Polymer, Fibres, Fibre reinforced polymers and Wood

1. Anisotropy and Isotropy

In a single crystal, the physical and mechanical properties often differ with orientation. It can be seen from looking at our models of crystalline structure that atoms should be able to slip over one another or distort in relation to one another easier in some directions than others. When the properties of a material vary with different crystallographic orientations, the material is said to be anisotropic.

Alternately, when the properties of a material are the same in all directions, the material is said to be isotropic. For many polycrystalline materials the grain orientations are random before any working (deformation) of the material is done. Therefore, even if the individual grains are anisotropic, the property differences tend to average out and, overall, the material is isotropic. When a material is formed, the grains are usually distorted and elongated in one or more directions which makes the material anisotropic. Material forming will be discussed later but let's continue discussing crystalline structure at the atomic level.

2. Polymers

Polymers are common in nature, in the form of wood, rubber, cotton, leather, wood, silk, proteins, enzymes, starches, cellulose. Artificial polymers are made mostly from oil. Their use has grown exponentially, especially after WW2. The key factor is the very low production cost and useful properties (e.g., combination of transparency and flexibility, long elongation).

Hydrocarbon Molecules

Most polymers are organic, and formed from hydrocarbon molecules. These molecules can have single, double, or triple carbon bonds. A *saturated hydrocarbon* is one where all bonds are single, that is, the number of atoms is maximum (or saturated). Among this type are the paraffin compounds, C_nH_{2n+2} (Table 15.1). In contrast, non-saturated hydrocarbons contain some double and triple bonds.

Isomers are molecules that contain the same molecules but in a different arrangement. An example is butane and isobutane.

Polymer Molecules

Polymer molecules are huge, macromolecules that have internal covalent bonds. For most polymers, these molecules form very long chains. The backbone is a string of carbon atoms, often single bonded.

Polymers are composed of basic structures called ***mer*** units. A molecule with just one mer is a monomer.

The Chemistry of Polymer Molecules

Examples of polymers are polyvinyl chloride (PVC), poly-tetra-chloro-ethylene (PTFE or Teflon), polypropylene, nylon and polystyrene. Chains are represented straight but in practice they have a three-dimensional, zig-zag structure (Fig. 15.1b).

When all the mers are the same, the molecule is called a homopolymer. When there is more than one type of mer present, the molecule is a *copolymer*.

Molecular Weight

The mass of a polymer is not fixed, but is distributed around a mean value, since polymer molecules have different lengths. The average molecular weight can be obtained by averaging the masses with the fraction of times they appear (number-average) or with the mass fraction of the molecules (called, improperly, a weight fraction).

The *degree of polymerization* is the average number of mer units, and is obtained by dividing the average mass of the polymer by the mass of a mer unit.

Polymers of low mass are liquid or gases, those of very high mass (called high-polymers, are solid). Waxes, paraffins and resins have intermediate masses.

Molecular Shape

Polymers are usually not linear; bending and rotations can occur around single C-C bonds (double and triple bonds are very rigid) (Fig. 15.5). Random kings and coils lead to entanglement, like in the spaghetti structure shown in Fig. 15.6.

Molecular Structure

- linear (end-to-end, flexible, like PVC, nylon)
- branched
- cross-linked (due to radiation, vulcanization, etc.)
- network (similar to highly cross-linked structures).

Molecular Configurations

The regularity and symmetry of the side-groups can affect strongly the properties of polymers. Side groups are atoms or molecules with free bonds, called free-radicals, like H, O, methyl, etc.

If the radicals are linked in the same order, the configuration is called *isostatic*

In a stereoisomer in a *syndiotactic* configuration, the radical groups alternative sides in the chain.

In the *atactic* configuration, the radical groups are positioned at random.

copolymers

Copolymers, polymers with at least two different types of mers can differ in the way the mers are arranged. Fig. 15.9 shows different arrangements: random, alternating, block, and graft.

Polymer Crystallinity

Crystallinity in polymers is more complex than in metals (fig. 15.10). Polymer molecules are often partially crystalline (*semicrystalline*), with crystalline regions dispersed within amorphous material. .

Chain disorder or misalignment, which is common, leads to amorphous material since twisting, kinking and coiling prevent strict ordering required in the crystalline state. Thus, linear polymers with small side groups, which are not too long form crystalline regions easier than branched, network, atactic polymers, random copolymers, or polymers with bulky side groups.

Crystalline polymers are denser than amorphous polymers, so the degree of crystallinity can be obtained from the measurement of density.

Polymer Crystals

Different models have been proposed to describe the arrangement of molecules in semicrytalline polymers. In the fringed-micelle model, the crystallites (micelles) are embedded in an amorphous matrix (Fig.15.11). Polymer single crystals grown are shaped in regular platelets (lamellae) (Fig. 15.12). Spherulites (Fig. 15.4) are chain-folded crystallites in an amorphous matrix that grow radially in spherical shape “grains”.

A polymeric solid can be thought of as a material that contains many chemically bonded parts or units which themselves are bonded together to form a solid. The word polymer literally means "many parts." Two industrially important polymeric materials are plastics and elastomers. Plastics are a large and varied group of synthetic materials which are processed by forming or molding into shape. Just as there are many types of metals such as aluminum and copper, there are many types of plastics, such as polyethylene and nylon. Elastomers or rubbers can be elastically deformed a large amount when a force is applied to them and can return to their original shape (or almost) when the force is released.

Polymers have many properties that make them attractive to use in certain conditions. Many polymers:

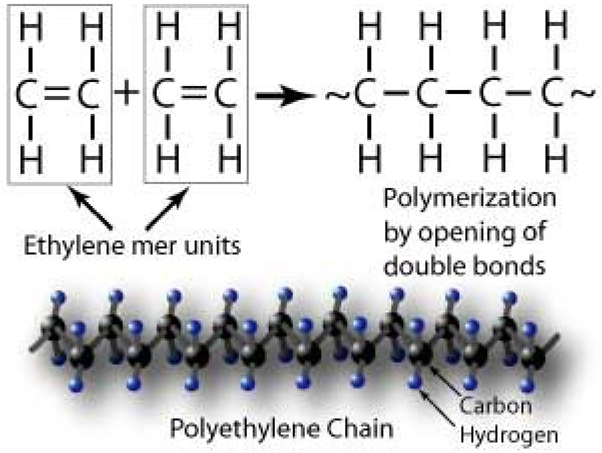
- are less dense than metals or ceramics,
- resist atmospheric and other forms of corrosion,
- offer good compatibility with human tissue, or
- exhibit excellent resistance to the conduction of electrical current.

The polymer plastics can be divided into two classes, thermoplastics and thermosetting plastics, depending on how they are structurally and chemically bonded. Thermoplastic polymers comprise the four most important commodity materials – polyethylene, polypropylene, polystyrene and polyvinyl chloride. There are also a number of specialized engineering polymers. The term ‘thermoplastic’ indicates that these materials melt on heating and may be processed by a variety of molding and extrusion techniques. Alternately, ‘thermosetting’ polymers can not be melted or remelted. Thermosetting polymers include alkyds, amino and phenolic resins, epoxies, polyurethanes, and unsaturated polyesters.

Rubber is a natural occurring polymer. However, most polymers are created by engineering the combination of hydrogen and carbon atoms and the arrangement of the chains they form. The polymer molecule is a long chain of covalent-bonded atoms and secondary bonds then hold groups of polymer chains together to form the polymeric material. Polymers are primarily produced from petroleum or natural gas raw products but the use of organic substances is growing. The super-material known as Kevlar is a man-made polymer. Kevlar is used in bullet-proof vests, strong/lightweight frames, and underwater cables that are 20 times stronger than steel.

2.1 Polymer Structure

Engineering polymers include natural materials such as rubber and synthetic materials such as plastics and elastomers. Polymers are very useful materials because their structures can be altered and tailored to produce materials 1) with a range of mechanical properties 2) in a wide spectrum of colors and 3) with different transparent properties.



Mer –
The repeating unit in a polymer chain
Monomer –
A single mer unit (n=1)
Polymer –
Many mer-units along a chain ($n=10^3$ or more)
Degree of Polymerization –
The average number of mer-units in a chain.

Mers

A polymer is composed of many simple molecules that are repeating structural units called monomers. A single polymer molecule may consist of hundreds to a million monomers and may have a linear, branched, or network structure. Covalent bonds hold the atoms in the polymer molecules together and secondary bonds then hold groups of polymer chains together to form the polymeric material. Copolymers are polymers composed of two or more different types of monomers.

Polymer Chains (Thermoplastics and Thermosets)

A polymer is an organic material and the backbone of every organic material is a chain of carbon atoms. The carbon atom has four electrons in the outer shell. Each of these valence electrons can form a covalent bond to another carbon atom or to a foreign atom. The key to the polymer structure is that two carbon atoms can have up to three common bonds and still bond with other atoms. The elements found most frequently in polymers and their valence numbers are: H, F, Cl, Bf, and I with 1 valence electron; O and S with 2 valence electrons; n with 3 valence electrons and C and Si with 4 valence electrons.

The ability for molecules to form long chains is a vital to producing polymers. Consider the material polyethylene, which is made from ethane gas, C_2H_6. Ethane gas has a two carbon atoms in the chain and each of the two carbon atoms share two valence electrons with the other. If two molecules of ethane are brought together, one of the carbon bonds in each molecule can be broken and the two molecules can be joined with a carbon to carbon bond. After the two mers are joined, there are still two free valence electrons at each end of the chain for joining other mers or polymer chains. The process can continue liking more mers and polymers together until it is stopped by the addition of anther chemical (a terminator), that fills the available bond at each end of the molecule. This is called a linear polymer and is building block for thermoplastic polymers.

The polymer chain is often shown in two dimensions, but it should be noted that they have a three dimensional structure. Each bond is at 109° to the next and, therefore, the carbon backbone extends through space like a twisted chain of TinkerToys. When stress is applied, these chains stretch and the elongation of polymers can be thousands of times greater than it is in crystalline structures.

The length of the polymer chain is very important. As the number of carbon atoms in the chain is increased to beyond several hundred, the material will pass through the liquid state and become a waxy solid. When the number of carbon atoms in the chain is over 1,000, the solid material polyethylene, with its characteristics of strength, flexibility and toughness, is obtained. The change in state occurs because as the length of the molecules increases, the total binding forces between molecules also increases.

It should also be noted that the molecules are not generally straight but are a tangled mass. Thermoplastic materials, such as polyethylene, can be pictured as a mass of intertwined worms randomly thrown into a pail. The binding forces are the result of van der Waals forces between molecules and mechanical entanglement between the chains. When thermoplastics are heated, there is more molecular movement and the bonds between molecules can be easily broken. This is why thermoplastic materials can be remelted.

16.2 Stress-Strain Behavior

The description of stress-strain behavior is similar to that of metals, but a very important consideration for polymers is that the mechanical properties depend on the strain *rate*, temperature, and environmental conditions.

The stress-strain behavior can be brittle, plastic and highly elastic (elastomeric or rubber-like), see Fig. 16. 1. Tensile modulus (modulus) and tensile strengths are orders of magnitude smaller than those of metals, but elongation can be up to 1000 % in some cases. The tensile strength is defined at the fracture point (Fig. 16.2) and can be lower than the yield strength.

Mechanical properties change dramatically with temperature, going from glass-like brittle behavior at low temperatures (like in the liquid-nitrogen demonstration) to a rubber-like behavior at high temperatures (Fig. 16.3).

In general, decreasing the strain rate has the same influence on the strain-strength characteristics as increasing the temperature: the material becomes softer and more ductile.

16.3 Deformation of Semicrystalline Polymers

Many semicrystalline polymers have the spherulitic structure and deform in the following steps (Fig. 16.4):

- elongation of amorphous tie chains

- tilting of lamellar chain folds towards the tensile direction
- separation of crystalline block segments
- orientation of segments and tie chains in the tensile direction

The macroscopic deformation involves an upper and lower yield point and necking. Unlike the case of metals, the neck gets stronger since the deformation aligns the chains so increasing the tensile stress leads to the growth of the neck. (Fig. 16.5).

16.4 Factors that Influence the Mechanical Properties of Polymers

The tensile modulus decreases with increasing temperature or diminishing strain rate.

Obstacles to the steps mentioned in **16.4** strengthen the polymer. Examples are cross-linking (aligned chains have more van der Waals inter-chain bonds) and a large mass (longer molecules have more inter-chain bonds). Crystallinity increases strength as the secondary bonding is enhanced when the molecular chains are closely packed and parallel. Pre-deformation by drawing, analogous to strain hardening in metals, increases strength by orienting the molecular chains. For undrawn polymers, heating increases the tensile modulus and yield strength, and reduces the ductility - opposite of what happens in metals.

16.5 Crystallization, Melting, and Glass Transition Phenomena

Crystallization rates are governed by the same type of S-curves we saw in the case of metals (Fig. 16.7). Nucleation becomes slower at higher temperatures.

The melting behavior of semicrystalline polymers is intermediate between that of crystalline materials (sharp density change at a melting temperature) and that of a pure amorphous material (slight change in slope of density at the glass-transition temperature). The glass transition temperature is between 0.5 and 0.8 of the melting temperature.

The melting temperature increases with the rate of heating, thickness of the lamellae, and depends on the temperature at which the polymer was crystallized.

Melting involves breaking of the inter-chain bonds, so the glass and melting temperatures depend on:

- chain stiffness (e.g., single vs. double bonds)
- size, shape of side groups
- size of molecule
- side branches, defects
- cross-linking

Rigid chains have higher melting temperatures.

16.6 Thermoplastic and Thermosetting Polymers

Thermoplastic polymers (thermoplasts) soften reversibly when heated (harden when cooled back)

Thermosetting polymers (thermosets) harden permanently when heated, as cross-linking hinder bending and rotations. Thermosets are harder, more dimensionally stable, and more brittle than thermoplasts.

16.7 Viscoelasticity

At low temperatures, amorphous polymers deform elastically, like glass, at small elongation. At high temperatures the behavior is viscous, like liquids. At intermediate temperatures, the behavior, like a rubbery solid, is termed *viscoelastic.*

Viscoelasticity is characterized by the viscoelastic relaxation modulus

$E_r = \square(t)/\square_0$.

If the material is strained to a value $\square_0$.it is found that the stress needs to be reduced with time to maintain this constant value of strain (see figs. 16.11 and 16.12).

In viscoelastic creep, the stress is kept constant at $\square_0$ and the change of deformation with time □t) is measured. The time-dependent *creep modulus* is given by

$E_c = \square_0/\square(t)$.

16.8 Deformation and Elastomers

Elastomers can be deformed to very large strains and the spring back elastically to the original length, a behavior first observed in natural rubber. Elastic elongation is due to uncoiling, untwisting and straightening of chains in the stress direction.

To be elastomeric, the polymer needs to meet several criteria:

- must not crystallize easily
- have relatively free chain rotations
- delayed plastic deformation by cross-linking (achieved by vulcanization).
- be above the glass transition temperature

16.9 Fracture of Polymers

As other mechanical properties, the fracture strength of polymers is much lower than that of metals. Fracture also starts with cracks at flaws, scratches, etc. Fracture involves breaking of covalent bonds in the chains. Thermoplasts can have both brittle and ductile fracture behaviors. Glassy thermosets have brittle fracture at low temperatures and ductile fracture at high temperatures.

Glassy thremoplasts often suffer *grazing* before brittle fracture. Crazes are associated with regions of highly localized yielding which leads to the formation of interconnected microvoids (Fig. 16.15). Crazing absorbs energy thus increasing the fracture strength of the polymer.

16.10 Miscellaneous Characteristics

Polymers are brittle at low temperatures and have low impact strengths (Izod or Charpy tests), and a brittle to ductile transition over a narrow temperature range.

Fatigue is similar to the case of metals but at reduced loads and is more sensitive to frequency due to heating which leads to softening.

16.11 Polymerization

Polymerization is the synthesis of high polymers from raw materials like oil or coal. It may occur by:

- addition (chain-reaction) polymerization, where monomer units are attached one at a time
- condensation polymerization, by stepwise intermolecular chemical reactions that produce the mer units.

3. Composites

A composite is commonly defined as a combination of two or more distinct materials, each of which retains its own distinctive properties, to create a new material with properties that cannot be achieved by any of the components acting alone. Using this definition, it can be determined that a wide range of engineering materials fall into this category. For example, concrete is a composite because it is a mixture of Portland cement and aggregate. Fiberglass sheet is a composite since it is made of glass fibers imbedded in a polymer.

Composite materials are said to have two phases. The reinforcing phase is the fibers, sheets, or particles that are embedded in the matrix phase. The reinforcing material and the matrix material can be metal, ceramic, or polymer. Typically, reinforcing materials are strong with low densities while the matrix is usually a ductile, or tough, material.

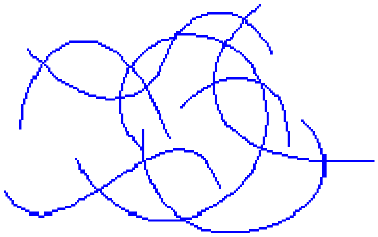
Some of the common classifications of composites are:

- Reinforced plastics
- Metal-matrix composites
- Ceramic-matrix composites
- Sandwich structures
- Concrete

Composite materials can take many forms but they can be separated into three categories based on the strengthening mechanism. These categories are dispersion strengthened, particle reinforced and fiber reinforced. Dispersion strengthened composites have a fine distribution of secondary particles in the matrix of the material. These particles impede the mechanisms that allow a material to deform. (These mechanisms include dislocation movement and slip, which will be discussed later). Many metal-matrix composites would fall into the dispersion strengthened composite category. Particle reinforced composites have a large volume fraction of particle dispersed in the matrix and the load is shared by the particles and the matrix. Most commercial ceramics and many filled polymers are particle-reinforced composites. In fiber-reinforced composites, the fiber is the primary load-bearing component. Fiberglass and carbon fiber composites are examples of fiber-reinforced composites.

If the composite is designed and fabricated correctly, it combines the strength of the reinforcement with the toughness of the matrix to achieve a combination of desirable properties not available in any single conventional material. Some composites also offer the advantage of being tailorable so that properties, such as strength and stiffness, can easily be changed by changing amount or orientation of the reinforcement material. The downside is that such composites are often more expensive than conventional materials.

Modern composites are usually made of two components, a *fiber* and *matrix.* The fiber is most often glass, but sometimes Kevlar, carbon fiber, or polyethylene. The matrix is usually a thermoset like an epoxy resin, polydicyclopentadiene, or a polyimide. The fiber is embedded in the matrix in order to make the matrix stronger. Fiber-reinforced composites have two things going for them. They are strong and light. They're often stronger than steel, but weigh much less. This means that composites can be used to make automobiles lighter, and thus much more fuel efficient. This means they pollute less, too.



glass fibers in Fiberglas™

The idea is that by combining two or more distinct materials one can engineer a new material with the desired combination of properties (e.g., light, strong, corrosion resistant). The idea that a better combination of properties can be achieved is called the principle of combined action.

New - High-tech materials, engineered to specific applications

Old - brick-straw composites, paper, known for > 5000 years.

A type of composite that has been discussed is perlitic steel, which combines hard, brittle cementite with soft, ductile ferrite to get a superior material.

Natural composites: wood (polymer-polymer), bones (polymer-ceramics).

Usual composites have just two phases:

- matrix (continuous)
- dispersed phase (particulates, fibers)

Properties of composites depend on

- properties of phases
- geometry of dispersed phase (particle size, distribution, orientation)

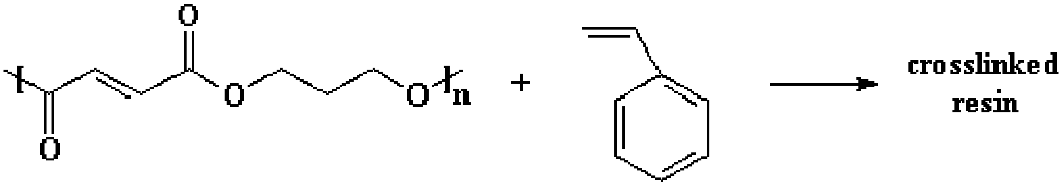
- amount of phase

Classification of composites: three main categories:

- particle-reinforced (large-particle and dispersion-strengthened)
- fiber-reinforced (continuous (aligned) and short fibers (aligned or random)
- structural (laminates and sandwich panels)

What Fibers Do

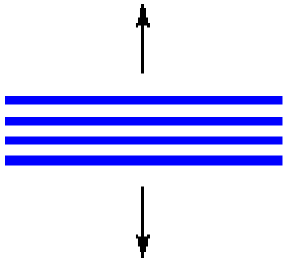
A common fiber-reinforced composite is Fiberglas^{TM}. Its matrix is made by reacting a polyester with carbon-carbon double bonds in its backbone, and styrene. We pour a mix of the styrene and polyester over a mass of glass fibers.



The styrene and the double bonds in the polyester react by free radical vinyl polymerization to form a crosslinked resin. The glass fibers are trapped inside, where they act as a reinforcement.

In Fiberglas^{TM} the fibers aren't lined up in any particular direction. They're just a tangled mass, like you see on the right. But we can make the composite stronger by lining up all the fibers in the same direction. Oriented fibers do some weird things to the composite. When you pull on the composite in the direction of the fibers, the composite is very strong. But if you pull on it at right angles to the fiber direction, it isn't very strong at all.

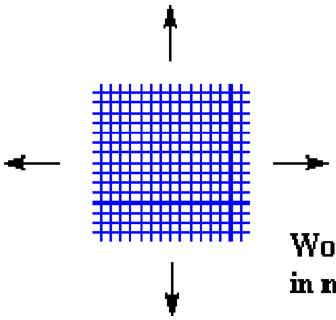
Oriented fibers are strong when you pull in the fiber direction.



But they're weak at right angles to the fiber direction.

This isn't always bad, because sometimes we only need the composite to be strong in one direction. Sometimes the item you're making will only be under stress in one direction.

But sometimes we need strength in more than one direction. So we simply point the fibers in more than one direction. We often do this by using a woven fabric of the fibers to reinforce the composite. The woven fibers give a composite good strength in many directions.



Woven fibers give strength in more than one direction.

What the Matrix Does

But what about the matrix? We've talked about what fibers do for the matrix, but what does the matrix do for the fiber? Why not just use fibers by themselves? First of all, the matrix holds the fibers together. A loose bundle of fibers wouldn't be of much use. Also, though fibers are strong, they can be brittle. The matrix can absorb energy by deforming under stress. This is to say, the matrix adds *toughness* to the composite. And finally, while fibers have good *tensile* strength (that is, they're strong when you pull on them), they usually have awful *compressional* strength. That is, they buckle when you squash them. The matrix gives compressional strength to the composite.

If you'd like to know more about just what it means to be strong and tough, and what the difference between strength and toughness is, visit our page dealing with the Mechanical Properties of Polymers.

Measuring up the Fibers

Not all fibers are the same. They all have good points and bad points. Glass is the most popular fiber. Why? Because it's really cheap. Now it may seem strange that glass is used as a reinforcement, as glass is really easy to break. I know this from years of destructive experience in the laboratory. But for some reason, when glass is spun into really tiny fibers, it acts very different. Glass fibers are strong, and flexible.

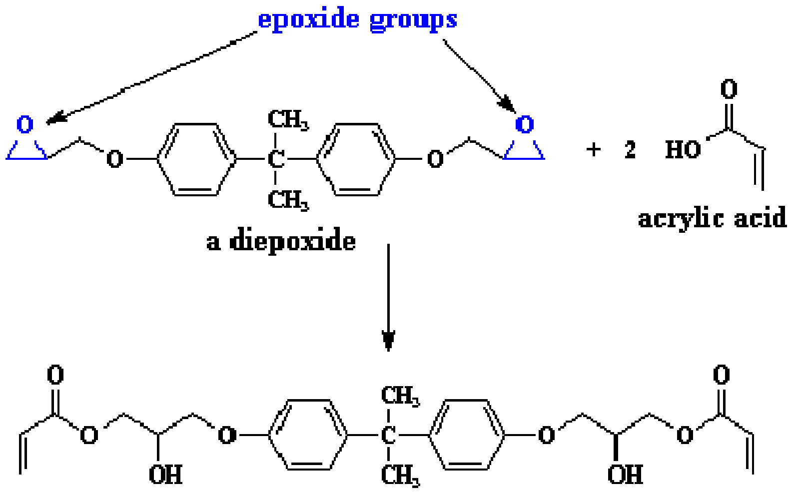
As a matter of fact...You know those glass slippers that Cinderella wore to the ball? They weren't made of plain old glass. They were actually made from a glass fiber-reinforced composite material. I mean, think about it. Glass shoes? They'd break the first time Cindy stepped on a piece of gravel in the driveway of Prince Charming's palace! And even if they didn't they'd definitely shatter when the clumsy prince stepped on Cinderella's foot dancing. But slippers made from glass-reinforced composites would be strong enough to handle a stomp by the biggest royal foot!

Still, there are stronger fibers out there. This is a good thing, because sometimes glass just isn't strong and tough enough. For some things, like airplane parts, that undergo a lot of stress, you need to break out the fancy fibers. When cost is no object, you can use stronger, but more expensive fibers, like Kevlar™, carbon fiber, or Spectra™. Carbon fiber is usually stronger than Kevlar®, that is, it can withstand more force without breaking. But Kevlar™ tends to be *tougher*. This means it can absorb more energy without breaking. It can stretch a little to keep from breaking, more so than carbon fiber can. But Spectra™, which is a kind of polyethylene, is stronger *and* tougher than both carbon fiber and Kevlar™.

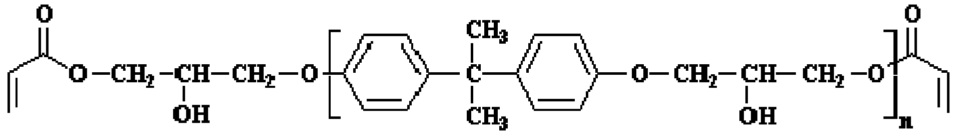
Measuring up the Matrices

Different jobs call for different matrices. When we want to save money, there are some cheap matrices that have decent properties. The unsaturated polyester/styrene systems we've already looked at are one example. They're fine for everyday applications. Chevrolet Corvette bodies are made from composites using unsaturated polyester matrices and glass fibers. But they have some drawbacks. They shrink a good deal when they're cured, they can absorb water very easily, and their impact strength is low. They're also not very chemically resistant.

Another low-cost system is the so-called vinyl ester resin. The first step to making a vinyl ester resin is reacting a di-epoxide with acrylic acid, or methacrylic acid:

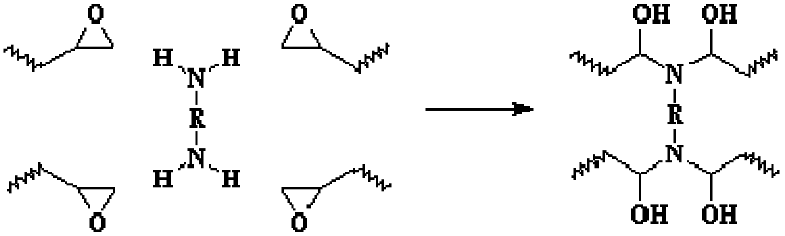


Then you polymerize the vinyl groups, and you've got a crosslinked resin. Sometimes we use bigger oligomers that look like this:



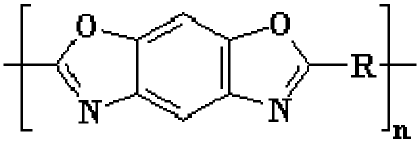
And they're cured the same way, by polymerizing the vinyl groups. Vinyl ester resins have some advantages over unsaturated polyesters. They don't absorb as much water, and they don't shrink nearly as much when cured. Plus, they have very good chemical resistance. Also, because of the hydroxyl groups, it bonds well to glass. This comes in handy if you're using glass as your fiber.

But neither vinyl ester resins nor unsaturated polyesters are very good for high temperature applications. For high temperatures, we need to use matrices like epoxy resins. To make these, we start with a di-epoxide, just like we did when we were making vinyl ester resins. Only this time, we don't react it with acrylic acid. Instead, we cure it with a diamine. The epoxide groups will react with the diamine, and the whole system becomes crosslinked:

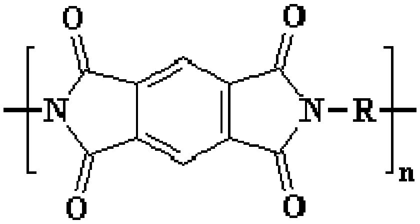


Because of all those hydroxyl groups, epoxy resins can bond well to glass fibers. But they have some properties you can't get with cheaper matrices. They don't absorb water, and they don't shrink very much when they're cured. And they can be used at higher temperatures, up to 160 °C in some cases.

But for REALLY high temperature applications, we're not sure what to do. There are a lot of options. Polyimides are good at resisting temperature, but they absorb a lot of water, which causes them to break down. Polybenzoxazoles are good at resisting temperatures, but they are almost impossible to process. Some people are interested in all-hydrocarbon matrices. Research is still underway in this field.



a polybenzoxazole



a polyimide

Most of the interest is in aerospace. There's a lot of interest right now in making a space-plane that can fly from Tokyo to Los Angeles in three hours. This plane would enter a low earth orbit during its flight. That means it would have to re-enter the atmosphere, and re-entry will generate a lot of heat on the surface of airplane. For the plane to make it through, it needs advanced composites that can stand up to the torture of all that heat.

Civil Structural Applications Using Composites

Many pedestrian bridge projects have been constructed throughout the United States using pultruded composite structural shapes. In states vulnerable to high seismic activity, concrete bridge columns are being retrofitted with a composite filament winding to increase ductility. Plate bonding using thin composite laminates to strengthen concrete and steel bridge members has been demonstrated. Composite prestressed piles are being applied to civil and marine structures in some of the coastal states.

The first US advanced composite vehicular bridge superstructure was dedicated into service on December 4, 1996 in Russell, Kansas. The deck panels were shop-fabricated with composite honeycomb cells which are sandwiched between two face sheets. These panels were then joined together with epoxy in the field. Demonstration bridge projects are being developed in other states such as Delaware, West Virginia and California. Continued research projects using composite reinforcing bars in concrete slabs are being studied in New Hampshire, Washington, D.C. and Michigan. Composite prestressing tendons and stay cables are being developed in Pennsylvania, Michigan, South Dakota and California.

Characteristics of Composites

The mechanical properties of composites depend on many variables such as fiber types, orientations, and architecture. The fiber architecture refers to the preformed textile configurations by braiding, knitting, or weaving. Composites are anisotropic materials with their strength being different in any direction. Their stress-strain curves are linearly elastic to the point of failure by rupture. The polymeric resin in a composite material, which consists of viscous fluid and elastic solids, responds viscoelastically to applied loads. Although the viscoelastic material will creep and relax under a sustained load, it can be designed to perform satisfactorily. Composites have many excellent structural qualities and some examples are high strength, material toughness, fatigue endurance, and light weight. Other highly desirable qualities are high resistance to elevated temperature, abrasion, corrosion, and chemical attack.

Some of the advantages in the use of composite structural members include the ease of manufacturing, fabrication, handling, and erection. Project delivery time can be short. It took the Russell county engineer one day to install the deck panels in the first vehicular composite bridge. Composites can be formulated and designed for high performance, durability and extended service life. They have excellent strength-to-weight ratios. If durability can be proven to last 75 years, composites can be economically justified using the life-cycle cost method.

Some of the disadvantages in the use of composites in bridges are high first cost, creep, and shrinkage. The design and construction require highly trained specialists from many engineering and material science disciplines. The composites have a potential for environmental degradation, for examples, alkalis' attack and ultraviolet radiation exposure. There are very little or nonexistant design guidance and/or standards. There is a lack of joining and/or fastening technology. Because of the use of thin sections, there are concerns in global and local buckling. Although the light weight feature may be an advantage in the response to earthquake loading, it could render the structure aerodynamically unstable. In manufacturing with the hand layup process, there is a concern about the consistency of the material properties.

What Is Really in Composites?

As the name implies, advance fiber reinforced polymer composites is made of fiber reinforcements, resin, fillers, and additives. The fibers provide increased stiffness and tensile capacity. The resin offers high compressive strength and binds the fibers into a firm matrix. The fillers serve to reduce cost and shrinkage. The additives help to improve not only the mechanical and physical properties of the composites but also workability. The discussions that follow immediately will explain the basic functions and behaviors of the constituents.

Fiber Reinforcements

The fiber is an important constituent in composites. A great deal of research and development has been done with the fibers on the effects in the types, volume fraction, architecture, and orientations. The fiber generally occupies 30% - 70% of the matrix volume in the composites. The fibers can be chopped, woven, stitched, and/or braided. They are usually treated with sizings such as starch, gelatin, oil or wax to improve the bond as well as binders to improve the handling. The most common types of fibers used in advanced composites for structural applications are the fiberglass, aramid, and carbon. The fiberglass is the least expensive and carbon being the most expensive. The cost of aramid fibers is about the same as the lower grades of the carbon fiber. "Other high-strength high-modulus fibers such as boron are at the present time considered to be economically prohibitive"[14].

- **Glass Fibers**

The glass fibers are divided into three classes -- E-glass, S-glass and C-glass. The E-glass is designated for electrical use and the S-glass for high strength. The C-glass is for high corrosion resistance, and it is uncommon for civil engineering application. Of the three fibers, the E-glass is the most common reinforcement material used in civil structures. It is produced from lime-alumina-borosilicate which can be easily obtained from abundance of raw materials like sand. The fibers are drawn into very fine filaments with diameters ranging from 2 to 13 X 10^{-6} m. The glass fiber strength and modulus can degrade with increasing temperature. Although the glass material creeps under a sustained load, it can be designed to perform satisfactorily. The fiber itself is regarded as an isotropic material and has a lower thermal expansion coefficient than that of steel.

Table 1 [5]

Typical Properties	**E-Glass**	**S-Glass**
Density (g/cm^3)	2.60	2.50
Young's Modulus (GPa)	72	87
Tensile Strength (GPa)	1.72	2.53
Tensile Elongation (%)	2.4	2.9

- **Aramid Fibers**

These are synthetic organic fibers consisting of aromatic polyamides. The aramid fibers have excellent fatigue and creep resistance. Although there are several commercial grades of aramid fibers available, the two most common ones used in structural applications are Kevlar® * 29 and Kevlar® 49. The Young's Modulus curve for Kevlar® 29 is linear to a value of 83 GPa but then becomes slightly concave upward to a value of 100 GPa at rupture; whereas, for Kevlar® 49 the curve is linear to a value of 124 GPa at rupture (see Table 2). As an anisotropic material, it's transverse and shear modulus are an order of magnitude less than those in the longitudinal direction. The fibers can have difficulty achieving a chemical or mechanical bond with the resin.

Table 2 [5]

Typical Properties	**Kevlar 29**	**Kevlar 49**
Density (g/cm^3)	1.44	1.44
Young's Modulus (GPa)	83/100	124
Tensile Strength (GPa)	2.27	2.27
Tensile Elongation (%)	2.8	1.8

- **Carbon Fibers**

The graphite or carbon fiber is made from three types of polymer precursors -- polyacrylonitrile (PAN) fiber, rayon fiber, and pitch. The tensile stress-strain curve is linear to the point of rupture. Although there are many carbon fibers available on the open market, they can be arbitrarily divided into three grades as shown in Table 3. They have lower thermal expansion coefficients than both the glass and aramid fibers. The carbon fiber is an anisotropic material, and its transverse modulus are an order of magnitude less than its longitudinal modulus. The material has a very high fatigue and creep resistance.

Table 3 [5]

Typical Properties	**High Strength**	**High Modulus**	**Ultra-High Modulus**
Density (g/cm^3)	1.8	1.9	2.0 - 2.1
Young's Modulus (GPa)	230	370	520 - 620
Tensile Strength (GPa)	2.48	1.79	1.03 - 1.31
Tensile Elongation (%)	1.1	0.5	0.2

Since its tensile strength decreases with increasing modulus, its strain at rupture will also be much lower. Because of the material brittleness at higher modulus, it becomes critical in joint and connection details, which can have high stress concentrations. As a result of this phenomenon, carbon composite laminates are more effective with adhesive bonding that eliminates mechanical fasteners.

Resin Systems

The resin is another important constituents in composites. The two classes of resins are the thermoplastics and thermosets. A thermoplastic resin remains a solid at room temperature. It melts when heated and solidifies when cooled. The long-chain polymers do not chemically cross link. Because they do not cure permanently, they are undesirable for structural application. Conversely, a thermosetting resin will cure permanently by irreversible cross linking at elevated temperatures. This characteristic makes the thermoset resin composites very desirable for structural applications. The most common resins used in composites are the unsaturated polyesters, epoxies, and vinyl esters; the least common ones are the polyurethanes and phenolics.

- **Unsaturated Polyesters**

The unsaturated polyester amounts to about 75% of all polyester resins used in USA. It is produced by the condensation polymerization of dicarboxylic acids and dihydric alcohols. The formulation contains an unsaturated material such as maleic anhydride or fumaric acid which is a part of the dicarboxylic acid component. The formulation affects the viscosity, reactivity, resiliency and heat deflection temperature (HDT). The viscosity controls the speed and degree of wet-out (saturation) of the fibers. The reactivity affects cure time and peak exotherm (heat generation) temperatures. High exotherm is needed for a thin section curing at room temperature and low exotherm for a thick section. Resiliency or flexible grade composites have a higher elongation, lower modulus, and HDT. The HDT is a short term thermal property which measures the thermal sensitivity and stability of the resins.

The advantages cited in the unsaturated polyester are its dimensional stability and affordable cost. Other advantages include ease in handling, processing, and fabricating. Some of the special formulations are high corrosion resistant and fire retardants. This resin is probably the best value for a balance between performance and structural capabilities.

- **Epoxies**

The epoxies used in composites are mainly the glycidyl ethers and amines. The material properties and cure rates can be formulated to meet the required performance. Epoxies are generally found in marine, automotive, electrical and appliance applications. The high viscosity in epoxy resins limits it use to certain processes such as molding, filament winding, and hand lay-up. The right curing agent should be carefully selected because it will affect the type of chemical reaction, pot life and final material properties. Although epoxies can be expensive, it may be worth the cost when high performance is required.

- **Vinyl Esters**

The vinyl ester resins were developed to take advantage of both the workability of the epoxy resins and the fast curing of the polyesters. The vinyl ester has higher physical properties than polyesters but costs less than epoxies. The acrylic esters are dissolved in a styrene monomer to produce vinyl ester resins which are cured with organic peroxides. A composite product containing a vinyl ester resin can withstand high toughness demand and offer excellent corrosion resistance.

- **Polyurethanes**

Polyurethanes are produced by combining polyisocyanate and polyol in a reaction injection molding process or in a reinforced reaction injection molding process. They are cured into very tough and high corrosion resistance materials which are found in many high performance paint coatings.

- **Phenolics**

The phenolic resins are made from phenols and formaldehyde, and they are divided into resole and novolac resins. The resoles are prepared under alkaline conditions with formaldehyde/phenol (F/P) ratios greater than one. On the contrary, novolacs are prepared under acidic conditions with F/P ratios less than one. Resoles are cured by applying heat and/or by adding acids. Novolacs are cured when reacting chemically with methylene groups in the hardener. The phenolics are rated for good resistance to high temperature, good thermal stability, and low smoke generation.

Fillers

Since resins are very expensive, it will not be cost effective to fill up the voids in a composite matrix purely with resins. Fillers are added to the resin matrix for controlling material cost and improving its mechanical and chemical properties. Some composites that are rich in resins can be subject to high shrinkage and creep and low tensile strength. Although these properties may be undesirable for structural applications, there may be a place for their use.

The three major types of fillers used in the composite industry are the calcium carbonate, kaolin, and alumina trihydrate. Other common fillers include mica, feldspar, wollastonite, silica, talc, and glasses. When one or more fillers are added to a properly formulated composite system, the improved performance includes fire and chemical resistance, high mechanical strength, and low shrinkage. Other improvements include toughness as well as high fatigue and creep resistance. Some fillers cause composites to have lower thermal expansion and exotherm coefficients. Wollastonite filler improves the composites' toughness for resistance to impact loading. Aluminum trihydrate improves on the fire resistance or flammability ratings. Some high strength formulations may not contain any filler because it increases the viscosity of the resin paste. High viscosity resins may have a problem wetting out completely for composite with heavy fiber reinforcement. A filler should not be used with fiber volume greater than 50% for the sheet molding composite production method.

Additives

A variety of additives are used in the composites to improve the material properties, aesthetics, manufacturing process, and performance. The additives can be divided into three groups -- catalysts, promoters, and inhibitors; coloring dyes; and, releasing agents. Their roles are as simple as their names imply, and they need no further discussion here.

Particle-reinforced composites

These are the cheapest and most widely used. They fall in two categories depending on the size of the particles:

- large-particle composites, which act by restraining the movement of the matrix, if well bonded.
- dispersion-strengthened composites, containing 10-100 nm particles, similar to what was discussed under precipitation hardening. The matrix bears the major portion of the applied load and the small particles hinder dislocation motion, limiting plastic deformation.

17.2 Large-Particle Composites

Properties are a combination of those of the components. The ***rule of mixtures*** predicts that an upper limit of the elastic modulus of the composite is given in terms of the elastic moduli of the matrix (E_m) and the particulate (E_p) phases by:

$$E_c = E_m V_m + E_p V_p$$

where V_m and V_p are the volume fraction of the two phases. A lower bound is given by:

$$E_c = E_m E_p / (E_p V_m + E_m V_p)$$

Fig. 17.3 - modulus of composite of WC particles in Cu matrix vs. WC concentration.

Concrete

The most common large-particle composite is concrete, made of a cement matrix that bonds particles of different size (gravel and sand.) Cement was already known to the Egyptians and the Greek. Romans made cement by mixing lime (CaO) with volcanic ice.

In its general from, cement is a fine mixture of lime, alumina, silica, and water. Portland cement is a fine powder of chalk, clay and lime-bearing minerals fired to 1500° C (calcinated). It forms a paste when dissolved in water. It sets into a solid in minutes and hardens slowly (takes 4 months for full strength). Properties depend on how well it is mixed, and the amount of water: too little - incomplete bonding, too much - excessive porosity.

The advantage of cement is that it can be poured in place, it hardens at room temperature and even under water, and it is very cheap. The disadvantages are that it is weak and brittle, and that water in the pores can produce crack when it freezes in cold weather.

Concrete is cement strengthened by adding particulates. The use of different size (stone and sand) allows better packing factor than when using particles of similar size.

Concrete is improved by making the pores smaller (using finer powder, adding polymeric lubricants, and applying pressure during hardening.

Reinforced concrete is obtained by adding steel rods, wires, mesh. Steel has the advantage of a similar thermal expansion coefficient, so there is reduced danger of cracking due to thermal stresses. *Pre-stressed concrete* is obtained by applying tensile stress to the steel rods while the cement is setting and hardening. When the tensile stress is removed, the concrete is left under compressive stress, enabling it to sustain tensile loads without fracturing. Pre-stressed concrete shapes are usually prefabricated. A common use is in railroad or highway bridges.

17.3 Dispersion-Strengthened Composites

Use of very hard, small particles to strengthen metals and metal alloys. The effect is like precipitation hardening but not so strong. Particles like oxides do not react so the strengthening action is retained at high temperatures.

Fiber-reinforced composites

In many applications, like in aircraft parts, there is a need for high strength per unit weight (specific strength). This can be achieved by composites consisting of a low-density (and soft) matrix reinforced with stiff fibers.

The strength depends on the fiber length and its orientation with respect to the stress direction.

The efficiency of load transfer between matrix and fiber depends on the interfacial bond.

17.4 Influence of Fiber Length

Normally the matrix has a much lower modulus than the fiber so it strains more. This occurs at a distance from the fiber. Right next to the fiber, the strain is limited by the fiber. Thus, for a composite under tension, a shear stress appears in the matrix that pulls from the fiber. The pull is uniform over the area of the fiber. This makes the force on the fiber be minimum at the ends and maximum in the middle, like in the tug-of-war game.

To achieve effective strengthening and stiffening, the fibers must be larger than a *critical length* l_c, defined as the minimum length at which the center of the fiber reaches the ultimate (tensile) strength $\square_f$, when the matrix achieves the maximum shear strength $\square_m$:

$$l_c = s_f d / 2 t_m$$

Since it is proportional to the diameter of the fiber d, a more unified condition for effective strengthening is that the aspect ratio of the fiber is $l/d > \square_f / 2 \square_m$.

17.5 Influence of Fiber Orientation

The composite is stronger along the direction of orientation of the fibers and weakest in a direction perpendicular to the fiber. For discontinuous, random fibers, the properties are isotropic.

Largest and most diverse use of composites due to ease of fabrication, low cost and good properties.

Glass-fiber reinforced composites (GFRC) are strong, corrosion resistant and lightweight, but not very stiff and cannot be used at high temperatures. Applications include auto and boat bodies, aircraft components.

Carbon-fiber reinforced composites (CFRC) use carbon fibers, which have the highest specific module (module divided by weight). CFRC are strong, inert, allow high temperature use. Applications include fishing rods, golf clubs, aircraft components.

Kevlar, and aremid-fiber composite (Fig. 17.9) can be used as textile fibers. Applications include bullet-proof vests, tires, brake and clutch linings.

Wood

This is one of the oldest and the most widely used structural material. It is a composite of strong and flexible cellulose fibers (linear polymer) surrounded and held together by a matrix of lignin and other polymers. The properties are anisotropic and vary widely among types of wood. Wood is ten times stronger in the axial direction than in the radial or tangential directions.