



COMPOSITE MATERIALS DESIGN

2. Materials/Components



Fibers and matrices

Materials

In this chapter, the underlying science of fibers and matrices is described. Some specific examples are given to illustrate the key factors involved. A wide range of reinforcements, mostly in the form of fiber is now available commercially. Their properties can be related directly to the atomic arrangement and the defect content of the reinforcement which must be controlled in the manufacturing processes. Matrices may be based on polymers, metals or ceramic. The choice of matrix is related to the required properties, the intended applications of the composite and the method of manufacture. The properties of the matrix depend on microstructure which, in turn, depends on manufacturing route and subsequent thermal and mechanical treatments. Certain properties of the composite may be sensitive to the nature of the reinforcement/matrix interface.



Fiber Reinforcement

Composite Materials

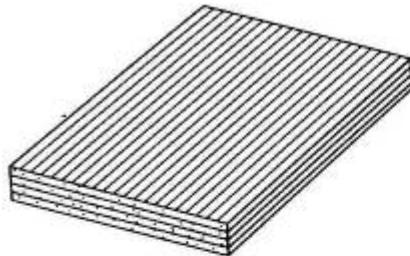
The role of the reinforcement in a composite material is fundamentally one of increasing the mechanical properties of the neat resin system. All of the different fibres used in composites have different properties and so affect the properties of the composite in different ways. The properties and characteristics of common fibres are explained later.

However, individual fibres or fibre bundles can only be used on their own in a few processes such as filament winding (described later). For most other applications, the fibres need to be arranged into some form of sheet, known as a fabric, to make handling possible. Different ways for assembling fibres into sheets and the variety of fibre orientations possible lead to there being many different types of fabrics, each of which has its own characteristics. These different fabric types and constructions are explained later.

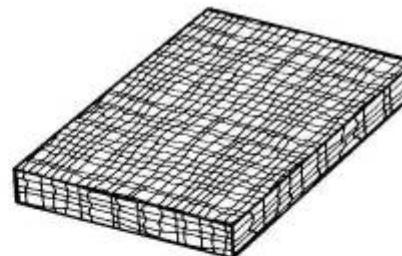
Fiber Reinforcement

Types of Fiber-Reinforced Composites

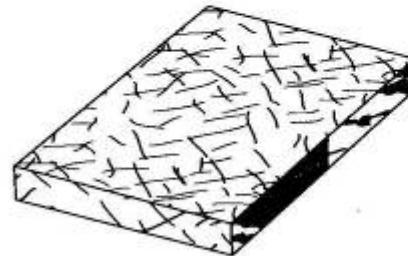
One generally finds four types of fiber-reinforced composites as shown below. They differ in how the fibers are used to make the composite (orientation and length of fibers).



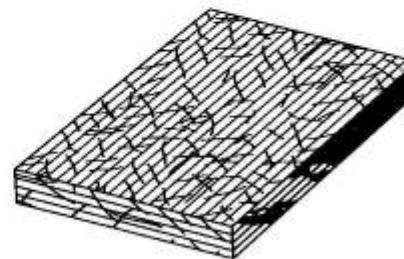
(a) Continuous fiber composite



(b) Woven fiber composite



(c) Chopped fiber composite



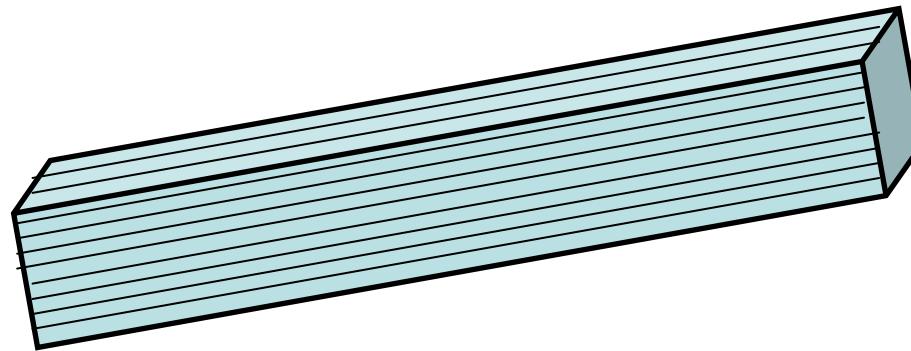
(d) Hybrid composite

Types of fiber-reinforced composites.

Fiber Reinforcement

Continuous fiber composites

Are generally "laid-up" in *plies* (or *laminae*) with each ply having fibers oriented in the same direction. A layer of fibers all oriented in the same direction is imbedded in a homogeneous material (called the *matrix*) to make a single ply or laminae. For example, glass-epoxy has a layer of glass fibers running more-or-less parallel within an epoxy resin matrix material.



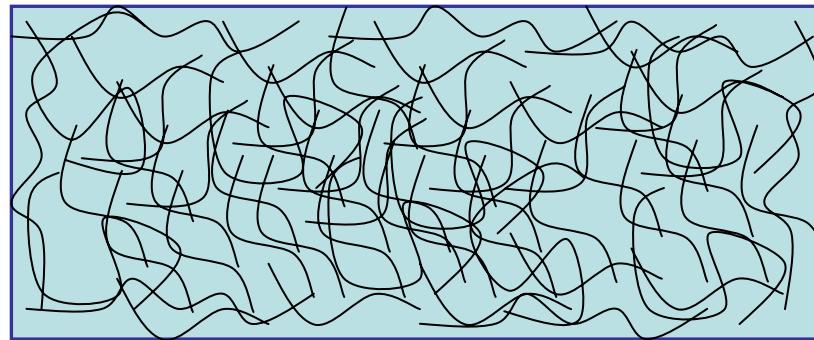
Individual plies can be stacked or layered and bonded together with individual ply fiber directions being selected so as to *tailor* the lay-up (or *laminate*) to have desired overall structural characteristics of the laminate. Under loading, the potential for delamination (or separation of the laminae) is a major problem because the interlaminar strength is matrix dominated (i.e., if the matrix is weak, ply delamination can occur).



Fiber Reinforcement

Chopped fiber composites

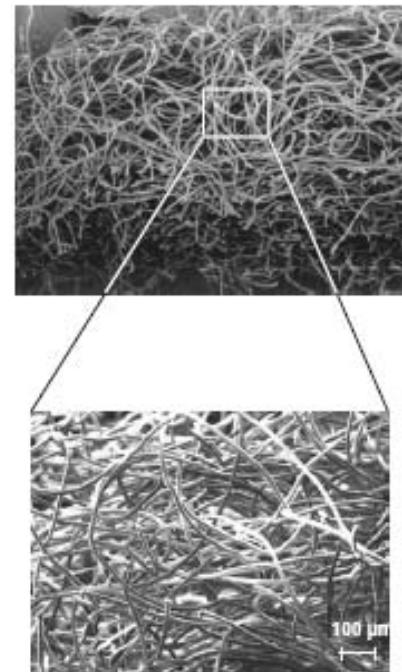
Have fibers that are relatively short and have a random orientation and distribution of the fibers. Chopped fiber composites generally have mechanical properties that are considerably poorer than those of continuous fiber composites. However they are cheaper to manufacture and are used in high-volume applications .



Non Woven



Nonwoven bonding
with needlepunch



Absorbable Nonwoven

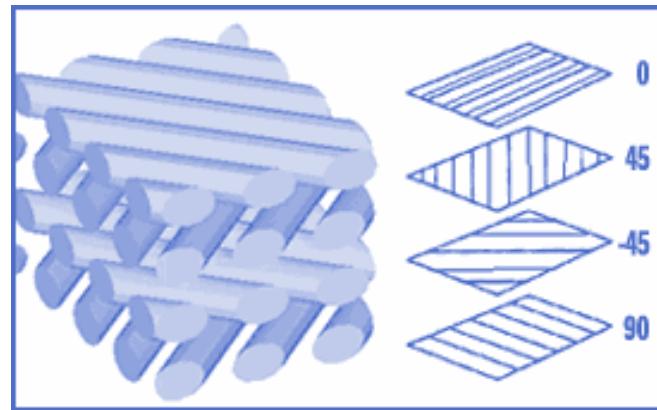


Fiber Reinforcement

Hybrid composites

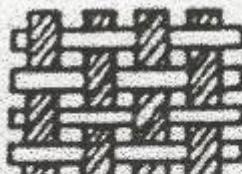
Composite Materials

Generally, consist of mixed chopped and continuous fibers; or mixed fiber types such as glass/CARBON or Kevlar/CARBON





manufacturing processes



Biaxial woven



High modulus woven



Multilayer woven



Triaxial woven



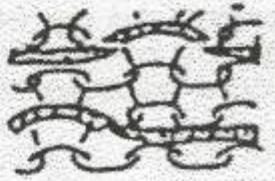
Tubular braid



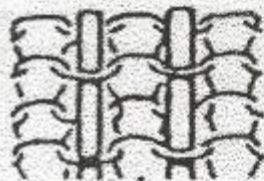
Tubular braid laid in warp



Weft knit



Weft knit laid in weft



Weft knit laid in warp



Weft knit laid in weft laid in warp



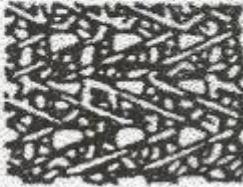
Square braid



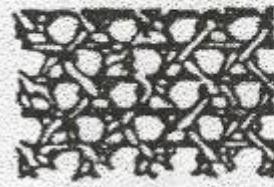
Square braid laid in warp



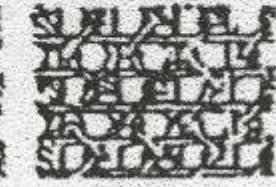
Warp knit



Warp knit laid in warp



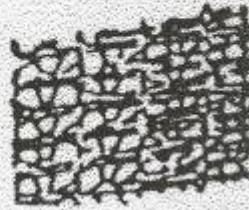
Weft inserted warp knit



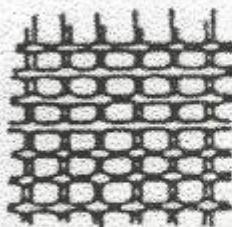
Weft inserted warp knit laid in warp



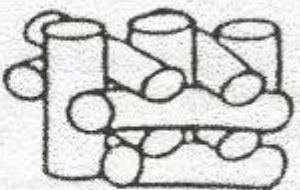
XD



Stitchbonded laid in warp



Biaxial bonded



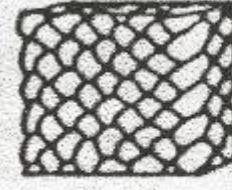
XYZ laid in system



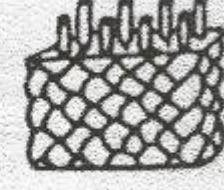
Flat braid



Flat braid laid in warp



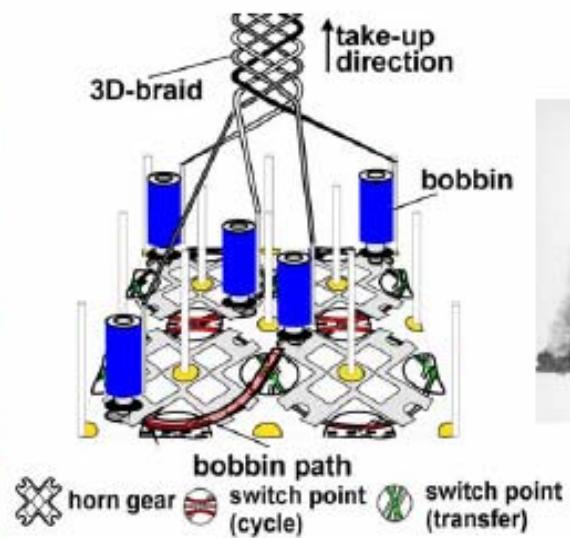
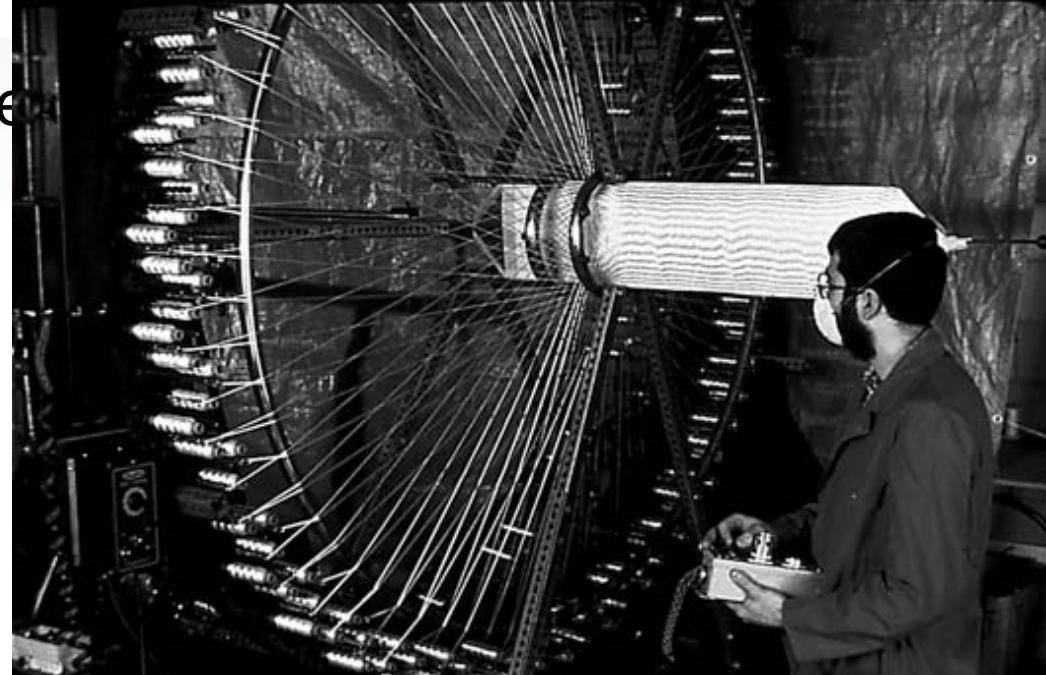
3-D braid

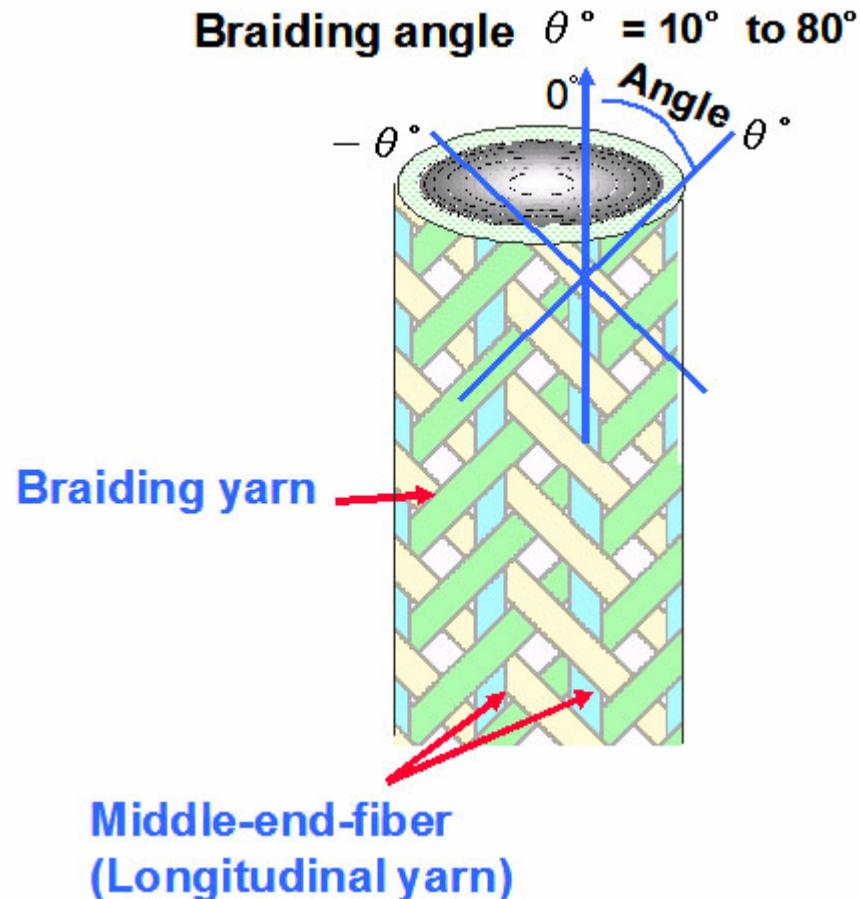


3-D braid laid in warp

Fiber Reinforcement

Braiding



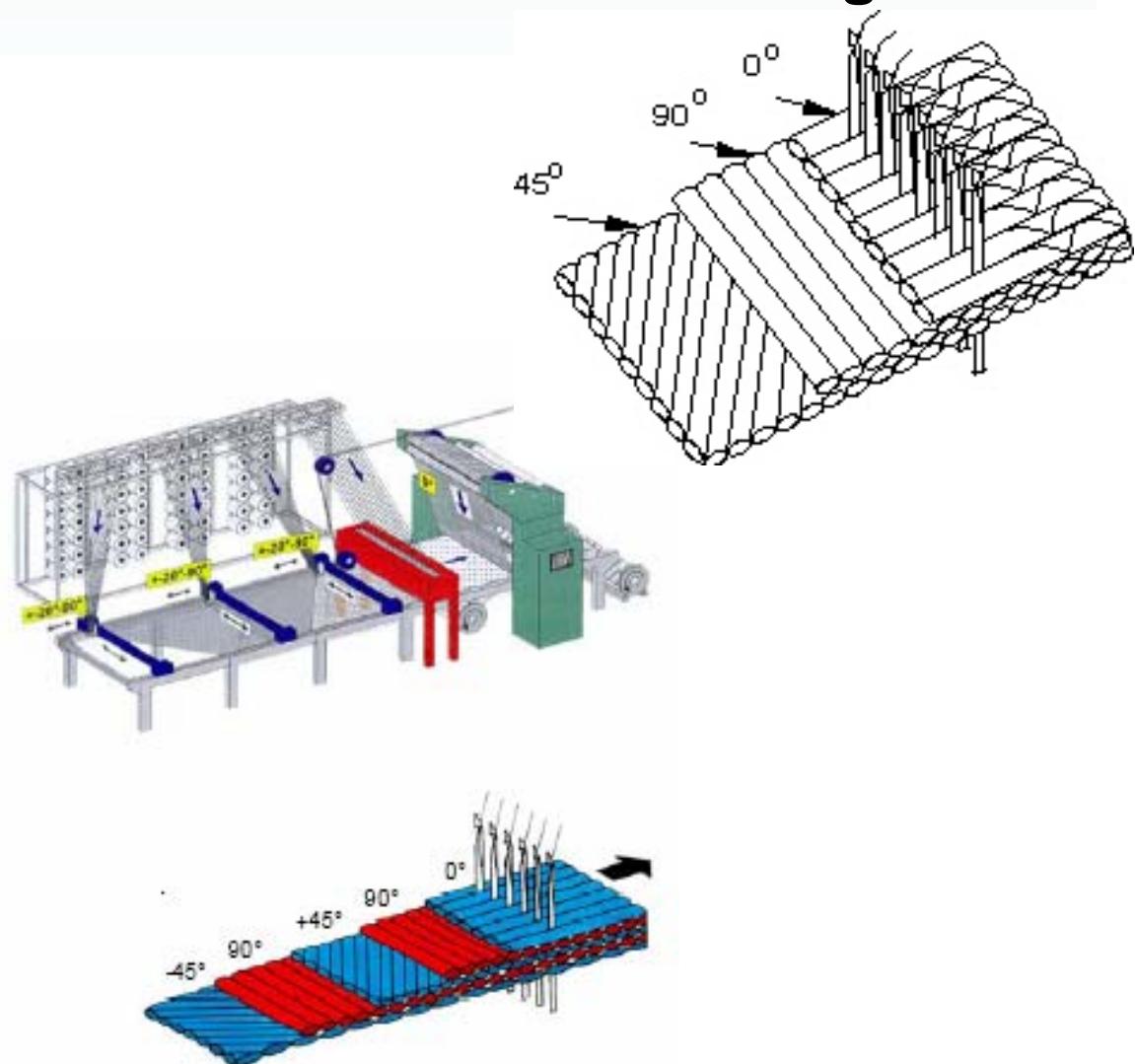


Warp Knitting



Multi-axial Warp Knitting Machine

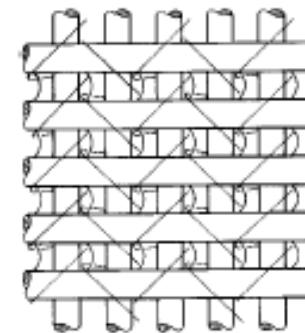
MECHATRONICS
December 2007



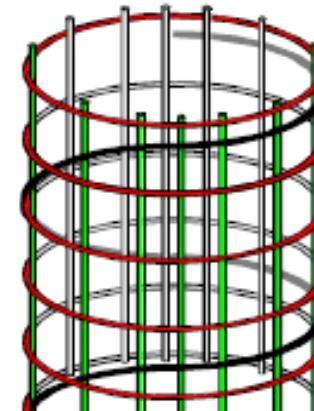
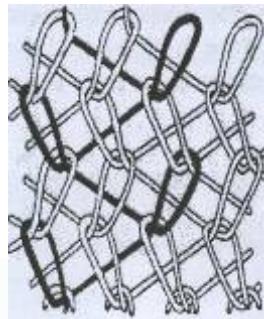
xavier.colom@upc.edu

Warp Knitting

Warp Knitting Machine



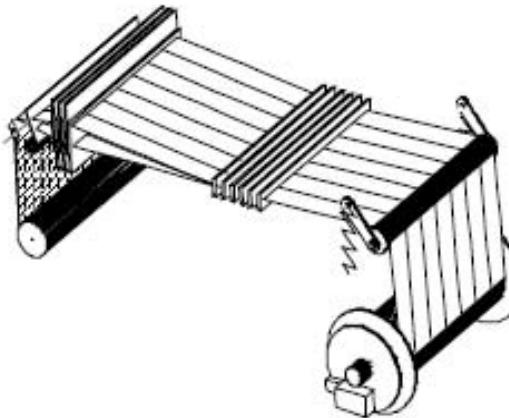
Circular Warp Knitting Machine



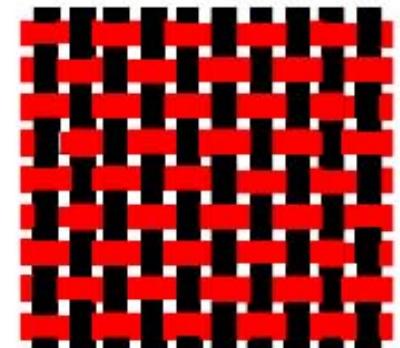
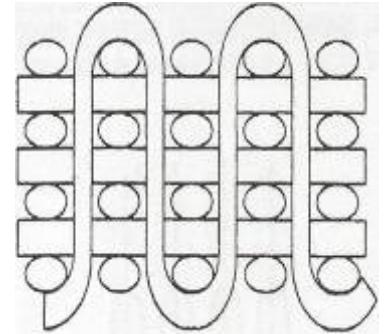
Woven fabric



Air-bulk weaving machine



Scheme of a weaving machine

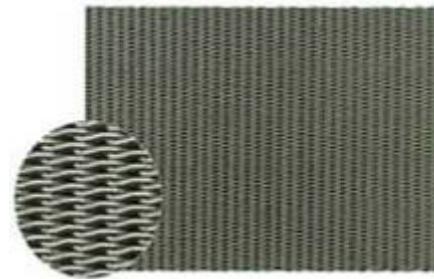
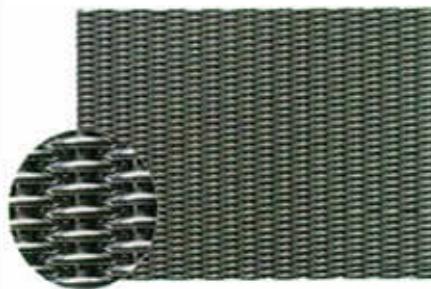


Woven fabric

Fiber Reinforcement

Woven fiber composites

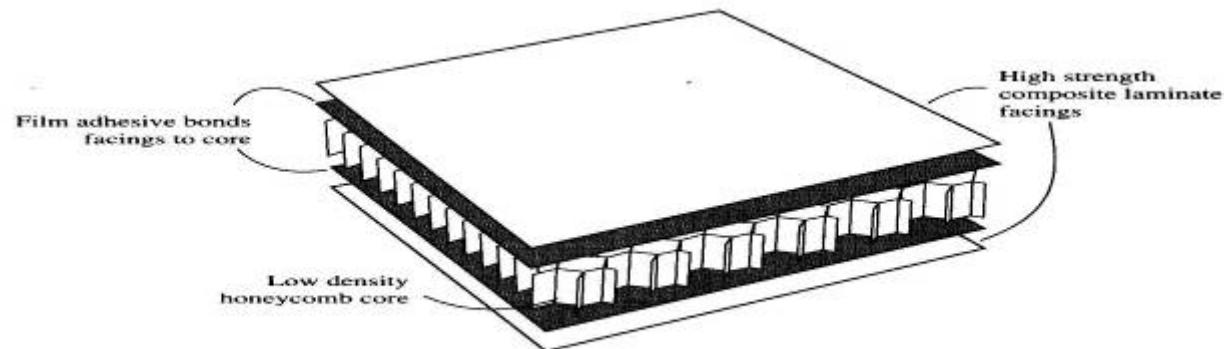
Are similar to ordinary cloth used in the textile industry. The woven fiber may be 2-D (fibers interwoven in 2 directions) or 3-D (fibers interwoven in 3 directions). Woven fiber composites do not generally have distinct laminae and are not nearly as susceptible to delamination; however, strength and stiffness are sacrificed due to the fact that the fibers are not as straight (because of the weaving) as in the continuous fiber laminate .



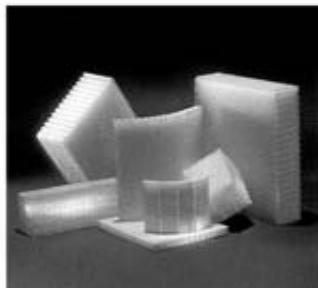
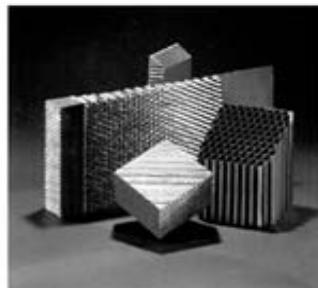
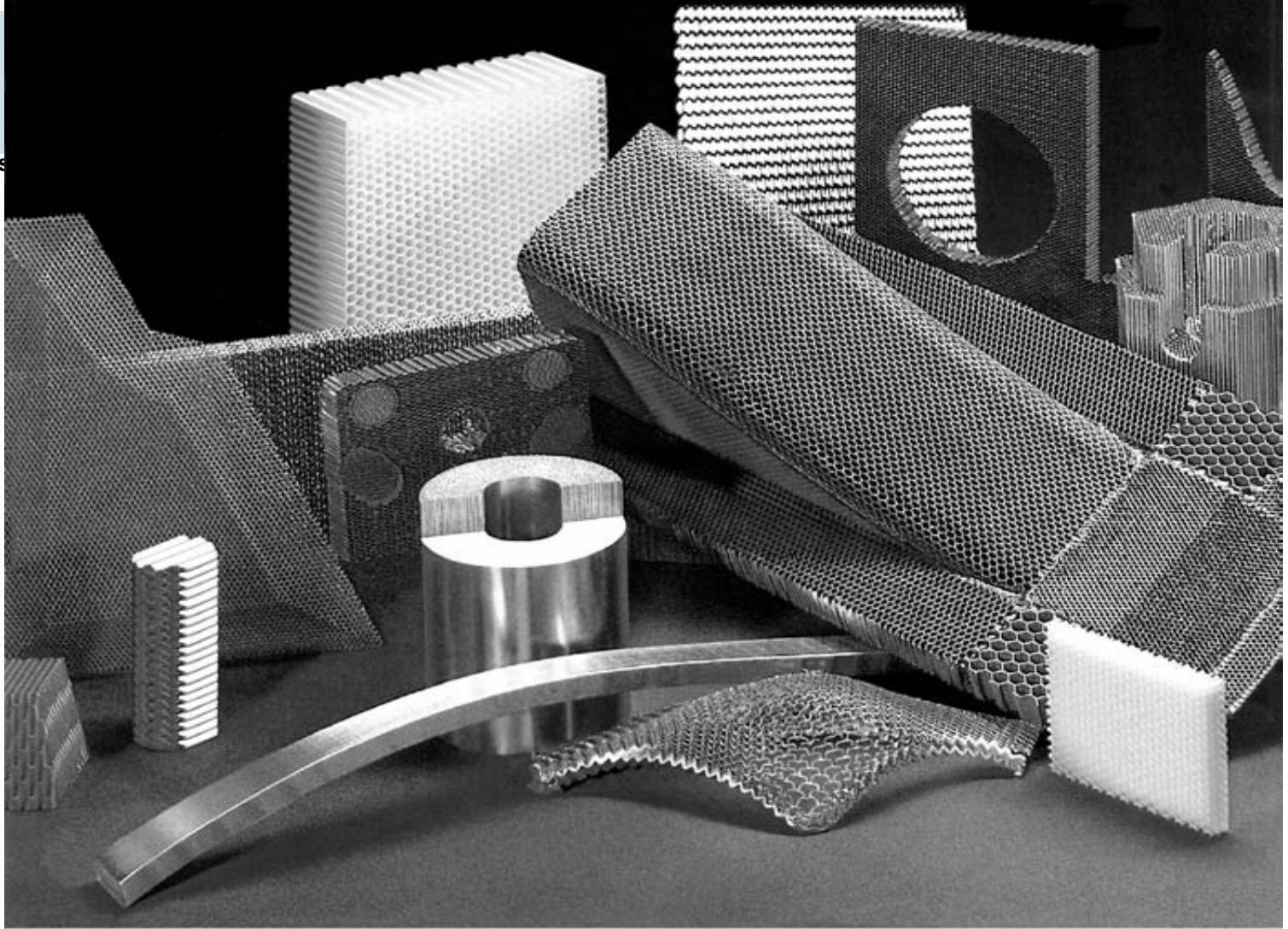


Sandwich composites

They consist of high strength composite facing sheets (which may be any of the four fiber composites discussed above) bonded to a lightweight foam or honeycomb core.

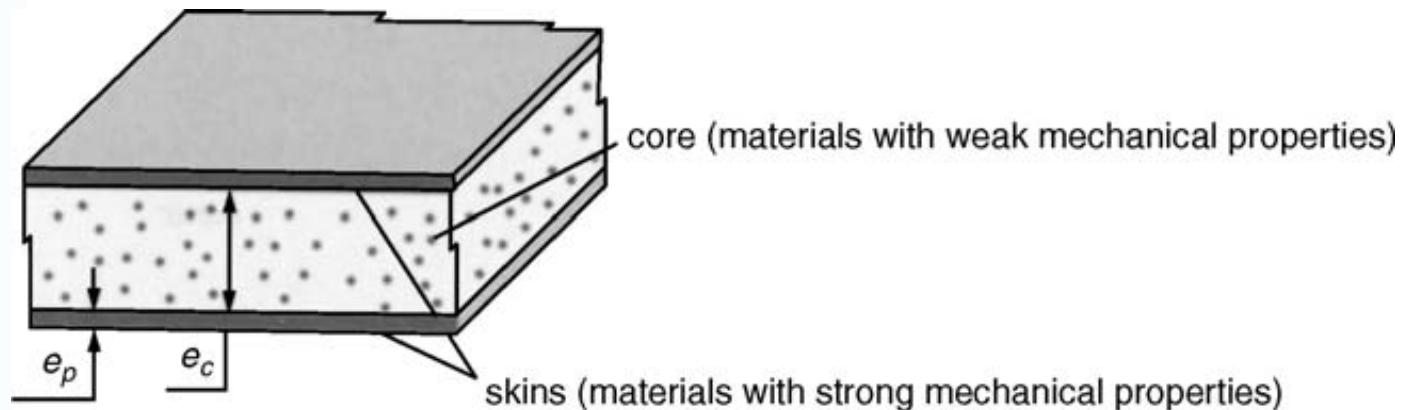


Sandwich structures have extremely high flexural stiffness-to-weight ratios and are widely used in aerospace structures. The design flexibility offered by these and other composite configurations is obviously quite attractive to designers, and the potential now exist to design not only the structure, but also the structural material itself.



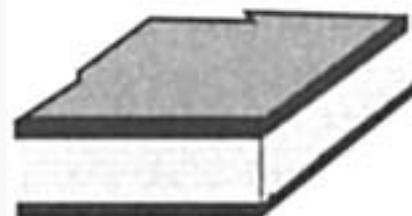


Sandwich Structure





Constituents of Sandwich Materials

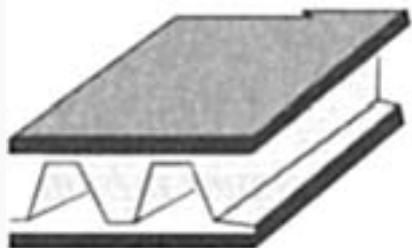


Facings

metal
lamine
wood
thermoplastics
asbestos/cement

Core

expanded materials

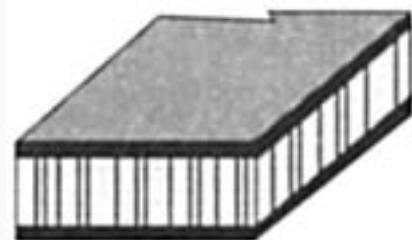


metal
lamine

↔
ribbed plate in metal
or lamine

laminated
wood plate

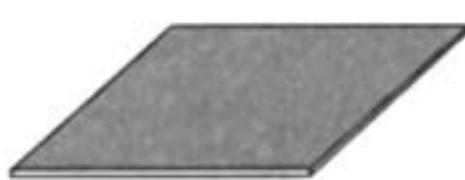
↔
wood plate
impregnated carbon
(honeycombs)



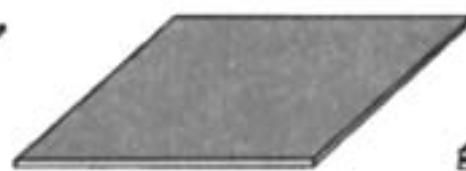
aluminum
lamine

↔
stretched aluminum
(honeycomb)

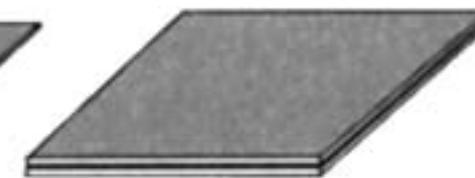
Comparison of Plates Having Similar Flexural Rigidity EI



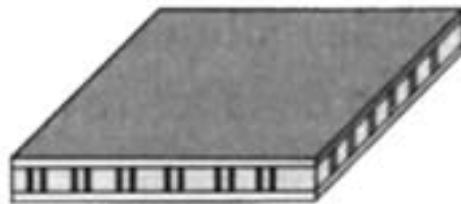
steel sheet
mass = 16



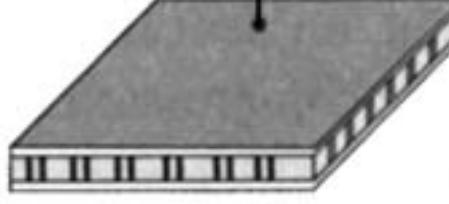
aluminum sheet
10



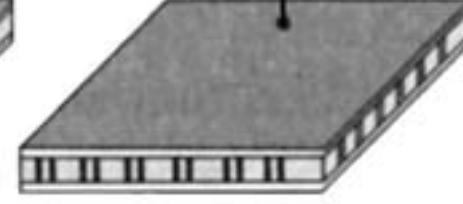
wooden plate
5



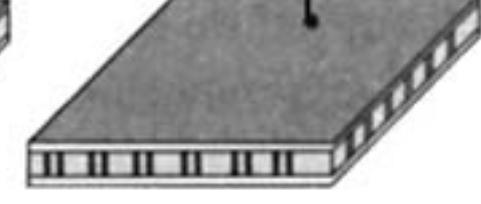
sandwich:
nida-aluminum
skins
mass = 1.
cost: 1



sandwich:
nida Nomex-
glass skins
1.12
cost: 1



sandwich:
nida-Kevlar
skins
0.86
cost: 1.57

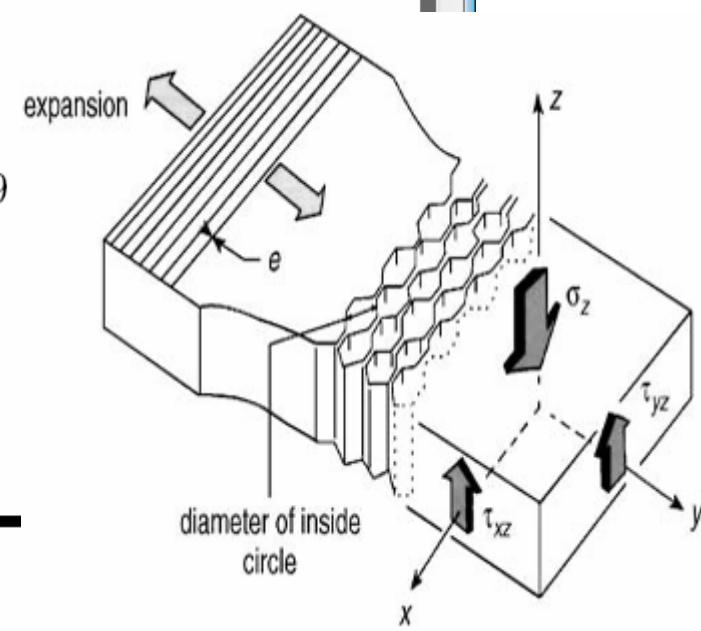


sandwich:
nida-carbon
skins
0.69
cost: 2.42

Table 4.1 Properties of Some Honeycomb

	Bonded Sheets of Polyamide: Nomex ^a	Light Alloy AG3	Light Alloy 2024
Dia. (D): inscribed circle (mm)	6; 8; 12	4	6
Thickness e (mm)		0.05	0.04
Specific mass (kg/m ³)	64	80	46
Shear strength $\tau_{xz\ rup}$ (MPa)	1.7	3.2	1.5
Shear modulus: G_{xz} (MPa) # 1.5 $G_{mat}(e/D)$	58	520	280
Shear strength $\tau_{yz\ rup}$ (MPa)	0.85	2	0.9
Shear modulus: G_{yz} (MPa)	24	250	140
Compression strength: $\sigma_z\ rup$ (MPa)	2.8	4.4	2

^aNomex® is a product of Du Pont de Nemours.

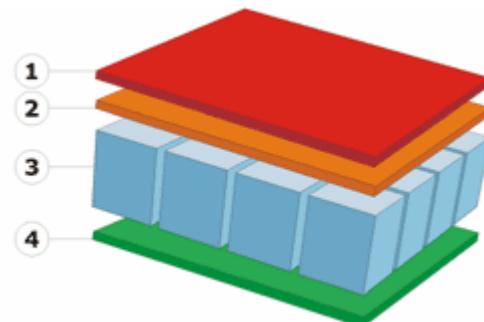


Fiber Reinforcement

Sandwich composites

Almost all of the fiber-reinforced composite types discussed above can be utilized in complex curved geometries although the manufacturing process may be much more costly and difficult. For example, wound fiber-reinforced pressure vessels are common and are manufactured by winding either individual fiber filaments on a mandrel (having the shape of the vessel) or individual plies are wound on the mandrel. Curved composite material panels on aircraft wings, fuselage and nacelles are common

- 1.- Decor** - the top layer that gives kayak its color and protects from the environment
- 2.- Top fiber reinforced plastic layer** - protection against tears and impacts
- 3.- The foam core** - makes the kayak rigid and unsinkable
- 4.- Inner fiber reinforced plastic layer** - more rigidity and inner finish of the kayak



Fiber Reinforcement

Sandwich composites

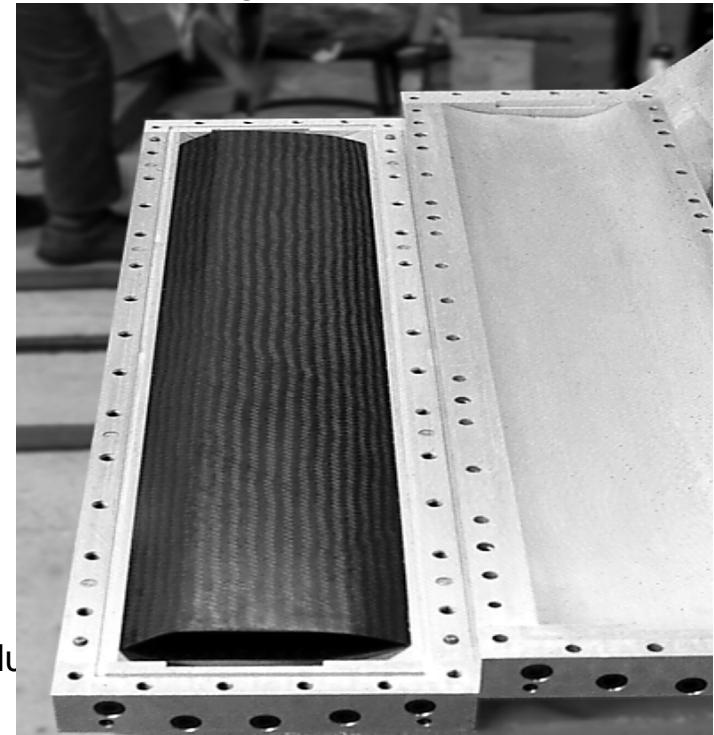
All of the composite types have various manufacturing processes required to bond individual plies. Common glass-epoxy composites must be *cured* using a high temperature and vacuum (or pressure) process designed not only to bond individual plies but also to minimize residual laminae and interlaminar stresses.



Fiber Reinforcement

CARBON FIBER

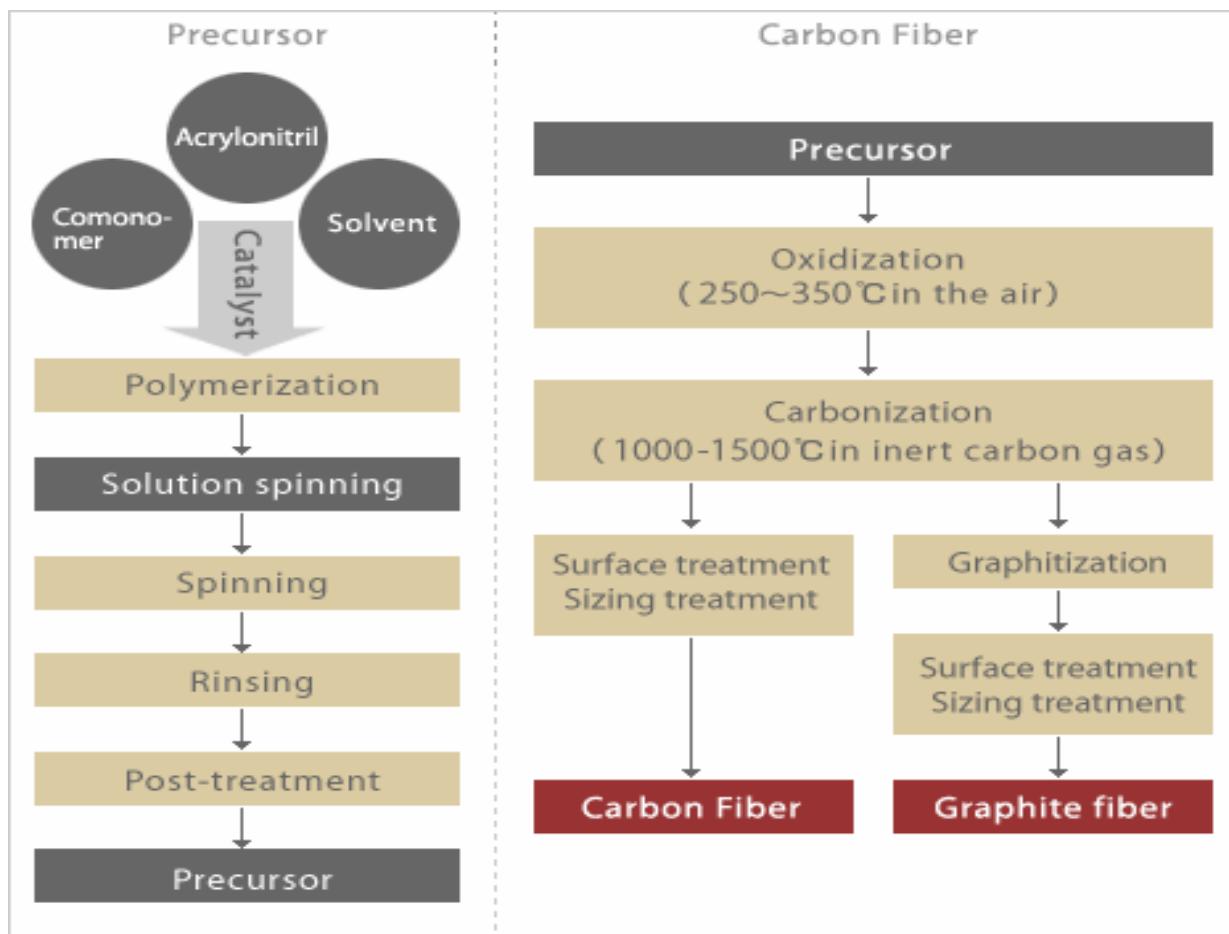
Graphite or carbon fibers are the most widely used advanced fiber, and graphite/epoxy or carbon/epoxy composites are now used routinely in aerospace structures. The actual fibers are usually produced by subjecting organic precursor fibers such as polyacrylonitrile (PAN) or rayon to a sequence of heat treatments, so that the precursor is converted to carbon by pyrolysis. Graphite fibers are typically subjected to higher heat treatments than are carbon fibers. Carbon fibers are typically 90-95% carbon, whereas graphite fibers are at least 99% carbon.



Fiber Reinforcement

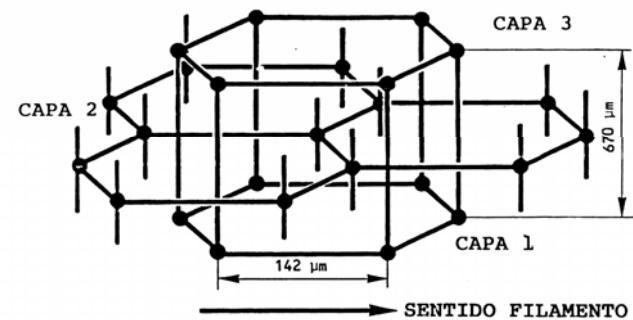
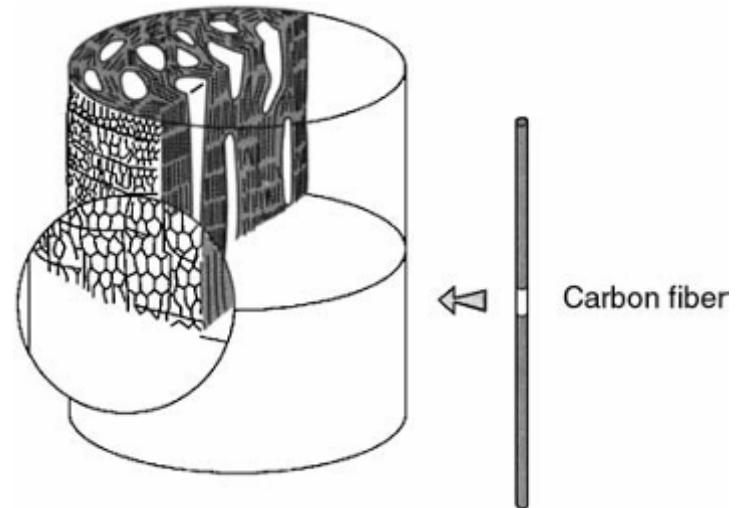
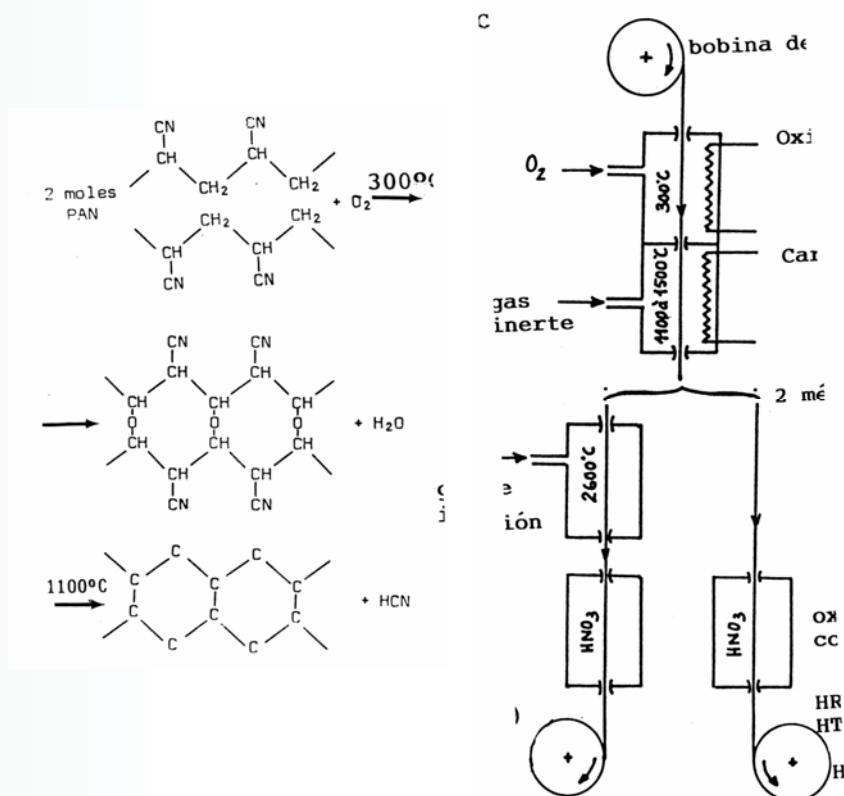
How obtain CARBON FIBER?

Manufacturing process of carbon fiber (PAN based) I



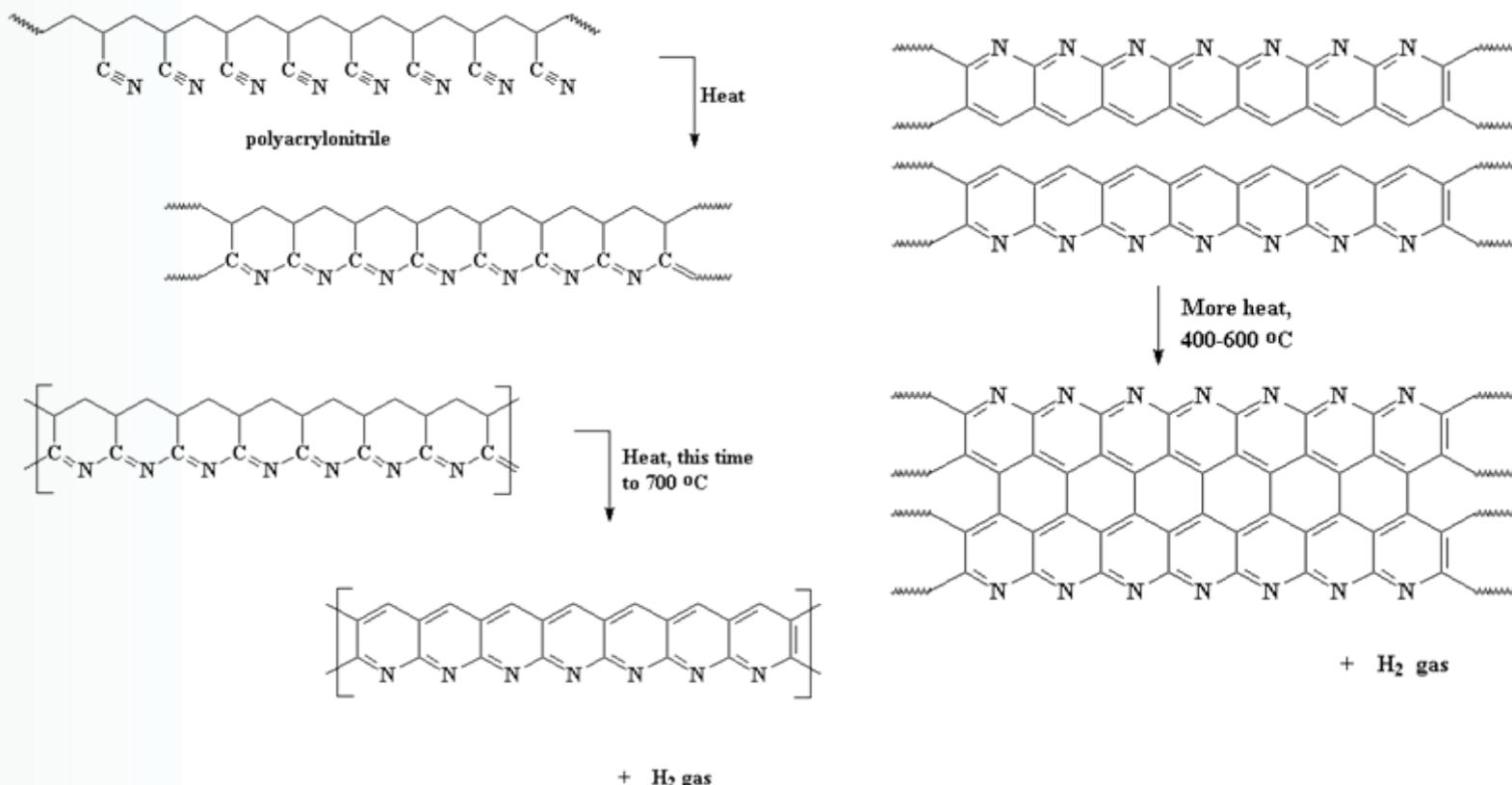


Manufacturing process of carbon fiber (PAN based) II





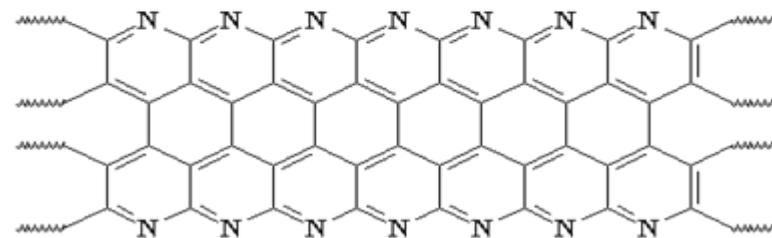
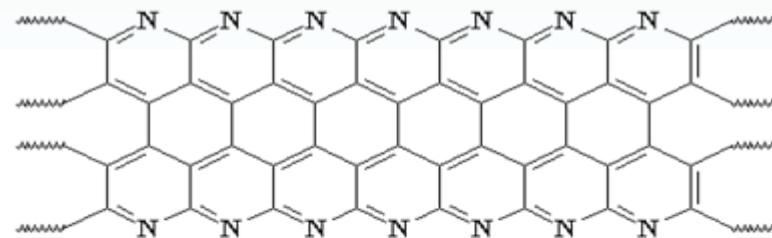
Manufacturing process of carbon fiber (PAN based) III



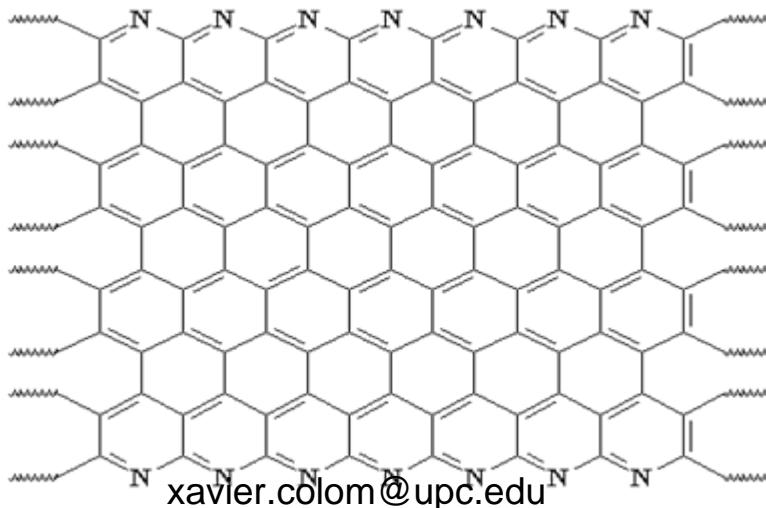


Fiber Reinforcement

CARBON FIBER

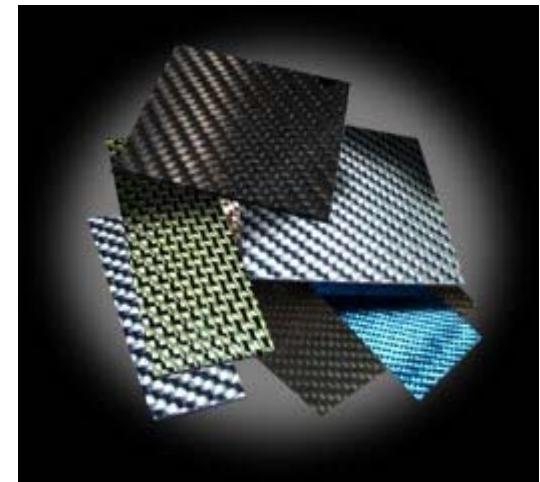


↓
still more heat,
600 to 1300 °C



Forms of Reinforcement Architectures

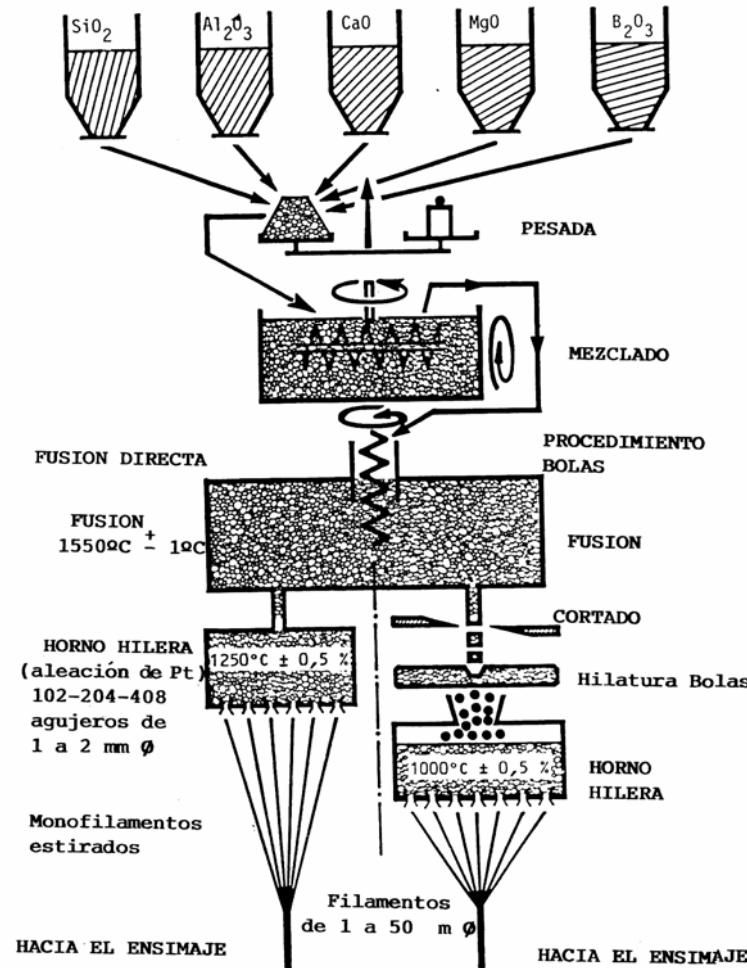
Twill-Weave Carbon Fiber Sheets: Twill-Weave sheets have a very bold appearance. Great for cosmetic applications, as well as when you need a lightweight, yet rigid material. The thicker you choose, the more rigid the sheet.



Glass fibers consist primarily of silica (silicon dioxide) and metallic-oxide-modifying elements are generally produced by mechanical drawing of molten glass through a small orifice. E-glass accounts for most of the glass fiber production and is the most widely used reinforcement for composites. The second most popular glass fiber, S-glass, has roughly 30 percent greater tensile strength and 20 percent greater modulus of elasticity than E-glass but is not as widely used because of its higher cost.

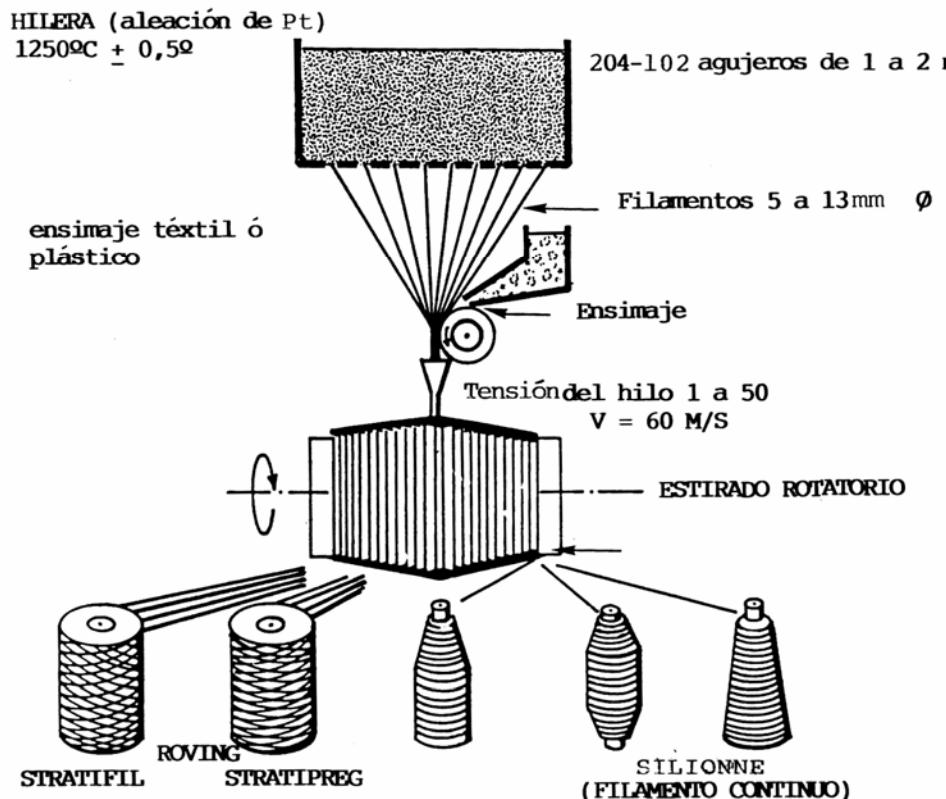


Manufacturing process of Glass Fiber





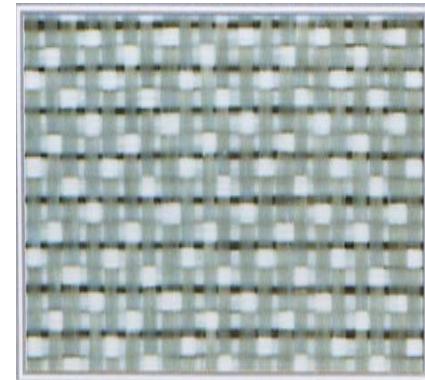
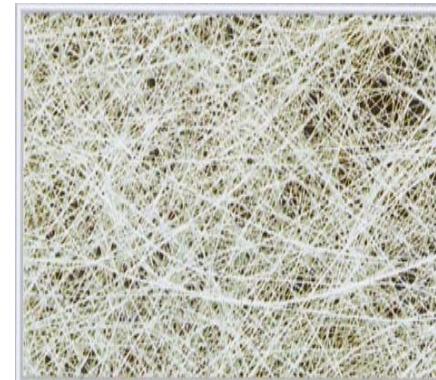
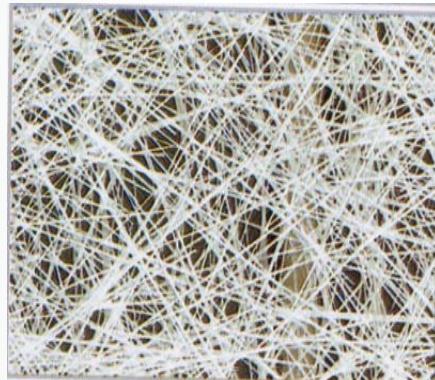
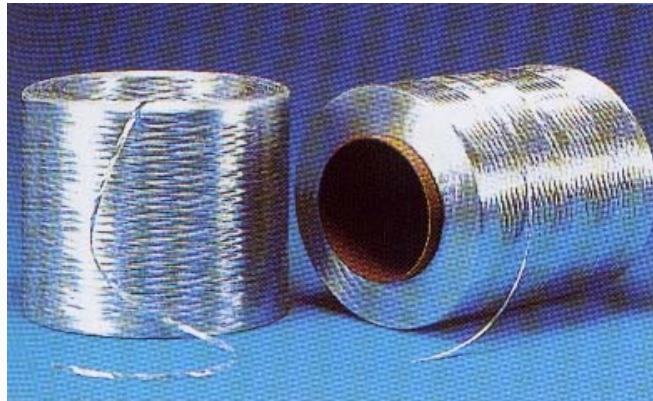
Manufacturing process of Glass Fiber





Fiber Reinforcement

GLASS FIBER



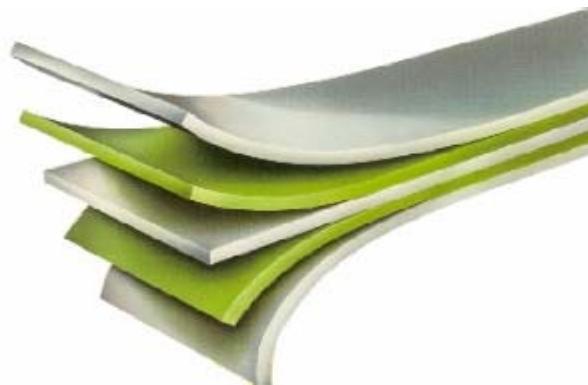


Fiber Reinforcement

ARAMID FIBER

Composite Materials

Aramid polymer fibers, produced primarily by E.I. DuPont de Nemours & Company under the tradename "Kevlar®," were originally developed for use in radial tires. The density of Kevlar is about half that of glass and its specific strength is among the highest of currently available fibers. Kevlar also has excellent toughness, ductility, and impact resistance; unlike brittle glass or graphite fibers.

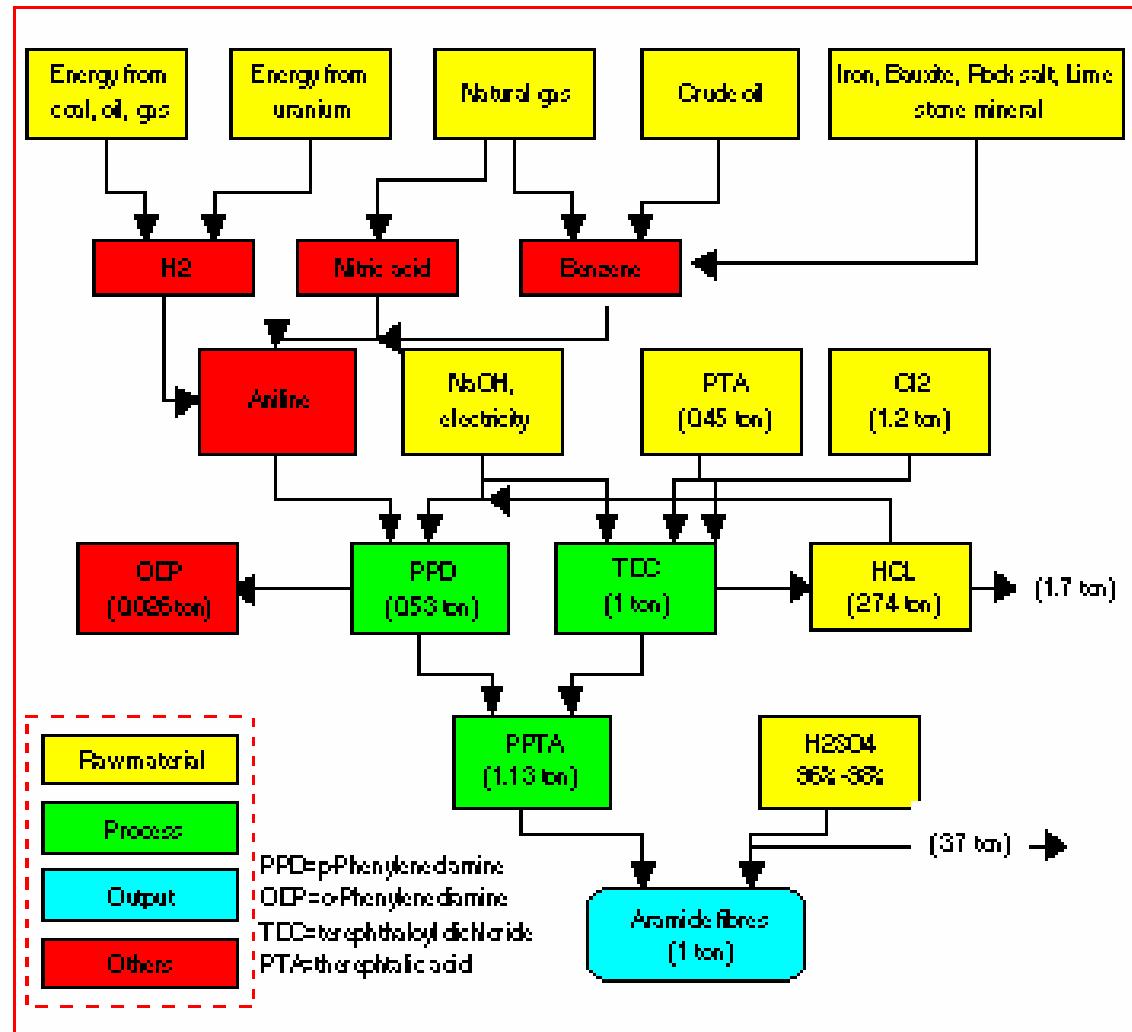




Fiber Reinforcement

ARAMID FIBER

Composite Materials





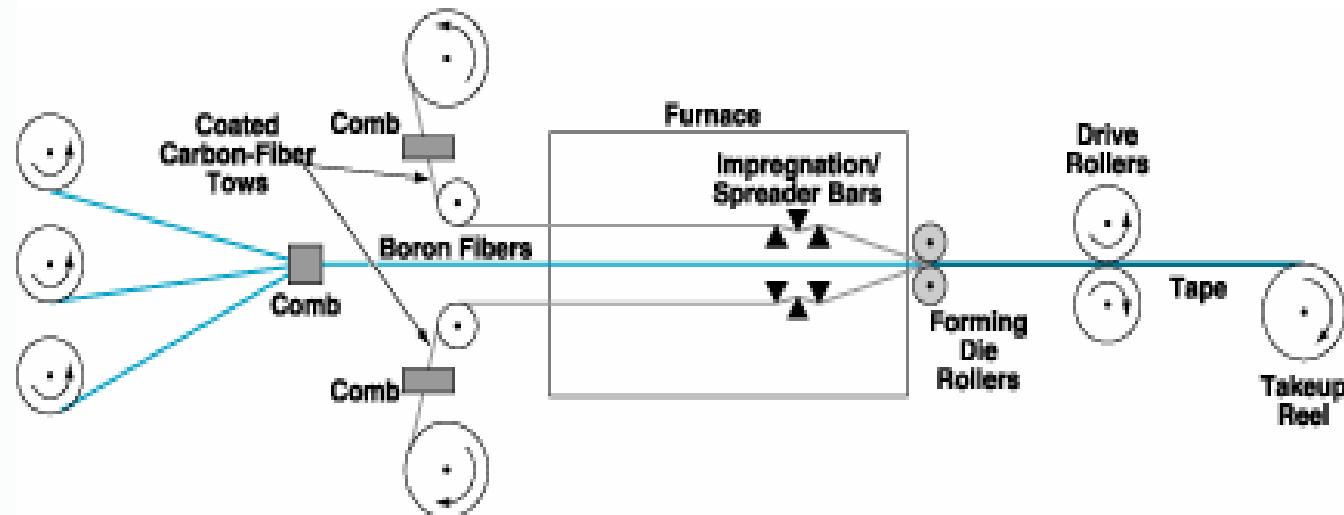
Fiber Reinforcement

BORON FIBER

Composite Materials

Boron fibers are actually composites consisting of a boron coating on a substrate of tungsten or carbon. The diameter of boron fibers is among the largest of all the advanced fibers, typically 20-25 microns. Boron fibers have much higher strength and stiffness than graphite, but they also have higher density. Boron/epoxy and boron/aluminum composites are widely used in aerospace structures, but high cost prevents more widespread use.

This is used for vertical stabilizer boxes and horizontal stabilizer boxes



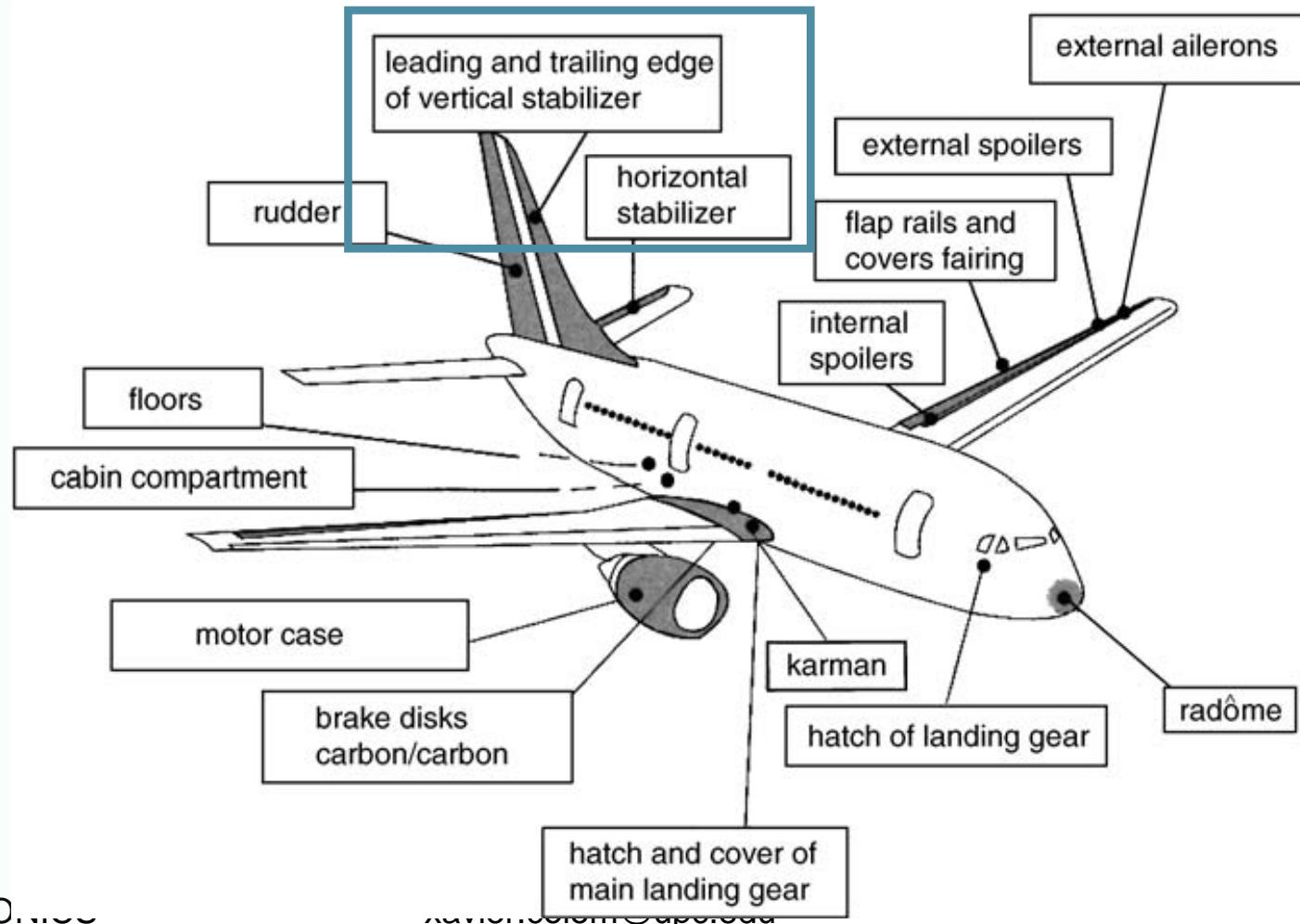


Fiber Reinforcement

BORON FIBER

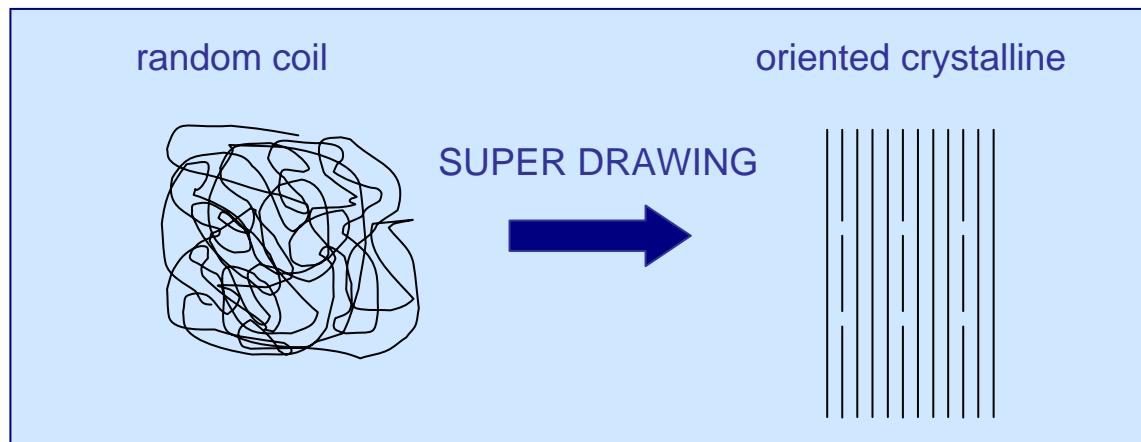
Composite Materials

This is used for vertical stabilizer boxes and horizontal stabilizer boxes





Ultra-high molecular weight polyethylene is dissolved in a solvent and then spun through small orifices (spinneret). Successively, the **spun solution is solidified by cooling, which fixes a molecular structure** which contains a very low entanglement density of molecular chain. This structure gives an extremely high draw ratio and results in extremely high strength. The highly drawn fiber contains an almost **100% crystalline structure with perfectly arranged molecules**, which promotes its extremely high strength, modulus, and other excellent properties.

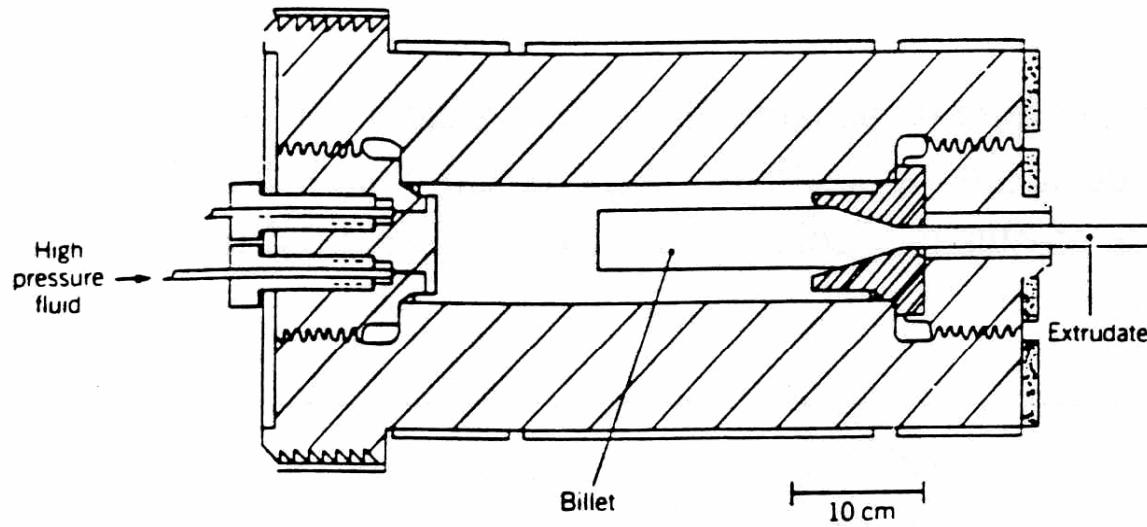




Fiber Reinforcement

UHMWPE FIBER

Composite Materials



Fiber Reinforcement

UHMWPE FIBER

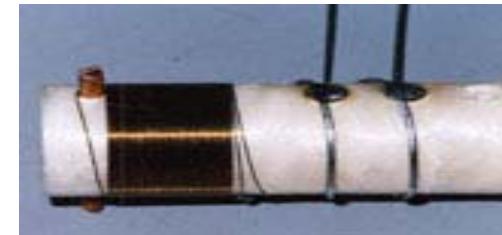
Ropes



nets



Sports/cryogenic





Fiber Reinforcement

MECHANICAL PROPERTIES

REFUERZO	VIDRIO		OLEF	FC			ARAMIDA	
	E	S	PE	HT	HST	HM	K29	K49
Densidad (g/mL)	2.6	2.5	0.97	1.7	1.7	1.75	1.4	1.43
Resistencia Tracción (GPa)	3.4	4.5	3.0	3.3	6.2	3.0	2.9	3.0
Deformación a rotura (%)	4.3	5.0	3.4	1.3	2.2	0.7	4.1	2.1
Módulo de Young (GPa)	73	87	150	230	250	450	64	150
Φ filamento (micras)	20	20	35	7	6	6	12	12



Fiber Reinforcement

MECHANICAL PROPERTIES : COMPARATIVE STUDY BEETWEN MATERIALS

✿ Acero

◆ Al

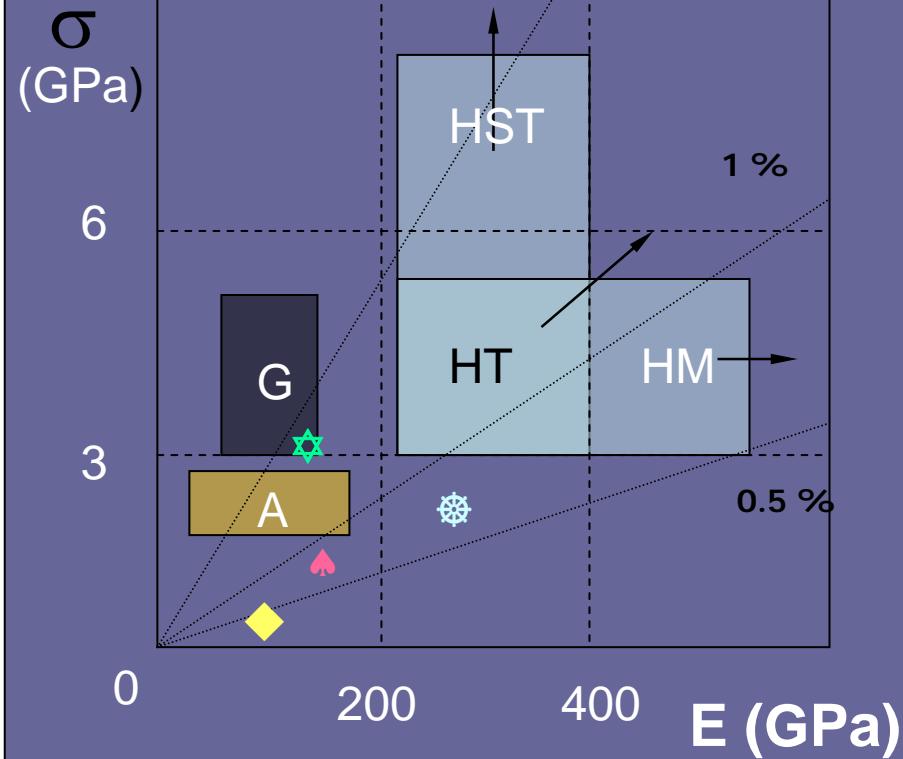
♠ Ti

◊ UHMWPE

2 %

1 %

0.5 %



2 %

1 %

0.5 %

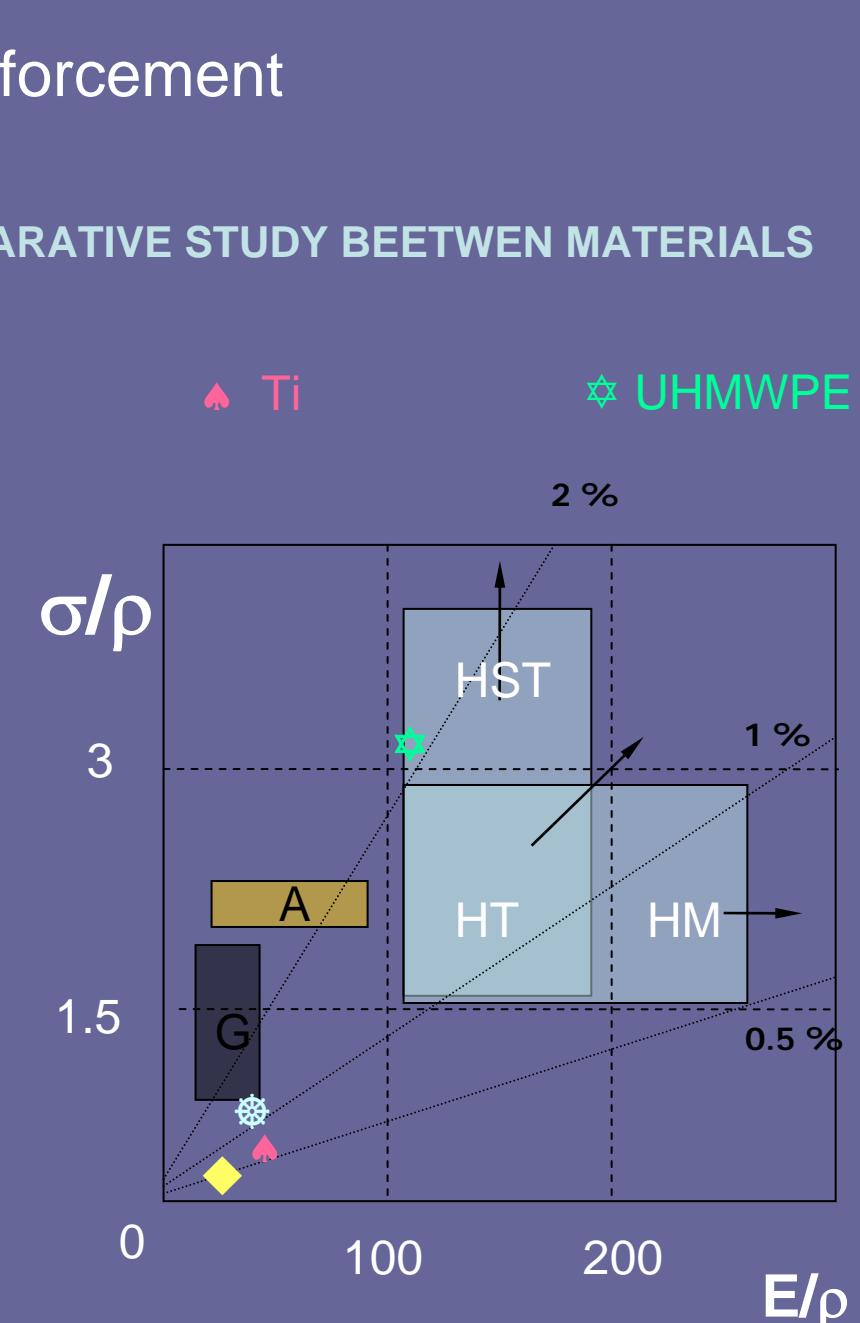
σ/ρ

1.5

3

0

E/ρ





Fiber Reinforcement

MECHANICAL PROPERTIES : COMPARATIVE STUDY COMPOSITES

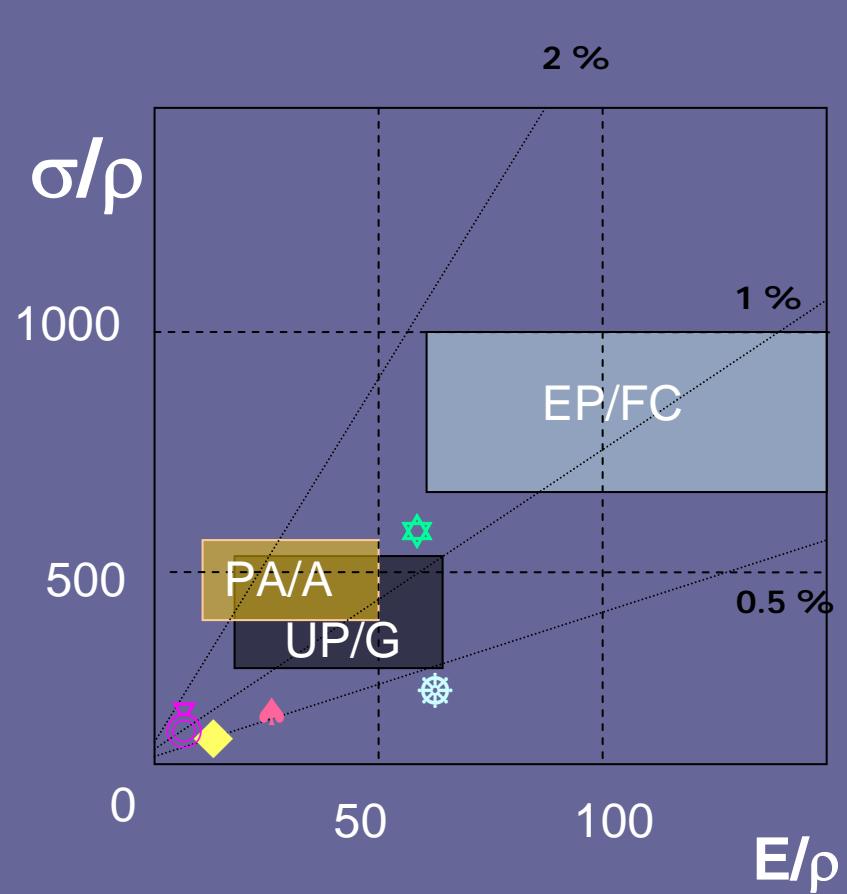
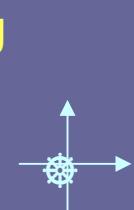
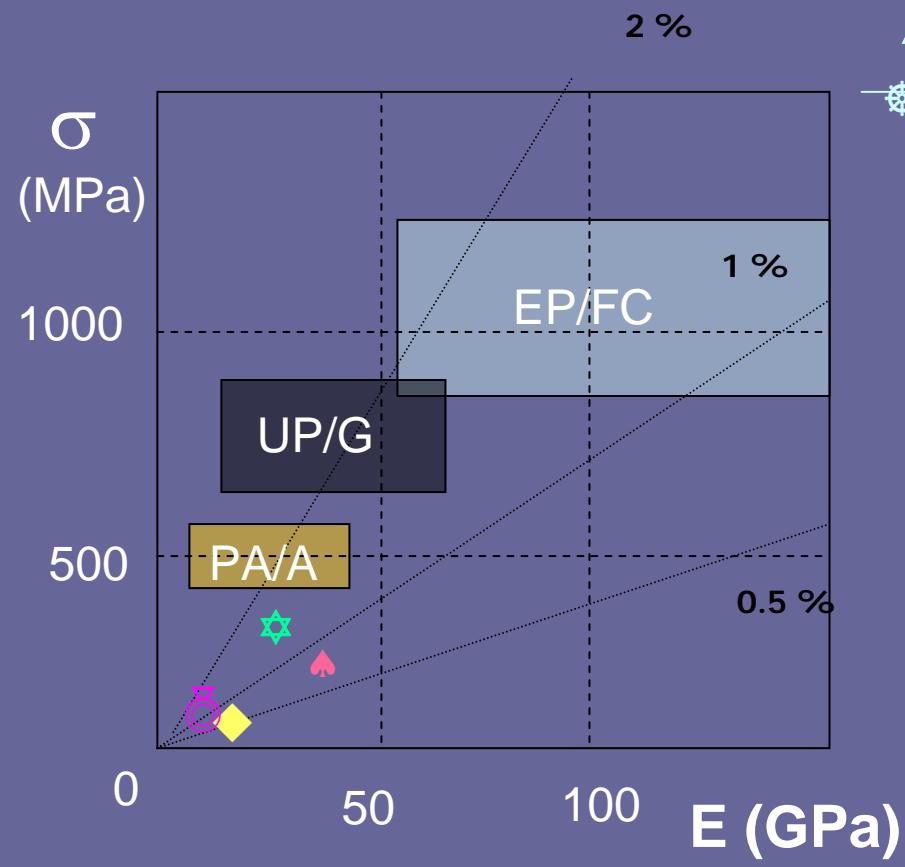
✿ Acero

◆ Al-Zn-Mg

○ Ni

♠ Ti

◊ UHMWPE / PP



Polymers, metals and ceramics are all used as matrix materials in composites. The matrix holds the fibers together in a structural unit, protects them from external damage, transfers and distributes the applied loads to the fibers, contributes some needed property such as **ductility, toughness, or electrical insulation**.

Because the matrix must transfer load to the fibers, a strong interface bond between the fiber and matrix is extremely important; either through a mechanical or chemical bond between fibers and matrix. Fibers and matrix must obviously be chemically compatible to prevent undesirable reactions at the interface; this is especially important at high temperature where chemical reactions can be accelerated.

Service temperature is quite often a controlling factor in consideration of a matrix material.



Matrix

Composite Materials

Polymers are the most widely used matrix materials. They may be either thermosets (e.g., epoxy, polyester, phenolics) or thermoplastics (e.g., polyimide (PI), polyetheretherketone (PEEK), polyphenylene sulfide (PPS)).

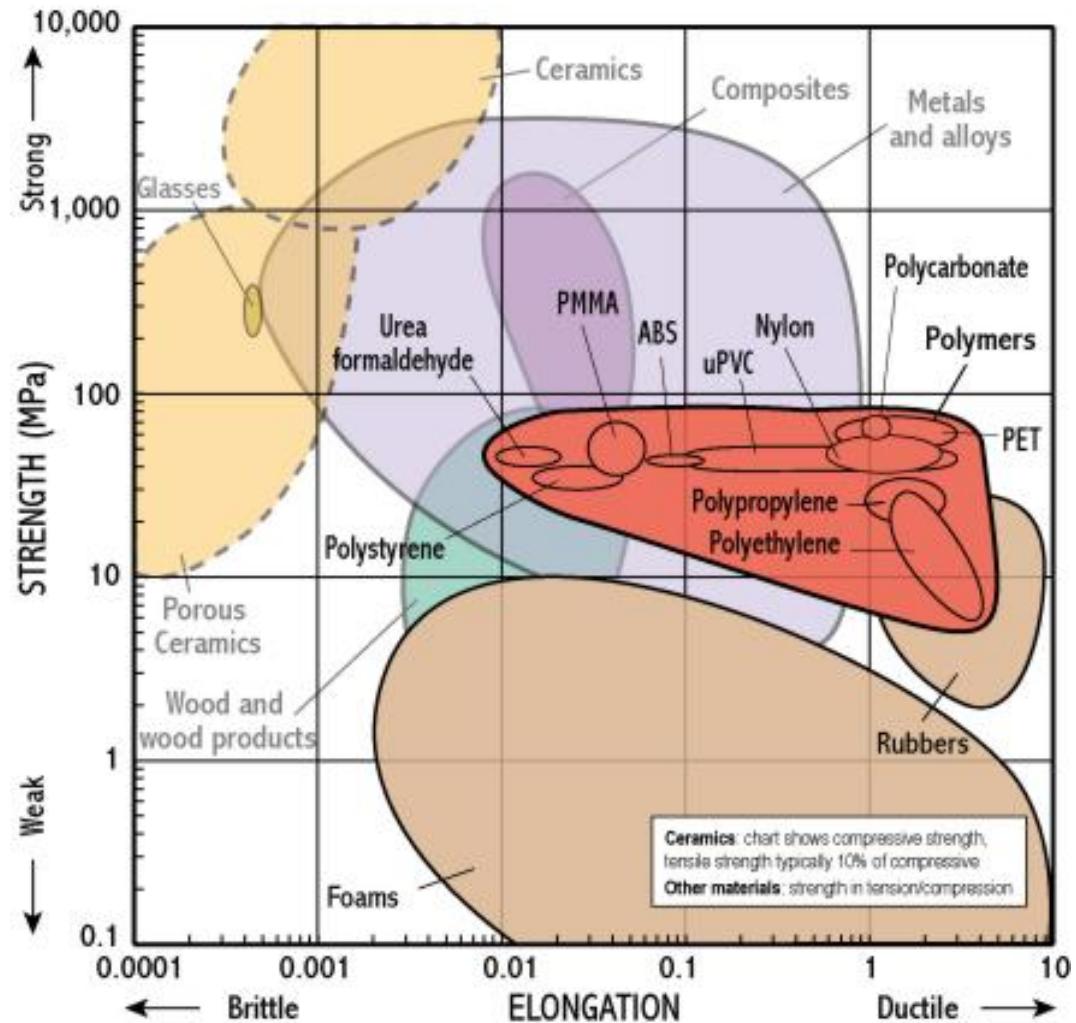
Upon curing, thermosets form a highly cross-linked, three-dimensional molecular network which does not melt at high temperature. Thermoplastics, however, are based on polymer chains that do not cross-link. As a result, thermoplastics will soften and melt at high temperature, then harden again upon cooling.



Polymer Matrix Composites

Basic Concepts

Resin systems such as epoxies and polyesters have limited use for the manufacture of structures on their own, since their mechanical properties are not very high when compared to, for example, most metals. However, they have desirable properties, most notably their ability to be easily formed into complex shapes.





Thermoplastics versus thermosets

Advantages of thermoplastic matrices

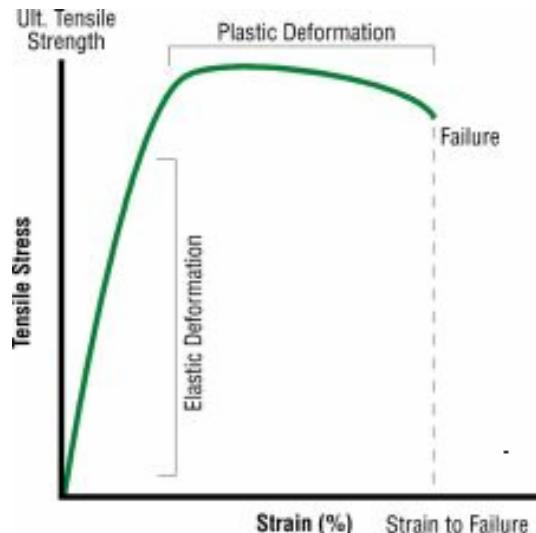
- Impact resistance
- High elongation at break
- Good resistance of flexion and compression
- Inert Chemical
- Recycled and sustainability
- No contraction

Disadvantages of thermoplastic matrices

- High T and P to mold
- Problems with the reinforced impregnation
- Compatibility

Any resin system for use in a composite material will require the following properties:

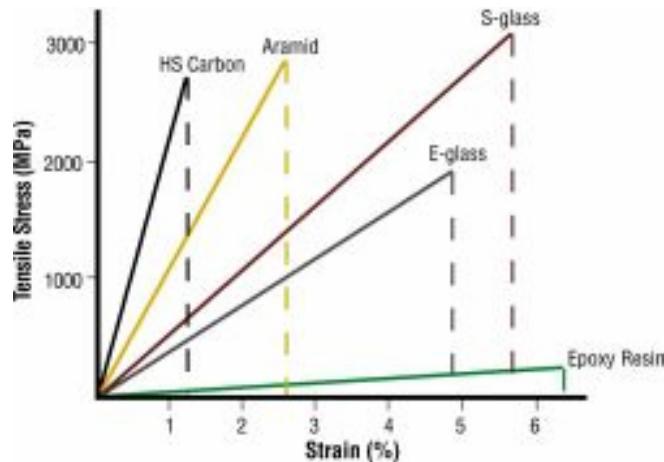
- Good mechanical properties
- Good adhesive properties
- Good toughness properties
- Good resistance to environmental degradation

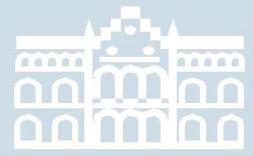


Mechanical Properties of the Resin System

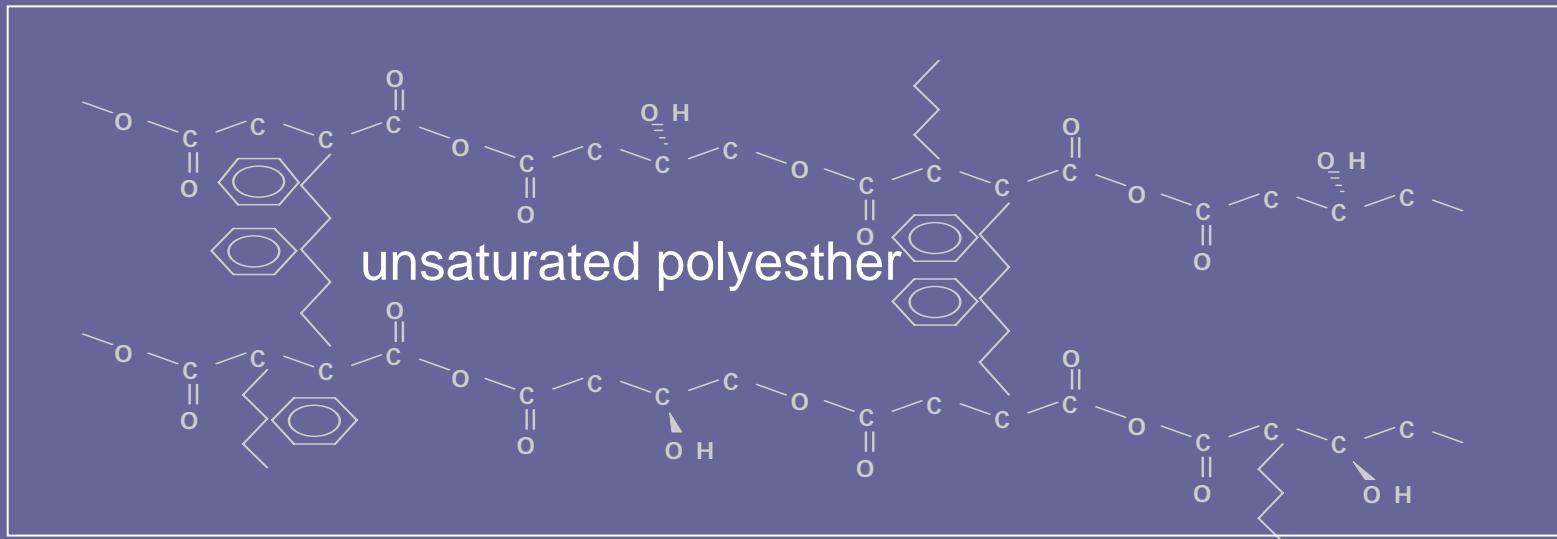
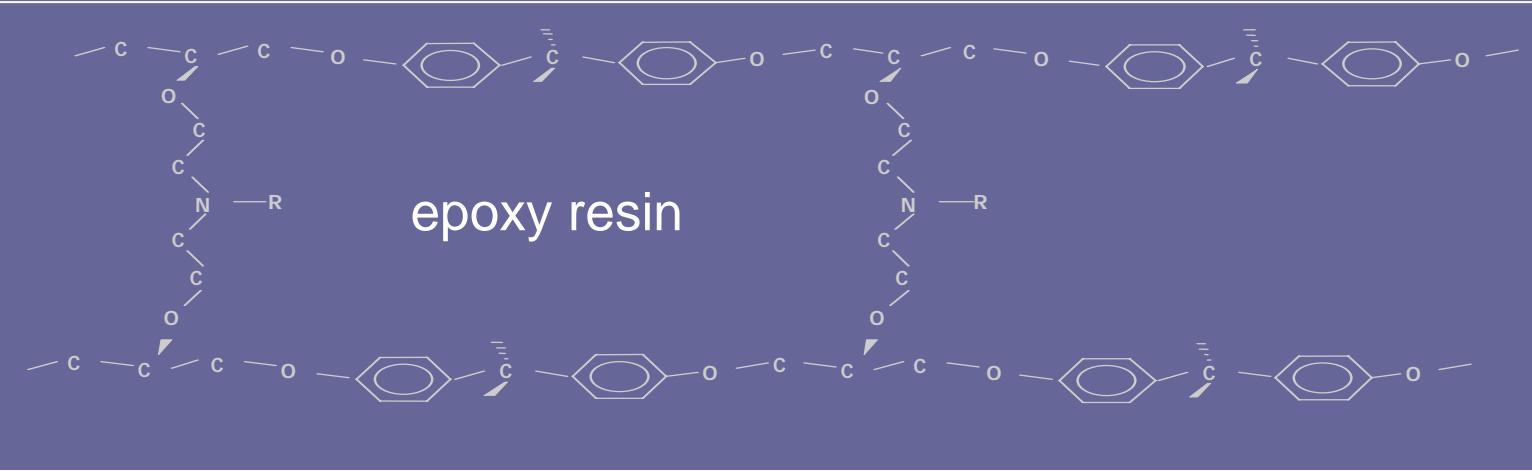
The figure shows the stress / strain curve for an 'ideal' resin system. The curve for this resin shows high ultimate strength, high stiffness (indicated by the initial gradient) and a high strain to failure. This means that the resin is initially stiff but at the same time will not suffer from brittle failure.

It should also be noted that when a composite is loaded in tension, for the full mechanical properties of the fibre component to be achieved, the resin must be able to deform to at least the same extent as the fibre. The figure below gives the strain to failure for E-glass, S-glass, aramid and high-strength grade carbon fibres on their own (i.e. not in a composite form). **Here it can be seen that, for example, the S-glass fibre, with an elongation to break of 5.3%, will require a resin with an elongation to break of at least this value to achieve maximum tensile properties.**





Thermoset matrices





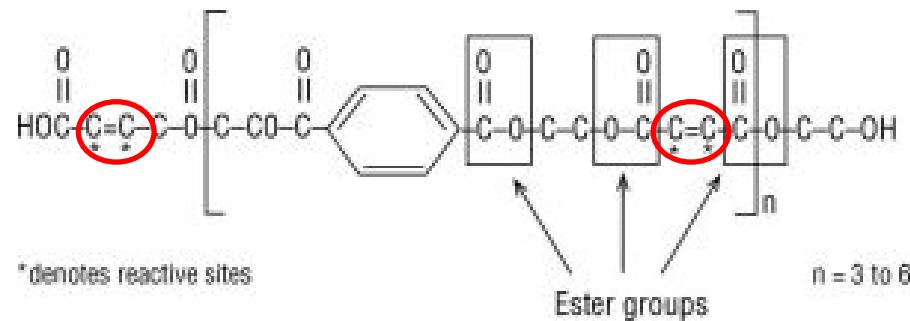
Polymer Matrix Composites

Polyester Resins

Polyester resins are the most widely used resin systems, particularly in the marine industry. (yachts and workboats built in composites make use of this resin system).

Polyester resins such as these are of the 'unsaturated' type. Unsaturated polyester resin is a thermoset, capable of being cured from a liquid or solid state when subject to the right conditions. There is a whole range of polyesters made from different acids, glycols and monomers, all having varying properties.

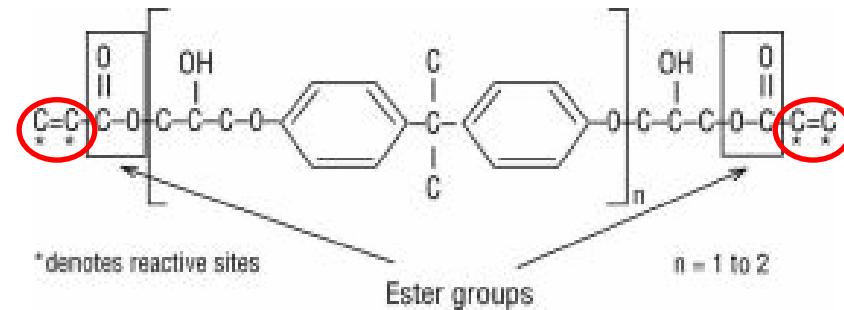
There are two principle types of polyester resin used as standard laminating systems in the composites industry. Orthophthalic polyester resin is the standard economic resin used by many people. Isophthalic polyester resin is now becoming the preferred material in industries such as marine where its superior water resistance is desirable.



Polymer Matrix Composites

Vinylester resins

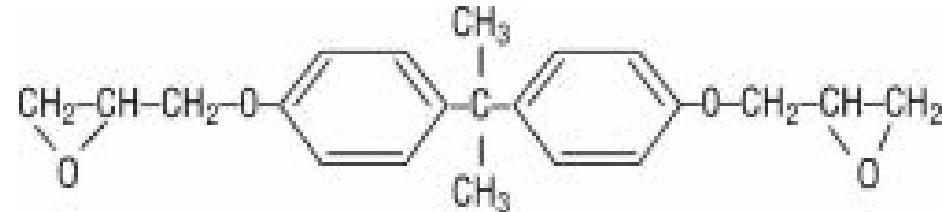
Vinylester resins are similar in their molecular structure to polyesters, but differ primarily in the location of their reactive sites, these being positioned only at the ends of the molecular chains. As the whole length of the molecular chain is available to absorb shock loadings **this makes vinylester resins tougher and more resilient than polyesters**. The vinylester molecule also features fewer ester groups. These ester groups are susceptible to water degradation by hydrolysis which means that vinylesters exhibit better resistance to water and many other chemicals than their polyester counterparts, **and are frequently found in applications such as pipelines and chemical storage tanks**.



Polymer Matrix Composites

Epoxy Resins

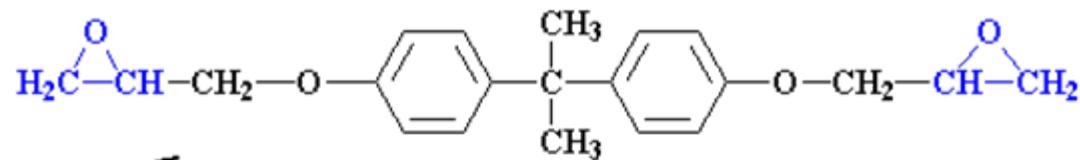
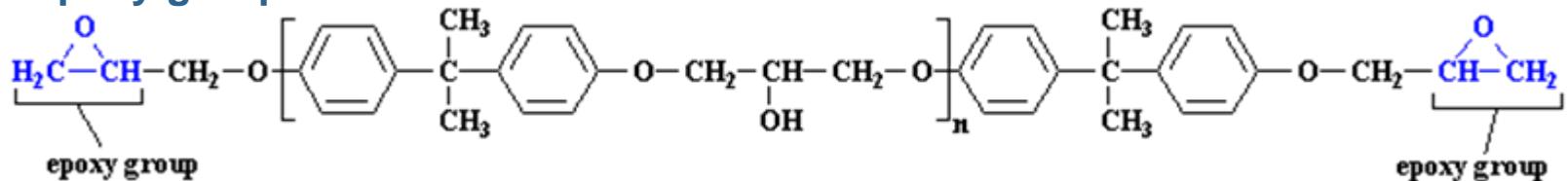
The large family of epoxy resins represent some of the highest performance resins of those available at this time. Epoxies generally out-perform most other resin types in terms of mechanical properties and resistance to environmental degradation, which leads to their almost exclusive use in aircraft components. **As a laminating resin their increased adhesive properties and resistance to water degradation make these resins ideal for use in applications such as boat building. Here epoxies are widely used as a primary construction material for high-performance boats or as a secondary application to sheath a hull or replace water-degraded polyester resins and gel coats.**



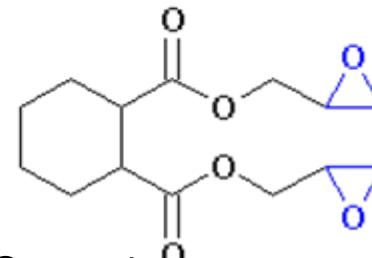
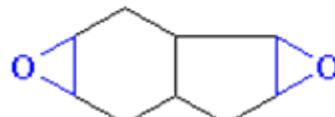
Epoxies differ from polyester resins in that they are cured by a 'hardener' rather than a catalyst. The hardener, often an amine, is used to cure the epoxy by an 'addition reaction' where both materials take place in the chemical reaction. The chemistry of this reaction means that there are usually two epoxy sites binding to each amine site. This forms a complex three-dimensional molecular structure.

Epoxy resins-Chemistry

The first part of the two-part epoxy is a low-molecular-weight polymer with epoxy groups at each end. In these prepolymers n can be as high as 25, but the diepoxy in two-part epoxy adhesive is more likely a small molecule with two epoxy groups.

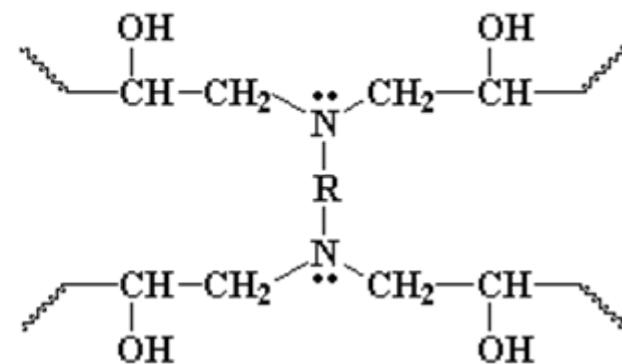
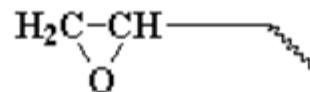
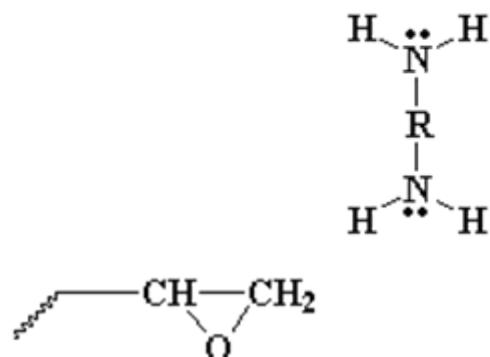
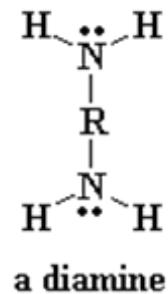
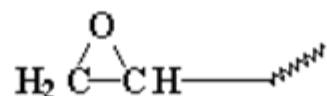
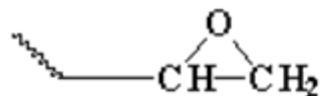


This is a small molecule diepoxy. You can think of it as the polymer shown above with a degree of polymerization of one. Some other diepoxy small molecules are shown below.



Epoxi resins-Chemistry

The second part is a diamine:

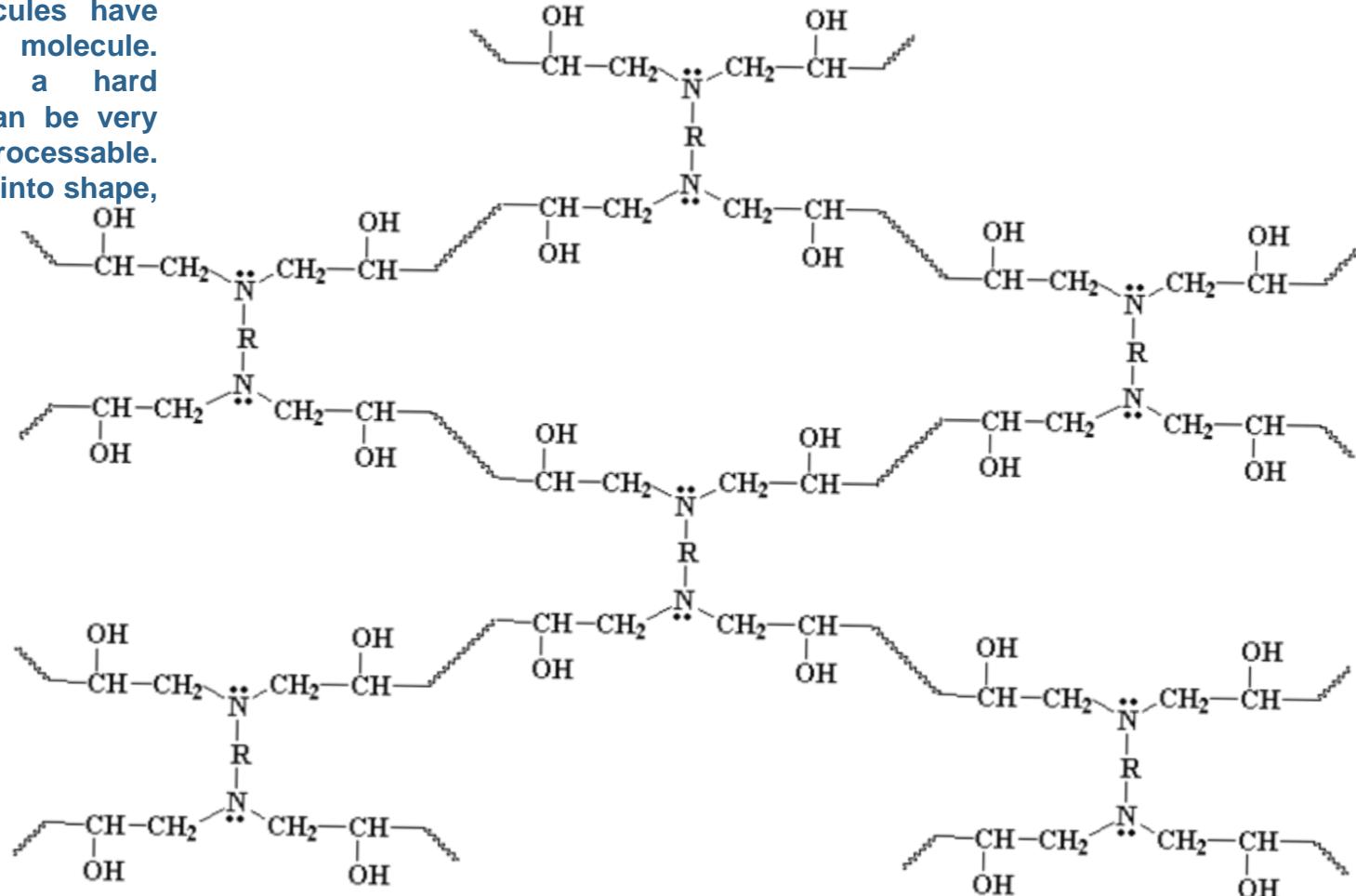


They react, and join together, in such a way that links all the diepoxy and diamine molecules together

Epoxi resins-Chemistry

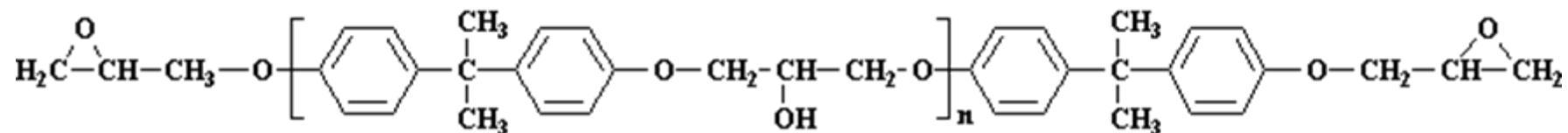
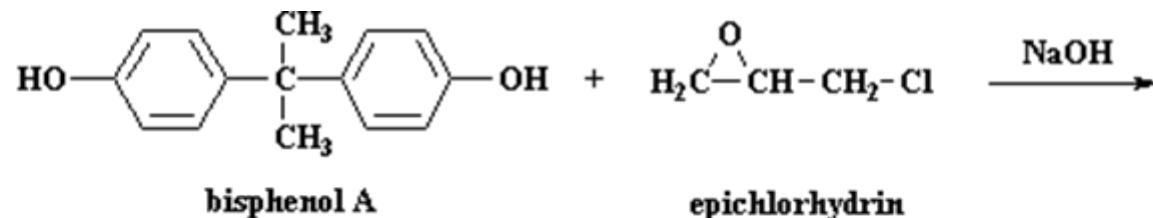
crosslinked network

The epoxy molecules have become one big molecule. The result is a hard substance that can be very strong, but not processable. It can't be molded into shape, or even melted.



Epoxi resins-Chemistry

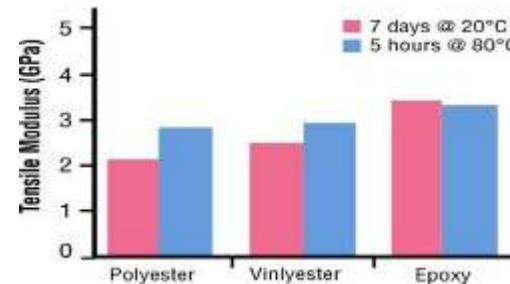
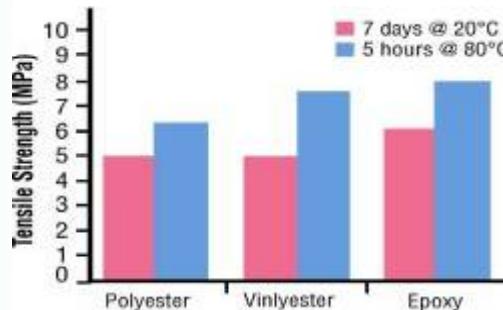
The first component is made by reacting bisphenol A with epichlorohydrin with some NaOH thrown in as a catalyst.



Polymer Matrix Composites

Mechanical Properties

Two important mechanical properties of any resin system are its tensile strength and stiffness. The two figures below show results for tests carried out on commercially available polyester, vinylester and epoxy resin systems



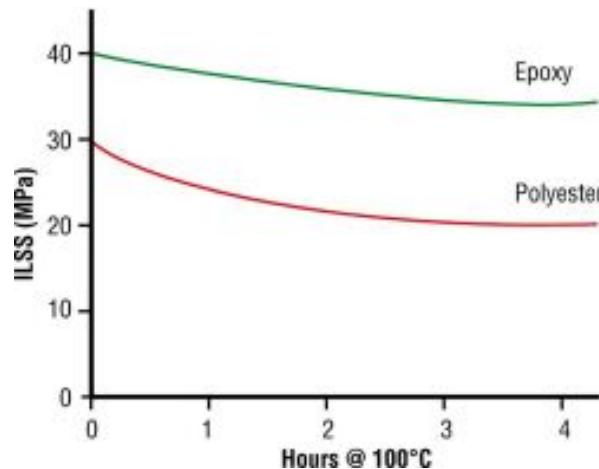
After a **cure period of seven days** at room temperature it can be seen that a typical epoxy will have higher properties than a typical polyester and vinylester for both strength and stiffness. The beneficial effect of a post cure at 80C for five hours can also be seen.

Also of importance to the composite designer and builder is the amount of shrinkage that occurs in a resin during and following its cure period. Shrinkage is due to the resin molecules rearranging and re-orientating themselves in the liquid and semi-gelled phase. **Polyester and vinylesters** require considerable molecular rearrangement to reach their cured state and **can show shrinkage of up to 8%**. The different nature of the epoxy reaction, however, leads to very little rearrangement and with no volatile by-products being evolved, **typical shrinkage of an epoxy is reduced to around 2%**. The absence of shrinkage is, in part, responsible for the improved mechanical properties of epoxies over polyester, as shrinkage is associated with built-in stresses that can weaken the material. Furthermore, shrinkage through the thickness of a laminate leads to 'print-through' of the pattern of the reinforcing fibres, a cosmetic defect that is difficult and expensive to eliminate.

Polymer Matrix Composites

Degradation from water

An important property of any resin, particularly in a marine environment, is its ability to withstand degradation from water ingress. All resins will absorb some moisture, adding to a laminate's weight, but what is more significant is how the absorbed water affects the resin and resin/fibre bond in a laminate, leading to a gradual and long-term loss in mechanical properties. Both polyester and vinylester resins are prone to water degradation due to the presence of hydrolysable ester groups in their molecular structures. **As a result, a thin polyester laminate can be expected to retain only 65% of its inter-laminar shear strength after immersion in water for a period of one year, whereas an epoxy laminate immersed for the same period will retain around 90%.**



Polymer Matrix Composites

Comparative summary of different resins

Resin matrix	advantage	disadvantage
Polyesters	Easy to use Lowest cost of resins available (1-2/kg)	Only moderate mechanical properties High styrene emissions in open moulds High cure shrinkage Limited range of working times
Vinylesters	Very high chemical/environmental resistance Higher mechanical properties than polyesters	Postcure generally required for high properties High styrene content Higher cost than polyesters (2-4/kg) High cure shrinkage
Epoxies	High mechanical and thermal properties High water resistance Long working times available Temperature resistance can be up to 140C wet / 220C dry Low cure shrinkage	More expensive than vinylesters (3-15/kg) Critical mixing Corrosive handling

Polymer Matrix Composites

Other polymers used as a matrix

Besides **polyesters, vinylesters and epoxies** there are a number of other thermosetting resin systems that are used where their unique properties are required:

- **Phenolics**

Primarily used where high fire-resistance is required, phenolics also retain their properties well at elevated temperatures. For room-temperature curing materials, corrosive acids are used which leads to unpleasant handling. The condensation nature of their curing process tends to lead to the inclusion of many voids and surface defects, and the resins tend to be brittle and do not have high mechanical properties.

- **Cyanate Esters**

Primarily used in the aerospace industry. The material's excellent dielectric properties make it very suitable for use with low dielectric fibres such as quartz for the manufacture of radomes. The material also has temperature stability up to around 200C wet.

- **Polyurethanes**

High toughness materials, sometimes hybridised with other resins, due to relatively low laminate mechanical properties in compression. Uses harmful isocyanates as curing agent.

Polymer Matrix Composites

Other polymers used as a matrix

- **Bismaleimides (BMI)**

Primarily used in aircraft composites where operation at higher temperatures (230C wet/250C dry) is required. e.g. engine inlets, high-speed aircraft flight surfaces.

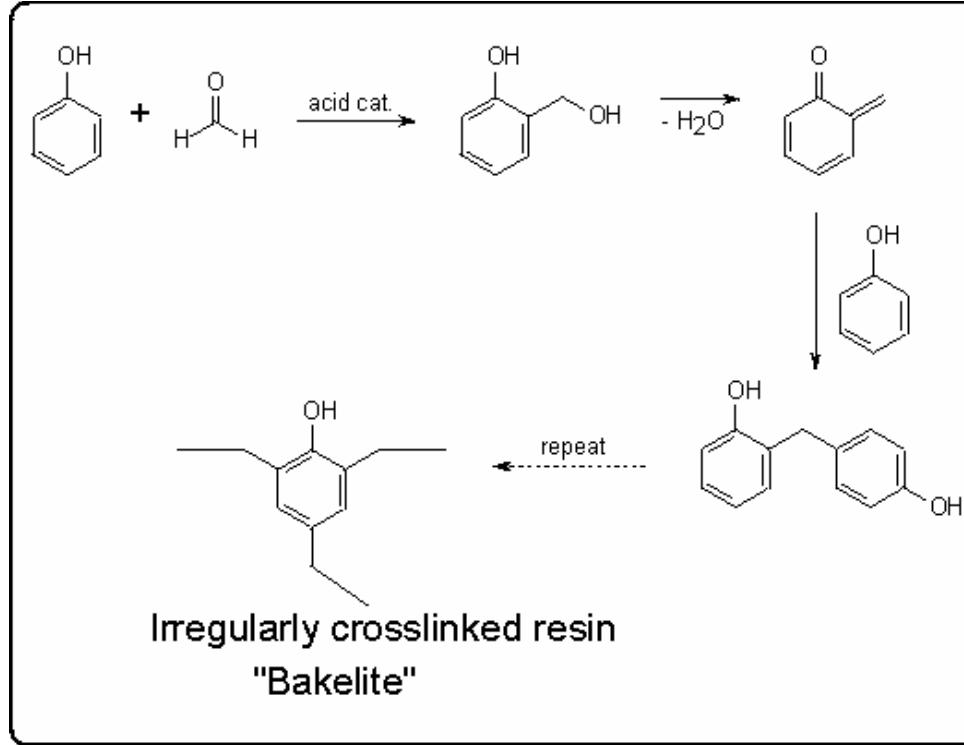
Typical costs: 50\$/kg.

- **Polyimides**

Used where operation at higher temperatures than bismaleimides can stand is required (use up to 250C wet/300C dry). Typical applications include missile and aero-engine components. Extremely expensive resin (>80\$/kg), which uses toxic raw materials in its manufacture. Polyimides also tend to be hard to process due to their condensation reaction emitting water during cure, and are relatively brittle when cured. PMR15 and LaRC160 are two of the most commonly used polyimides for composites.

Phenol formaldehyde resin

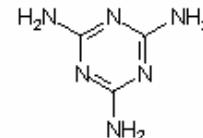
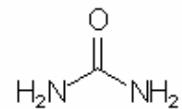
The earliest commercial synthetic resin is based on a Phenol formaldehyde resin with the commercial name **Bakelite**, and is formed from a elimination reaction of phenol with formaldehyde. Phenol is reactive towards formaldehyde at the ortho and para sites (sites 2, 4 and 6) allowing up to 3 units of formaldehyde to attach to the ring.



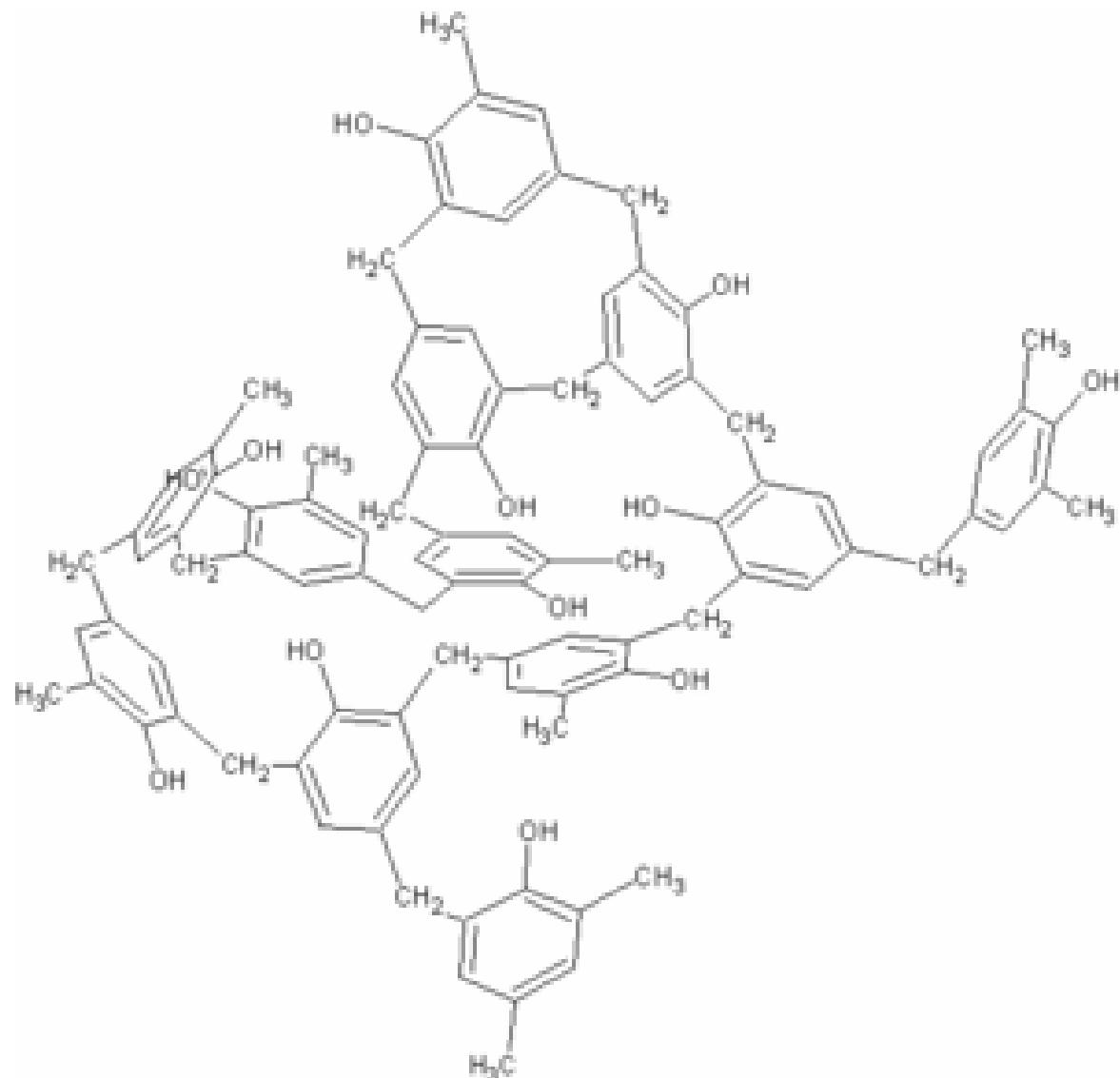
Phenol formaldehyde resins, as a group, are formed by a step-growth polymerization reaction which may be either acid or base catalysed. The pathway the reaction follows varies depending on the catalyst type used.

Relatives:

- cresol --> Novolak (photoresist polymer)
- urea - formaldehyde (outdoor plywood glue)
- melamine - formaldehyde (Formica countertops)



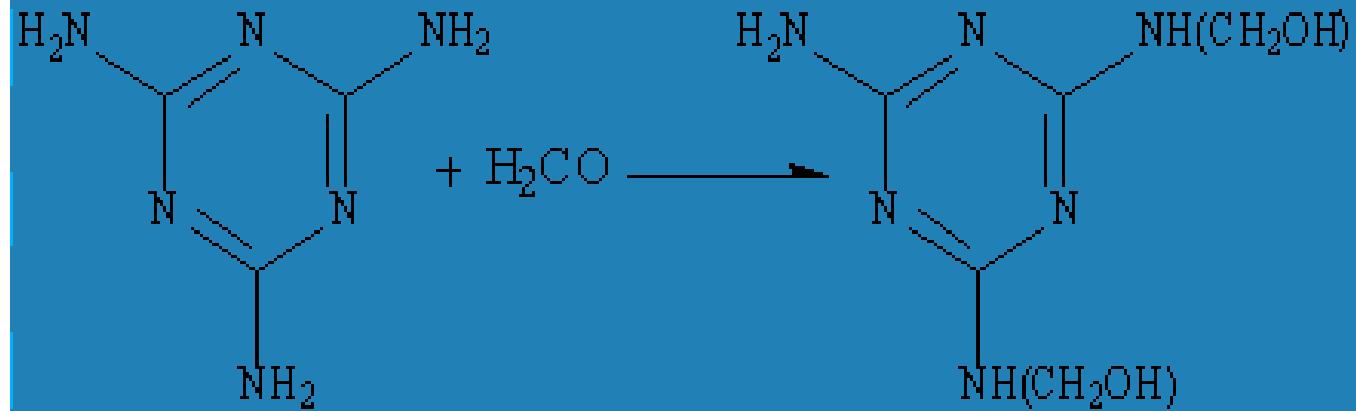
Phenol formaldehyde resin estructure of Bakelite



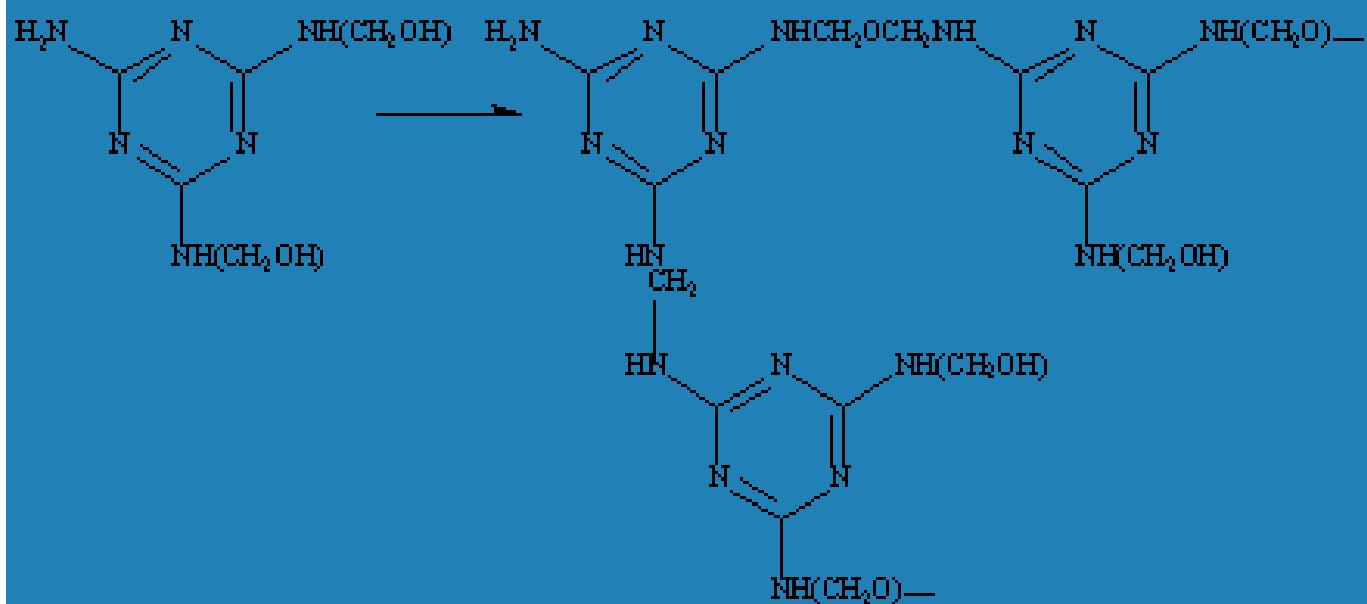
Urea Formaldehyde - UF Urea



Melamine and formaldehyde reaction – I. *(Methylation)*

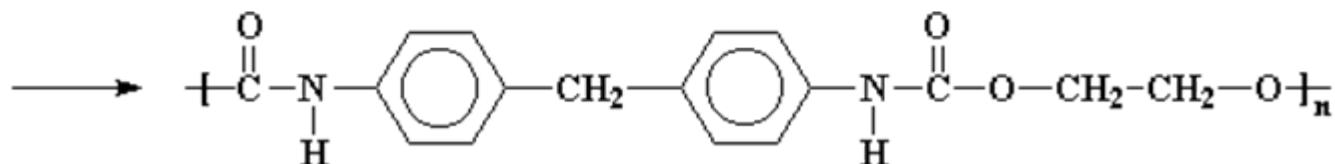
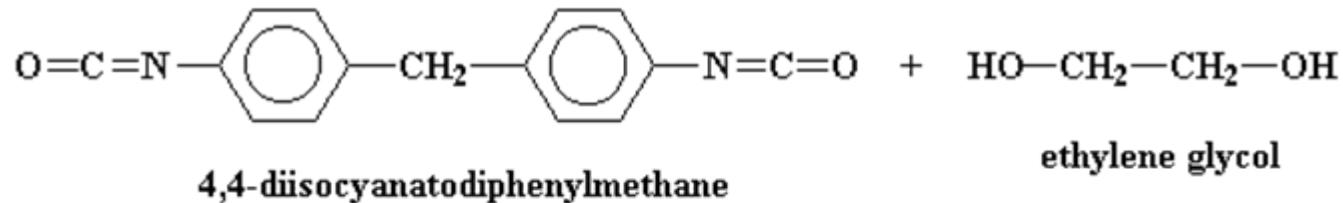


Melamine and formaldehyde reaction – II. *(Condensation)*



Polyurethanes PUR preparation

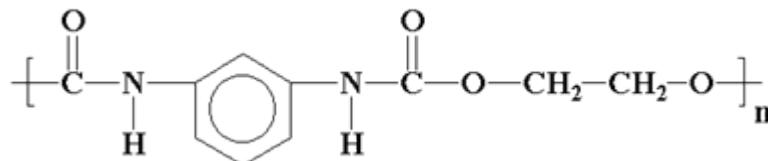
Polyurethanes are made by reacting diisocyanates with di-alcohols.



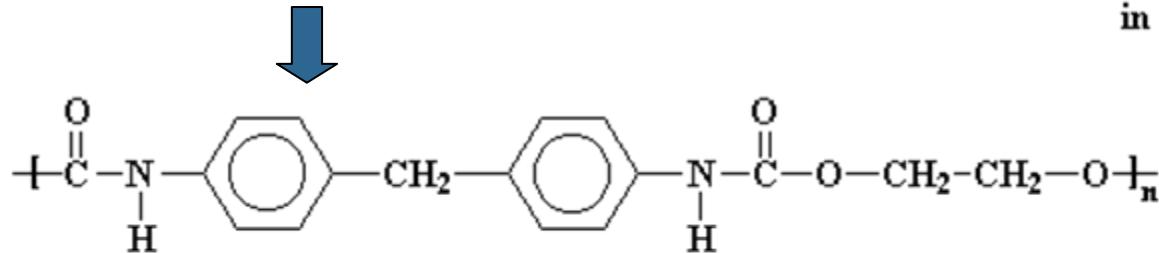
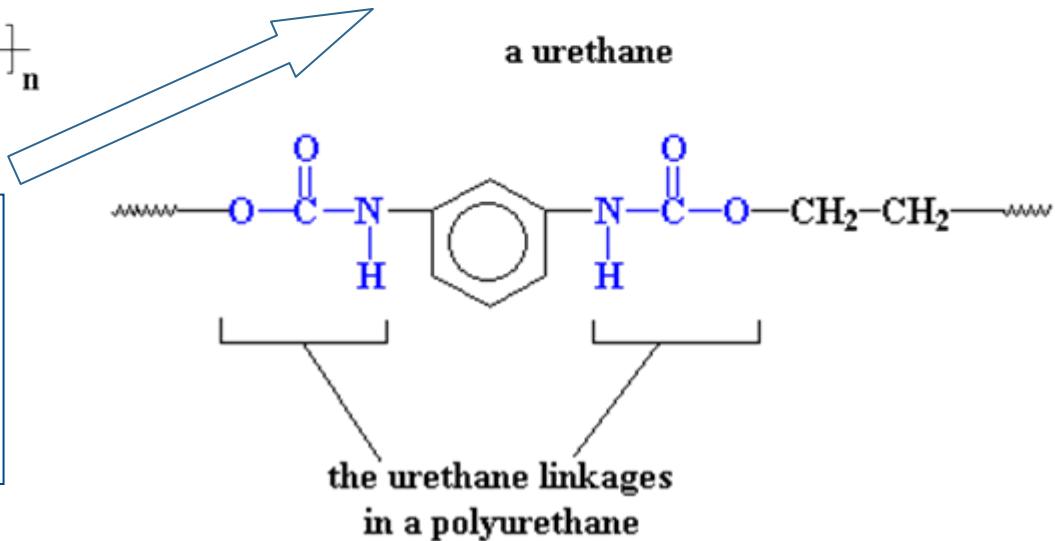
Polyurethanes can hydrogen bond very well, and thus can be very crystalline. For this reason they are often used to make block copolymers with soft rubbery polymers. These block copolymers have properties of thermoplastic.

Polyurethanes PUR

Polyurethanes are the most well known polymers used to make foams. Polyurethanes are the single most versatile family of polymers there is: can be elastomers, paints, fibers and adhesives.

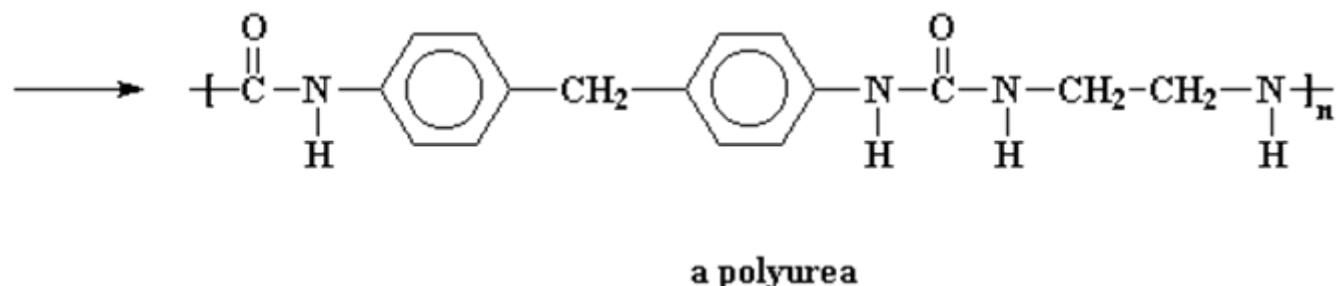
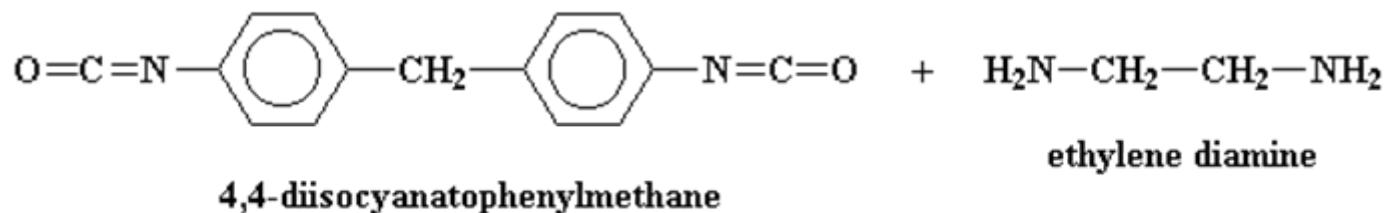


In their backbones they have a **urethane** linkage. A polyurethane can be any polymer containing the urethane linkage in its backbone chain. More sophisticated polyurethanes are possible, for example:



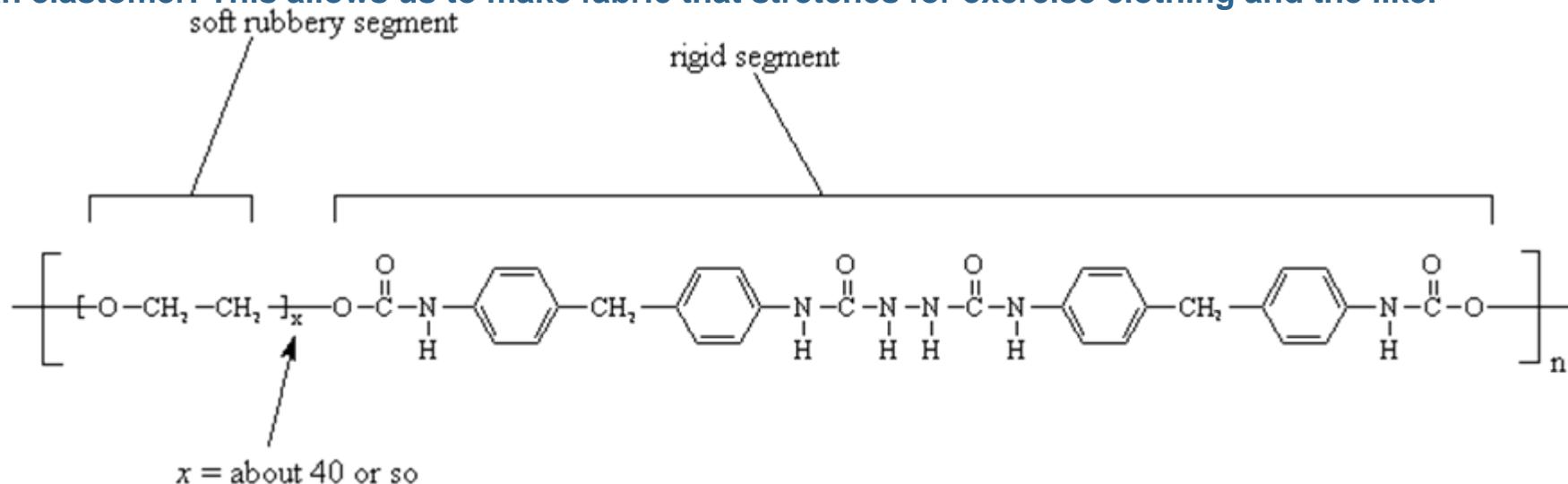
Polyurethanes PUR preparation

If the dialcohol is replaced with a diamine, the polymer is a polyurea, because it contains a urea linkage, rather than a urethane linkage. But they are usually called also polyurethanes.



Spandex

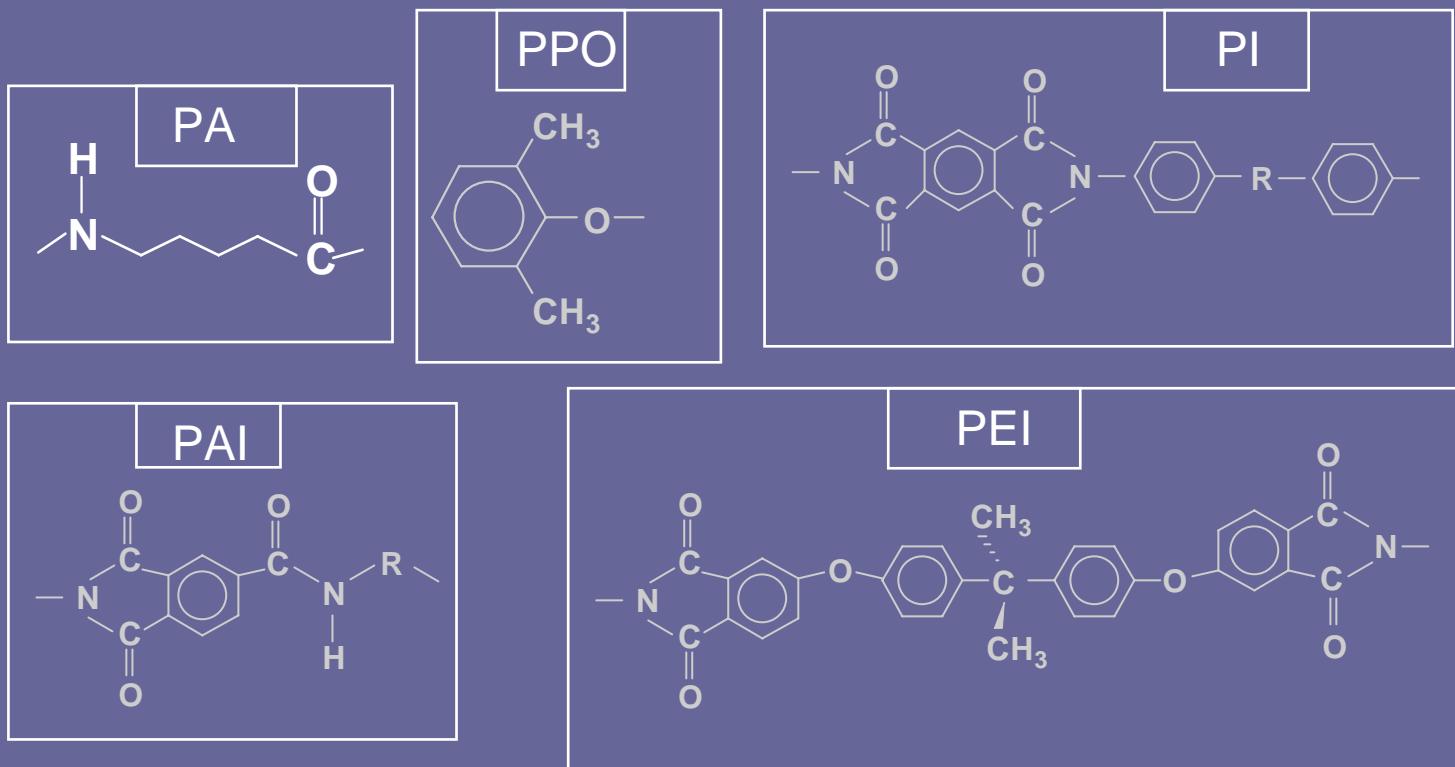
One unusual polyurethane thermoplastic elastomer is spandex, which DuPont sells under the trade name Lycra. It has both urea and urethane linkages in its backbone. What gives spandex its special properties is the fact that it has hard and soft blocks in its repeat structure. The short polymeric chain of a polyglycol, usually about forty or so repeats units long, is soft and rubbery. The rest of the repeat unit, you know, the stretch with the urethane linkages, the urea linkages, and the aromatic groups, is extremely rigid. This section is stiff enough that the rigid sections from different chains clump together and align to form fibers. Of course, they are unusual fibers, as the fibrous domains formed by the stiff blocks are linked together by the rubbery soft sections. The result is a fiber that acts like an elastomer! This allows us to make fabric that stretches for exercise clothing and the like.



Spandex has a complicated structure, with both urea and urethane linkages in the backbone chain.
xavier.colom@upc.edu



Thermoplastic matrices





Thermoset and thermoplastic matrices

MATRIZ	TERMOESTABLE			TERMOPLÁSTICO				
	UP	EP	FF	PP	PA	PEEK	PEI	PI
Densidad (g/mL)	1.4	1.3	1.29	0.9	1.14	1.31	1.27	1.43
Resistencia Tracción (MPa)	70	100	45	30	70	92	102	85
Deformación a rotura (%)	2	3	1.7	300	60	50	60	55
Temperatura max (°C)	170	300	240	145	210	280	260	210
Temperatura min (°C)	0	0	0	-60	-10	-15	-20	-5
Absorción de agua (%)	0.3	0.3	0.2	0.03	6	0.5	0.25	0.32





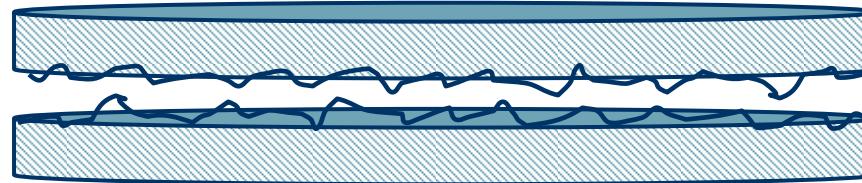
the interface region bonding mechanisme

- Adsorption and wetting
- Interdiffusion and chemical reaction
- Electrostatic attraction
- Mechanical keying



the interface region

Adsorption and wetting

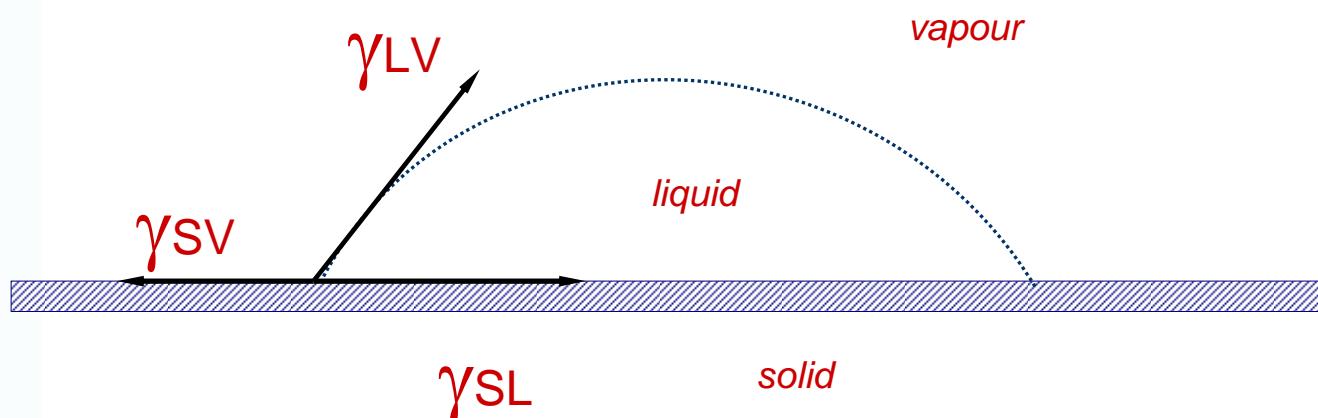


$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}$$

Work of adhesion (Dupré equation)

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta$$

Surface energy (Young equation)





Adsorption and wetting

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}$$

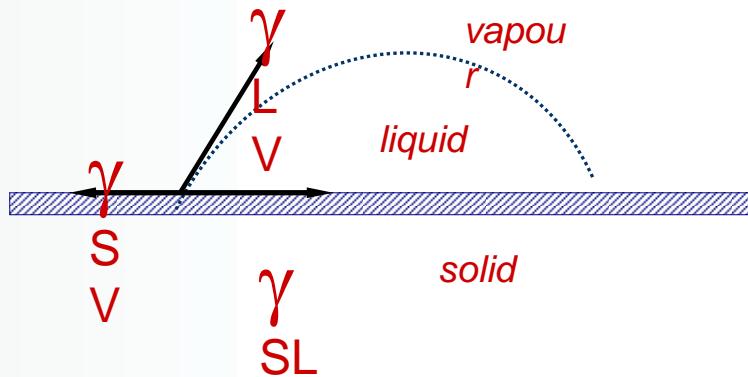
Work of adhesion (Dupré equation)

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta$$

Surface energy (Young equation)

According with this equation, wetting is strongly favoured if the surface Energy of two constituents are large and their interfacial energy is small.

A large value of the liquid surface energy inhibits the spreading of a liquid droplet.



$$\gamma_{SV} > (\gamma_{SL} + \gamma_{LV} \cos\theta)$$

G ($\gamma_{SV}=560\text{mJ/m}^2$) wetted by UP ($\gamma_{LV}=35\text{mJ/m}^2$)

CF ($\gamma_{SV}=70\text{mJ/m}^2$) wetted by Ep
($\gamma_{LV}=43\text{mJ/m}^2$)

PE ($\gamma_{SV}=31\text{mJ/m}^2$) isn't wetted neither by UP or Ep ($\gamma_{LV}=35\text{mJ/m}^2$)



Coupling agent and environmental effects

Many coatings have been developed to improve the durability and mechanical strength of the fiber-matrix bond and these are usually named coupling agents.

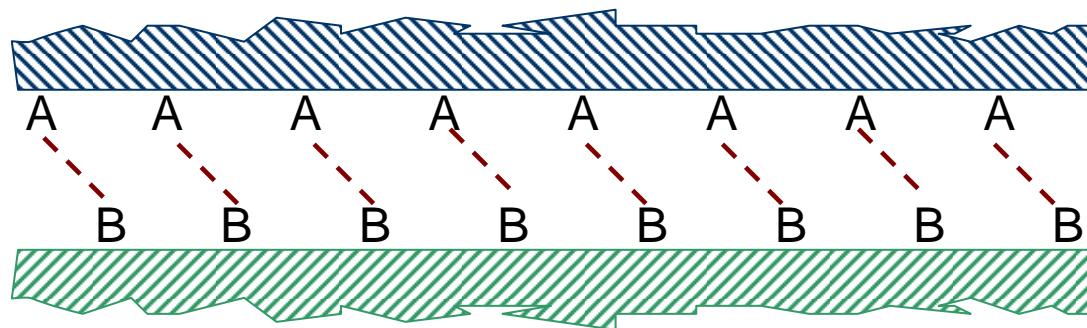
A good example is provided by those used on glass fiber which often suffer from problems caused by pick-up of water. (Different oxides form links with the water)

The presence of water also reduces the wettability of the fibers, reducing γ_{SV} from **560 mJ/m²** to **15 mJ/m²**. Coatings which function as coupling agent are designed to eliminate the leaching effect and raise the effective γ_{SV} at least about **50 mJ/m²**



the interface region

Chemical reaction

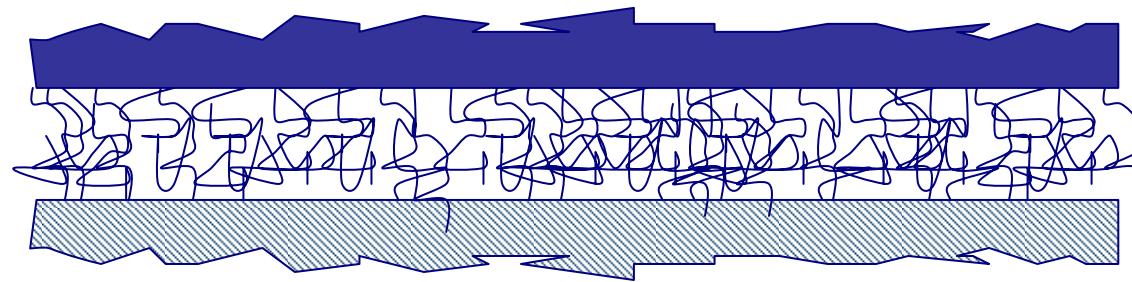


Various types of chemical reaction may occur at the interface, either deliberately promoted or inadvertent. These can be represented by new A --- B bonds being formed as a result of interface chemical reactions. These bonds may be covalent, ionic, metallic,... and in many cases are very strong



the interface region

Interdiffusion and chemical reaction



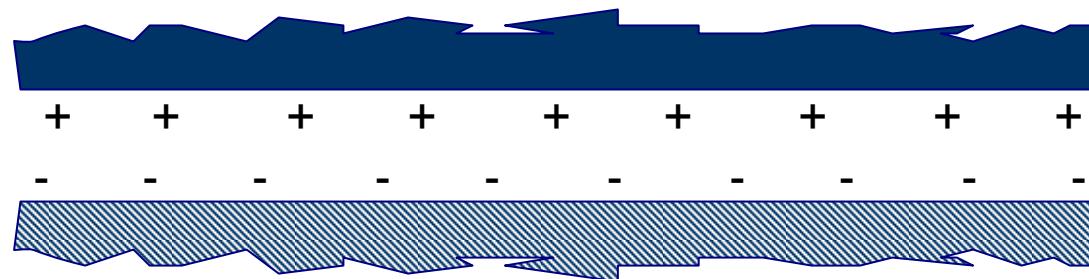
Diffusion of free chain ends at the interface between two polymers, which leads to chain entanglements and a rise in the adhesive strength.

Interdiffusion can also take place in non-polymeric systems, particularly if it accompanied by chemical reaction.



the interface region

Electrostatic attraction

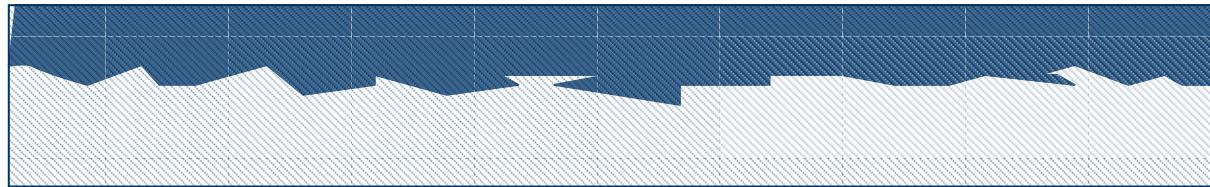


If the surface carry net electrical charges of opposite sign, then a sustained adhesive force may result. This effect is used in certain fibre treatment , as in the deposition of coupling agents on glass fibres.



the interface region

Mechanical keying



There may be a contribution to the strength of the interface from the surface roughness of the fibres if good wetting has occurred. The effects are much more significant under shear loading than for decohesion as a result of tensile stresses. Some improved resistance to tensile failure results if reentrant angles are present and there is an increase in strength under all types of loading as a consequence of the increased area of contact.

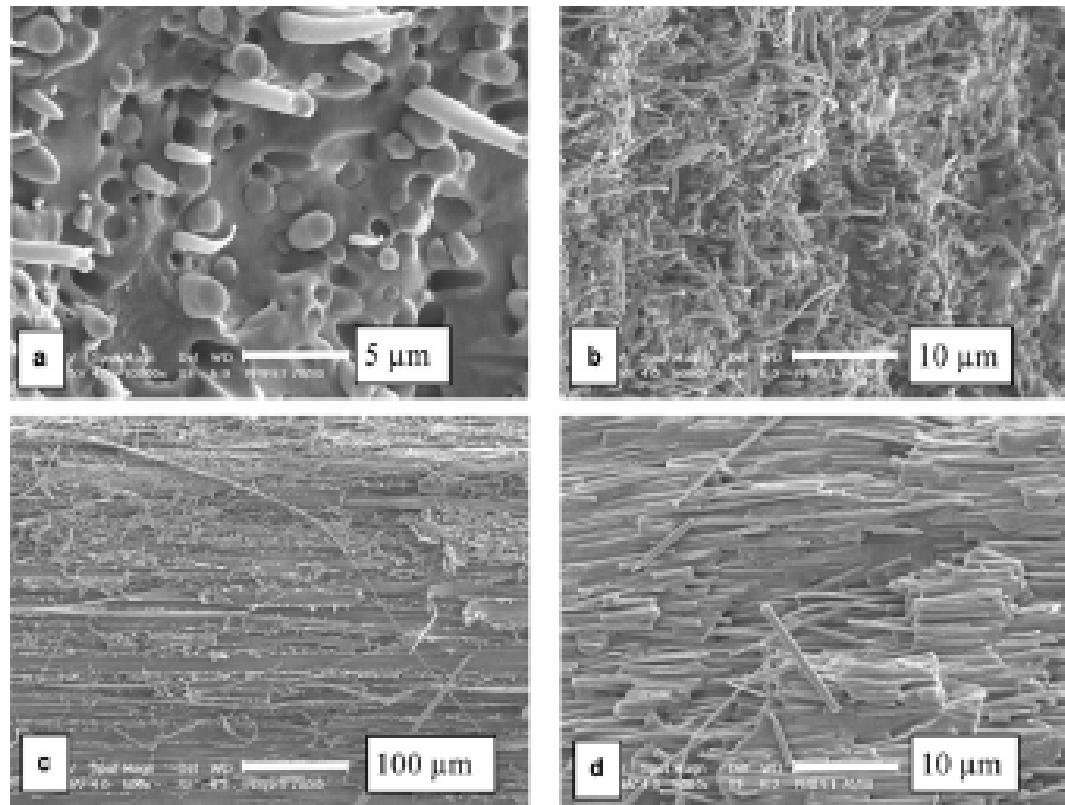


Fiber Reinforcement (SEM)

PP/PET

CST 66 (2006) 3161

Composite Materials





Fiber Reinforcement (SEM)

CARBON / PEEK

Composite Materials

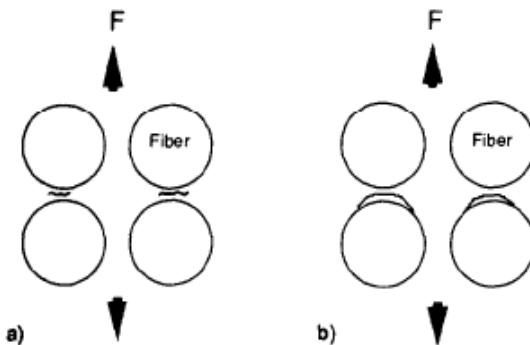
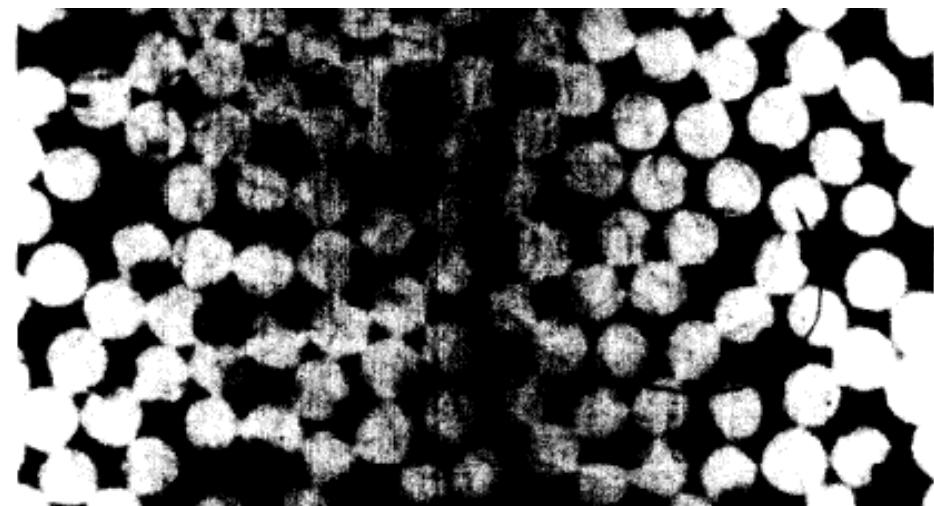


Fig. 1. Schematic illustration of initiation mechanisms for transverse cracks: (a) transverse crack initiation in the matrix; (b) transverse crack initiation at the fiber/matrix interface.





Composite Materials

ARAMID FIBER

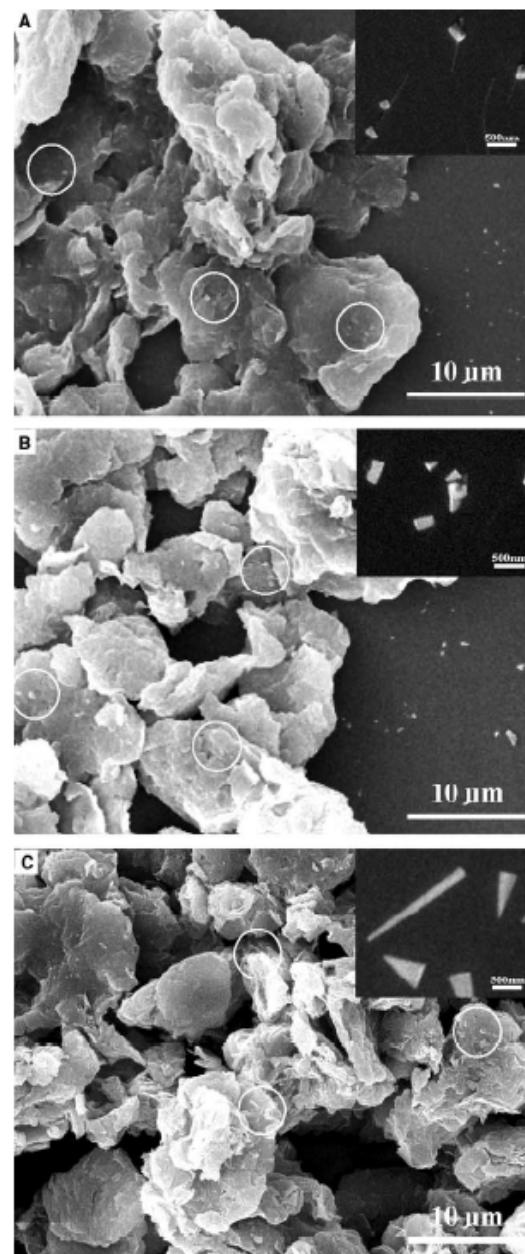
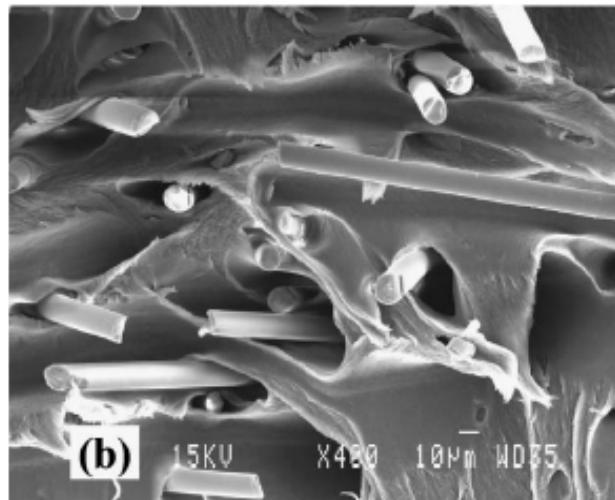
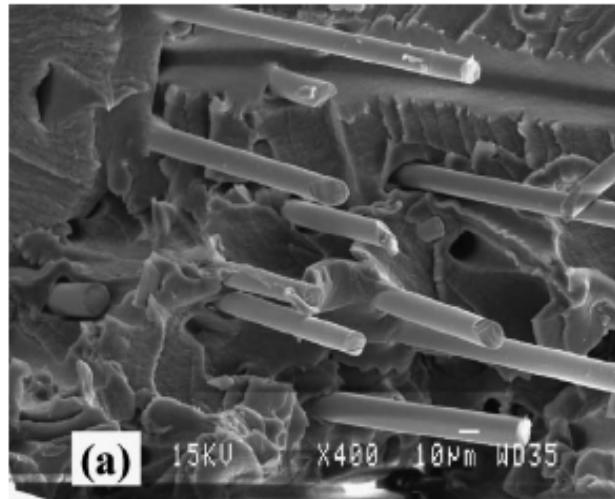


Fig. 1. SEM images of the Co(OH)_2 -nanoclay hybrids produced at pH 7.5 (A), 8.5 (B), and 9.5 (C).

Fiber Reinforcement

Composite Materials



PA66/GLASS FIBER SEBS g MA
CST 62(2002) 2017

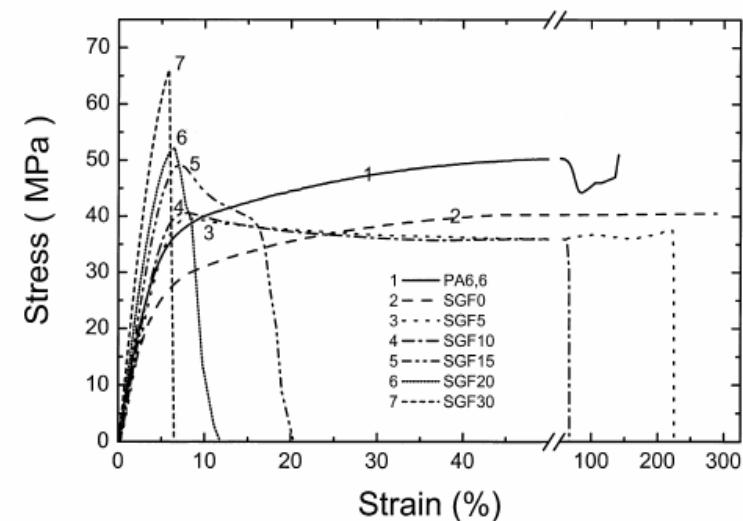


Fig. 5. Stress-strain curves of PA6,6 polymer, PA6,6/SEBS-g-MA 80/20 blend and its hybrids.

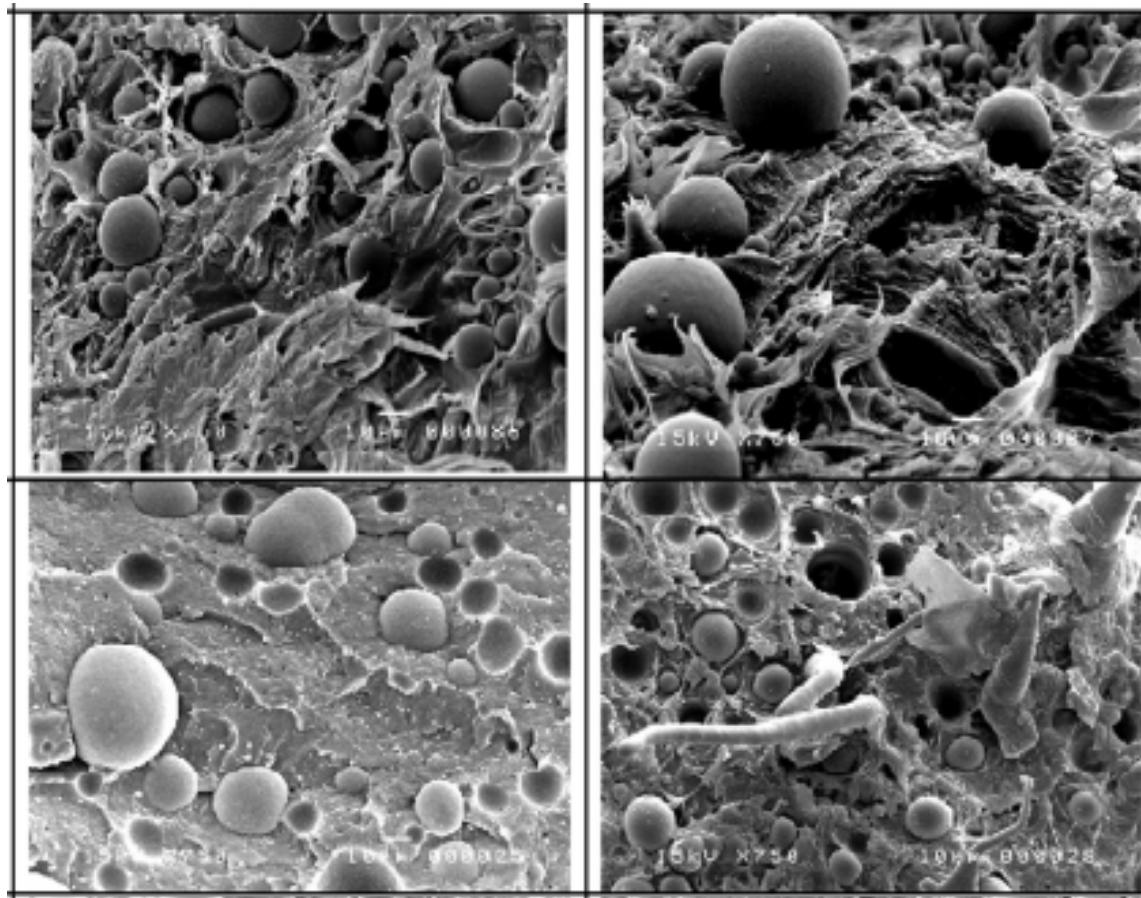


Fiber Reinforcement

PP/TLCP

CST 61(2001) 941

Composite Materials





Fiber Reinforcement

Composite Materials

Termo/PALM FIBER mod
CST 63(2003) 861

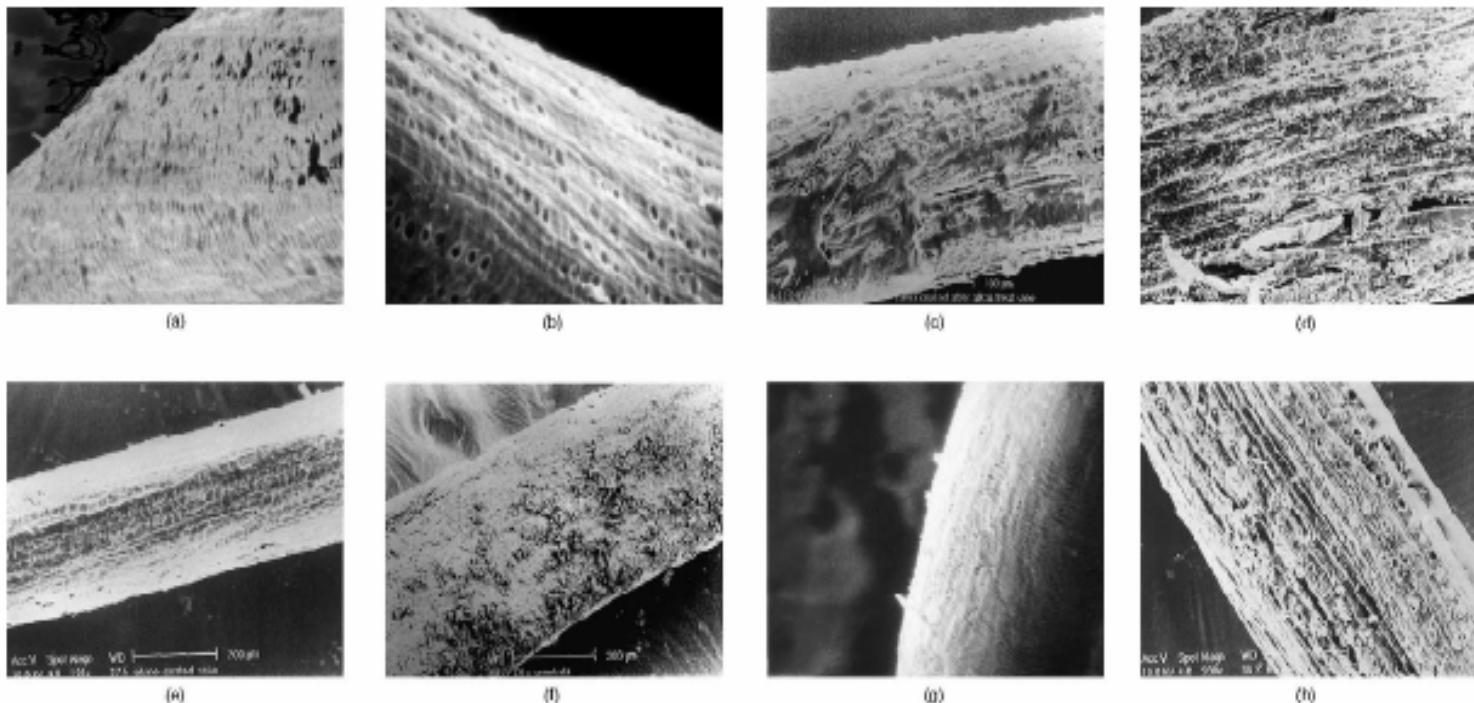


Fig. 5. Scanning electron micrographs of OPEFB fibre surface, (a) untreated ($\times 400$), (b) mercerized ($\times 400$), (c) latex coated ($\times 200$), (d) γ irradiated ($\times 200$), (e) silane treated ($\times 100$), (f) TDIC treated ($\times 100$), (g) acetylated ($\times 200$), (h) peroxide treated ($\times 200$).



Fiber Reinforcement

Composite Materia

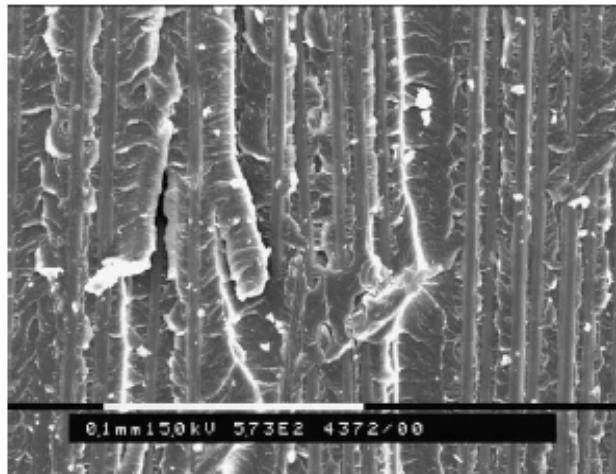
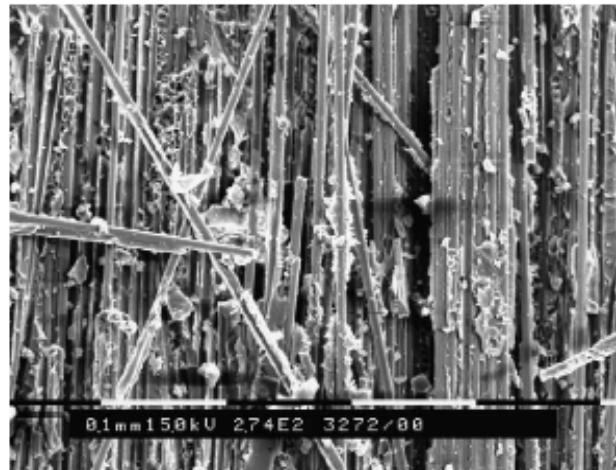


Fig. 5. SEM image showing the fracture surface of an unreinforced and untreated DCB sample.



EPOXY/CARBON
CST 63(2003) 531

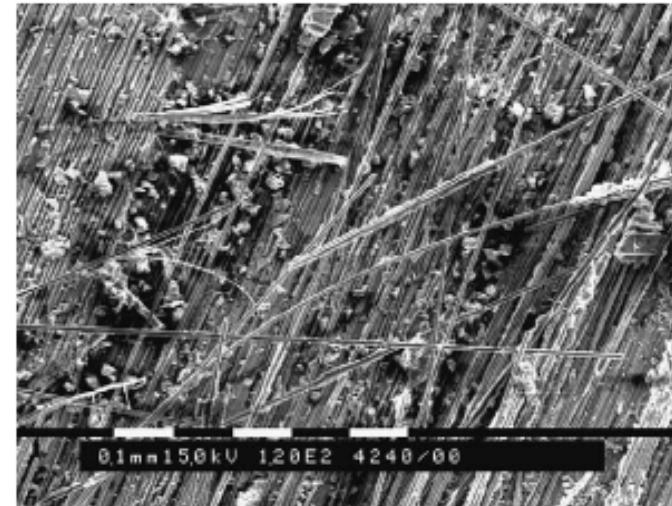


Fig. 9. SEM image showing the fracture surface of a treated sample

