

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Theory

The word "composite" means consisting of two or more distinct parts. Thus a material having two or more distinct constituent materials or phases may be considered as a composite material. It is only when the constituent phases have significantly different physical properties and the composite properties are noticeably different from the constituent properties. Classification of certain material as composites is often based on significant property changes due to the combination of constituents, and these property change will generally be more obvious when one of the phases is in platelet or fibrous form, or the volume fraction is greater than 10%, and the property of one constituent is much greater (≥ 5 times) than the other.

Composites consist of one or more discontinuous phase embedded in a continuous phase. Figure 1 represents reinforcing geometries of composites which can be roughly grouped by shape of the reinforcing elements. The discontinuous phase is usually harder and stronger than the continuous phase and which is called the reinforcement or reinforcing material, whereas the continuous phase is termed the matrix. Properties of composites are strongly influenced by the properties of their constituent materials, their distribution, and

their interaction. The composite properties may be volume fraction

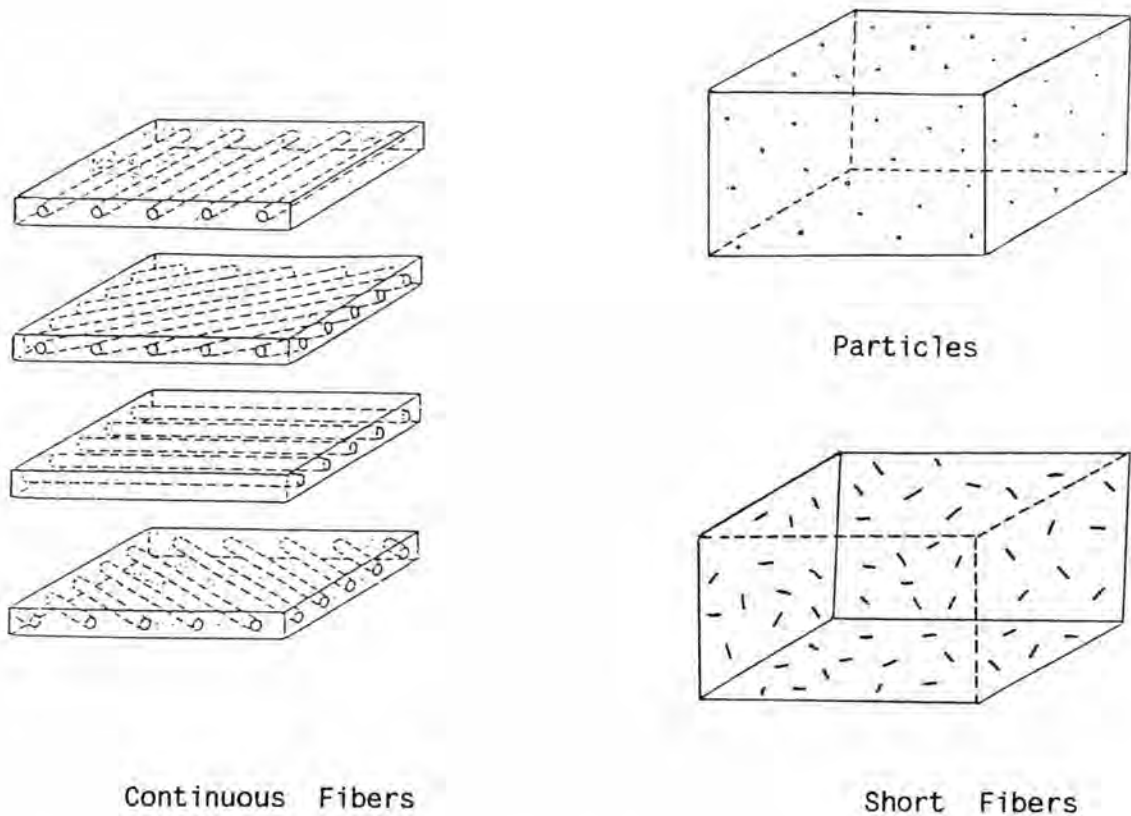


Figure 2.1 Reinforcing geometries of composites classified by shape of reinforcing elements (1)

sum of constituent properties, or that of synergistic interaction of the constituents. Thus to describe a composite material as a system, besides specifying the constituent materials and their properties, it is necessary to specify the geometry of reinforcement with reference to the system. The geometry of reinforcement may be described by shape, size and size distribution. However, systems containing reinforcements with identical geometry may differ from each other in many ways. For example, the reinforcement in the

systems may differ in concentration, concentration distribution, and orientation. Therefore, all these factors may be important in determining properties of the composites, but only some are accounted for the development of theoretical descriptions of composites.

Most composite materials have been developed to improve mechanical properties such as strength, stiffness, toughness, and high-temperature performance. It is usual to start with the composites having a common strengthening mechanism. The strengthening mechanism

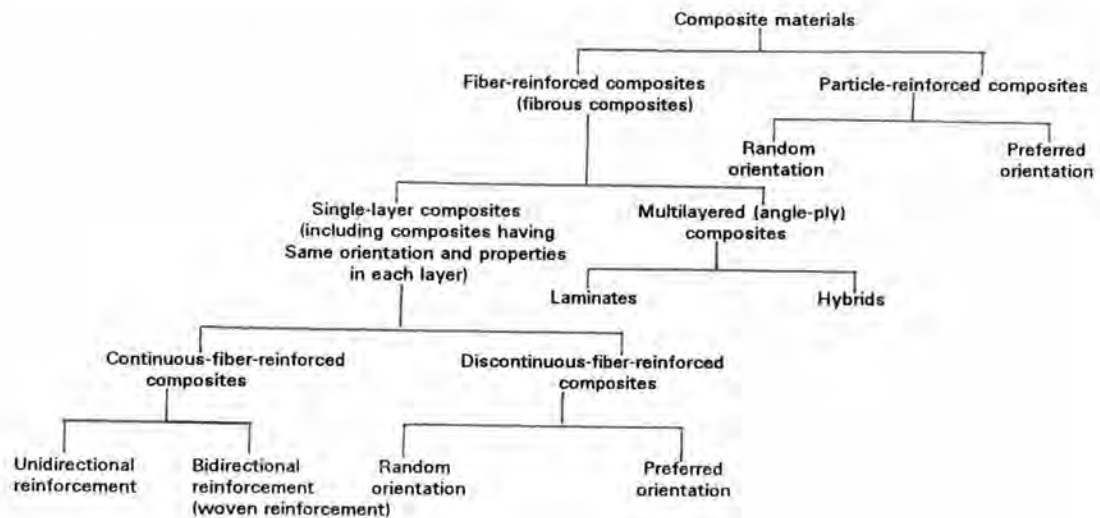


Figure 2.2 Classification of composite materials

strongly depends on the geometry of the reinforcement. Therefore, it is quite convenient to classify composite materials on the basis of the geometry of a representative unit of reinforcement. Figure 2.2 represents a commonly accepted classification scheme for composite materials. Regarding to this classification, the distinguishing characteristic of the particle is that it is nonfibrous in nature. It may be spherical, cubic, tetragonal, platelet, or other regular

or irregular shape, but it is approximately equiaxed. A fiber is characterized by its length which must be greater than its cross-sectional dimensions. Particle-reinforced composites are sometimes referred to as particulate composites and fiber-reinforced composites are called fibrous composites.

2.1.1 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 determines 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 load, 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.

2.1.2 Fibrous Composites

It is well known that the measured strengths of most materials are found to be much smaller (by a couple of orders of magnitude) 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, compare with the strength of bulk material, man-made filaments or fibers of nonpolymeric materials exhibit much higher strength along their lengths since large flaws, sometime 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 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 aramide 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 structures.

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.

Fibrous composites can be broadly classified on the basis of theoretical and experimental properties into single-layer and multi-layer (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, that is, 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

Table 2.1 Properties of fibers and conventional bulk materials

Material	Tensile modulus (E)	Tensile strength (σ_U)	Density (ρ) (g/cm ³)	Specific modulus (E/ ρ)	Specific strength (σ_U/ρ)
Fiber					
E-glass	72.4	3.5 ^a	2.54	28.5	1.38
S-glass	85.5	4.6 ^a	2.48	34.5	1.85
Graphite (high modulus)	390.0	2.1	1.90	205.0	1.1
Graphite (high tensile strength)	240.0	2.5	1.90	126.0	1.3
Boron	385.0	2.8	2.63	146.0	1.1
Silica	72.4	5.8	2.19	33.0	2.65
Tungsten	414.0	4.2	19.30	21.0	0.22
Beryllium	240.0	1.3	1.83	131.0	0.71
Kevlar-49 (aramide polymer)	130.0	2.8	1.50	87.0	1.87
Conventional materials					
Steel	210.0	0.34-2.1	7.8	26.9	0.043-0.27

Table 2.1 (cont.) Properties of Fibers and Conventional Bulk Materials

Material	Tensile modulus (E)	Tensile strength (δ_U)	Density (ρ) (g/cm ³)	Specific modulus (E/ ρ)	Specific strength (δ_U/ρ)
Aluminum alloys	70.0	0.14-0.62	2.7	25.9	0.052-0.23
Glass	70.0	0.7-2.1	2.5	28.0	0.28-0.84
Tungsten	350.0	1.1-4.1	19.3	18.1	0.057-0.21
Beryllium	300.0	0.7	1.83	164.0	0.38

^a Virgin strength values. Actual strength values prior to incorporation into composite are approximately 2.1 GN/m²

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 structural 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. The discontinuous-fiber composite can be considered to be the one in which fiber length affects properties of the composite. In case of continuous-fiber-reinforced composites, it may be assumed that the load is directly applied to fibers and the fibers in the same direction as load are the principal load-carrying constituent. The latter assumption is particularly valid when high-modulus fibers are used in high content. Thus the principal purpose of a matrix is not only as the load-carrying constituent but also essential for binding the fibers together and protect them. Failure of such a composite is also generally controlled by the fiber.

The continuous fibers in a "single-layer" composite may be all aligned in one direction to form a unidirectional composite. Such composites are fabricated by laying the fibers parallelly and saturating them with resinous material, such as polyester or epoxy resin, which holds the fibers in position and serves as the matrix material. Such form of preimpregnated fibers are called prepreg. Generally, a removable backing is also used to prevent the layers from sticking together while being stored. The backing also provides holding the fibers in position. The unidirectional composites are very strong in the fiber direction but generally weak in the direction perpendicular to the fibers. Therefore, the unidirectional preregs are stacked together in various orientations to form laminates for engineering applications. For heavy duty such as sealing application,

unidirectional glass reinforced adhesive tapes are widely used. Some unidirectional composites are used for fishing poles and other rodlike structures. The continuous reinforcement in a single layer may also be in a second direction to provide more balance properties. In case of bidirectional reinforcement, it may be provided in a single layer in mutually perpendicular direction as in a woven glass fabric. In bidirectional reinforcement, the secondary direction is perpendicular to the primary direction and provided only to prevent damage and fiber separation upon handling due to the poor strength in the transverse direction. In such case the transverse strength is much less than the strength in the direction of primary reinforcement.

The orientation of short or discontinuous 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. Alternatively, the chopped fibers may be converted to a lightly bonded preform or mat which can be later impregnated with resin to fabricate single-layer composites. In all these processes 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. The other advantages of fibrous composites include ease of processing and structural forms that are otherwise inconvenient or impossible to manufacture by other processes. Therefore, the utilization in aerospace and transportation industries is continuously increasing.(2)

Composite materials consist of a continuous matrix phase that surrounds the reinforcing phase structures. Possible acceptions are (a) a laminated stacking of sheets in which the phases are kept separately, and (b) two continuous interpenetrating phase, such as an impregnated sponge structure, in which it is arbitrary as to which phase is designated as the matrix. 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 determine the range of applications of this class of composites.

In the remaining two categories, cost is the more immediate consideration. The second category emphasizes 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.(3)

2.1.3 Thermoplastic Matrix Composites

In 1989, it was found that over 80% of the 23 billion kilograms(4) of plastic produced in the United States of America was thermoplastic polymers and the other 20% was thermosetting polymers. Most applications of thermoplastics take more advantage of the inherent ease of processing and excellent balance of properties. Thermosetting polymers are more time-consuming to process because they require chemical reactions for curing, and are generally less impact-resistance than the thermoplastic polymers.

However, the predominance of thermoplastic polymers over thermosetting polymers does not extend to composites. Over 85% of the 1 billion kilograms of composites in the United States of America in 1986 used thermosetting polymers as matrix.(5) Moreover, there is a significant difference in the applications of composites based on type

of the matrix polymer used. Composites of short fiber reinforced injection molding compounds largely used the thermoplastics as the matrix, while long and continuous fiber reinforced composites mostly used the thermosetting polymers as the matrix.

In long and continuous fiber reinforced composites, thermosetting polymers are particularly well suited for impregnation into the fibers by manual or semi-automated means, since they consist of low viscosity liquids that can be handled at room temperature with little difficulty. For low production runs, composites produced by manual or semiautomated production techniques have a strong economic advantage over those produced by fully automated methods of manufacturing. With the exception of injection molded short fiber reinforced composites, the number of any single composite part manufactured in a year has been small compared to the quantities of most thermoplastic parts. The recent growth of polymer composites during the 1980s has resulted in a need for higher productivity manufacturing processes which are currently extent with thermoset composite production methods.

The need for higher manufacturing productivity has provided the intensive to develop long and continuous fiber reinforced thermoplastic matrix composites that can potentially overcome some of the property limitations associated with the thermoset composites. The major property limitations of the thermoset composites are brittleness, solvent susceptibility, and problems associated with the fact that the polymers must be chemically reacted. These problems include the fact that the reactivity of the uncrosslinked thermoset polymers limits their shelf life, extends their processing time, re-

sults in difficulty of scrap reclaiming and cannot be easily repaired. These property limitations, by themselves, have not been sufficient to warrant a switch from thermosetting polymer matrices to thermoplastic polymer matrices, because of the economic advantage of thermoset composites production in low volume production runs.

While thermoplastics have a considerable advantage in enhancing toughness of the composite, unlimited shelf life and requiring only heat and pressure for processing. It has a potential for high volume processing, and low cost per part, that has spurred the current research and development activities on thermoplastic matrix composites. In fact, the use of thermoplastic composites requires high productivity applications because the process must be automated in order to handle high temperature and pressure requirement. Automated processes are best advantage for economics scale. Therefore, the use of thermoplastic polymers as the matrix for composites goes hand in hand with the requirement and need for high volume production. The widely use of glass fiber reinforced injection molded composites is an example of this fact. Developments of using high volume production techniques have been extended to long and continuous fiber reinforced thermoplastic matrix composites to serve increase demand of structural and advanced composites uses.

This article discusses three types of thermoplastic matrix composites. The first type is short fiber reinforced injection moldable composite. There are two major forms of reinforcement used in this type of composite: discontinuous synthetic fibers and short natural fibers and flakes. The second type of thermoplastic composite is long and/or continuous fiber reinforced sheet with random in-plane

fiber orientation and relatively low fiber content. The third type of composite is an advanced composite, usually consisting of a high temperature polymer with an oriented fiber construction. Carbon fibers are the preferred reinforcement for advanced composites because of their higher modulus than the glass fibers.(6)

2.1.4 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(PE), polypropylene(PP), polystyrene(PS), polyvinylchloride (PVC), polyethyleneterephthalate (PET), 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-resistant, capable of withstanding wide ranges of temperatures, resistant to weather, chemicals, and other hostile conditions. The engineering plastics consist of acrylonitrile butadiene styrene terpolymer(ABS), polycarbonate(PC), poly(ether ether ketone) (PEEK), etc.(7)

Hence, the commodity plastics are interested because they have

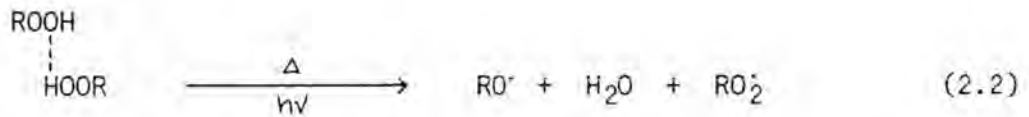
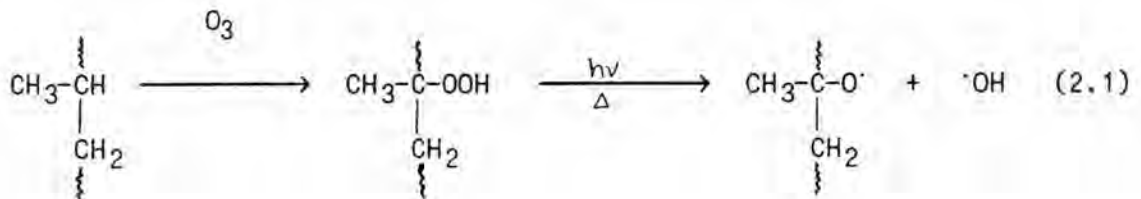
many advantages such as recyclability, cheap, etc. However, in the group of PS, PVC, and PET, toxic gases are generated during recycling process and mechanical properties will drop substantially when comparing to PE and PP. Due to the withstanding range of temperature of PP is greater than PE, (8) the PP was chosen for our research.

Polypropylene, (PP), has been commercially available for more than 15 years. However, it has started to take place some major thermoplastics just recent years due to lacking direct production of the monomer. The monomer is usually a byproduct from either refinery operations or from steam cracking of ethane and higher feedstocks for ethylene production. Another factor which has been considered to delay polypropylene development was the lack of catalysts to produce a stereoregular polymer. Unlike ethylene, propylene has a methyl group in the molecule. Upon polymerization propylene may produce one of the three structures: isotactic, where the methyl groups attached to the carbon chain are in the same plane; syndiotactic, where the methyl groups are alternately distributed in the same plane; and atactic, where the methyl group are randomly distributed in the same plane.

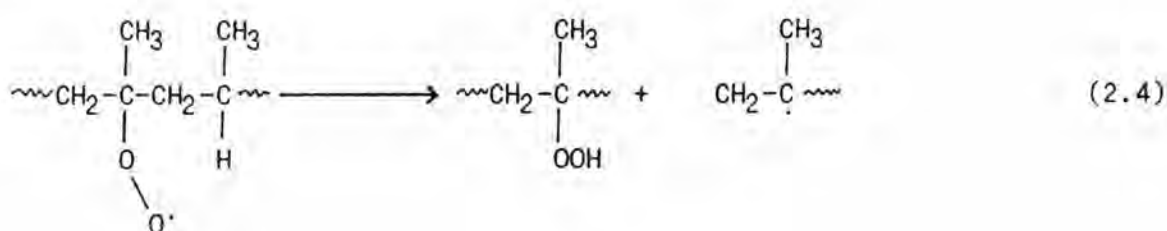
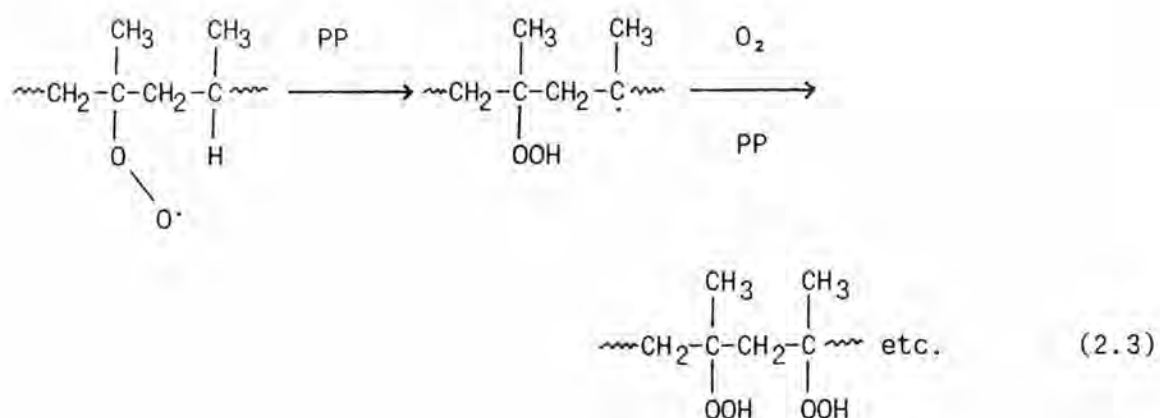
Polypropylene has good electrical and chemical resistance and low water absorption. It has good heat resistance and can be sterilized at 100°C. Because of the flex fatigue resistance of polypropylene, self hinged articles made from polypropylene have long life expectancy. Other important properties of polypropylene are toughness, high abrasive resistance, good dimensional stability, nontoxicity, high impact strength, and good transparency.(9)

2.1.4.1 Degradation of Polypropylene(PP)

Polypropylene is susceptible to thermal oxidation,(10) even at ambient temperatures, so that it is never used without an antioxidant. Initiation of thermal oxidation in the solid polymer is usually attributed to the formation of hydroperoxides or peroxides during process or storage, perhaps in part, as a result of slow attack by ozone (O_3) (eq.2.1). Ozone attack on PP leads to an efficient escape of free radicals from the primary cage, possibly because of the intermediate or the mobile hydroxy radical(11) (eq.2.1).Ozone probably also attacks oxidation products, especially peroxidic species. Thermal decomposition of PP hydroperoxide is complex, either because of the simultaneous unimolecular and pseudobimolecular process (eqs. 2.1&2.2) or because



of the neighboring group assisted reactions.(12) The bimolecular process is approximately 10 times faster than the unimolecular process. The bimolecular process may be associated with the presence of α , β , γ , ϵ , ..., ω sequences of adjacent hydroperoxide groups.(13)



2.1.5 Fiber reinforcement

A fiber is a long fine filament of matter with a general diameter in the order of $10 \mu\text{m}$ and with an aspect ratio of length to diameter between 100 and virtually infinity for continuous fibers. Fibers can be divided into three groups: natural, regenerated and synthetic.

The first truly synthetic organic fibers were produced from short molecular compounds in 1938. Continuous glass fibers were also commercially produced just before the time. Both polyamide and glass fibers were developed in U.S.A., by E.I du Pont de Nemours and Owens Corning, respectively. Almost simultaneously with the work of theirs Caro at du pont, polyamide was produced in Germany by I.G. Farben.(14) Fiber reinforcement can be divided into many types.

2.1.6 Glass Fibers

Glass fibers were firstly used by the ancient Egyptians. They used coarse fibers drawn from heat-softened glass for manufacturing vessels by wrapping the fibers around clay mandrels and heating them to fuse the glass into a solid container. The clay mandrel was removed after glass cooled. In the mid-1600s Robert Hooke, an English physicist, described experiments with glass filaments. In the next century, Rene' Antoine Ferchault de Re' aumur, a French scientist, predicted that fine glass fibers would be pliable enough to weave into fabric. Glass fabric was made in 1893 by Edward Libbey who was the founder of Libbey Glass Company. A dress made from this fabric was exhibited at the columbian Exposition held that year in Chicago. It was not until 1931 that a commercial process for the production of glass fibers was demonstrated by the Owens Illinois Glass Company. By 1936 the company had developed a process for continuous glass filament production. Owens Illinois merged with corning Glass Works in 1938 to form Owens-Corning Fiberglass. This marked the beginning of the modern fiberglass industry. In the late 1940s and early 1950s, Owens-Corning granted the licenses to Pittsburgh Plate Glass (now PPG), Libbey-Owens-Ford. st.Gobain in France, and Pilkington in England.(15)

Initially the glass fibers were destined for textile applications. However, the developement of heat-setting resins opened up the possibility of fiber-reinforced composites, and in the years after World WarII, the fiber came to dominate the market for this type of material.(16)

Structure of all glass fiber is based on silica, which is mixed with other materials according to the desired properties. The structure is vitreous, with no definite compounds being formed and no crystallization taking place. The silica forms an irregular three-dimensional network. This open network is a result of the rapid cooling that takes place in fiber production from about 1500°C to 200°C within 0.1-0.3 second. Despite this rapid rate of cooling, there appear to be no appreciable residual stress within the fiber, and the structure is isotropic.(17)

Glass fibers require specialized treatments during the production process and subsequent use. Each treatment, generally organic, provides some specific beneficial quality such as providing lubrication, protecting the individual filaments, holding the strands together, or providing compatibility with the resin system used in the manufacture of the glass reinforced end-product. Glass fiber reinforcements are supplied in several basic forms. These forms allow cost flexibility, strength and choice of process. Many variations of the basic forms have been developed over the years to meet performance and economic needs which vary over a wide range. Variations of each form occur in the manufacture of the basic glass fiber. Most fibers are made by mechanically drawing a filament from a stream of molten glass. During the early stages of processing, a chemical treatment is applied to the surface of the glass fiber.(18)

Surface treatment specifications vary with performance requirements. A few industry terms are useful for understanding this point. A size is a chemical surface treatment applied immediately after fibers are formed. It protects strands and couples strands to

plastic resin. A finish is a chemical coupling agent applied to fabric after it is woven and cleaned to make fabric compatible with molding resin. A binder is a bonding resin to hold strands of glass fiber together in a mat or preform during manufacture of the molded object.(19)

2.1.7 Types of Glass Fiber Reinforcements

The general types or structures of glass fiber reinforcement products which are commercially available in transportable form are as follows:

2.1.7.1. Continuous Strand

A 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.

2.1.7.2 Mats

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

a. Reinforcing Mats

(1) Chopped strand mat is constructed from multiple-length, chopped fine strands and bonded in a mat form with a resinous binder.

(2) Continuous strand mat is made from multiple layers of continuous filament strands in a swirl pattern, which are held together with resinous binder. This mat is recommended for matched metal die molding where relatively deep and complex contours require maximum draw characteristics.

(3) Fabmat, a trademark of Fiber Glass Industries, Inc., is a combination reinforcement consisting of one ply of fast-wetting Araton, a trademark of Owens-Corning Fiberglass Corp., woven roving, chemically bonded to chopped-strand mat.

b. Surfacing mat is commonly used with other glass fiber reinforcements for laminate surface appearance and weathering. It is also used to provide reinforcement of a resin-rich surface where serious corrosion considerations are involved.

c. Overlay mat is very similar to surfacing mat and commonly used in matched-die molding to improve surface properties.

2.1.7.3. Chopped Strands

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

2.1.7.4. Fabrics and Tapes

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.

a. Continuous filament yarn fabric is available in open, medium, and close weaves. Continuous filament-ply yarns are normally used in weaving cloth fabrics, but single yarns are also used.

b. Woven roving fabric is manufactured from continuous filament roving, spun strand roving, or a combination of the both. It is processed as bulking coarse texture and as fabric which offers the highest strength at the lowest cost.

c. Spun strand roving fabric, recently developed one does not offer as much bidirectional strength as does continuous strand roving fabric. It does, however, provide multidirectional strength, better wet-out, and improved layer-to-layer bonding characteristics (interlaminar shear).

Mechanical strength depends on combined effect of fiber content and fiber arrangement in a finished object.

2.1.8 Arrangement and Amount of Reinforcements

As shown below in the Figure 2.4, strength of the finished laminate increases in direct relation to the amount of glass. It is shown that a part containing 80 percent glass and 20 percent resin is almost four times stronger than a part containing opposite proportions

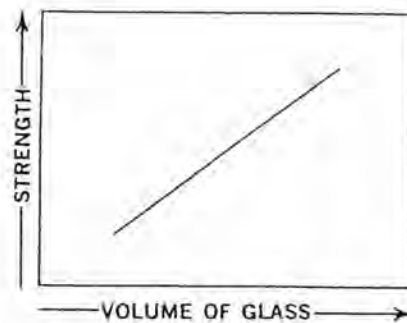


Figure 2.3 Dependence of strength on fiber content

opposite proportions of the two materials. Glass arrangement also affects strength of the finished product which may be considered as the following three cases:

(1) When all strands are laid parallel to each other (unidirectional), maximum strength results in one direction. This strength is supplied for end uses such as solid rods or solid bars. Product application includes guy strain insulators, golf clubs, and fishing rods. Strength perpendicular to the axis of the fibers is dependent on the shear strength of the resin.

(2) When half of the strands are laid at right angles to the other half (bidirectional), strength is the highest in those two directions. Strength in any directions are less than the parallel arrangement. This pattern of glass reinforcement is used in structural shapes.

(3) When glass fibers are arranged in a random manner (isotropic), strength is equal in all directions. This arrangement is generally found in safety helmets, chairs, premix molded parts, luggages, and machine housings. There is a relationship between the

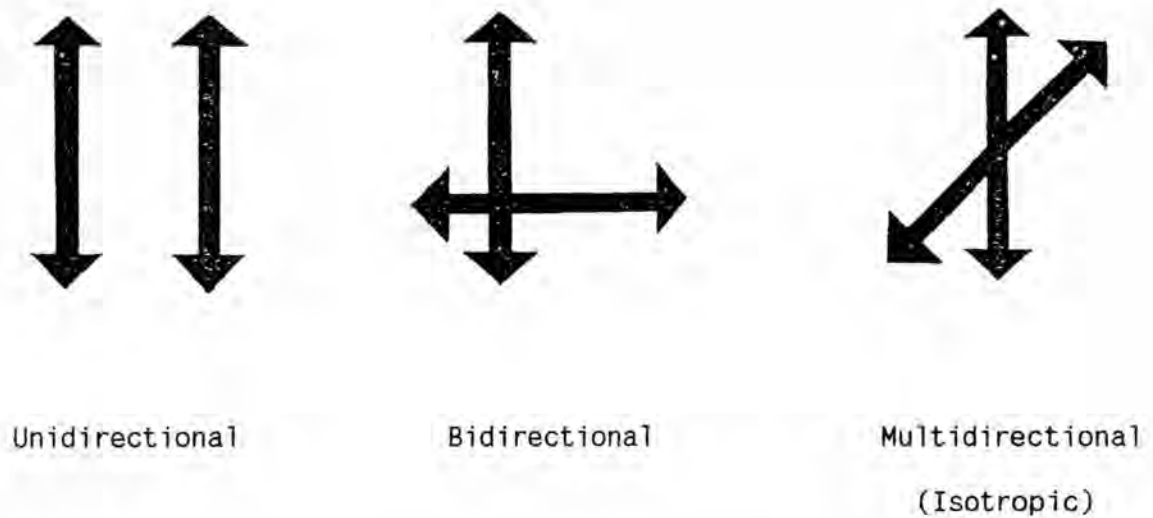


Figure 2.4 Three strength patterns available in glass fiber reinforced plastics

glass arrangement and the glass content that can be loaded into a given object or product. Then the neater arrangement or the more precise placement, the greater amount of reinforcement can be placed.

In the case of unidirectional arrangement, glass loadings from 45 percent to 90 percent can be obtained. The maximum theoretical amount is about 92 percent, while the practicable desired maximum is less than 80 percent. The bidirectional arrangement, glass loadings range from 55 percent to 75 percent. The random arrangement gives glass loading in a range of 15 percent to 50 percent. Dependence of strength characteristics on glass content and glass arrangement is shown in Figure 2.6. The figure shows that continuous parallel strands give higher strength than both bidirectional random arrangements. Reinforcements are sold in a form which permits the designer or user to utilize the directionality to maximize their advantages. The basic

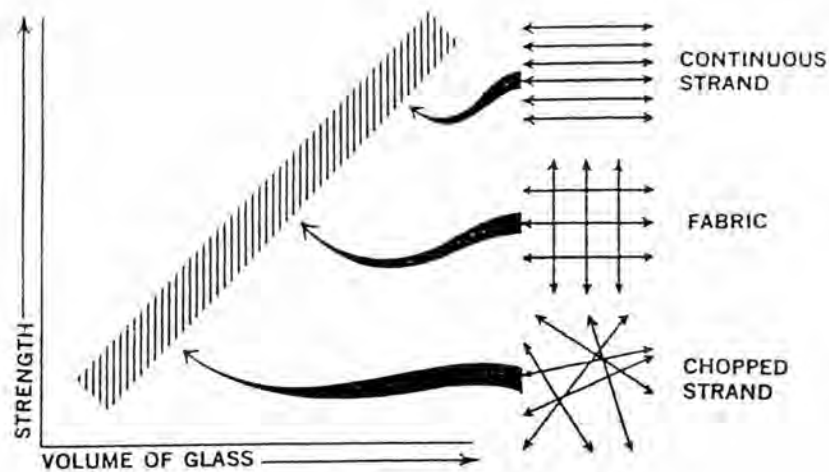


Figure 2.5 Dependence of strength characteristics on glass content and glass arrangement

forms are continuous strand, fabric, woven roving, chopped strand, reinforcing mat, and surfacing mat.

Continuous strand, the lowest cost, gives unidirectional reinforcement. In filament windings it is utilized to give a balance of reinforcement in the desirable directions and angles. The reinforcement of glass fibers can be summarized as follows:

1. Fabric essentially reinforces the object in two directions.
2. Woven roving gives higher strength and lower cost than conventional glass fabrics.
3. Chopped strand gives random reinforcement.
4. Reinforcing mats are lower cost than fabric and give random reinforcement.
5. Surfacing mats give virtually no reinforcement but permit a decorative and smoother surface finish.

As mentioned earlier, a definite relationship exists among

reinforcement, molding methods, and engineering properties. In general, an increase of molding pressure will decrease laminate thickness and increase glass content. As a result, strength properties will be improved. (20)

2.1.9 Production of Glass Fiber Reinforced Polypropylene

There are currently two main ways to produce staple polypropylene thermoplastic prepreg sheets in an industrial scale. The most common is the melt impregnation process (Figure 2.6). Here, two glass mat layers are sandwiched between three PP layers, the inner layer being melted PP, while the top and bottom layers are either film or melted PP. The sandwich is compacted at a temperature higher than the melting temperature of PP and then cooled. It is finally cut into three sheets. BASF, Shell and GE Plastics are the major prepreg manufacturers using this process. In the melt process the mat is a very

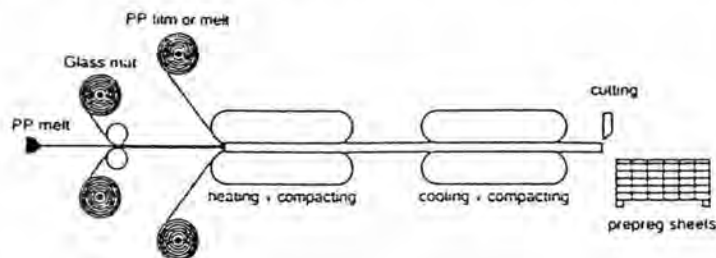


Figure 2.6 Melt Glass Fiber Reinforced Polypropylene

critical element. In general, a typical chopped strand mat or continuous mat is used when only minimal flow is needed in the mold. Where optimal flow is required, a specially needled mat produced from glass fiber roving is used.

The second main industrial technique used to produce PP prepreg sheets is the wet/paper process (Figure 2.7), which was developed on paper machines. Glass fibers having length between 6 to 25 mm are dispersed in water, together with powder and latex. Then flocculating additive is added to the suspension to cause the latex to coagulate with the powder which will separate from the water on the screen of hydroformer machine. The resulting belt is then consolidated by pressure at a temperature superior to the PP melting temperature. This process was originally developed by the paper companies, Arjomari and Wiggins Teape. The major thermoplastic manufacturers using this process are Exxon and GE Plastics. While they have their own specific peculiarities, each of these process requires optimum performance of glass fibers. For this reason, glass fibers are tailor-made for each process. Numerous automotive parts, such as bumper beam, structure

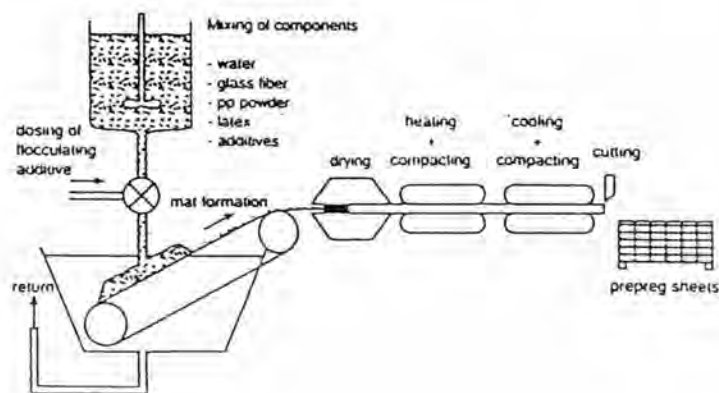


Figure 2.7 Wet/paper glass fiber reinforced PP process

front ends, are now produced by this process. Most are non-appearance parts. A second generation of glass mat thermoplastic (GMT) sheet, launched on the market about one year ago, has better adhesion between

the fibers and the matrix, as a result to improve modulus and strength. This improvement results from using new, tailor-made sizing and modifications of the matrix. Further works is the improvement of flow, surface finish and homogeneity of the material. The term COFIT is used to define the field of composite manufacturing based on the use of continuous fiber roving impregnated with thermoplastic. Numerous processes are used but the most important processes are the melt impregnation (or pultrusion) process and powder impregnation process.

The melt impregnation process (Figure 2.8) consists of passing cosmostrand roving through an impregnation chamber specially designed to wet the roving with melted resin. The chamber is fed by an extruder, while the chamber exit is fitted with a die which provide the required The impregnated strand is then cooled and pulled by a belt puller. The

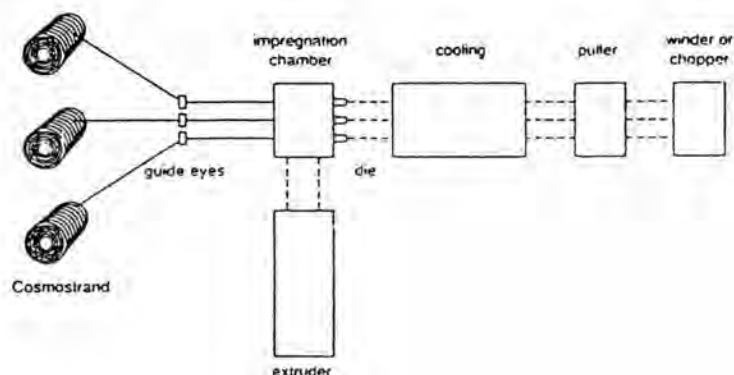


Figure 2.8 Melt impregnation process

resulting rods or tapes can be wound or chopped, depending on application. This process is attractive because it combines the versatility of melt compounding with a standard raw material. As a result, it is

extensively developed. For this application, cosmostrand offers the following advantages:

1. It can be externally unwound without a twist, which considerably facilitates impregnation
2. It offers considerably better protection against abrasion failure at the impregnation stage.

In the powder impregnation process (Figure 2.9), Cosmostrand roving is opened by tensioning bars and then passes through a bed of PP powder which is suspended in an air current behaving a liquid suspension. Opening the roving allows the powder to be trapped between the filaments. There are several different approaches to opening the

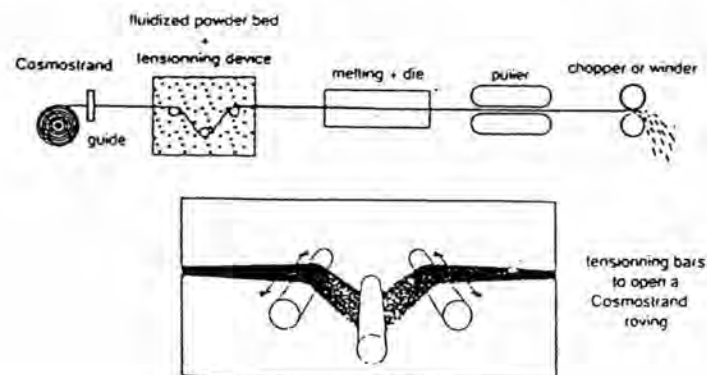


Figure 2.9 Powder impregnation process

strand and handling the powder-air mixture. The principal processes related to this technique have been developed by Spliflex, ATO (FIT), Flexline and Picther.

Main advantages of the powder impregnation process are high speed of impregnation and ease to obtain a high molecular weight polymer between the filaments, which would be more difficult to achieve by

using the melt process. Two limitations are the need of fine powder with high grade and the fact that melting after impregnation limits the operation speed. Other processes such as fiber entanglement, solvent impregnation and powder/water impregnation are also available. However, it seems that their cost and efficiency will limit them from being used with expensive polymers.(21)

2.1.10 Void Formation in Melt Flow Thermoplastic Composites

Voids may be intentionally introduced into polymer composites to reduce density, however, in most cases voids are considered to determine mechanical property of the polymer composites.(22) The voids act as initiation sites for crack formation and propagation in addition to residual stress in the material.(23) Thus, the void content should be kept below a certain limit unless other phenomena such as microcracking will become important. As the result, either strength or modulus of the material will change significantly.

Kavanagh presented a simple mechanical model for void content effect on the stiffness of fiber-reinforced composites.(24) In this model, the voids and the matrix material are combined and represented by an "effective matrix material" having a modulus E_m^{eff} as shown below (eq. 2.5)

$$E_m^{eff} = E_m [(1 - \sqrt{V_p}) / (1 - \sqrt{V_p} + V_p)] \quad (2.5)$$

where

E_m = matrix modulus

V_p = void volume fraction based on the combined volumes of matrix and voids.

Consequently, computation of the composite properties can follow a rule of mixture approach, in which the matrix properties have been corrected for the presence of voids. In the production of thermoplastic structural foams, bubbles nucleate and then grow by diffusion of gas molecules through the melt to the growing bubbles followed by some bubble coalescence. Numerous factors influence and control the process of void formation, void content, and shape of the composites. Examples of the factors are pressure and temperature gradients in the compounding and in the melt flow processing steps, extrusion rate, viscosity of the melted polymer, and fiber length, fiber content, and fiber orientation. The complex interactions of these variables had led to various studies concerning basic aspects of void formation in the thermoplastic composites.

2.1.10.1 Void Formation Mechanism

The mechanism of bubble formation in molten polymer is that of nucleation and growth expansion in a viscous medium.(25) The total work, W , required for nucleation is the work necessary to inflate a bubble minus the energy consumed in the creation of a new surface (eq. 2.6).

$$W = P [(4\pi r^3) / 3] - \sigma (4\pi r^2) \quad (2.6)$$

where

r = bubble radius

P = pressure

σ = surface tension

At equilibrium the forces are equal and the maximum work required for nucleation as well as the critical radius, r , can be obtained by differentiation of Eq.(2.6) to give eq. 2.7 as shown below.

$$W_{\max} = 16\pi\sigma^3 / 3P^2 \quad (2.7)$$

Experimental evidence suggests that bubble nucleation in fiber containing melt takes place at the fiber end.(26) Diffusion of gas from small bubbles into the larger ones occurs as a result of the pressure difference between the both as shown below (eq. 2.8).

$$P = 2\sigma [(1/r) - 1/R] \quad (2.8)$$

where

P = pressure different small bubbles and larger bubbles

R = radius of large bubbles

r = radius of small bubbles

σ = surface tension of the polymer melt

Rate of the bubble growth depends largely on diffusivity and concentration of the gas, viscosity of the polymer melt, and the temperature and pressure gradients. No bubble growth is predicted to occur during initial drop of the melt pressure but depending on

shear modulus of the melt and the critical radius above which growth falls very sharply to a micron or less. The number of bubbles growing due to a given pressure drop depends on ratio of the critical radius to the average radius of the bubbles assumed to be present in the melt. Appreciable reduction of the bubble growth rate resulting from diffusion of small bubbles into the larger ones occurs only when the internal bubble pressure is very low or when the bubble wall thickness is very thin. In all cases a growing bubble will ultimately reach its asymptotic growth rate. No bubbles that have begun to grow will disappear or collapse as a result of diffusion into the larger neighboring bubbles or agglomerate due to fracture of bubble walls. This is because the interbubble gas diffusion rate is smaller than the growth rate even at small values of the interbubble distances.

In conclusion, voids are formed in short-fiber thermoplastic composites mainly because of entrapped air introduced during melt compounding and the subsequent processing steps and probably also because of uneven volume contraction resulting from temperature gradients during melt solidification. Voids usually nucleate at fiber ends. The void content depends on processing method and conditions, fiber concentration, and fiber length. In injection molding, a low void level is obtained by cooling under high pressure in closed mold. In extrudates, relatively high void contents are obtained through post-die cooling at atmospheric pressure. The void content in extrudates increases with increasing fiber content and fiber length. Higher shear rates and temperatures also result in higher void levels. Hot drawing of extrudates changes the void shape from spherical to elongated and decreases its content. From the practical viewpoint,

one can conclude that low void content short fiber reinforced thermoplastic extruded profiles may be produced only in vented machines under specific narrow-window, well-defined processing conditions.(27)

2.1.11 Mechanical Properties

Composites compete with materials such as metals, ceramics, and wood for structural applications. In order to overcome these materials, composites must have mechanical properties comparable to those of metals, ceramics, and wood, and superior to those available with unfilled polymer. The primary mechanical properties interested for evaluating composites are tensile strength, tensile modulus, and impact strength. Other important properties include flexural strength and modulus, chemical resistance, creep behavior, ultimate fatigue stress, and upper use temperature. For advanced composites, a common method for comparing mechanical properties is on an equivalent weight basis. This is not always a valid method of comparison for the short fiber reinforced composites because such composites are not usually intended for long term high stress applications since they still exhibit creep under high tensile loads. However, in order to evaluate potential for the composites in structural applications, the three basic mechanical properties must be known for design purposes. In this section, theoretical analyses are presented to provide estimation of mechanical properties of various fiber reinforced composites.

As the shape of a filler particle is elongated from a spherical shape to a fiber, the filler stiffens the composite to a greater extent, and begins to carry increasing fractions of the load. Useful

fibers exist several types such as glass, boron, graphite, or other polymers and may exist in various configurations from discrete whiskers or fiber to woven cloth. With short, discontinuous fibers of a high modulus material, mechanical load is shared between the matrix and the filler, and most mechanical properties of the composite are improved to greater or lesser extents in comparison to the matrix. With continuous fibers, on the other hand, the fibers carry most of mechanical load while the matrix serves to transfer stress to the load-bearing fibers and to protect them against damage.(28) In this case, the presence of the matrix makes possibly better utilization of the inherently high levels of property characteristic of fibers. Indeed, fiber polymer composites are the strongest and stiffest engineering materials, especially on a property/density basis.(29)

2.1.11.1 Tensile Strength

A detailed theoretical analysis of the tensile strength of short fiber reinforced composites is well beyond the scope of this section. A number of excellent presentations have been made to provide complete theoretical analysis of the tensile strength of short fiber reinforced polymer matrix composites.(30) For a reasonable engineering estimation of the tensile strength of a short fiber reinforced composite, a modification to a simple rule of mixtures has been effectively used (31) as shown below in eq. 2.9.

$$\sigma_c = \sigma_p \phi_p + \sigma_f \phi_f \epsilon_1 \epsilon_0 \quad (2.9)$$

where

σ_c = tensile strength of the composite

σ_p = tensile strength of the polymer

σ_f = tensile strength of the reinforcing fibers

ϕ_p = volume fraction of the polymer in the composite

ϕ_f = volume fraction of the fibers in the composite

ϵ_0 = efficiency factor related to the orientation of the fibers in the composite

ϵ_1 = efficiency factor related to the effectiveness of load transfer between the fiber and matrix

If the fibers are unidirectionally oriented, ϵ_0 will be 1.0. When they are randomly dispersed in a plane, the value of ϵ_0 is approximately 0.33. For very small particulate reinforcing fibers, three-dimensional random isotropy is possible, in which ϵ_0 is approximately 0.162. In a complex part ϵ_0 can have different localized values. In such cases a finite element analysis of the part can be made by taking the localized fiber orientation into account. One of the primary problems associated with designing with short fiber reinforced composites is their anisotropy. Different regions of a molded part will have not only different in fiber orientations but also different in fiber concentrations. Moreover, the fiber orientations may be varied not only in the in-plane dimension but also in the thickness of the part.

Despite the problems associated with determining ϵ_0 , the value of ϵ_1 is even more difficult to determine because it is different for each polymer-fiber combination. For example, the value of ϵ_1 is strongly affected by the effectiveness of coupling agent. ϵ_1

is equal to 1.0 for continuous fibers. For discontinuous fibers, ξ_1 relates to the critical aspect ratio for the fiber matrix combination. The equation used to establish the critical fiber aspect ratio is:

$$(L/D)_c = \sigma_f / 2\tau_I \quad (2.10)$$

where

σ_f = tensile strength of the fiber

τ_I = interfacial strength between the fiber and the matrix

Shear strength of the polymer is often used as an estimation of τ_I .(32) This provides a relationship between the shear strength of a polymer and the critical aspect ratio for glass fiber reinforced composite as shown in Figure 2.10. In most cases, however, τ_I is determined from fiber pull-out experiments. For many polymer fiber combinations, the critical aspect ratio is between 15:1 and 30:1. As might be expected, the interfacial strength is strongly influenced by coupling agents. Coupling agents improve the wetting of thermoplastic polymers to the fibers. There is no evidence that coupling agents affect a chemical reaction with the polymer, as they do in the case of thermoset polymers. Coupling agents drive away the moisture that is present on the surface of the glass fiber. This enhances wetting between the polymer and the fiber and improves the strength of the composite.(33) (The relationship between τ_I and the critical aspect ratio can be represented in a general fashion by a curve shown in Figure 2.11. This plot reveals that in a short fiber reinforced com-

posite, the maximum degree of reinforcement is achieved when the average fiber length is approximately 10 times the critical aspect ratio. Therefore, in order to obtain maximum reinforcement from a discontinuous fiber reinforced composite, the fibers in the composite should have an aspect ratio of at least 500:1).

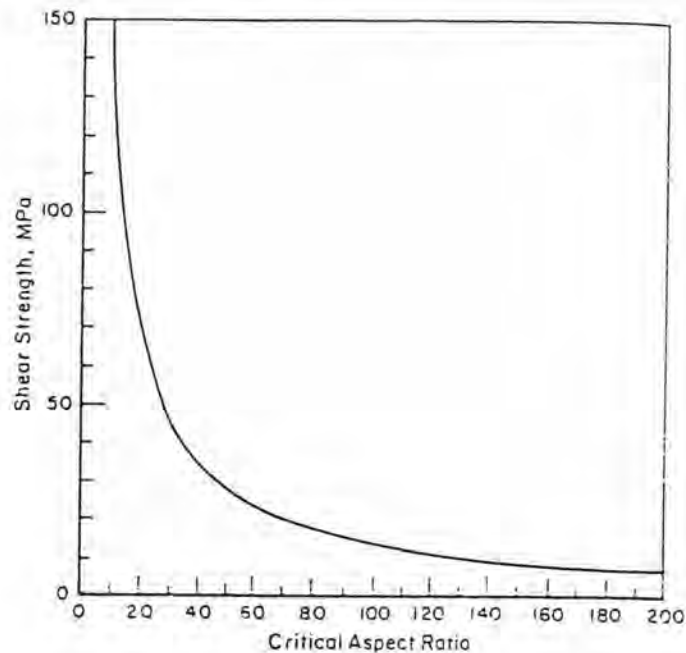


Figure 2.10 Relationship between the shear strength of a polymer and the critical aspect ratio for glass fiber reinforced composites

A significant conclusion that can be drawn from this plot is that composites containing long chopped fibers can potentially have mechanical properties almost equal to composites containing continuous fiber reinforcement. The critical fiber aspect ratio for many polymer fiber combination is in the range of 20-50 : 1. The average fiber aspect ratio for a 20 volume percent loaded injection

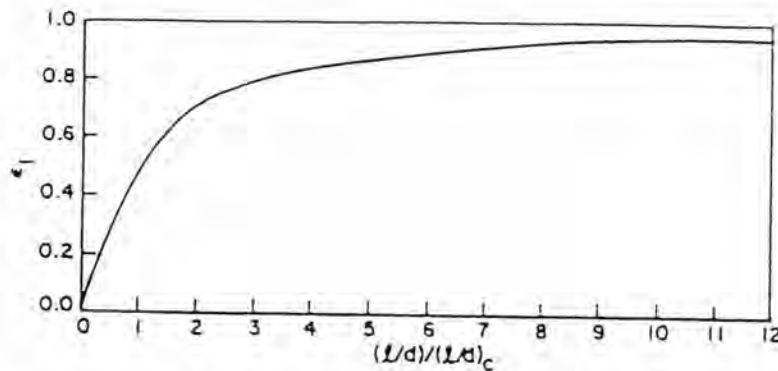


Figure 2.11 Relationship between the reinforcement efficiency ϵ_1 and the critical aspect ratio for short fiber reinforced composites

molded fiber reinforced composite is approximately 30 : 1. This is considerably less than ten times the critical aspect ratio for most polymer fiber combinations, even with very effective coupling agents. Therefore, the strength of injection molded fiber reinforced composites is considerably less than theoretically possible.(34)

2.1.11.2 Modulus

A relationship similar to that for the strength of composites can be used to describe the modulus of composites. The modified rule of mixtures equation for modulus enhancement is:

$$E_c = E_p \rho_p + E_f \rho_f e \quad (2.11)$$

where

e = efficiency factor

This efficiency factor depends on many of the same factors as the efficiency factors used in the modified rule of mixtures equation for tensile strength. There are significant differences in the application of the rule of mixtures to the determination of modulus and tensile strength, however. Specifically, while the tensile strength of the composite is strongly dependent on the degree of adhesion between the fibers and the matrix for short fibers, this is not the case for modulus enhancement. The effect of interfacial adhesion on modulus enhancement is considerably less than its effect on tensile strength. This is evident from the fact that nonreinforcing fillers will enhance the modulus, but not the strength of polymers. Therefore, the efficiency factor in Eq.(2.11) will have no numerical relationship to the efficiency factors in Eq.(2.9).

The tensile strength of a composite is very strongly affected by orientation of the fibers. The tensile modulus, which is sensitive to the fibers orientation is not as strongly affected as the strength. For example, if the reinforcement is in the form of a square weave fabric and the composite is tested in the same direction as the orientation of the warp fibers, the fibers in the warp direction contribute strongly to both the tensile strength and the modulus of the composite. The fibers in the transverse, or fill, direction, however, do not contribute to the strength of the composite, but they do contribute to the modulus. Therefore, the effect of orientation on the strength of the composite is greater than the effect on its

modulus. (35)

2.1.11.3. Role of the Matrix and Interface

While it is true that in fibrous composites the fibers bear major fraction of the load, the matrix and nature of the fiber matrix adhesion are often exceedingly important. In fact, the matrix is the strength limiting variable in the following cases: aligned continuous fibers, tested off-axis; cross-piled continuous fibers, tested at all angles; discontinuous fibers more or less aligned, and tested at all angles; and incompletely dispersed random in a plane discontinuous fibers, tested at all angles. Thus, in many common cases, matrix strength and static or dynamic toughness, as well as modulus are not often achieved as desired.

In all these cases, the nature of the interface must be carefully controlled. Fracture energy of a fiber reinforced composite is a complex function of the properties of the reinforcement, the matrix, and the interface. Several modes of energy dissipation may be involved:

1. Debonding of the fibers from the matrix as a crack impinges upon a fiber. Such a debonding may occur when the fracture strain of the fiber is greater than the fracture strain of the matrix, and the extent of debonding will depend on strength of the interfacial bond relative to that of the matrix (Figure 2.12). A related type of debonding, in which the tensile component in the stress field ahead of the crack can induce interfacial failure, has previously been proposed.

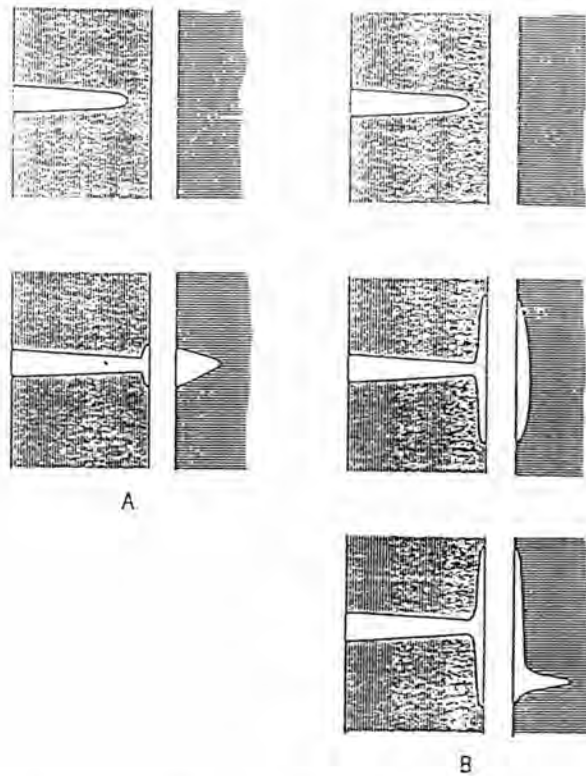


Figure 2.12 Effect of glass polymer interface on advancing crack. (A) Adhesive strength of bond equals cohesive strength of matrix. (B) Adhesive strength of bond is much less than cohesive strength of matrix

2. Pulling of broken filaments out of the matrix following the fracture.

3. Redistribution of strain energy from a fiber to the matrix after fracture of the fiber.

4. Fracture of the fibers and matrix themselves, the former contributing little to the overall fracture energy. The case of the interface has already been included in 2, the interfacial fracture energy will, of course, be added to the strain energy taken up by the fiber, the latter constituting the "debonding" energy per se. (36)

2.1.11.4. Adhesive Bonding

Strength of the glass fiber reinforced plastic depends on the interface of adhesion bonding between polymer matrix and reinforcement. Modification of the interface may produce any desirable changes in the composites. Surface treatment of a mineral or filler may improve wetting as well as dispersion with a polymer. The treatment protects the mineral against cleavage and may even heal flaws in the surface. The polymer layer may be strengthened by interface modification that promotes alignment of polymer segments and interdiffuses with the polymer, possibly forming interpenetrating polymer networks (IPNs). (37) Adhesive bonding is a technique for joining materials which has recently shown itself capable of replacing or supplementing conventional methods such as riveting, welding, and mechanical fastening in a variety of applications. Another system for classifying adhesives is based on chemical type or major ingredient from which the adhesive is formulated (Table 2.2).

Thermoplastic, comprising either natural or synthetic resins. Thermoplastic adhesives are fusible, soluble, soften with heat, and creep under stress. The poor creep strength must be compensated by modifying joint design to include folded overlaps or auxiliary stiffeners. Thus, the nature of these adhesives restricts their use with low load assemblies based on metal, wood, plastics, and porous materials which are not intended for service under extreme conditions. They differ from the natural product adhesives in their increased bond strength and almost complete resistance to moisture and biodeterioration. (38)

Table 2.2 Classification of Adhesives According to Chemical Type.

Category	Representative types	Physical forms	Joint properties	Joint materials	Applications
Natural	Starch, dextrin, animal and fish glues, casein, rosin, shellac, Canada balsam, and gums	Solvent dispersions, emulsions, pastes, solids, and powder	Low strength with poor moisture resistance, but fair resistance to heat and chemicals	Paper, cork, packaging materials, textiles, wood (furniture), some plastics, and metals	General domestic purposes, industrial packaging, and other rapid set assemblies
Thermoplastics	Cellulose derivatives, polyvinyl acetate, polyvinyl alcohol, polyacrylates, polyethers, and oleoresins	Solvent dispersions or water emulsions, films, and solids	Fair peel strength, but low shear strength and subject to creep under high loads; maximum service temperature approximately 90°C	Non-metallic materials: wood, plastics, leather, textiles, and paper	Generally in assemblies subject to low loads in service
Thermosets	Urea and melamine formaldehydes, polyesters, polyimides, furanes epoxides, and phenolics	Liquids, films, pastes, and powder	High shear strength and resistant to creep, but low peel strength; maximum service temperature is between 200°C and 250°C	Metals, wood, ceramics, and glass	Structural assemblies involving stressed joints based on metals and wood
Elastomers	Natural and reclaim rubbers, acrylonitrile-butadiene, polyurethane, polychloroprene silicone, butyl, butadiene-styrene, and polysulphide	Films, solvent dispersions, and water emulsions	High peel strength and flexibility, but low shear strength and poor creep resistance; maximum service temperature is between 80°C and 100°C, with silicones exceeding 200°C	Plastics, rubber, fabrics, and leather	Unstressed joints of light materials and flexible bonds
Two-polymer types	Phenolic-nitrile, phenolic-neoprene, phenolic-polyvinyl acetal, and epoxide (modified)	Liquids, films, and pastes	Strength properties dependent on formulation, but generally higher strength over a broader temperature range than other types; good resistance to chemicals	Metals, ceramics, glass, and thermosets	Structures subject to high stresses or adverse service conditions such as heat and moisture

Glass fiber reinforced plastic composites have been developed into high performance materials. Along with modest improvements in resins and glass fibers, the greatest advance has been the development of coupling agents to strengthen the bonding of resin to glass. The present coupling agents may have attained the ultimate in performance, since failure no longer takes place at the interface, but only in the glass or matrix resin.(39)

2.2 Surface Treatment on Polymer-Filler Interactions

In the case of plastics, addition of many fillers results to a loss of strength. This is because when it is deformed, the resin which is more elastic than the filler will pull away from it, as a result of void formation. Bonding of the filler to the resin with a coupling agent helps to prevent separation and result to a stronger material. It is shown that reaction between the silane coupling agent and the filler is more complex than suggested above and is dependent on concentration of hydroxyl groups on the surface of the filler. In case of precipitated silica which contains high concentration of hydroxyl group, a monomolecular layer of polysiloxane will be formed on the filler. While the silica from a flame-process which contains lower concentration of hydroxyl groups, a three-dimensional network, which may be seven or eight molecular layers, will be formed.(40)

Coupling agents are primarily defined as materials that improve the adhesive bond of dissimilar surfaces. This must involve an increase in true adhesion, but it may also involve better wetting, rheology, and other handling properties. Bonding of silane coupling agents to matrix resin can take several forms:

1. The oligomeric siloxanol layer may be compatible with the liquid matrix resin and form a true copolymer during a cure period of resin.

2. The oligomeric siloxanol may be partially compatible with the matrix resin and form an interpenetrating polymer network. In this case the siloxanols and the matrix resin separately cure with a limited degree of copolymerization.

3. The oligomeric siloxanol layer may diffuse into a nonreactive thermoplastic layer and then crosslink at a fabrication temperature. Structures in which crosslink occur only on the interpenetrating phase have been designated as pseudo-interpenetrating networks (pseudo-IPN).

4. Polymeric siloxane segments may interdiffuse into a thermoplastic polymer with no crosslinking in either phase that may be molded as in Figure 2.13.

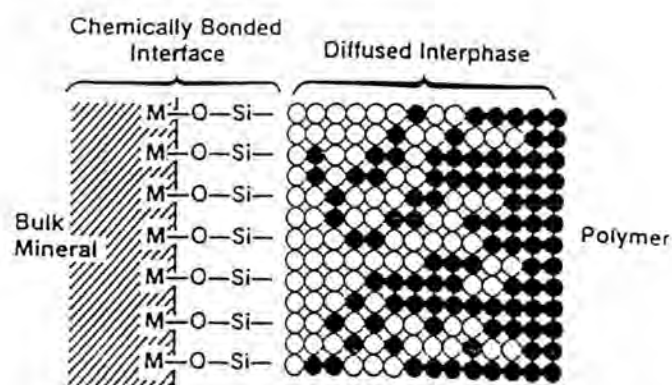


Figure 2.13 Inter-diffusion model for adhesion of a thermoplastic to silane-primed glass: open circles indicate regions of coupling agent, closed circles indicate regions of polymer

Thermoplastic may also be coupled to a glass through reactive silanes; however, coupling through solution compatibility, i.e., interdiffusion, is also possible. Laminate properties are greatly improved with silanes having optimum compatibility with the polymer, as predicted from solubility parameters of the organofunctional silane and the resin. This type of coupling is most successful with glassy

polymers such as polystyrene, but less effective with crystallizing polymers such as polyethylene or polypropylene. Coupling agents often used for non reactive thermoplastics such as polyolefins are methacrylate, amino and cationic styrylsilanes.(41)

2.3 Applications and Recycling

The first European application for glass mat thermoplastic (GMT) was as under body engine shields in the early 1980s. These shield cut down road noise, held keep the engine clean and reduce air resistance. Although they will account for about 300 tonnes of material in 1992, they will not be a major application for GMT in the future, Schmahl believes. GMT has been widely used for bumpers in the USA, however, bumpers on European cars are different and the material seems to be used not so much in this application.

GMT front ends will grow to about 8000 tonnes/year in 1995 according to Schmahl's estimates. Rear seat backs are already an established application. GMT is lighter than metal and offers an opportunity for parts consolidation. An additional advantage is the ability to cover a textile with the GMT part in one step. Other applications are pallets, electrical goods and the building industry.

GMT's other major attraction, in addition to its mechanical properties and light weight, is its recyclability. Two techniques have been developed for reusing the material. Parts can simply be heated up in an oven and remolded to a new part of the same weight. This can be done three or four times without any significant reduction in properties. The second, preferable method involves using the GMT scrap

to remold a new part. Up to 25% of shredded GMT can be used without any significant detriment to properties. GMT's rapid take up by automotive manufacturers combine with its "green credentials" indicate that the material will see substantial growth in Europe in the 1990s.(42)

2.4 Review of the Literatures

The concept of thermoplastic stamping has recently moved from the R&D laboratory to the production environment. Evidence of the commercial reality of the process as a viable means for parts production is provided by the emergence of a number of thermoplastic materials specially designed for stamping or compression molding. Among these, AZDEL, a continuous glass reinforced thermoplastic laminate, has gained wide acceptance as an engineering material.

Richard Margolis (43) developed cost/performance relationships for the Azdel composites and compared to similar analyses of steel assemblies die cast aluminium, SCM and other thermoplastic materials. It was found that the system's approach to materials and processing technology provides the most cost effective structural and process advantages.

From the materials engineering standpoint, stamped glass reinforced components offer economical structural performance and light weight. Continuous glass reinforcement provided improved toughness and extended temperature ranges over equivalent molding materials.

From the processing point of view, the rapid cycle times for

stamping operations due to no requirement of curing cycle, along with the capability to handle complex shapes allows stamped thermoplastics to complete effectively with metal assemblies which require multiple operations.

The AZDEL composites are glass mat thermoplastics (GMT's) manufactured by impregnating a pre-formed glass mat with molten extrudate, and laminating films onto both surfaces were developed by AZDEL Inc., a joint venture in composites technology by the United States companies General Electric Plastics and PPG Industries. The composite structures were developed through the synergistic use of GE Plastics engineering resins and PPG Industries proprietary fiberglass mat technology.

In addition to GMT's, AZDEL Inc. has also obtained the licence for a complementary new technology call " Radlite ", developed by Wiggins Teape, manufacturers of speciality papers, and based on the modification of a papermaking process.(44-45)

Radlite is reinforced not by a continuous or chopped strand mat of many hundred of fibers bundled together, as in GMT, by discrete, uniformly dispersed, single long fibers. The fiber-to-polymer ratio and the material's thickness may be precisely tailored to suit a customer's requirements. This system of reinforcement creates a completely uniform fiber dispersion within a flow molded part, leaving no polymer-rich areas.

An essential element of Radlite technology is a foaming agent, which makes a water-based foam that acts as a support for the fiber. This foam provides the ideal way of obtaining a homogeneous mixture of powdered polymer and long glass fiber-longer than those used in the

extrusion process. D.F. Hiscock and D.M. Bigg(46) found that the degree of homogeneity of the mixture and the subsequent ability to handle the dry sheet have been significantly improved by the addition of less than 5% by weight of thermoplastic pulp fibers, based on solids concentration, to the slurry.

The AZDEL(47) and Radlite processes therefore give mutually complementary products that, though obtained in different ways, offer substantially identical advantages over other materials. But the feature of the Technopolymers (TM) obtained by both processes is that they can be very accurately tailored to suit specific and often widely differing applications.

The Technopolymers (TM) are divided into three families: AZDEL (R), AZMET (TM) and AZLOY (TM). Each family may comprise products based on mat or long fibers. Each product type is identified by a suffix: M for AZDEL composites containing continuous-fiber glass mat, and F for long-fiber composites obtained by the Radlite process.

AZDEL (R) is the brand of the polypropylene-based sheets. They are materials containing 30% and 40% of glass fiber mat. A new type with 40% of unidirectional glass fiber mat has reached the development stage and is already available for the European market. These materials find their main uses in the motor industry for components like seat shells, load decks, bumpers, battery trays, spare-wheel compartments and engine-block shields.

They have wider potential, however, and are now being suggested for office furniture and for chair shells; when compression-moulded they are a cheaper alternative to injection-moulded shells, for example. In Herman Miller's chairs the seat and back can be

produced as a single moulding with satisfactory springiness, thank to continuous-fiber mat's excellent bending performance.

High impact strength and lightness also make AZDEL (R) products ideal for materials handling, in such form as pallets, boxes for industry, and cases for military use, for example for transporting computers and other delicate electronic equipment.

A self-extinguishing type has also been developed, for junction boxes, particularly for joining large electric cables where high strength and lightness are the main requirements.

AZDEL (R) sheet is already finding a market for lining commercial vehicle bodies, and there are good prospects in the building industry as a replacement for plywood shuttering for concrete.

The second family, AZMET (TM), comprises Technopolymers (TM) based on crystalline resins such as Valox thermoplastic polyester, having greater thermal stability and higher modulus modulus than the polypropylene-based AZDEL (R).

These composites also are mainly suitable for uses in the motor industry, when the main requirements are high thermal stability and good chemical resistance, for example, for oil sumps, which have to withstand temperatures of up to 150°C. Those characteristics extend the scope to applications such as tappet and engine covers and practically any semistructural component in the engine compartment.

The third and latest group are the AZLOY (TM) products, based on the more traditional GEP resins: Lexan polycarbonate, Xenoy polymer alloys and Noryl modified PPO, all three being amorphous semicrystalline materials with higher modulus and thermal stability than polypropylene. As its very first application, AZMET M was chosen

by a motor manufacturer for engine covers for sound-deadening and heat-insulating purposes. The manufacturer not only managed to produce a single moulding in place of what had previously been assembled from a large number of parts but also obtained a significant increase in productivity and appreciable reduction in costs.

The first use of AZDEL M in Europe was in the motor accessory field. It was chosen by a German company, UMO, for moulding its universal roof racks, owing to the material's lightness, short cycle times and excellent ductility, which greatly reduces the risk of breakage, especially during removal from the mould and handling.

The roof racks have various profiles to suit a large number of cars, are adjustable and are supplied with various accessories for quick and easy fixing of such things as bicycles, skis and surfboards.

The high modulus of AZDEL R reinforced with unidirectional fiber made it possible to give the racks an excellent streamline section, so that they can be left permanently mounted without a penalty in fuel consumption.

An AZLOY F base on PPO reinforced with 30% of glass is now on trial as a replacement for other materials in a power station exhaust gas scrubbing system.

These composites " under development " are very well suited to environmental engineering, where the global characteristics of materials are of particular interest. This is a market sector where thermoplastic resins had already made some headway on account of their high thermal stability and corrosion resistance. But hitherto their use necessitated some compromise, because the PPO matrix by itself is rather difficult to work, whereas with the addition of glass-fiber mat

by the Radlite technique an easily press-formed material is now available.

Components of the exact shape required can be produced in one piece. Being incorrodible and resistant to temperature fluctuations between 60°C and 160°C, frequently found in this application, AZLOY can ensure a much longer component life. It also maintains its mechanical properties up to 200°C and therefore offers a wide margin of safety.

The press conference ended with a presentation of some outline concepts that might become economic industrial reality in the 1990s.

CAR ROOFS

The roof is made in a single operation, with the fabric lining fitted direct during moulding; it also incorporates the assembly points and the sealing rim for the sunroof. Its loading strength rules out the need for a roof rack and it incorporates a load space that improves the vehicle's aerodynamics and line and at the same time extends its scope for both private and commercial use.

BUMPERS

AZDEL is already being used for bumper beams to ECE and FMVSS standards and weighing up to 10 kg less than steel or aluminium beams, but its potential has not yet been fully exploited. This bumper cuts out the need for a fairing strip or expensive painting by having the beam joined direct to the injection-moulded face. Assembly has been simplified by having the mounting brackets built into the face.

FRONT AND REAR ENDS

Complete front and rear ends not only gain a new line but may also revolutionize the system of assembling the whole vehicle. By incorporating the lamp housings and bonnet and tailgate closing plates in the ends, or by using the front end as a frame for the radiator, maximum use can be made of off-line assembly and the concept of "just-in-time" delivery.

DASHBOARDS

The same principle applies to a unit on which the dashboard is mounted. A key feature of this project is the incorporation of a knee-guard supporting bar, which in combination with various types of seatbelt and airbag may increase passenger safety.

Making use of its resistance to high temperatures, AZDEL is used for housing parts of the heating and ventilation system, such as the fan and motor, and the radiant panel, condenser and hot and cold air mixer. The new composites' mechanical properties allow the steering column and the pedals - the latter usually mounted on the engine compartment bulkhead - to be mounted as a single unit.

EXTERNAL BODYWORK

The wheel carrier, mudguard and step of commercial vehicles are traditionally made by welding various steel pressings, in a process that requires a large number of dies and fittings. A one-piece moulding eliminates this problem and has the advantage of being lighter and resisting corrosion and dents.

An additional possibility is to overmould the component with a rubbing strip of flexible rubber to improve the aerodynamics and reduce consumption while also containing spray when travelling at high speeds. In that way there would be no need to make holes for bolting a rubbing strip to the body.

The rear panel of a truck's cab is a simple steel pressing that is not paid much attention by designers, but all that will change in the future. When more complex shapes and deeper drawing depths are required, without having to use complicated and expensive dies, the new composites will be able to make a great contribution.

In addition, K-Plasheet(48), a stampable sheet based on polypropylene and 10-13 mm chopped glass fibers having 30-40% glass content, was introduced by a partnership involving Kawasaki Steel with 60% share, Sumitomo Chemical with 20% share and plastic moulders, along with Takiron and Trading company C-Itoh with 10% share each. A key selling point of the K-Plasheet is the material's high formability—sheets can be rapidly heat formed to shape using a variation of steel-stamping technology. K-Plasheet offers a tensile modulus of between 4 and 5 GPa.

C. Y. Yue and W. L. Cheung(49) investigated interfacial strength of glass fiber reinforced polypropylene where the composite was water-quenched, air-cooled and oven-cooled (50°C), respectively. They found that the water-quenched composite had the highest interfacial strength of 1.0 MPa, comparing with that of 0.9 MPa for the air-cooled one and 0.8 MPa for the oven-cooled one. The results demonstrate that amorphous polypropylene exhibits higher interfacial strength than crystalline polypropylene. They also found that silane

surface treatment of the glass fiber showed further enhance in the interfacial strength upto 3.5 MPa for the water-quenched composites. Thus, water-quenching technique was used in the present study.