CHAPTER II

THEORY

2.1 Composite materials

There has been a rapid growth in the use of fiber reinforced material in engineering application in the last few years. The main purposes in the development of composite materials are to obtain materials with controlled properties and to find reinforcing materials and polymer matrices whose mixture have improved properties and not attainable by the components of the composite isolately [Wang *et al.* 1983].

By definition, composite materials are composed of a reinforcing structure, surrounded by a continuous matrix [Richardson *et al.* 1987].

Generally, properties of composites depends on:

1. Properties of fibers and matrices
2. Fiber volume fraction (V_f) and fiber orientation
3. Flaws and voids
4. Interfacial bonding between fibers and matrices

Advantages and disadvantages of composites [Schwartz 1997]

The advantages of composites include:

1. Weight reduction (high strength-or modulus-to-weigh ratio)
2. Longer life (less corrosion)
3. Lower manufacturing costs because of lower part count
4. Inherent damping property
5. Increased (or decreased) thermal or electric conductivity

The disadvantages include:

1. Cost of raw material and fabrication
2. Environmental degradation of matrix
3. Difficulty in attaching (e.g. welding)
4. Difficulty with analysis

Composite structural elements are now uses in a variety of components for automotive, aerospace, marine, and architectural structures in addition to consumer products, such as skis, golf clubs, tennis rackets, I - beam, channel section, and other structural elements used in building.

Polymer matrices

Polymers are popular as the matrices for composites because they can be easily fabricated, low density, and offered good mechanical and dielectric. Matrices are the materials that give body and grip or hold the reinforcements of composite together, and are usually of lower strength than the reinforcement. The major roles of the matrix in a fiber-reinforced composite are

1) To transfer stresses between the fibers
2) To provide a barrier against an adverse environment damage before, during, and after composite processing
3) To protect the surface of the fibers from mechanical abrasion.

The matrix plays a minor role in the tensile load-carrying capacity of a composite structure.

Matrices can be divided into two groups: -

1. Thermosets: - such as epoxy, polyester, polyimide, etc.
2. Thermoplastics: - such as polycarbonate (PC), polyethylene (PE), etc.

Thermoplastic polymers

Thermoplastic matrices are normally used with short fiber reinforcement for applications in products made by injection molding. The feedstock is usually in the form of pellets that contain the short fibers, typically 1 to 3 millimeters long. Thermoplastics readily flow under stress at elevated temperature, so allowing them to be fabricated into the required component, and become solid and retain their shapes when cooled to room temperature. These polymers may be repeatedly heated, fabricated and cooled consequently scrap may be recycled, though there is evidence that this slightly degrades the properties probably because of a reduction in molecular weight.

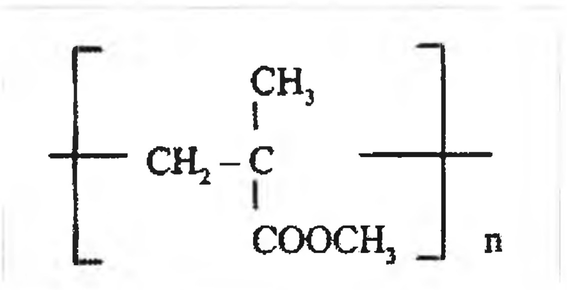
Advantages of thermoplastic polymers include:

1. Unlimited storage (shelf) life at room temperature
2. Shorter fabrication time
3. Post-form ability (e.g., by thermoforming)
4. Ease of repair by welding, solvent bonding, etc.
5. Ease of handing (no tackiness)
6. Can be recycled (recyclability)

2.2 Poly(methyl methacrylate) (PMMA)

PMMA is an important commercial thermoplastic material. PMMA is polymerized by solution, suspension, and emulsion processes via free radical polymerization of methyl methacrylate using the usual peroxide or azo initiators, or by thermal or photochemical initiation. PMMA is completely amorphous but has high strength and excellent dimensional stability due to the rigid polymer chains (T_g = 105°C) [Ordain 1991]. PMMA is clear, colorless transparent plastic with a high soften point, impact resistance, good resistance to many chemicals, and very good weather resistance ability. but attacked by organic solvents. It is available in molding and extrusion composition, syrups, and cast sheets, rods, and tubes.

Molecular structures of PMMA can be shown as figure 2.1: -



$$\left[-CH_2-\underset{COOCH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}- \right]_n$$

Figure 2.1 Molecular Structure of PMMA [Ordain 1991].

PMMA can be modified by copolymerization of methyl methacrylate with other monomer, such as, acrylate, styrene, butadiene, and acrylonitrile; MMA is by far the most important methacrylate ester monomer, accounting for 90 % of the volume of methacrylic ester monomer [Balagaru *et al.* 1992]. The structure and molecule formula, physical properties and rate and heat of polymerization of MMA can be shown in Table 2.1 [Pattamage 1996].

Table 2.1 Structure ana molecule formula, rate and heat of polymerization, and physical properties of MMA [Pattamage 1996].

Structure and molecular formula of MMA monomer	
Formula	$C_5H_8O_2$
Structure	$CH_2=C(CH_3)COOCH_3$
Physical properties of MMA monomer	
Boiling Range (°C)	100 –101
Flash point (°F)	55^a
Solubility at 25°C	
- in water , parts /100	0.015
- parts / 100 monomers	-
Density (g/cm^3)	0.939
Heat of vaporization (cal/g)	86
Specific heat (cal/g°C)	0.45
Heat of polymerization, H_p (kcal / mole)	12.9
When, a = open cup	
Rate and heat of polymerization	
ΔH (kcal /mole)	13.8
K_a at 44.1 (°C)	27 ^{a}
at 60 (°C)	123^a
When, a = Measured in the bulk	

Examples for the use of PMMA

Major uses of PMMA are safety glazing fixtures, windows, skylight and PMMA molding compound in the automotive industry for taillights. Applications include electrical components, lens, etc. Physical properties of thermoplastics at test according to ASTM shown in Tables 2.2 [McCrum *et al.* 1988].

Table 2.2 Physical properties of thermoplastics at the tests according at ATSM

	ASTM Test	HDPE	PP	ABS	PMMA	PC	PBT
Young's modulus	D790	0.8	1.5	2.1	3.2	2.3	2.2
Yield / fracture stress (MPa)	D638	28	33	41	72	65	50
Elongation at break (%)	D638	300	50	20	4	100	300
Heat distortion temperature ($^{\circ}C$)	D648	<23	<23	110	95	140	55
Limiting oxygen index	D2863	18	18	19	17	25	20
Coefficient of linear expansion (10^{-6} K^{-1})	D696	90	110	96	68	70	70
Specific gravity	D792	0.96	0.90	1.04	1.18	1.20	1.31

2.3 Poly(methyl methacrylate) in dental application

[Available from: http://www.ucc.ie/ucc/depts/restorative/dentext/dchap4.pdf]

Poly(methyl methacrylate) (PMMA), produced through the free-radical polymerization of the liquid monomer methyl methacrylate (MMA) (Figure 2.2) is an atactic polymer of high average molecular weight with a glass-transition temperature of 105°C (approx.). Thus, at ambient temperatures, the material is a brittle & transparent organic glass. At temperatures above the transition temperature, the material softens and becomes viscoelastic. Being a non-crystalline system, the plastic can be plasticized by compatible solvents (including the monomer).

Materials based on PMMA are the most common 'plastics' used in the dental laboratory, where their uses include the production of denture bases & soft linings for dentures, together with close-fitting impression trays & orthodontic devices, and the repair of dentures. In general, a device is not fabricated from bulk plastic, but through the combination of spherical polymer beads (obtained by polymerizing an emulsion of monomer in soap solution) with liquid monomer. In this form, the plasticized polymer can be shaped, as required, before the monomer present is polymerized to yield a relatively rigid and permanent result.

There are two main approaches to the polymerization of the monomer in the monomer / polymer combination and materials are formulated appropriately:

1. By heating to ca 70°C (Heat-Cured PMMA, Section 2.3.2)
2. By Chemical activation at room temperature (Cold-Curing, or Auto-Polymerizing PMMA, Section 2.3.3)

However, before these techniques are discussed, the effects of combining the polymer and monomer must be considered (Section 2.3.1).

2.3.1 Plasticization of PMMA by Methyl methacrylate

Since atactic PMMA is non-crystalline, appropriate solvents will be absorbed by, and swell, the polymer. The effect is purely of physical significance, as a chemical reaction is not involved. The value of T_g for the polymer is reduced. When this value is lowered to below room temperature, the polymer/monomer combination acts as a gel and may be shaped as desired. In practice the combination of polymer with liquid results in following sequence of effects.

1. Wet Sand Stage

   Very little attack on the polymer by the monomer.

2. Stringy Stage

   Some polymer from the outer surface of the polymer beads has dissolved in the monomer to give a very viscous solution of polymer in monomer.

3. Gel (Full Dough) Stage

   The polymer beads have absorbed all of the available monomer to yield a gel. In this condition. the flow properties of the combination are maximized and it is at this stage that the material is shaped, as required (usually by packing into a mould), before the monomer is polymerized. The polymer beads may be plasticized, by the manufacturer, to assist in the absorption of monomer.

The time taken for the combination to reach the Dough State 'doughing' time is mainly determined by the temperature of the mix and may be controlled accordingly. Other factors involved are the average size of the polymer beads, the average molecular weight of the polymer and the presence of plasticized.

If the evaporation of monomer can be prevented, the mix can be maintained indefinitely in the dough stage.

4. Elastomeric stage

   If the mixture is allowed to stand further, in the open laboratory, evaporation of monomer will take place from the gel to yield a rubber-like consistency.

2.3.2 Heat-Cured PMMA-Procedure

Polymerization of methyl methacrylate in the MMA/PMMA dough can be activated by the unstable organic peroxide, Dibenzoyl Peroxide (BPO, white crystalline solid, Figure 2.2), which composes to form phenyl free radicals at a temperature of *ca* 70°C. This can be achieved through the use of dry heat, as in an oven, or via a heated water bath. Once polymerization has been initiated, it is important that an excessive temperature rise not take place in the dough (the polymerization is exothermic). If this temperature exceeds the boiling point of the monomer (100.3°C under 1 atm pressure, but may be higher under processing conditions), the monomer will evaporate such that the processed artefact will feature gaseous porosity.

This is characterized by a microporosity evident at the bulkier aspects of the artefact, where the temperature rise has been greatest. A suitable protocol for the processing of acrylic dentures, without inducing gaseous porosity, is as follows:

Step 1: From 20°C to 70°C over 1 hour
Step 2: 4 hours at 70°C
Step 3: From 70°C to 100°C over 1 hour
Step 4: 1 hour at 100°C

The effect of Step 4 is to ensure that the quantity of residual monomer in the polymerized article is minimized (which should not be greater than 0.5 % wt. for correct heat curing) and takes place when most of the monomer has been converted to polymer. After processing, the acrylic artefact is allowed to cool to room temperature slowly so as to avoid the effects of stress-relief.

2.3.2.1 Main Components of Heat-Cured PMMA Powder

a) Emulsion-polymerized beads of PMMA, of average molecular weight 10^5-10^6.

b) Plasticized (e.g. dibutyl phthalate)

The polymer beads are plasticized in the manufacturing process to allow facile absorption of the monomer.

c) Initiator (Dibenzoyl peroxide, Figure 2.2): 1%.

d) Pigment

Inorganic, or organic, pigments to color the denture base; may include HgS, CdS and Fe_2O_3.

2.3.2.2 Main Components of Heat-Cured PMMA Liquid

a) Monomer (methyl methacrylate, Figure 2.2)

b) Cross-linking agent (e.g. glycoldimethacrylate, Figure 2.2): 1-2%

The cross-linking agent has the effect of increasing the surface hardness of the polymer and reduces the incidence of surface crazing. An excess of the material must be avoided due to the increased reaction exotherm involved, and the increased polymerization contraction.

c) Inhibitor (e.g. Hydroquinone, Figure 2.2): 0.1 %

Hydroquinone (colorless crystalline solid, soluble in MMA) can donate Hydrogen atoms readily to free-radical species (hydrogen abstraction). Thus, spontaneously formed monomer radicals (through thermal effects, or the action of light) do not initiate a premature polymerization but are consumed through the abstraction of hydrogen atoms from hydroquinone.

2.3.2.3 Strength & Physical Properties of Heat-Cured PMMA

A) Strength

The main physical properties of heat-cured PMMA are summarized in Table 2.3. As PMMA is an organic glass, the material is brittle and the presence of surface cracks/pores, and internal faults, will adversely affect the tensile strength of the material. The effect of such faults is to raise the stress locally (stress-raisers). Because of the relevance of tensile strength in a brittle material, the strength commonly measured in the laboratory is the flexural strength, measured by loading beam centrally between two supports. The deformation of such a beam involves both tensile, and compressive, stress. Tests must be carried out on similar beams for comparative results (Table 2.3).

The failure of a denture base material may often involve impact failure. Impact failure involves rapid stressing of the material such as by dropping the denture on a hard surface. Denture base materials with increased resistance to impact failure are available.

B) Thermal Expansion

The coefficient of thermal expansion of PMMA is 81 ppm/°C. This indicates a linear contraction of 0.65% on cooling from 100°C to 20°C. While this suggests that a processed denture might initially be a tight fit in the mouth, the relevance of the contraction to the fit is not simply demonstrable.

C) Surface Cracking

If a strip of PMMA is bent and the tensile surface treated with a solvent (e.g. monomer) may small cracks, called crazes, travel into the surface at 90°C to the tensile loading. Both a tensile stress and the presence of a solvent are necessary for the effect, which appears to involve a reduction of the T_g value for the polymer by the solvent. Crazing may also occur without an external stress due to residual stresses within the material due to processing. However, a certain minimum stress is required for the effect to be observed with a given solvent. Cross-linking of the polymer chains reduces the incidence of crazing.

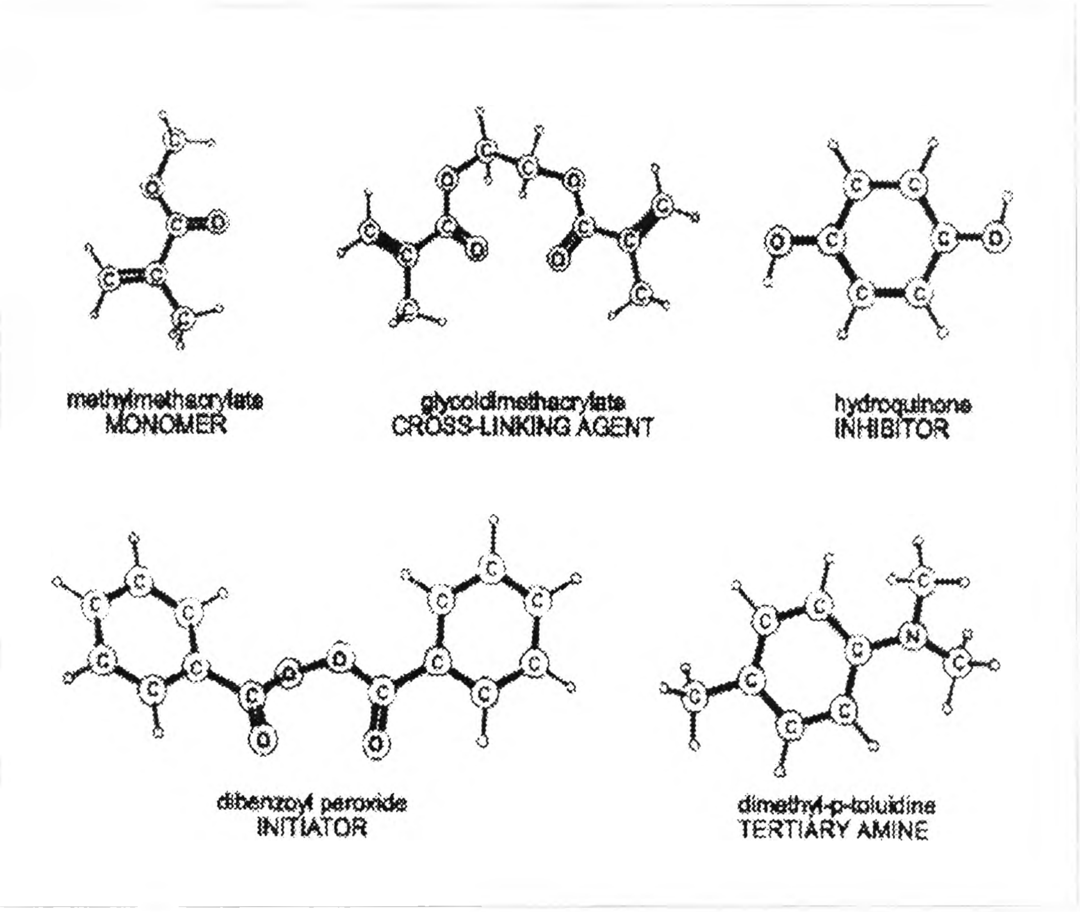


Figure 2.2 Some chemicals relevant to the polymerization of methyl methacrylate [http://www.ucc.ie/ucc/depts/restorative/dentext/dchap4.pdf].

2.3.3 Cold-Curing PMMA

Methyl methacrylate may be polymerized through the induced chemical decomposition of Dibenzoyl peroxide by suitable tertiary amine, at room temperature. Dimethyl-p-toluidine (DMPT, figure 2.2) may be used. Such materials are called 'Cool-Curing' or 'Auto-Polymerizing' acrylic. In practice, the peroxide is added to the polymer beads, as with the heat-processed material, while the amine is dissolved in the monomer. Combination of the powder with the liquid activates the system through the generation of free radicals, which ultimately initiate polymerization. It is found, however, that many of the properties of the cold-curing materials are inferior to the relevant heat-processed system. Uses of cold-curing acrylic include the fabrication of close-fitting impression trays, orthodontic devices, and 'pour & cure' denture resins and denture repairs.

While the addition of polymer powder to monomer initiates a similar series of physical transformations as with the heat-polymerized material (sandy-stringy-dough-elastomeric), it is commonly known that the free radicals are being produced immediately on mixing. However, rapid conversion of monomer to polymer is delayed due to the following effects:

1. Neutralization of inhibitor (consumes radicals)
2. Inhibiting effect of air (O_2 dissolved in monomer)
3. Early termination of short & mobile polymer chains

Thus, significant conversion to polymer only occurs after the system has achieved the dough state. This conversion is accompanied by an evolution of heat, which may result in gaseous porosity in the final article, as with the heat-polymerized material. Cold-Curing acrylic is often processed under pressure (inert gas pressure) to raise the boiling point of the monomer.

2.3.3.1 Main Components of Cold-Curing PMMA Powder

a) Emulsion-Polymerized bead of PMMA, of average molecular weight 10^5-10^6

b) Plasticizer: the polymer beads are more heavily plasticized than the heat-curing materials

c) Initiator (Dibenzoyl peroxide): 1 %

d) Pigment

2.3.3.2 Main Components of Cold-Curing PMMA Liquid

a) Cross-linking agent (e.g. glycoldimethacrylate): 0-10 %. The effectiveness of cross-linking agents in cold-curing acrylic is not established.

b) Inhibitor (e.g. Hydroquinone)

c) Tertiary amine(e.g. DMPT)

2.3.3.3 Comparison cold-curing with heat-cured material

A) Strength

The transverse strength of cold-cured PMMA is approximately 80 % of the heat-cured material (Table 2.3). The average polymer chain length appears to be less in the cold-cured material and this effect together with other factors such as the increased residual monomer content and the reduced attack by the monomer on the polymer grains, undoubtedly contribute to the reduction in strength.

B) Residual Monomer Content

The residual monomer content may be as high as 5 % wt. This will have the effect of plasticizing the acrylic.

Table 2.3 Selected physical properties of acrylic denture-base materials [http://www.ucc.ie/ucc/depts/restorative/dentext/dchap4.pdf].

	Heat-Cured	Cold-Cured
Compressive Strength (MPa)	76	-
Tensile Strength (MPa)	55	-
Young's Modulus (GPa)	3.2	3
Flexural Strength (MPa)	72.5	60
Impact strength (notched Hounsfield, kJ/square meter)	1.6	1.35
Water Absorption (24hrs, at saturation, % wt)	0.3	0.25

2.4 Natural Fibers

Fibers are the principal constituent in fiber reinforced composite materials. They occupy the largest volume fraction in a composite laminate and share the major portion of the load acting on a composite structure. Fiber is a fundamental form of solid (usually crystalline) characterized by relatively high tenacity and an extremely and high ratio of length to diameter. Proper selections of types, amount, and orientation of fibers are very important since they affect the following characteristics of the composites, i.e.,

1. Specific gravity
2. Tensile strength and modulus
3. Compressive strength and modulus
4. Fatigue strength and fatigue failure mechanisms
5. Electric conductivity and thermal conductivity
6. Cost

Fibers can be divided into three types, i.e., [Lewis 1993].

1. Synthetic fibers are made from high polymers (polyamides, polyesters, acrylics, and polyolefins) by extruding from spinneret, such as, nylon, polyethylene, etc.

2. Semisynthesis fibers include rayon and inorganic substances extruded in fibrous forms, such as, glass, boron carbide, boron nitride, carbon, graphite, aluminum silicate, fused silica, and some metal (steel).

3. Natural fibers can be divided into two types :
   3.1) animal fibers consist of primary component of a protein, such as, wool and silk,
   3.2) Vegetable fibers consist of primary component of cellulose, such as, ramie fibers, coconut fibers, cotton fibers, etc.

2.4.1 Advantages and disadvantages of natural fibers

Advantages and disadvantages of natural fibers can be concluded in Table 2.4

Table 2.4 Advantages and disadvantages of natural fibers [Lewis 1993]

Advantages	Disadvantages
1. Low density 2. Low production cost 3. High strength-to-weight ratio 4. Abundant availability	1. High water absorption 2. Low fiber-polymer interfacial Adhesion

Examples of natural fibers into composites

Natural fibers used in composites include akawara, bamboo, coconut, flax, jute, sisal, wood, and others, Mechanical properties of some of these fibers are presented in Table 2.5. The following sections provide a brief description of these fibers.

Table 2.5 Properties of naturally occurring fibers [Balaguru *et al.*, 1992].

Fiber type	Coconut	Sisal	Bamboo	Jute	Flax	Elephant grass	Wood Fiber (Kraft pulp)
Fiber length (mm.)	50-350	NA*	NA	180-300	500	NA	2.5-5
Fiber diameter (mm.)	0.1-0.4	NA*	0.2-0.4	0.1-0.2	NA	NA	0.015-0.08
Specific gravity	1.12-1.15	NA	1.5	1.02-1.04	NA	NA	1.5
Modulus of Elasticity (GPa)	19-26	13-26	33-40	26-32	100	4.9	NA
Ultimate tensile Strength (MPa)	120-200	280-568	350-500	250-350	1000	178	700
Elongation at break (%)	10-25	3-5	NA	1.5-1.9	1.8-2.2	3.6	NA
Water Absorption (%)	130-180	60-70	40-45	NA	NA	NA	50-75

*Properties are not readily available or not applicable.

2.4.2 Bamboo fibers [Balagaru *et al.*, 1992]

Bamboo, which is a member of the grass family, grows in tropical and subtropical regions. Their hollow stalks have intermediate joints. The diameters of these stalks range from 0.4 to 4.0 inches (1 to 10 centimeters), Special techniques are needed to extract the fiber from bamboo.

Coconut fibers

A mature coconut has an outer fibrous husk. Coconut fibers, called "coir", can be extracted simply the husk in water or, alternatively, by using mechanical processes. These short stiff fibers have been used for making rope for centuries. Coir has a low elastic modulus and is also sensitive to moisture changes.

Flax and elephant grass fibers

Flax fibers are strong under tension and also possess a high modulus of elasticity (Table 2.5). Elephant grass fibers are extracted from elephant grass stems, which grow up to 10 feet (3 meters) tall and are packed with tough, sharp fibers bonded together by lignin.

Sisal fibers

A number of researchers have studied the properties of composite made with sisal fibers. These fibers, extracted from the leaves of *Agava sisalana*, are primarily made of hemicellulose, lignin, and pectin.

Wood fibers

The advantages of wood fibers are their availability, high tensile strength, high modulus of elasticity, and the well-developed technology to extract the fibers.

Jute fibers

Jute, grown solely for its fiber content, is cultivated mainly in Bangladesh, China, India, and Thailand. Jute plants can grow to a height of 8 feet (2.4 meters) with stalk diameters normally less than 1 inches (2.5 millimeters). They are relatively strong in tension as shown in Table 2.5. Traditionally the fibers have been used for making ropes and for weaving into gunny cloth used for making ropes and bags for transporting grains.

2.4.3 General Aspects of Bamboo

Bamboo is particularly attractive as a commercial crop because of its rapid growth. It can be used in three to six years after planting, at which time it reaches its maximum strength. Its advantages are low cost, abundant, ease of transport, its shape, high resistance to tension, compression, and flexion.

The bamboo as well as several groups of herbaceous grasses is classified by botanists as a subfamily (*Bambusoideae*) of the grass family (*Graminene*). Bamboo generally grows well in places with temperature ranging from 8.8 to 36°C. It grows best on well drained sandy-loam to clay-loam soil.

2.4.3.1 Status of development in the utilization of bamboo [Samapuddhi 1959 and Shriner 1964]

Bamboo can be used for a variety of purposes. Some of which are mentioned below:

1. Constructional, such as, scaffolding, bridges, support members, fencing, etc.
2. Cottage and rural industries, e.g., household goods including bed frames, brooms, blinds, umbrella handles, brushes, chopsticks, ladle, etc.
3. Others, including Polo mallets.

2.4.3.2 Culm structure of bamboo

Culm structure of bamboo can be divided into three groups, i.e., peripheral tissues, and ground tissue.

1. Peripheral tissues consist of sclerified parenchyma, chlorenchyma, and epidermis.
2. Fibrovascular bundles consist of both phloem and xylem with patches on sheaths of fibers on the outsides. A large number of vascular bundles scattered irregularly among the ground tissue.
3. Ground tissue composes mainly of continuous parenchymatous cells throughout the entired thickness of the culm.

The total culm consists of about 50% parenchyma, 40 % fibers, and 10 % conducting cell (vessels and sieve tubes). Figure 2.3 shows culm structure of bamboo and Figure 2.4 shows vascular bundle with large metaxylem vessels and phloem surrounded by fibers.

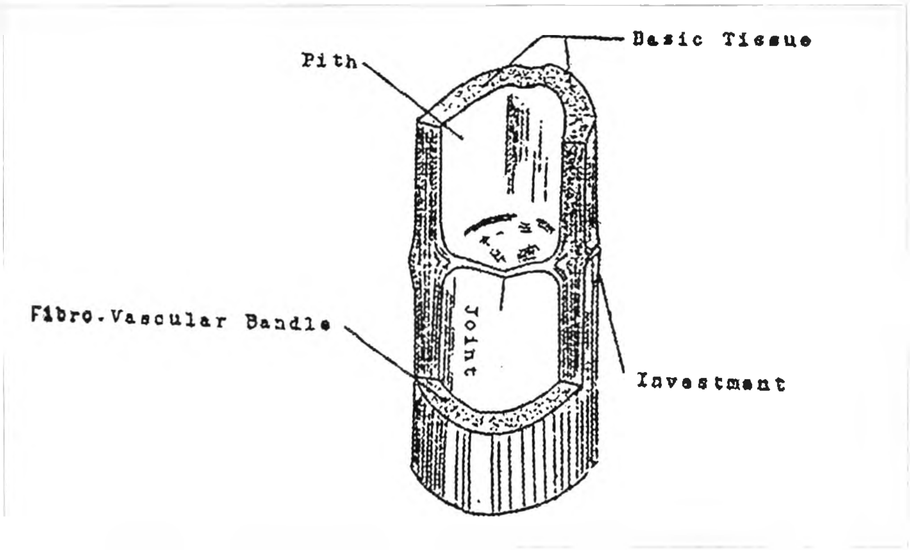


Figure 2.3 Culm structure of bamboo [Mohmod, 1996]

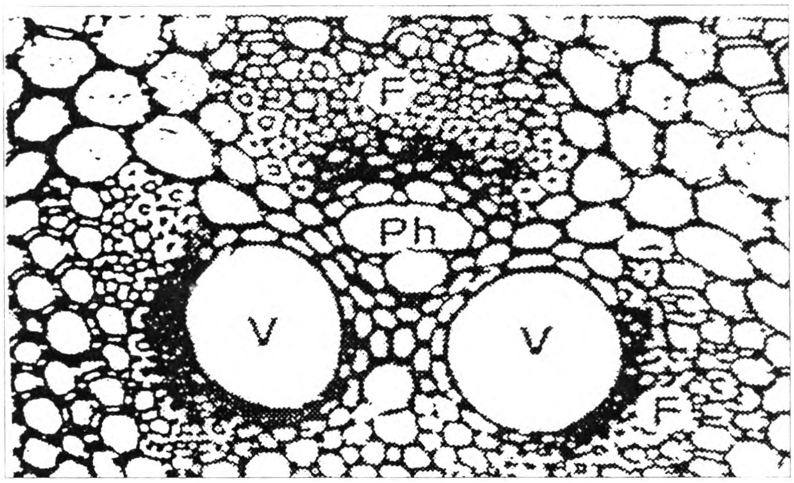


Figure 2.4 Vascular bundle with two large metaxylem Vessels (V), Phloem (Ph) surrounded by Fiber (F) [Mohmod, 1996]

2.4.3.3 Anatomical properties of bamboo

Bamboo fibers

Bamboo is a natural ligno-cellulose composite, which the cellulose fibers are embedded in a lignin matrix. Table 2.6 shows fiber morphology of *Bambusa asper Schult*.

Table 2.6 Approximate Fiber morphology of *Bambusa asper Schult* [Mohmod *et al*.1996].

Portion	Fiber			
	Length (mm)	Diameter (μm)	Cell Wall Thickness (μm)	Lumen Diameter (μm)
Basal	2.3	23.5	6.5	10.0
Middle	2.4	19.1	5.5	9.1
Top	2.1	24.1	8.5	7.2

The fibers constitute the sclerenchymatous tissue and occur in the internodes as caps of vascular bundles and in some species additionally as isolated strands. They contribute to 40 to 50 % of the total culm tissue and 60 to 70 % by weight [Sharma.1983]. The fibers are long and tapered at their ends. Natural fibers, except silk, have three distinct parts-an outer skin (or cuticle) an inner area and a central core that may be hollow. All of the celluloses, most of the hemicellulose, and about one half of the lignin, are found in the cell walls.

2.4.3.4 Physical properties of bamboo

Physical properties of bamboo can be shown in Table 2.7 and 2.8 respectively.

Table 2.7 Physical properties of bamboo [S. Jain et al. 1992]

Bamboo	Density $(10^{3}\ \mathrm{kgm}^{-3})$	Tensile Strength (CoV)^{a} (MNm^{-2})	Elongation (mm)	Flexural Strength (CoV)^{a} (MNm^{-2})	Deflection (mm)	Impact strength (CoV)^{a} (kJm^{-2})
Across the fibers	0.802	8.6(±1.02)	0.10	9.04(±0.3)	Fiber Split	3.02(±1.08)
Along the fibers	0.802	200.5((±7.08)	10.2	230.09(±9.06)	6.3	63.54(±4.63)

^{a} Coefficient of variance

Table 2.8 Proximate specific gravity of *Bambusa asper Schult* [Mohmod et al.1996]

Vertical portion			
Basal	Middle	Top	Average
0.51	0.60	0.62	0.58

2.4.3.5 The chemical of bamboo

The basic chemical constituents of bamboo are cellulose, hemicellulose, and lignin. In the bamboo, cellulose and hemicellulose are present in the form of holocellulose, which amounts to more than 50 % of the total chemical constituents. Most of the cellulose is present in the fiber. The second most abundant chemical constituent of the bamboo is lignin. It functions as a binder or a matrix for the cellulose fibers. Minor constituents, such as, extractives consist of resins, tannins, waxes, pectin, oil, protein, etc. [T.R.Soderstrom 1973]. The composition varies according to species, condition of growth, age of the bamboo and part of the culm. Table 2.9 shows proximate chemical analysis (%) of *Bambusa aspera Schultes*.

Table 2.9 Proximate chemical analysis (%) of the *Bambusa aspera Schultes* [Mohmod *et al.*1996]

	Ash	Holocellulose	Alcohol-benzene solubles	1 % NaOH solubles	Lignin	Hot Water solubles	Cold Water solubles
% Average	3.4	70.8	3.9	24.2	24.3	7.7	5.5

This works used *Bambusa aspera Schultes* [Kamnueng 1999], whose local Name is “Pai dton” [Rimmington 1995]. It is native to Java, Malaysia and is now especially found in the central region of Thailand. It is a large bamboo, with the largest stem diameter 8 to 18 centimeters. The stem is yellow or brown hard and smooth. It grows in dense clumps, especially at the base. It is widely used in construction and agricultural implements.

2.4.3.6 Cellulose / Lignin

Cellulose is a polysaccharide made up of β - D (+) – glucose residues joined linear chains. Its chemical structure can be shown as the below: -

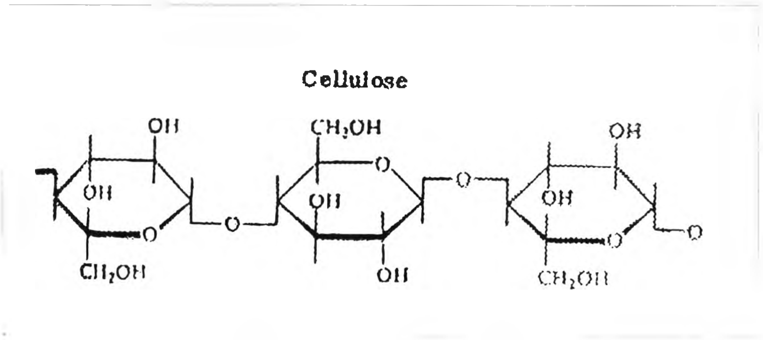


Figure 2.5 cellulose chain

With its three-hydroxyl groups, cellulose has the opportunity of forming a number of hydrogen bonds. The resulting high intermolecular forces and the regular structure of the polymer yield an unusually high degree of crystallinity. The crystalline melting point of cellulose is far above its decomposition temperature. Figure 2.6 shows relationships of ultrastructural components of cellulose in wood. The linear nature conferred upon cellulose as a consequence of the β - (1-> 4)- glycosidic linkage results in a rigid, rod-like molecule. Each chain of cellulose may be as long as 8,000 to 12,000 glucose monomers, or up to 4 micrometers long. They are arranged linearly, with no side branching. Cellulose chains are aggregated into bundle of approximately 40 chains each call the cellulose micelles which are held together by hydrogen bonds. The micelles themselves are embedded in the matrix of other polysaccharides known as the hemicellulose, Micelles, in bundles of variable numbers, are bound together into the cellulose microfibril. These, in turn, are bound together into macrofibrils.

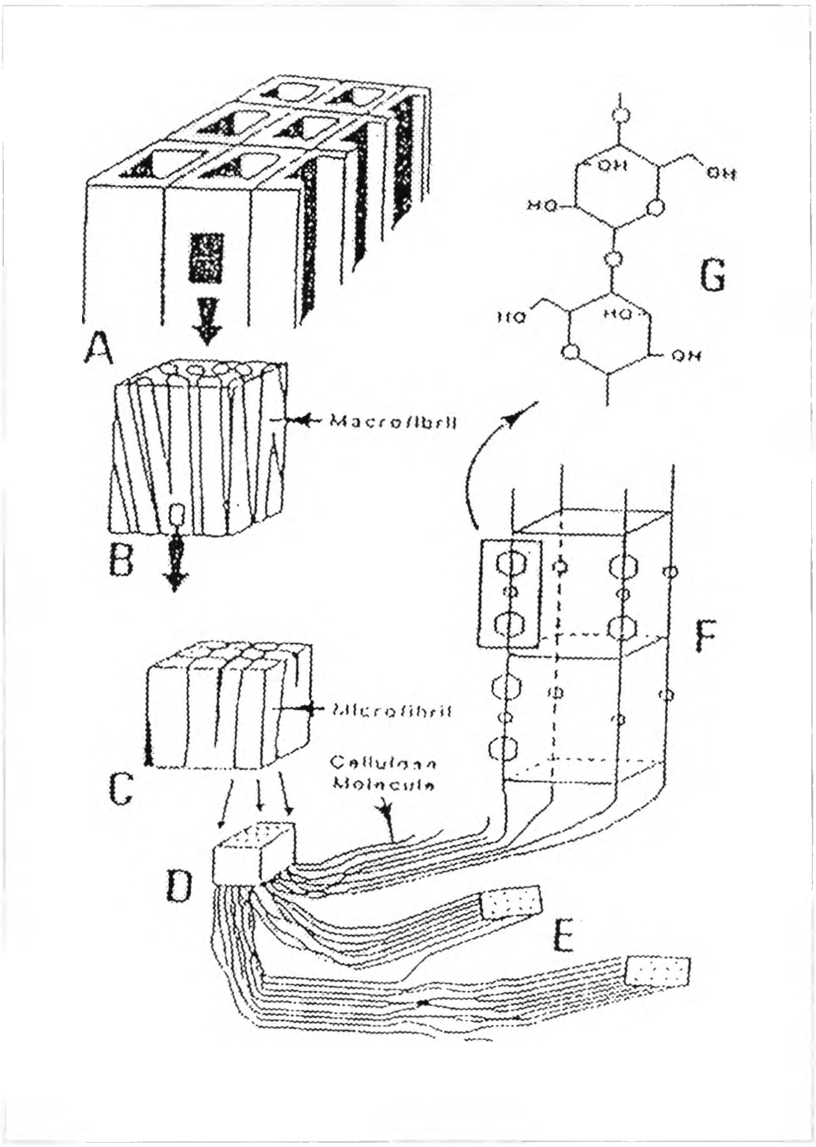


Figure 2.6 Schematic relationships of ultrastructural components of cellulose in wood [Salamone 1996]

a) Gross wood structure, b) Macrofibrils, c) Portion of macrofibril showing aggregates of microfibrils, d) A single microfibril,

e) Cellulose crystallite, f)Unit cell of crystallite,

and g) Cellobiose repeat

2.4.3.7 Cellulose solvents

In nature, cellulose is generally admixed with other substances, including lignin, hemicellulose, pectins, fats, waxes and protein. The solubility of the cellulose is very low, as it is insoluble in water and in most organic solvents. Cellulose swells, however, in hydrogen bonding solvents, The swelling is, of course, restricted to the amorphous regions of the structure. Pure cellulose is obtained by removing all incrustations of lignin and other organic and inorganic matter by treatment with alkali, acid, sodium sulphite, etc. [Salamone. 1996]. Several known systems dissolve cellulose. These systems range from solutions in protomic acids (e.g., 78% phosphoric acid) to metallic complexes (e.g., cuprammonium).

a) Hemicellulose

Hemicellulose is carbohydrates related to cellulose, but mixed with polysaccharides containing other sugars beside glucose, such as, hexoses (mannose, galactos, and glucose) And pentoses (xylose and arabinose) [Verma.1984]. They are found in cell wall of plants which are extractable by dilute alkaline or hot dilute mineral acids by forming simple sugars. More than 90 % of forming a 4-0- methyl-D-glucuronic acid, L- arabinose, and D-xylose in a molar ratio of 10:1.3:2.5, respectively. Formula of hemicellulose is $(C_6H_{10}O_5)_{2n}$.

b) Lignin

Lignin is a complex organic material found in the woody tissue of plants, often combined with hemicellulose materials to help bind the cells together and cellulose [Chapman *et al*. 1971]. Lignin acts as glue to hold the cellulose fibers in place with in the cell wall [Burdette 1988] Lignin is usually insoluble in all solvents, unless they are degraded by physical or chemical treatment. Formula of lignin can be shown in Figure 2.7. It is noted that actual structure is three-dimensional.

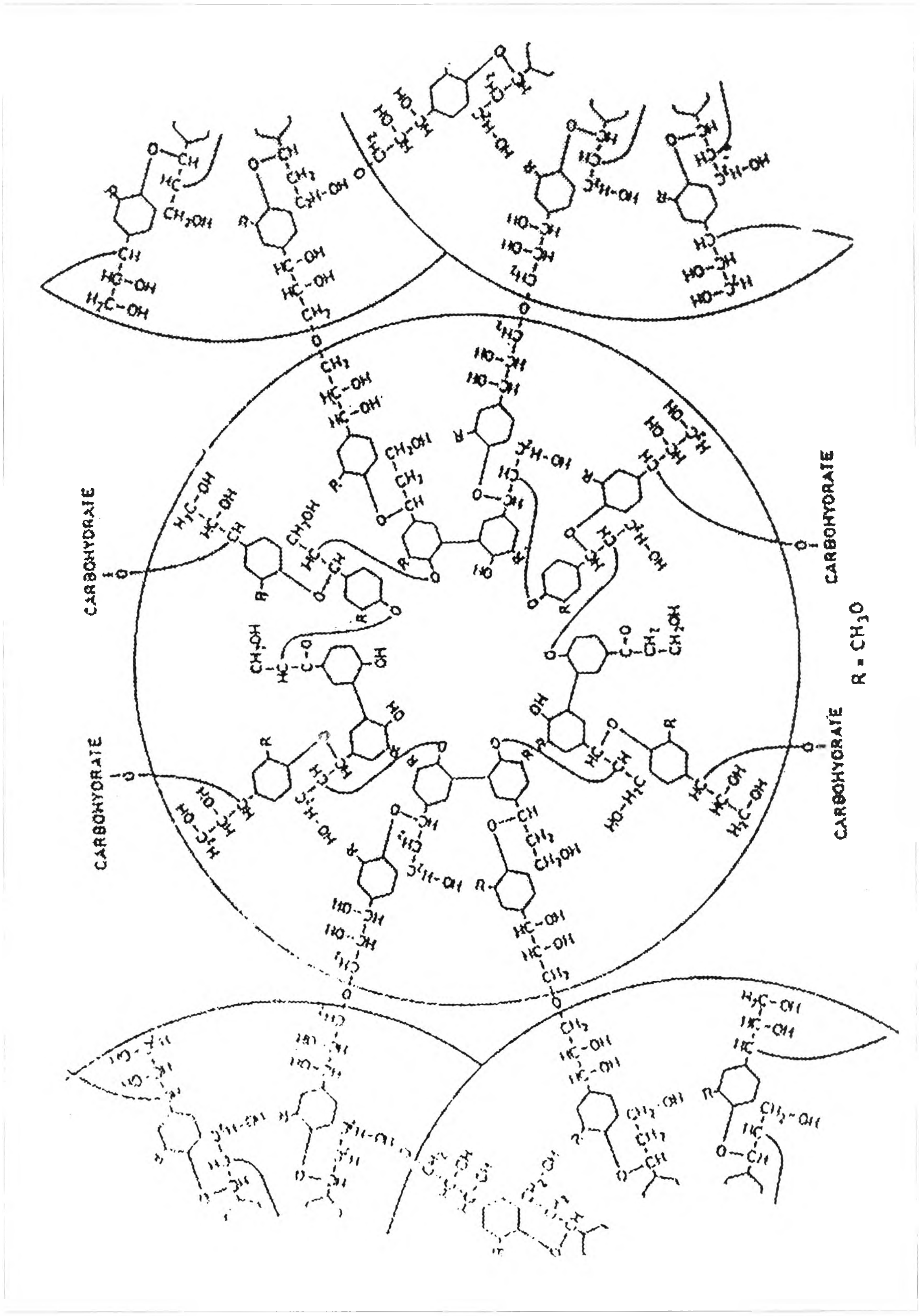


Figure 2.7 Formulation for the repeating unit of lignin [Pinyo Panitchapun 1996]

2.5 Interfacial bonding

Once the matrix is in intimate contact with the reinforcement, bonding will occur, A number of different types of bond may be formed. Furthermore, for a given system more than one bonding mechanism may be operative at the same time, e.g., mechanical and electrostatic bonding, and the bonding mechanism may change during the various production stages or during service, e.g., electrostatic bonding changing to reaction bonding. The type of bonding varies from system to system and depends on fine details such as the presence of surface contaminants or of added surface active agents (coupling agents). The main features of the different bonding mechanisms are shown as below

2.5.1 Mechanical bonding

A mechanical interlocking or keying of two surfaces, as shown in the Figure 2.8, can lead to a reasonable bond. Clearly the interlocking is greater, and hence the mechanical bonding more effective, the rougher the interface. Also any contraction of the matrix onto the reinforcement is favorable to bonding.

The mechanical bond is most effective when the force is applied parallel to the interface, in other words, the shear strength may be considerable. On the other hand, when the interface is being pulled apart by tensile force the strength is likely to be low unless there is a high density of features with re-entrant angles. In most cases a purely mechanical bond is not encountered and mechanical bonding operates in conjunction with another bonding mechanism.

2.5.2 Electrostatic bonding

Bonding occurs between the matrix and the reinforcement when one surface is positively charged and the other negatively charged (Figure 2.8). This leads to an electrostatic attraction between the components of the composite, which will depend on the difference in charge on their surfaces. Electrostatic interactions are short range and are only effective over small distances of the order of atomic dimensions therefore it is essential that the matrix and reinforcement are in intimate contact and that surface contamination and entrapped gases will decrease the effectiveness of this bonding mechanism.

2.5.3 Chemical bonding

In the context of composite science, chemical bonding is the bond formed between chemical groups on the reforcement surface (marked X in Figure 2.8) and compatible groups (mark R in Figure 2.8) in the matrix. Not surprisingly the strength of the chemical bond depends on the number of bonds per unit area and the type of bond.

Chemical bonding may account for the success of some coupling agents. For example, silanes are commonly employed for coupling the oxide groups on a glass surface to the molecules of a polymer matrix. At one end (A) of the silane molecules a hydrogen bond forms between the oxide (silanol) groups on the glass and the partially hydrolyzed silane, whereas at the other end (B) it reacted with a compatible group in the polymer (Figure 2.8)

2.5.4 Reaction or interdiffusion bonding

The atoms or molecules of the two components of the composites may interdiffuse at the interface to give what is known as reaction or interdiffusion bonding. For interfaces involving polymers this type of bonding can, in simple term, be considered as due top the intertwining of molecules (Figure 2.8) Many factors control the strength of this interface including the entanglement of the molecules and the number of molecules per unit area of interface.

For systems involving metals and ceramics the interdiffusion of species from the two components can produce an interfacial layer of different composition and structure from either of the components (Figure 2.8). The interfacial layer will also have different mechanical properties from either the matrix or reinforcement and this consequently greatly affects the characteristics of the interface. In metal matrix composites the interfacial layer is often a brittle intermatallic compound which is a compound that exists at or around a stoichiometric composition such as AB, A_2B, A_3B, e.g., $CuAl_2$.

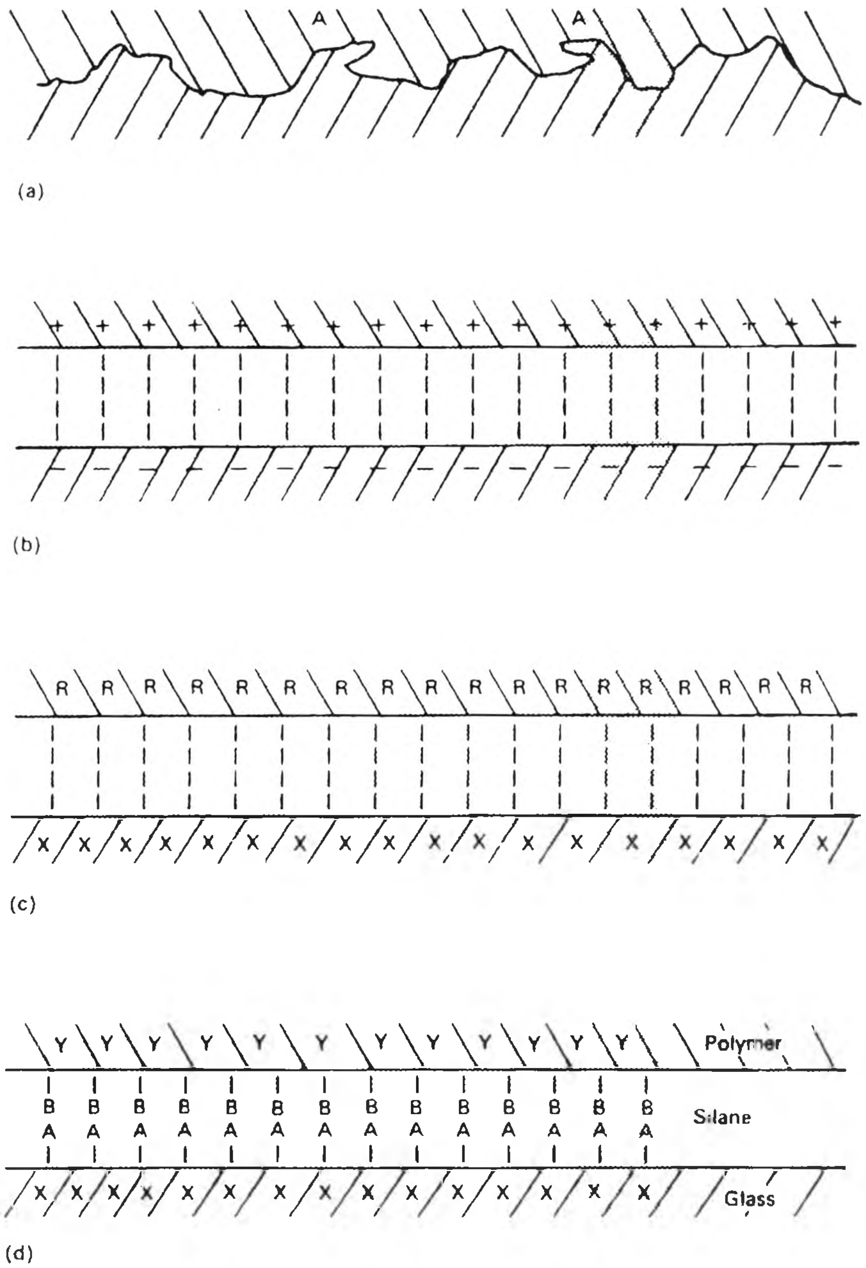
One of the main reasons why interfacial layers are formed is that ceramic matrix and metal matrix composite production invariably involve high temperatures. Diffusion is rapid at high temperatures as the rate of diffusion, or the diffusion coefficient, D_d, increases exponentially with temperature according to the Arrhenius-type equation

$$D_d = D_o \exp(-Q_d/RT) \qquad (2.1)$$

Where Q_d is the activation energy for diffusion, D_o is a constant, R is the gas constant and T is the temperature, Temperature has a marked effect on the diffusion coefficient; substituting a typical value for Q_d of 250 kJ/mol into the above equation it can be shown that D_d is 2×10^{34} greater at 1000 °C than at room temperature. The extent of the interdiffusion X, and hence the thickness of the reaction layer, depends on time, t, as well as temperature and is given by the approximate relationship

$$X = (D_d t)^{1/2} \qquad (2.2)$$

An interface can change during service. In particular interfacial layers can form during service at elevated temperature. In addition, previously formed layers may continue to grow and complex multilayer interfaces may develop.


A
A
(a)
+
−
(b)
R
X
(c)
Y
Polymer
B
A
Silane
X
Glass
(d)

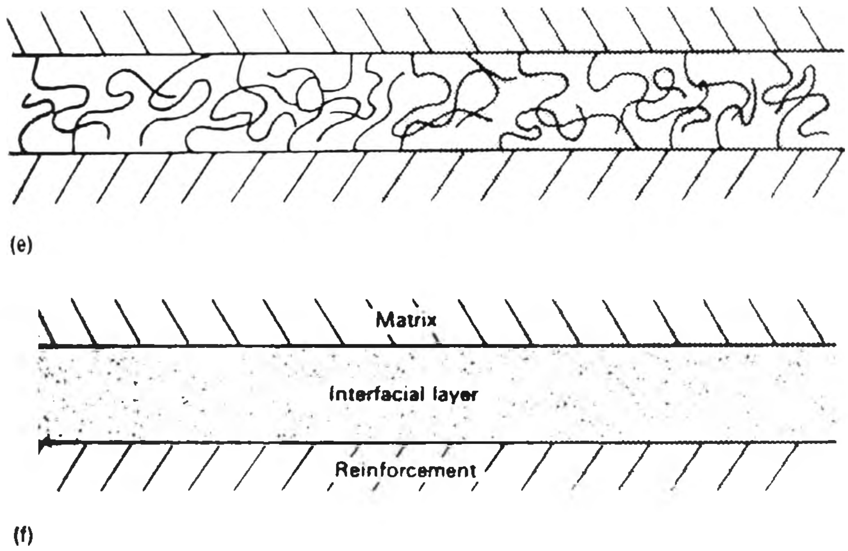


Figure 2.8 Schematic diagrams of the interfacial bonding mechanism:

[Matthews 1994]

(a) mechanical bonding (features designated A have a re-entrant angle);

(b) electrostatic bonding;

(c) chemical bonding (R and X represent compatible chemical groups);

(d) chemical bonding as applied to a silane coupling agent;

(e) reaction bonding involving polymers;

(f) interfacial layer formed by interdiffusion.

2.6 Coupling Agents [Brydson 1988]

Filler cannot be used to best advantage in a polymer unless there is good adhesion between them. In particular the filler particle/polymer interface will not be stress- bearing and therefore provides a point of mechanical weakness.

One way of improving the adhesion between polymer and filler is to improve the level of wetting of the filler by the polymer. One approach, which has been used for many years, is to coat the filler with an additive that may be considered to have two active parts. One part is compatible with the filler, the other with the polymer. Probably the best known example is the coating of calcium carbonate with stearic acid. Such coated or 'activated' whiting have been used particularly with hydrocarbon rubbers. It is generally believed that the polar end attaches itself to the filler particle. Whilst the aliphatic hydrocarbon end is compatible with the rubbery matrix. In a similar manner clays have been treated with amines.

A much more positive attempt to increase the adhesion between polymer and filler was to link them by covalent bonds using coupling agent. The earliest of these were the methacrylato-chrome chloride coupling agents introduced in the mid of 1940s. These materials were used primarily in conjunction with glass fibers and marketed as Volan treatments for use in polyester-glass reinforced plastics. They were believed to react as shown in Figure 2.9. Chemical bonding to the surface of the glass fiber occurs through Cr-O-Si links. Bonding to the unsaturated polyester resin occurs via a polymerization reaction involving double bonds in the polyester, in styrene monomer present as diluent and in the methacrylato groups present in the coupling agent. Reaction is also sometimes possible with saturated polymers via the hydroxyl, CrCl, CrOH and carboxyl groups that are present.

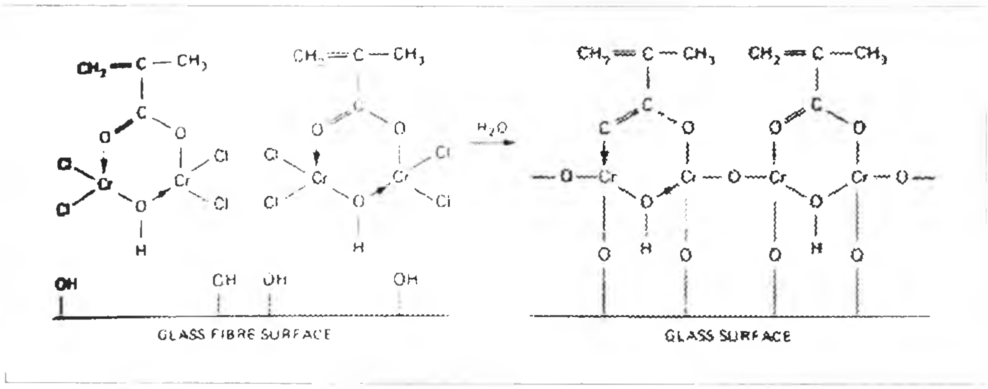


Figure 2.9 Glass fiber surface and Volan coupling agent
[Brydson 1988]

The appearance of the methacrylato-chrome chloride treatments was soon followed by glass fiber treatments involving silanes. One of the first such materials was vinyltrichlorsilane. As can be seen in figure 2.10 these are joined to the glass via Si-O-Si (siloxane) linkages. As with the chrome complexes the coupling agent may then be linked to an unsaturated polyester resin via the unsaturated vinyl group.

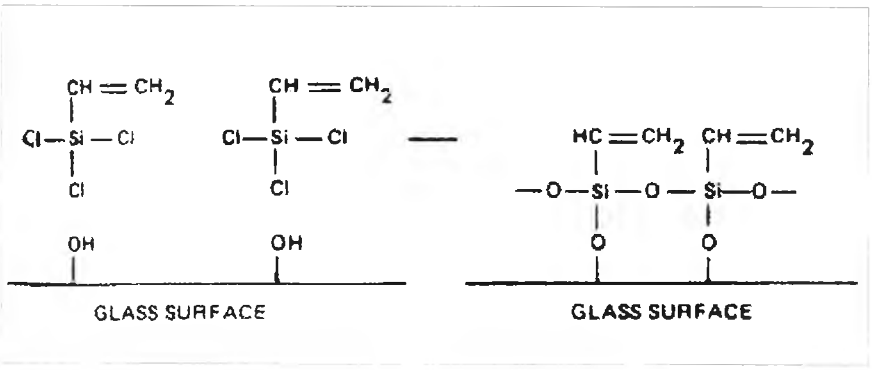
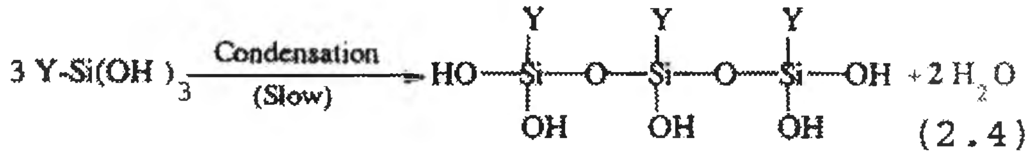


Figure 2.10 Si-O-Si linkage on glass surface [Brydson 1988]

2.6.1 Organosilane Coupling agent

In composite materials, coupling agents are generally employed to improve the bonding between the polymer matrix and the reinforcing fibers. Organosilane coupling agents are widely used for glass fiber reinforcement. They have the general structure of Y-Si(X_3), where Y is an alkyl or group containing an alkyl function and X is a hydrolyzable group such as alkoxy or halide group. These coupling agents are used in the form of silane triols after the hydrolysis of X, which is fast in dilute acid (Eq. 2.3). The silanols that form have to be used quickly to avoid condensation which will lead to the formation of polysiloxane oligomer (Eq. 2.4). These oligomers are insoluble in aqueous medium and will precipitate out.

$$\text{Y-Si}(\text{OCH}_3)_3 + 3\text{H}_2\text{O} \xrightarrow[\text{(Fast)}]{\text{Hydrolysis}} \text{Y-Si(OH})_3 + 3\text{CH}_3\text{OH} \qquad (2.3)$$

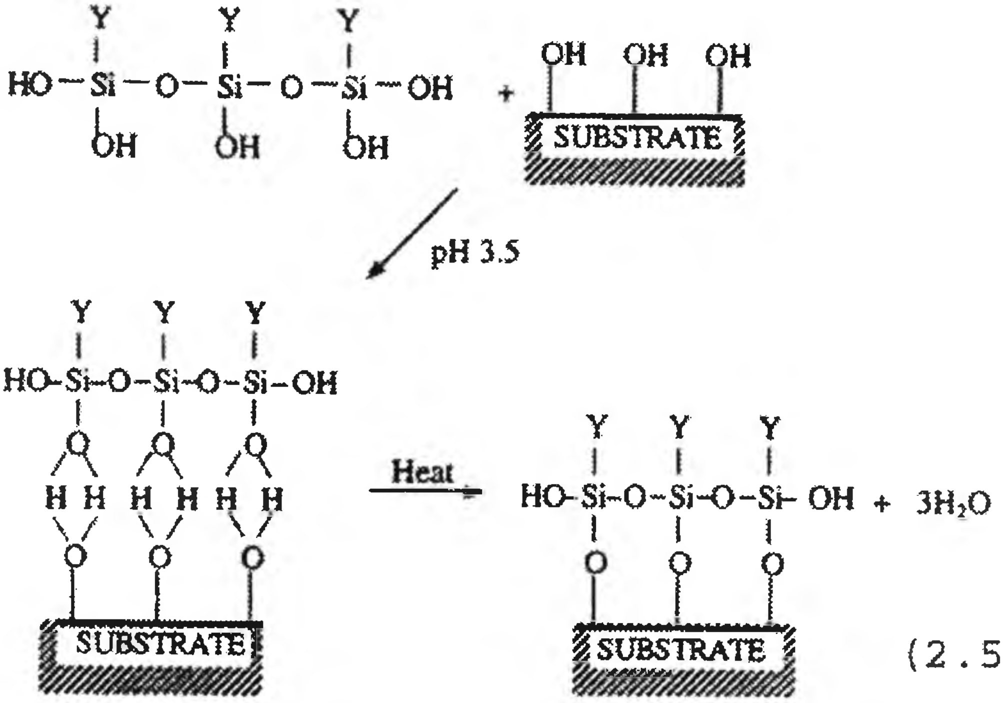


$$3\ \text{Y-Si(OH)}_3 \xrightarrow[\text{(Slow)}]{\text{Condensation}} \text{HO}-\underset{\text{OH}}{\overset{\text{Y}}{\text{Si}}}-\text{O}-\underset{\text{OH}}{\overset{\text{Y}}{\text{Si}}}-\text{O}-\underset{\text{OH}}{\overset{\text{Y}}{\text{Si}}}-\text{OH} + 2\,\text{H}_2\text{O} \qquad (2.4)$$

Silanetriols can react directly with the hydroxyl group of a substrate to form oxan bonds or they may condense with the surface hydroxyl groups, and with each other, to form an organosilicone-bonded surface (Eq. 2.5). The siloxane thus formed on the substrate surface can act a a linking agent between fiber and polymer matrix via the interaction between organofunctional groups (Y) and polymer matrix.

The organofunctional group,Y, in the coupling agent can interact with the polymer matrix to form an IPN (interpenetrating network). The final curing reaction of a silane treated substrate in a composite enhances the adhesion of the polymer matrix to the fiber substrate. In composite processing, the Y group should be chosen according to its chemical reactivity with the resin for maximum interaction.

Generally, the reaction between cellulosic materials and silanes is not simple. It is known that silane coupling agents react with cellulose moisture (or additional water) to form silanol (Si-OH) groups. After hydrolysis, the coupling agent can develop either covalent or hydrogen bonds with cellulose hydroxyl groups [Matias, M. C., *et al* 1999].



(2.5)

2.6.2 Gamma-methacryloxypropyltrimethoxysilane

Gamma-methacryloxypropyltrimethoxysilane (γ-MPS) is one of the organosilane coupling agents used to improve the physical and electrical properties of glass-reinforced and mineral-filled thermosetting resins under exposure to heat and/or moisture. It is typically employed as a blend additive in resin systems that cure via a free radical mechanism (e.g. polyester, acrylic) and in filled or reinforced thermoplastic polymers, including polyolefins and polyurethanes. It is also used to functionalize resins via radical initiated processes - copolymerization or grafting - and to modify surfaces. Furthermore, its application is to enhance initial and wet strength of reinforced polyester resin composites and to enhance the wet electrical properties of many mineral-filled and reinforced composites.

It can be soluble in methanol, ethanol, isopropanol, acetone, benzene, toluene, and xylene. After hydrolysis, it is soluble in water with adequate stirring if the pH is adjusted to 3.0-4.0. Hydrolysis releases methanol. It shows copolymerization or grafting reactions when catalyzed by (organic) initiator systems, e.g. peroxides or by radiation (e.g. UV).

γ-MPS is a clear, light and heat sensitive liquid with a faintly sweet odor. It is used as adhesion promoter at organic/inorganic interfaces, as surface modifier (e.g. imparting water repellency, organophilic surface adjustment) or as crosslinking of polymers). Its properties are presented in Table 2.10.

Table 2.10 properties of Gamma-methacryloxypropyltrimethoxysilane

Formula	C H O Si $H_2C=C(CH_3)CO_2(CH_2)_3Si(OCH_3)_3$
Color and Appearance	Colorless transparent liquid
Molecular Weight	248.4
Boiling Point	255 C [760mmHg]
Refractive Index	1.4202 +/- 0.0005 [25 C]
Viscosity $_{25}{}^{\circ}\mathrm{C}$	2 cSt
Density $_{25/25}\,\mathrm{C}$	1.045
Flash point	108 C

2.7 Compression molding [Billmeyer, 1984].

Compression molding is one of the common methods used in thermosets and also thermoplastics. In general, compression molding used for polymers is illustrated in Figure 2.11. The polymer is placed in the lower half of a heated mold, the upper half is then moved down and the pressure is applied. The pressure and temperature can be varied considerably depending upon the thermal and rheological properties of the polymers. In practice, the polymer is often preheated to reduce the temperature different from the mold and to assist early flow in the mold. In addition, a slight excess of material is usually placed in the mold to ensure its being completely filled. The rest of the polymer is squeezed out to take the shape of the mold. The advantages of compression molding over other procession techniques are:

a) Polymer flow over shorter distances thus reducing frozen-in stresses.

b) Polymers are not forced through small gates, which can lead to reduction in mechanical properties.

c) Mold maintenance cost is low.

d) Tooling costs are inexpensive because of the simplicity.

e) Material is not wasted because of the absence of sprues and runners.

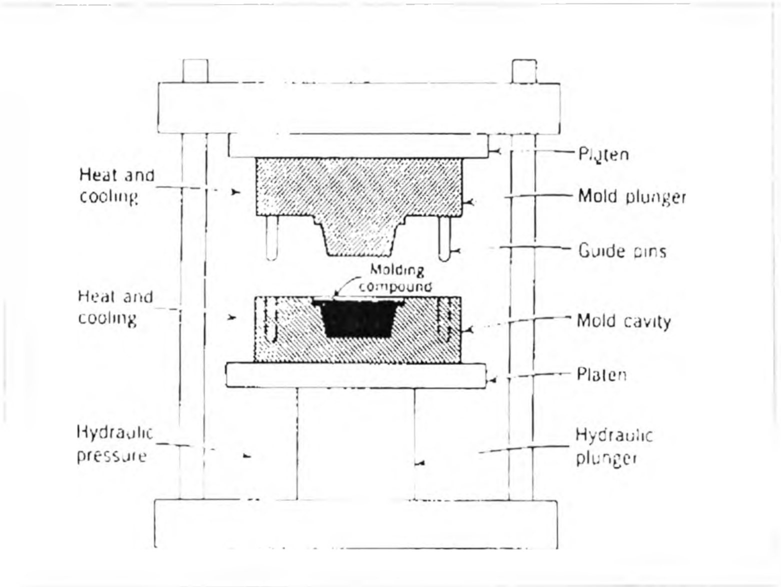


Figure 2.11 Principle of compression molding [Billmeyer, 1984].