2.5 Machine for producing sheet-molding compound (SMC)[1].

Compression molding is used to manufacture small and intermediate-sized high quality parts at relatively high rates. A typical mold is shown schematically in Figure 2.6. The desired number of layers of preimpregnated composite is placed in

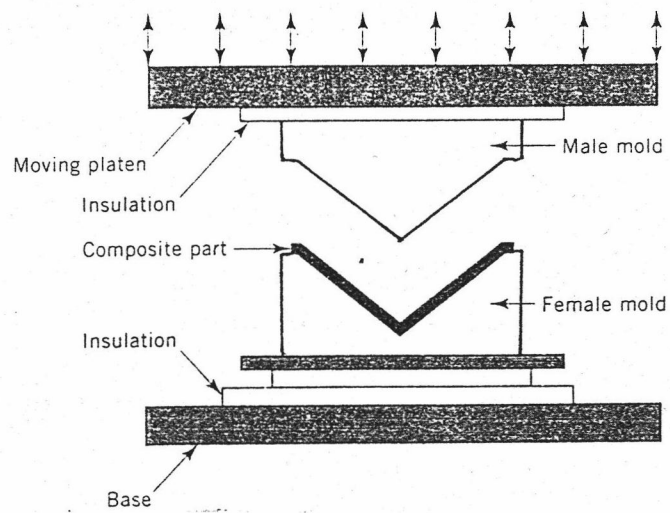


Figure 2.6 Compression molding in matched dies[1].

the lower mold, and the upper mold is lowered until the required pressure is achieved. The composite is then heated according to the required cycle. In order to achieve a high quality surface, great care has to be taken in the manufacture of the mold surfaces. After continued use, the surfaces need to be replaced in order to maintain the desired tolerances. In spite of the costs involved in the production and maintenance of the mold, compression molding represents a relatively inexpensive and practical means of producing high quality composite parts.

Filament winding (Figure 2.7), which involves winding resin-coated fibers onto a rotating mandrel, may be used to produce any composite structure which has the form of a body of revolution. Fiber orientation is controlled by the traverse speed of the fiber winding head and the rotational speed of mandrel.

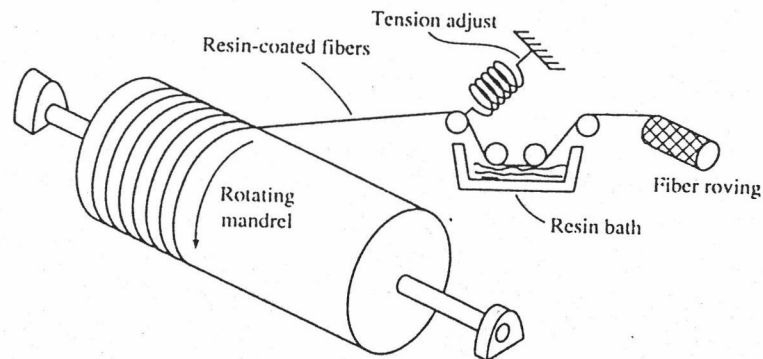


Figure 2.7 Filament winding process[1].

Reinforced reaction injection molding (RRIM) is a very fast process which is widely used to produce such components as automobile body panels. The RRIM process (Figure 2.8) involves injection of a chopped fiber/resin mixture into a mold under high pressure and then curing at the required temperature.

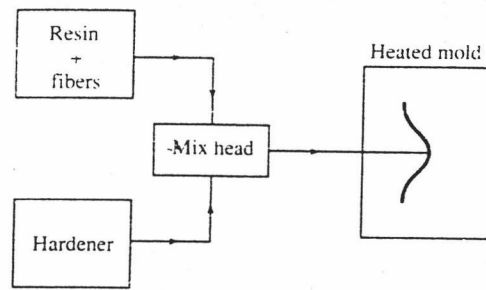


Figure 2.8 Reinforced reaction injection molding (RRIM) process[1].

“Pultrusion” (Figure 2.9) is the process of pulling a continuous fiber/resin mixture through a heated die to form structural elements.

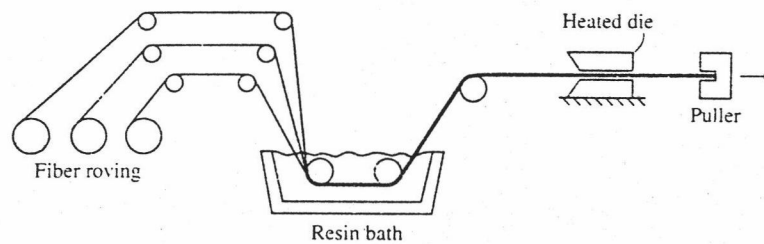


Figure 2.9 Pultrusion process[1].

Resin transfer molding allows the economical manufacture of high quality composites. Dry fibers, which may have the form of continuous strand mat, unidirectional, woven or knitted preforms, are placed in a closed mold and resin is then introduced into the mold under external pressure or vacuum. The resin cures under the action of its own exotherm, or heat may be applied to the mold to complete the curing process.

## 2.2 Polymer Matrix

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

**Commodity plastic:** In general, properties of the plastic are intermediate and the product has many applications. For example, polyethylene, polypropylene, polystyrene, poly(vinyl chloride), poly(ethylene terephthalate), etc.

**Engineering plastic:** 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.

Hence, the commodity plastics are interested because they have many advantages such as recyclability, cheap, etc.

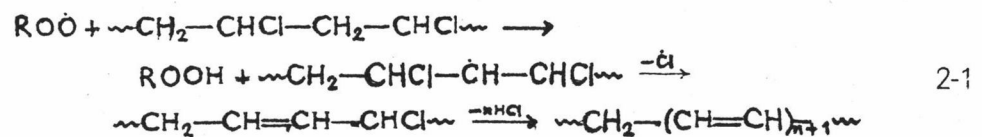
### 2.2.1 Poly(vinyl chloride)

In 1930, rigid PVC technology was emphasized in Germany. Rigid poly(vinyl chloride) (PVC) is characterized by strength and excellent chemical resistance. The homopolymer has repeating units of vinyl chloride monomer (VCM).

PVC is a “head-to-tail” amorphous polymer with a low degree of crystallinity. It contains 0.4 to 1.1 branches per 100 carbon atom chains. Its glass-transition temperature of about 80°C varies with polymerization temperature. The melting point

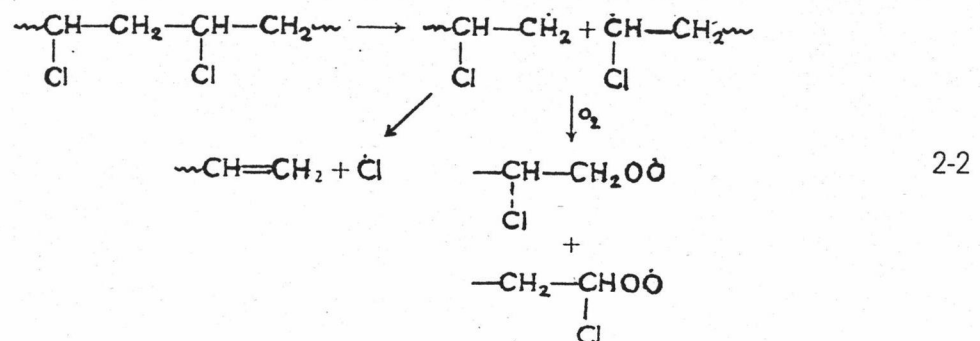
varies with molecular weight, molecular weight distribution, and polymerization temperature.

Commercial PVC resin degrades at moderate processing temperatures which cause thermal dehydrochlorination. In addition, the presence of oxygen will lead to thermooxidative degradation. Oxygen and peroxy radical will react with the polyenes, forming peroxides. In this way, the polymers become shorter. The peroxy radicals may also abstract hydrogen from intact monomer units and initiate further HCl loss by thermal dehydrochlorination as scheme herebelow.



Besides heat and oxygen, the polymer may be influenced by mechanical energy during processing also. The shear forces will reach a maximum in the beginning of the processing. Scott *et al.* [7] have suggested that chain scission occur at this stage. The radicals formed then react with oxygen. The Cl atoms, as well as the alkyl and alkyl peroxide radicals, could initiate zipper dehydrochlorination as scheme above.

Scott and co-workers [7] consider that the chain scission process in Eq.2-2 is important for the initiation of the degradation in the first stage of the process. In the work, the accelerating effect of HCl is caused by a catalytic effect on the radical decomposition of peroxides, resulting in increased random dehydrochlorination.



The adding of heat stabilizer that inhibit degradation enabled processors to use PVC. The introducing of Lubricant into the PVC composite can improve flow and processing properties.

Rigid PVC plastic is a formulated and compounded product with outstanding properties such as high strength, good chemical resistance, good stiffness, excellent electrical properties, etc. This versatile product, which offers the possibility of an almost infinite number of compounds, is made from a low-cost feedstock. As noted, 56.7% of the molecule is chlorine. This means that the polymer's availability and pricing are not wholly related to oil or gas feedstocks.

The disadvantages of rigid PVC are

- Processing difficulty caused by polymer stability
- Low heat deflection
- Poor creep at elevated temperatures.

In order to improve these deficiency properties of rigid PVC, polymer blends are utilized. Blending of PVC with other polymers is done by melt mixing. It should be noted that a blend component may be a homopolymer, copolymer (standard, graft or block) or a blend itself. Thus, styrene-acrylonitrile copolymer (SAN), styrene-acrylonitrile-methacrylate-butadiene (SAMB) copolymer, poly(methyl methacrylate), could be used to blend with rigid PVC[8].

### 2.2.2 Styrene-Acrylonitrile Copolymer

SAN is a transparent plastic resin composed the polymerization of styrene and acrylonitrile monomers. The process of manufacturing SAN is a bulk process which, uses a catalyst for the reaction without water as a heat transfer medium. Therefore, drying step is not necessary leading to product purification. Polymer acquired is in transparent liquid form[9,10].

As temperature is the most sensitive factor for the SAN product application, therefore temperature control should be considered as follows:

1. Drying temperature (80-82° C for 2-3 hours)
2. Molding temperature (50-85° C)
3. Melt polymer temperature (220-260° C)

### 2.3 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[11].

#### 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  $\mu\text{m}$  for most applications (Figure 2.10).

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).

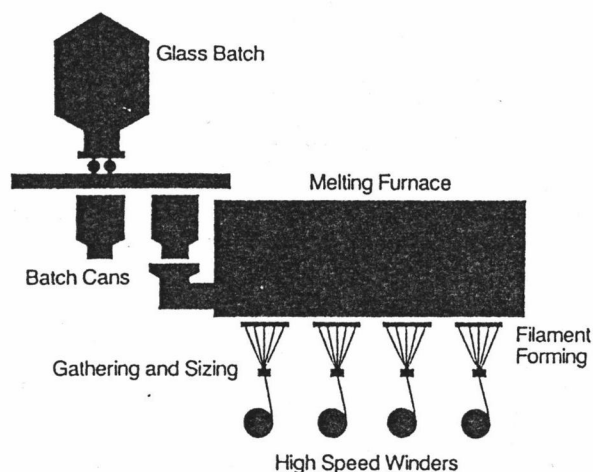


Figure 2.10 Direct melt continuous filament process

### Types of Glass

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

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

3. Chopped Strands are produced by cutting continuous filament strands or 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 be ranged 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 interlacing (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 determined 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 costs. On the other hand, flexural modulus increases linearly with the volume fraction loading of 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 positioned 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. Manufacturers compounding their own composites will obtain this orientation.

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. Figure 2.3 illustrates how part strength is affected by glass reinforcement percentage by weight, as well as by fiber orientation.

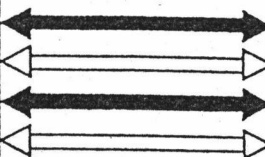
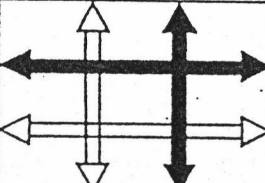
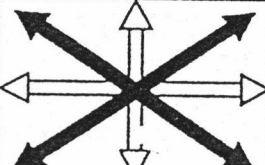
<b>Unidirectional Fiber Orientation</b>	Percentage of Fiberglass reinforcement increases strength in direction of fiber orientation		<b>REINFORCEMENT TYPES:</b> Continuous Strand Roving <b>PROCESSES:</b> Continuous Pultrusion
<b>Bidirectional Fiber Orientation</b>			<b>REINFORCEMENT TYPES:</b> Continuous Strand Roving <b>PROCESSES:</b> Filament Winding <b>REINFORCEMENT TYPES:</b> Woven Fabrics & Woven Roving <b>PROCESSES:</b> Hand Lay-up
<b>Multidirectional Fiber Orientation</b>			<b>REINFORCEMENT TYPES:</b> Chopped Strands Continuous & Chopped Strand Mat <b>PROCESSES:</b> Compression and Injection Molding Spray-up, Pressure Bag, Preform.

Figure 2.11 Arrangement of fibers

Also shown are reinforcement products that yield directional arrangements indicated, together with widely used processing methods with which they are compatible.

#### 2.4 Coupling agent

In recent years, there has been increasing interest in composite technology among those in the thermoplastic industry. The use of mineral and fiber reinforcement has allowed the compounder and fabricator to keep pace with the increasingly rigorous demands of the marketplace. End-user specifications are continually being rewritten to demand better material performance.

The art of compounding requires selecting the most cost-effective system that will fulfill the end user's performance requirements. A key to this art is achieving maximum possible physical properties with a selected resin-reinforcement/filler system and maintaining properties in the environment. This can occur only if applied stresses can be efficiently transferred from the resin matrix to the reinforcement and maintained in the environment. This requires intimate contact at the interface. Coupling agents provide this interfacial bonding and have become a very important tool in the quest for cost-effective, maximum performance.

Figure 2.12 illustrates the functions of a coupling agent. First a reaction must occur between the mineral surface and the coupling agent. This modifies the mineral surface, which prevents agglomeration. Coupling agents improve dispersion of minerals, leading to improvements in composite properties. Second, the coupling agent must be capable of reaction with the resin.[12,13]

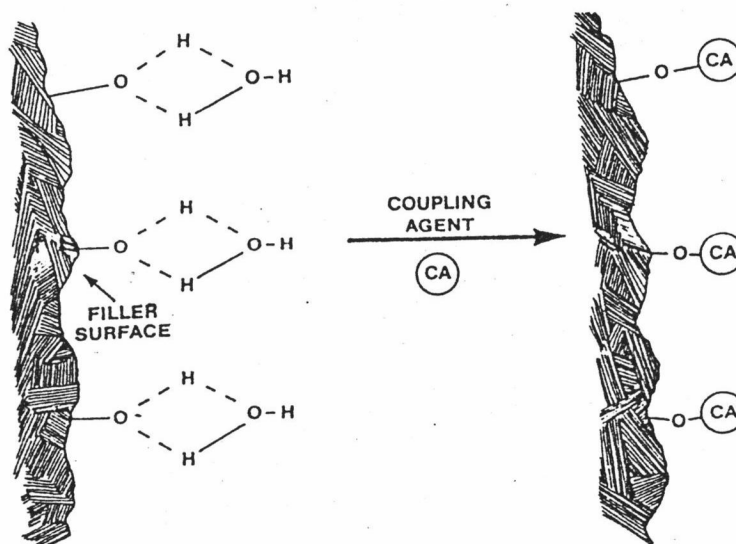
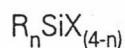


Figure 2.12 Functions of Coupling Agent.

#### 2.4.1 Chemistry of Organofunctional Silane Coupling Agents

The general formula of an alkoxy silane shows two classes of moieties attached to the silicon atom[14]:



R is a nonhydrolyzable organic moiety that can be either an alkyl, aromatic, organofunctional, or a combination of any of these groups. These groups provide the organic compatibility, which allows the silane to form IPNs, or in the case of reactive organofunctional silanes, to co-react with the coating polymer. Alkyl and aryl silanes are utilized to improve glass, hiding power, mixing time, and other properties. Alkyl and aryl silanes are also utilized to provide hydrophobic surfaces.

The X represents alkoxy moieties, most typically the methoxy or ethoxy, which react with the various forms of hydroxyl groups and liberate methanol or ethanol. These groups can provide the linkage with glass fiber, pigment or filler to improve

adhesion. The methoxy groups are also capable of reaction with hydroxy functional polymers.

Reaction of these silanes involves four steps (Figure 2.13). Initially, hydrolysis of the alkoxy (X) groups occurs. It is after the first and second alkoxy groups are

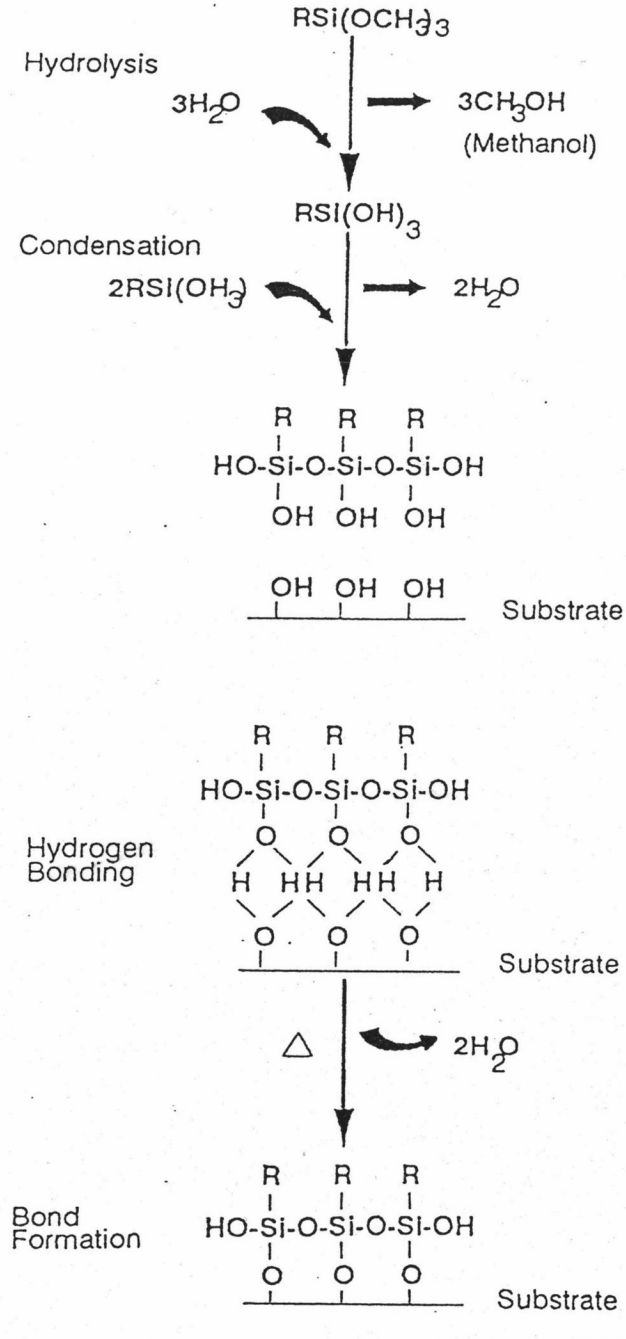


Figure 2.13 Reaction process of alkoxy silanes[14].

hydrolyzed that condensation to oligomers follows. Compared to the hydrogen of a carbinol moiety, the silanol hydrogen is more electrophilic and much more reactive. This is due to the larger, more electropositive, atomic structure of silicon which results in a high dipole moment for the silanol group and greater hydrogen bonding. The tendency toward self-condensation can be controlled by using fresh solutions, alcoholic solvents, dilution, and by careful selection of pH ranges. Silanetriols are most stable at pH 3-6, but condense rapidly at pH 7-9.

The third methoxy group upon hydrolysis is oriented towards, and hydrogen bonds with, hydroxy sites on the substrate. Finally, during drying or curing, a covalent bond is formed with the substrate and water is liberated. At the interface, there is usually only one bond from each silicon of the organosilane to the substrate surface. A suitable drying cycle will leave silanol groups remaining in a free form and, along with any silane organofunctionality, and provide improved adhesion.

#### 2.4.2 Mode of Silane Addition

For application of the silane to the mineral surface is critical to achieve the greatest coupling activity. It is a matter of thoroughly coating the mineral in an environment that will allow the bonding interaction to occur. It is usually accomplished in one of two ways.

Filler pretreatment: This method consists of

- a) diluting the silane with a suitable solvent (generally alcohol and water),
- b) thoroughly mixing the dry filler with the diluted silane and
- c) drying the coated filler to remove solvent and water.

Integral addition: This method is the in-situ blending of the resin/filler mixture with the neat silane. This method may require a higher loading of silane to achieve

the desired effect, but the elimination of a separate pretreatment step could make this the most economical mode of addition for some users[12].

Glass fibers are routinely sized with formulations that usually include silanes. Although these formulations are generally high proprietary, glass fiber manufacturers will be happy to specify which resins are compatible with their various fiberglass grades. Additional silane can be added to sized glass for further improvements in composite properties.

## 2.5 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 the material properties of the fibers, the polymer matrix, the additives and the polymer–fiber interface modification. In this literature survey, the works of fiber reinforced polymer are reviewed.

Rahrig, D. B. [15] studied poly(vinyl chloride) and chlorinated poly(vinyl chloride) reinforced with glass fibers, which have been sized with a particular aminosilane coupling agent and an alkylene oxide-containing film former. This combination of sizing components, among all others generated allylic Cl atoms in the vinyl chloride chain of the polymer. Though the vinyl chloride resin contained an adequate amount of stabilizer to counter the formation of such allylic Cl atoms in the mass of the resin, enough were generated near the surface of the glass to cause a reaction with the aminosilane so as to bond the glass fibers to the vinyl chloride resin so strongly that a composite only failed in coherent failure. The sizing consisted essentially of (i) an aminosilane coupling agent having a reactive amino moiety, which upon reaction with



the VC resin resulted in a compound having a peak in a proton magnetic resonance spectra at 5.65 ppm in Figure 2.7, and (ii) a film former consisted essentially of a polymer having a ring-opened lower alkylene oxide. The wet strength of the composite was about equal to or greater than the dry strength of an identical composite which had no film former in the sizing. The data are presented in Table 2.3.

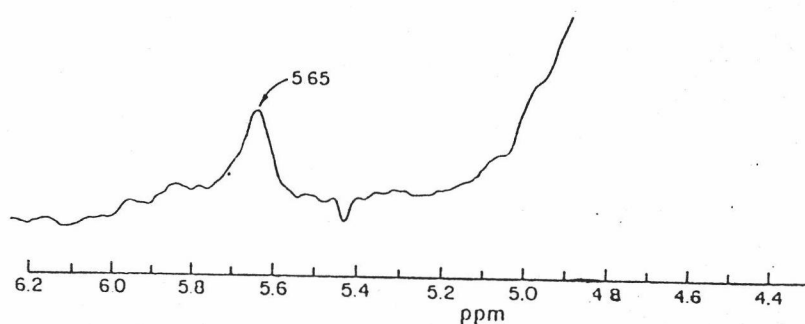


Figure 2.14  $^1\text{H-NMR}$  spectra of GFR PVC composite in which the glass fibers were sized with an aminosilane having a reactive primary amine moiety[15].

Table 2.3 Physical properties of the composites[15].

	Glass content of blend, % by wt		
	Rahrig '360		
	10	20	30
Tensile strength, $\text{psi} \times 10^3$	10.5	12.8	13.9
Tensile modulus, $\text{psi} \times 10^4$	56.	96.	129.
Elongation, %	6.0	2.7	2.0
Flexural strength, $\text{psi} \times 10^4$	64.	97.	119.
Izod, notched, ft-lb/in	0.8	1.0	1.1
@ $-40^\circ\text{C}$ .	0.7	0.8	0.9
Specific gravity	1.43	1.5	1.57
HDT (annealed) 264 psi, $^\circ\text{F}$ .	167	167	169
Coeff of Therm Exp*, $\times 10^{-5}$	2.0	1.3	1.2
Relative Spiral Flow, in.	32	28	25

\*in/in  $^\circ\text{F}$ .

Kim, J. H., Barlow, J. W., and Paul, D. R. [16] reported the phase behavior of blends of poly(vinyl chloride) with an  $\alpha$ -methyl styrene/acrylonitrile copolymer using differential scanning calorimetry for blends prepared by several methods. Melt blending gave single  $T_g$  mixtures (Figure 2.15); whereas, solution techniques gave results that depended on the solvent choice and the manner in which it was removed. These blends did not phase separate on heating prior to significant PVC decomposition ( $\sim 250^\circ\text{C}$ ) in contrast to PVC/SAN blends which have much lower cloud points. Repulsion between  $\alpha$ -methyl styrene and acrylonitrile units in the copolymer was the principal cause for miscibility of this system as shown by an analysis based on a binary interaction model using calorimetry data for low molecular weight liquid analog compounds.

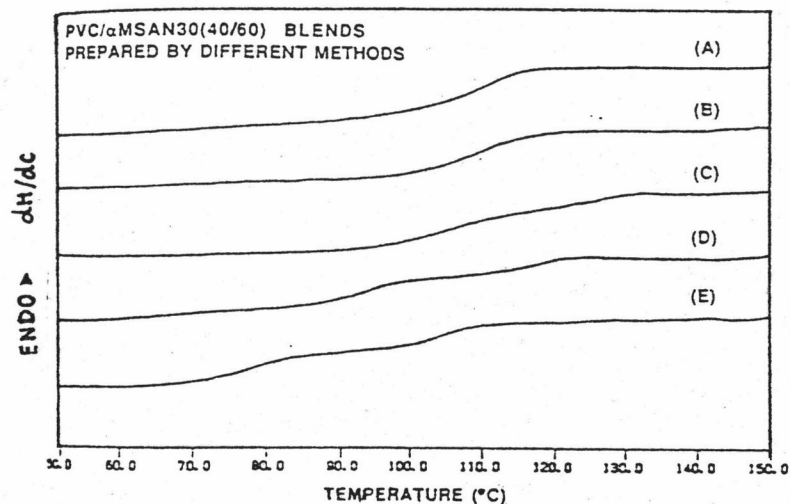


Figure 2.15 DSC thermograms for PVC/ $\alpha$ -MSAN30 (40/60) blends prepared by  
 (A) melt-mixing, (B) precipitation from MEK solution with methanol,  
 (C) precipitation from THF solution with methanol,  
 (D) casting from MEK solution at  $75^\circ\text{C}$ , and  
 (E) same as (D) except cast at room temperature[16].

Eckstein, Y. and Berger, E. J. [17] studied the effect of silane on glass/resin adhesion strength in a system consisting of silane coated single filaments embedded in a polymeric resin. The interfacial shear strength and the resin wetting were found to be dependent on the concentration of the silanes in the coating solution. The dependence on silane concentration was a significant factor in determining the molecular structure of a film deposited from that solution. Hydrolysis and polymerization took place in solutions at all concentrations; however, more dilute solutions formed lower molecular weight products than do solutions at higher concentrations. For the more concentrated solutions, both an uncross-linked species and a relatively highly cross-linked species were present. These characters were studied by GPC, DMA and FT-IR. In glass fiber/epoxy composites, silane concentration of the fiber coating solution affected interfacial adhesion and thermodynamic wetting by liquid epoxy resin. The optimum concentration with respect to maximum shear strength varied with the silane organofunctionality. For gamma-methacryloxy propyl trimethoxy silane ( $\gamma$ -MPS) and gamma-amino propyl triethoxy silane ( $\gamma$ -APS) are 0.2 and 1.0 wt%, respectively (Figure 2.16).

As the adhesion of glass single filaments in epoxy resin increased, so does the interfacial glass/resin adhesion increased. For stronger interfacial adhesion was achieved by increasing the amine or the alkoxy functionality in a series of aminosilane compounds. While the amine functionality did not strongly affect the degree of degradation of the interfacial adhesion by water, the alkoxy functionality did, with more alkoxy groups, give better hydrolytic stability.

From Figure 2.17, a decreased (N)H/SiOX ratio implied a lower magnitude of polar silane-epoxy interactions or a higher hydrophobicity of the silane coating which diminished degradation by water. Enhanced interdiffusion and chemical bonding were the most important mechanisms in formation of strong interfacial adhesion. On the

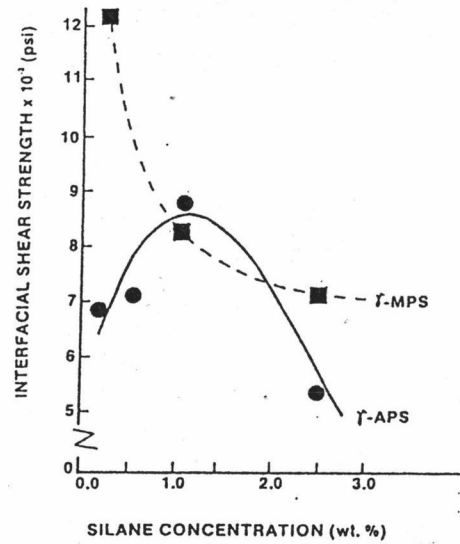


Figure 2.16 Interfacial shear strength as a function of silane concentration in solution[17].

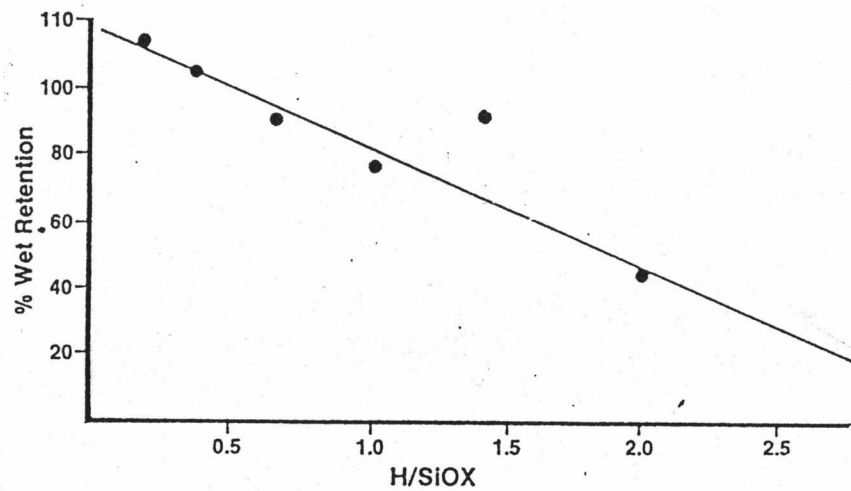


Figure 2.17 Ratio of number of hydrogen bond to nitrogens to number of alkoxy groups[17].

other hand, reduced silane-resin polar interaction and increased hydrophobicity of the silane coatings were of major consequence in producing glass/resin interfaces resistant to degradation by water.

Kinson, P. L. and Fober, E. M. [18] 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 processing 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 HDT and equivalent tensile strength as listed data in Table 2.4, compared to that of Rahrig's invention in Table 2.3.

Table 2.4 Physical properties of the composites [18].

	Glass content of blend, % by wt		
	This invention		
	10	20	30
Tensile strength, psi $\times 10^3$	10.	11.1	12.2
Tensile modulus, psi $\times 10^4$	66.	90.	122.5
Elongation, %	3.3	2.4	1.5
Flexural strength, psi $\times 10^4$	65.	96.	120.
Izod, notched, ft-lb/in	0.8	1.0	1.0
@ -40° C.	0.8	1.0	1.0
Specific gravity	1.31	1.40	1.49
HDT (annealed) 264 psi, °F.	185	185	185
Coeff of Therm Exp*, $\times 10^{-5}$	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 2.5

Table 2.5 Physical properties in each mixing[18].

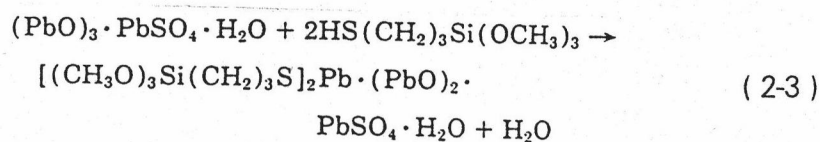
Physical Property	Run 1	Run 2	Run 3
Tensile strength (psi)	10,068	10,829	8,938
Tensile Modulus (psi)	730,000	768,000	657,000
Elongation at yield (%)	2.5	2.4	2.5
Yield Work (ft-lbs/cu.in.)	14.2	14.1	12.6
Flexural Strength (psi)	16,606	17,436	14,896
Flexural Modulus (psi)	644,000	682,000	598,000
Notched Izod (ft-lb/in)	0.7	0.8	0.6
Unnotched Izod (ft-lb/in)	3.9	3.7	3.3
Annealed HDT (°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.

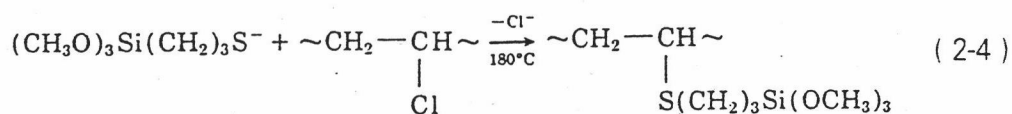
Run 2 : PVC and copolymer are blended before mixing with glass fibers.

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

Kelnar, I. and Schatz, M. [19] reported silane cross-linking of PVC. The reaction of poly(vinyl chloride) with mercapto alkyl trialkoxy silanes yielded silane-grafted PVC that could be cross-linked by the hydrolytic mechanism. The grafting of the silanes on the plasticized and unplasticized PVC was carried out at 180°C during processing in the presence of basic lead-containing stabilizers. These stabilizers reacted with mercaptosilane at the laboratory temperature to yield a yellow compound according to Eq.2-3:



Dissociation of this compound at processing temperatures then leads to the formation of the thiolate anion, which was capable of substituting, a chlorine atom in the PVC chain according to Eq.2-4:



The reaction was favourably affected by the presence of plasticizers and lubricants containing polar, preferably ester, groups. The silane-grafted and cross-linked polymers had satisfactory thermal stability. The results of strength measurements at elevated temperatures after cross-linking by water indicated that the material obtained had greatly improved parameters that were suitable for a number of applications.

Table 2.6 Tensile Tests of Unplasticized PVC cross-linked with mercaptosilane[19].

Test Temperature(°C)	Strength at Break (MPa)	Elongation at Break (%)
20	46	23
120	6.1	290
150	1.85	200

Otaigke, J. U. [20] studied the effect of introduction of a silane coupling agent and absorbed moisture (i.e. equilibrium hygroscopic state) on the tensile properties of a thermoplastic reinforced reaction injection molding (RRIM) composite, having a fiber volume fraction of 0.33, was evaluated. The composite was produced by anionically polymerizing caprolactam monomer within a continuous strand (swirl) glass fiber mat using a RRIM method. In addition to the expected strong dependence of the composite tensile stiffness and strength on an introduction of 1.5 wt% (based on the total weight of glass fibers) of  $\gamma$ -amino propyl triethoxy silane coupling agent, the effect of the mode of application of the coupling agent on resultant composite properties, under tensile loading, was observed to be insignificant in the dry state but

quite important in the wet state.

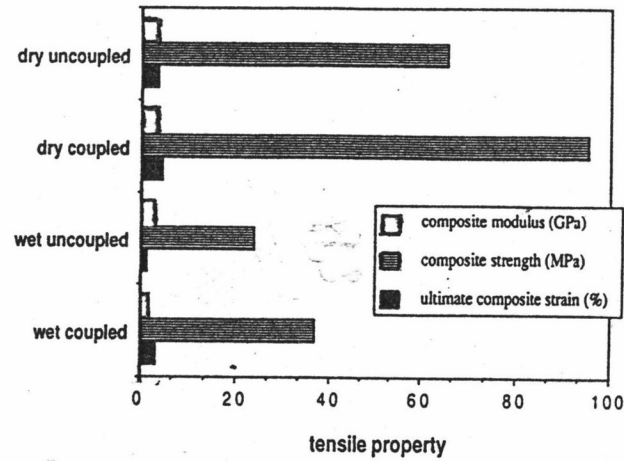
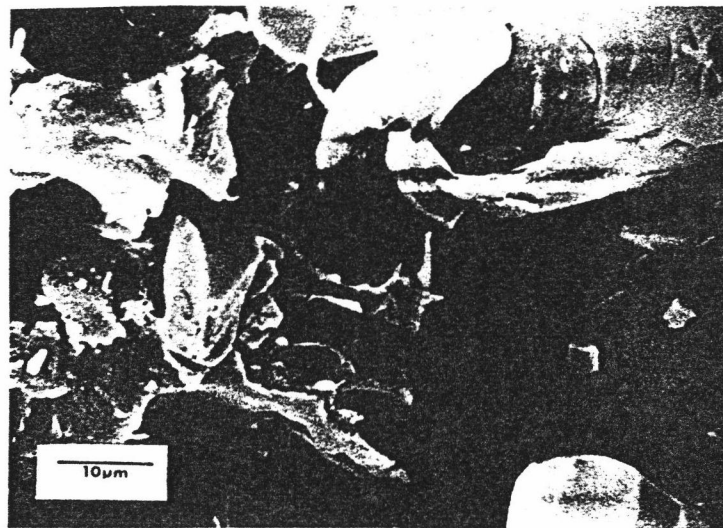


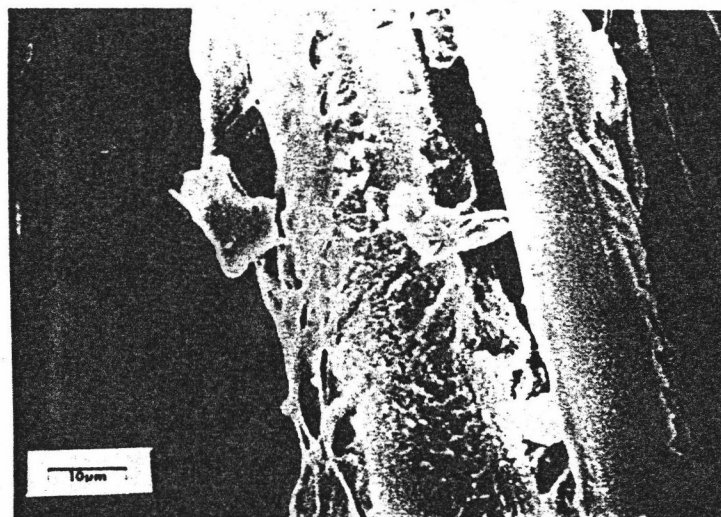
Figure 2.18 Effect of coupling agent and absorbed moisture on the Young's modulus strength (or peak stress), and ultimate strain of the composites[20].

Microscopic examination of the fracture surfaces revealed a three-stage tensile failure mechanism that was associated with debonding at low strains of the fibers, fiber failure (at the weakest point), and pull-out of the fibers resulting in catastrophic failure, at the ultimate tensile strain, of the composites as shown in Figure 2.19.





(a) Uncoupled



(b) Coupled

Figure 2.19 SEM photomicrographs showing the effect of coupling agent:

(a) uncoupled (b) coupled [20].