

Matrix Materials

Fibers and whiskers in composites are held together by a binder known as matrix. This is required since fibers by themselves—given their small cross-sectional area, cannot be directly loaded. Further, they cannot transmit load between themselves. This limitation is addressed by embedding fibers in a matrix material. Matrix material serves several functions, the important ones being: Binds fibers together; transfers loads and stresses within the composite structure; Support the overall structure; protects the composite from incursion of external agents such as humidity, chemicals; protects fibers from damage due to handling. Matrix material strongly influences composite's overall transverse modulus, shear properties, and compression properties. Matrix material also significantly limits a composite's maximum permissible operating temperature. Most of the matrix materials are relatively lighter more compliant and weaker vis-à-vis fibers and whiskers.

However, the combination of fibers/whiskers and matrix can be very stiff, very strong, and yet very light. Thus most of modern composites have very high specific strengths, i.e. very high strength/density ratios. This makes them very useful in aerospace applications, where weight minimization is a key design consideration.

Matrix materials can be broadly classified on the basis of their usable temperature ranges.

Matrix Material	Usable Temperature Range (C)
Polymers	< 260
Metals	260-750
Glass	750 -1150
Ceramic and carbon	1150 -1400

Choosing the Right Matrix Materials.

While selecting matrix material for a composite system, several considerations have to be factored into, principal ones being: Physical properties such as specific gravity; Mechanical properties such as modulus,

strength, CTE, conductivity, etc; Melting of curing temperature for the matrix

Material; Viscosity: It strongly affects processing attributes of the composite and also uniform flow of matrix material into the composite system.

Reactivity with fibers: One would certainly not desire possibility of chemical reactions between fibers and matrix material.

Fabrication process compatible with matrix and fibers –Reactivity with ambient environment
–Cost

Polymers as Matrix Materials

Polymers: Most widely used matrix materials.

Common examples: Polyesters, vinylesters, PEEK, PPS, nylon, polycarbonate, polyacetals, polyamides, polyether imides, polystyrene, epoxies, ureas, melamines, silicones.

Advantages: –Low cost , Easy to process, Low density, Superior chemical resistance.

Limitations: –Low strength, Low modulus, Limited range for operating temperature, Sensitivity to UV radiation, specific solvents, and occasionally humidity.

Polymer classification –Thermoplastics

Soften or melt when heated. This process is reversible. Their structure has long chains of molecules with strong intra-molecular bonds but weak inter-molecular bonds. When exposed to heat, these inter-molecular bonds break down, and the material starts “flowing”. Semi-crystalline or amorphous in structure. Examples: polyethylene, PEEK, polyamides, polyacetals, polysulfone, PPS, nylon, polystyrene

Thermosets: These polymers do not melt, but breakdown (decompose) when heated.

Amorphous structure: They have networked structures with strong covalent bonds linking all molecules. These networks permanently breakdown upon heating. Hence, these polymers, once “set”, cannot be reshaped.

Examples: epoxies, polyesters, phenolics, urea, melamine, silicone, polyimides.

Polymers behave significantly differently vis-à-vis metals and ceramics. – Performance of polymers is highly sensitive to several environmental variables. For instance, while mechanical properties of metals are temperature sensitive only in

the proximity of melt temperature, polymers' mechanical properties are highly sensitive to heat.

Polymers have significant behavioral sensitivity to increased temperatures. This sensitivity is strongly dependent on the structure of a polymer.

As mentioned earlier, polymers may either be thermoplastics, or thermosets. While thermosets have amorphous structure, thermoplastics may have either semi-crystalline structure, or amorphous structure.

Temperature sensitivity of amorphous thermoplastics –

When these plastics are heated, their specific volume slowly increases somewhat linearly with increasing temperature. However, if the temperature exceeds their glass transition

temperature T_g , their specific volume increases at a faster rate.

This is accompanied with a significant change in their mechanical properties.

Hence the maximum use temperature for these materials should not exceed T_g .

If these materials are heated beyond T_g , then the material melts at T_m .

Examples of these materials are polystyrene, polycarbonate, and polymethylmethacrylate.

Temperature sensitivity of semi-crystalline thermoplastics –

When these plastics are heated, their specific volume slowly increases somewhat linearly with increasing temperature. Further, if the temperature exceeds their glass transition temperature T_g , their specific volume increases at a somewhat faster rate. This is so, because presence of crystalline structure in these materials tends to limit the extent of changes in material's mechanical properties. It is only when the temperature exceeds their melting point T_m , that their material properties change significantly, and this change is accompanied by very significant increase in specific volume. This happens because at melting point, the crystalline bonds in the material breakdown, and all properties of the material undergo sudden and large changes. Thus, maximum use temperature for semi-crystalline thermoplastics is determined more by their melting point, and not so-much by their glass transition temperature. Examples of these materials are linear polyethylene (PE), polyethylene terephthalate (PET),

polytetrafluoroethylene (PTFE) or isotactic polypropylene (PP).

Unlike thermoplastics, thermosets do not melt upon heating. Rather, they decompose when they are heated beyond a certain threshold. Hence thermoset polymers are associated only with glass transition temperature T_g , and have no melting point. When these plastics are heated, their specific volume slowly increases somewhat linearly with increasing temperature.

However, if the temperature exceeds their glass transition temperature T_g , their specific volume increases at a faster rate. However, the change in mechanical properties for these materials at temperature corresponding to glass transition temperature is much less vis-à-vis for amorphous thermoplastics. Their relative reduced sensitivity to temperature at T_g , is attributable to high degree of cross-linked bonds, which sustain material's mechanical properties even at T_g .

Even then, maximum use temperatures for these materials are dictated by T_g . Common examples of these materials include epoxies, polyesters, and phenolics.

Thermoset: Polyesters and epoxies are very popular as thermoset matrix materials. Other thermoset materials used for matrix applications are vinyl esters, polyimides, and phenolics.

Polyesters: Polyester matrix material is produced by “curing” a “polyester resin” using a “curing agent”. Polyester resin comes in solid form. It is essentially unsaturated polyester. The structure of unsaturated polymer constitutes of mutually disconnected long chains of linear polymers. These long polymeric chains have a series of unsaturated bonds, occurring periodically along their length. It is at these locations, that cross-linking can occur.

This is accomplished by providing for reactive and polymerizable monomers such as styrene at these unsaturated bond locations.

Towards this end, polyester resin is dissolved in styrene. This monomer (styrene) acts as a cross linking agent between long linear polymeric chains of polyester. Further, it reduces viscosity of the polyester, thereby helping the processing.

However, the cross-linking process does not happen by mere presence of styrene. The cross-linking process needs a “trigger” or “initiation”. This is accomplished by addition of a small amount of “curing agent” also known as “initiator”.

Benzoylperoxide is a very popular curing agent for polyesters.

The cross-linking process reaction does not have any by-products since all of styrene gets used up for purposes of cross-linking polymeric chains. This is an exothermic reaction, which occurs at room temperature and at atmospheric pressure. The chemical undergoes shrinkage during this process.

Properties of polyesters can be modified and tailored as per design requirements.

Towards this end, several variables can be manipulated. Some of these variables are –Raw materials used for producing polyester resin: Typically, polyester resin is produced from reaction of diethylene glycol and maleic acid. However, by selecting alternative glycols and acids, properties of final polyester matrix material may be modified.

Solvent monomers: Styrene is a very popular monomer used to cross-link polyester chains. However, other monomers may as well be used for purposes of modifying matrix material’s properties.

Processing variables.

Epoxies

Epoxy thermosets, like polyester thermosets, are produced from epoxy resins.

These resins come in viscous liquid form, and have low molecular weight.

The viscosity of these resins strongly depends on the extent of polymerization of its molecules.

Common epoxy resins are produced through a reaction between epichlorohydrin and bisphenol-A. Alternative formulations replace bisphenol-A with other chemicals.

A “curing agent” (or hardener, or activator) triggers the polymerization process amongst

resin molecules, thereby generating a very dense network of cross-linked polymer. Diethylene triamine is a very commonly used curing agent.

The exothermic reaction between hardener (curing agent) and resin (compound) does not produce a by-product. Further, like polyesters, epoxies also undergo shrinkage during the curing process.

Epoxies, like polyesters, can be produced at room temperatures. However, by proper selection of curing agents, the curing process can be conducted at elevated temperatures as well.

The curing process time strongly depends on the choice of resin as well as curing agent. It can vary between minutes to 24 hours.

Many a times, heat is applied to accelerate the curing process. Typically, curing time decreases, almost exponentially, with increasing temperature.

Commercially, epoxies are available as “two-part” system, as well as “one-part” system. While the “two-part” epoxies require mixing of hardener and resin, “one-part” systems come essentially as pre-mixed systems (of hardener and resin).

Typically, one-part systems have to be stored at low temperatures, so that curing process gets significantly slowed down, and the epoxy does not get cured while being stored.

Vinylesters

Similar in behavior to polyesters.

Low viscosity and reduced curing time

Slightly more expensive compared to polyesters

Very good mechanical properties

Unlike polyesters, these materials have superior resistance to UV
Chemical performance is superior vis-à-vis polyesters

Works well in humid and wet environments

Overall performance is somewhere in between polyesters, and epoxies.

Common applications include chemical vessels, pipes, etc.

Polyimides

Relatively higher maximum use temperature (300 C)
Excellent resistance to solvents and chemical agents
Very strong and stiff amongst thermosets.

Bis-maleimides(BMI) are most popular thermosets in this class of materials.

However, BMIs are very brittle. Hence, they are combined with other thermoplastics to address this limitation. Typical additives include poly-sulfones, polyether imides, and other

Thermoplastics

Phenolics

Very low flammability

Produce less smoke during oxidation/charring process
Dimensionally stable when subjected to changes in temperature
Good adhesion properties

Good candidates for public transportation systems, where flammability and smoke concerns are very significant

Also used in aircraft applications for similar reasons.

Thermoplastics are very commonly used for short-fiber large-scale composite applications. This is so, since thermoplastic based short-fiber composites can be relatively easily and quickly processed.

These plastics are often used in injection molding machines, where solid thermoplastics impregnated with short glass fibers, are molded at high temperatures and pressures.

In such applications, these composites are essentially higher strength/modulus alternatives for non-reinforced plastics used in mass scale applications. Thus, such composites are not used to bear very high loads or provide high stiffness, where normally metals and other structural materials are deployed.

Polypropylene (PP), polysulfone, polyamide-imide, polycarbonates, and ABS (acrylonitrile-butadiene styrene) are commonly used thermoplastics for such applications.

However, there are also certain thermoplastic resins with maximum use temperatures well exceeding those of most epoxies and BMIs.

PEEK, i.e. polyether-ether-ketone is one such thermoplastic candidate whose maximum use temperature can be as high as 310 C. Such materials are used in high-temperature and high-performance application areas.

Metal Matrix Materials

Metals are very useful matrix materials. They offer following key advantages: High strength, High modulus, High toughness, High impact strength, Relative immunity to temperature changes, Immunity to a large range of environmental variables.

However, metals are not very popular matrix materials because: – They can only be processed at high temperature, as their melting points are high, They have high density, They have a propensity to react with several types of fibers, Metals are susceptible to corrosion.

Titanium, and aluminum are most commonly used for metal matrix applications.

They are used on account of their low specific gravities, which are 4.5 and 2.7, respectively. Magnesium is also a very light material as its specific gravity is 1.74. However, it reacts vigorously with oxygen, thereby promoting fire, and also corrosion.

In super alloy applications, nickel and cobalt are frequently used as metal matrices

However, when such metals are alloyed with specific elements, they tend to promote fiber oxidation, particularly at higher temperatures.

Metal matrices are used as binders for graphite fibers, as well as ceramic fibers. Special care is taken to inhibit the fiber-matrix reactivity in such fibers.

Special care is taken to inhibit the fiber matrix reactivity in such systems particularly at high temperatures.

Aluminum based matrices –Pure aluminum has very good corrosion resistance. Al-6061 and Al-2024 are commonly used alloys for high strength applications. Graphite is the most frequently used fiber with aluminum based matrices. Such fiber matrix systems are used where high strength, high modulus is needed at elevated temperatures.

Carbon has a propensity to react with aluminum at temperatures in excess of 500 C. To avoid such reactions, graphite fibers are coated with protective layers. These protective coatings also enhance fiber-matrix wetting.

Titanium based matrices

Titanium based alloys are known for high strength-to-weight ratios. These alloys, unlike aluminum alloys, also have better strength retention attributes at temperatures as high as 500 C.

However, these alloys react with boron/alumina fibers. Thus they are used either with SiC fibers or with borsic fibers (boron core, and SiC coating).

Ceramic and Carbon Matrices

These matrices are used for applications where operating temperatures exceed 1000 C. Typical applications include nose cones of missiles, reentry vehicles, turbine blades, etc.

Glass-ceramic matrices are made from lithium aluminosilicate(LAS) and calcium aluminosilicate(CAS).

Ceramics are typically reaction bonded silicon trinitride.

These matrix materials are used in conjunction with fibers, which can take high temperatures as well. Thus, they are quite often used with SiC fibers.

Carbon matrix is produced by vapor deposition of pyrolytic graphite onto a graphite fiber. The resulting composite, known as carbon-carbon composite, can take temperatures as high as 2700 C. These composites are used for re-entry vehicles, and missile nose cones. They are coated with a protective layer to protect them against oxidation.

Fillers

Polymeric composites, especially those with short-fibers commonly have “fillers” for purposes of reducing cost, and/or to improve performance. Some of the commonly used fillers are: –

Calcium carbonate: Used to reduce cost, control shrinkage, provide surface smoothness, and eliminate sink marks.

Kaolin (China clay): Increase resin viscosity to prevent fibers from extruding out of molding surfaces enhance fire resistance.

Natural silicas: Used in thermosets to provide dimensional stability , enhance electrical insulation and improve thermal conductivity.

Talc: Used to improve stiffness, and creep properties.

Glass or polymer hollow micro-spheres: Used for weight reduction

Antimony oxide: Fire resistance

Graphite flakes: Used to provide UV immunity.