FRP Composites
A Primer on Modern High-performance Fibres

– BY JAMES KAY –

Modern fibre-reinforced polymer (frp) composites have distinct advantages over conventional structural materials: their properties can be tailored precisely for specific purposes; and, perhaps most importantly, they can provide enormous strength and stiffness at a fraction of the weight.

FRP composite materials are made up of two parts: a polymer matrix and reinforcing fibres embedded in the matrix. The matrix is most commonly a vinyl-ester or epoxy polymer, and its task is to protect, support and transfer loads to the fibres. The reinforcing fibres bear the loads and give the material its excellent mechanical properties. The most common types of fibres used in frp composites are glass, carbon, and polymer. Glass is the most widely used (worldwide production is 4-5 million tons annually). In comparison, the annual production of carbon and polymer fibres is around 100,000 tons each. Below is an overview of how these different types of high performance fibres are made along with some of their basic structural properties.

GLASS FIBRES

Glass fibres are the original high-performance composite fibre and were first produced commercially in the 1930s by drawing fibres from high temperature melts. Today most glass fibres are still produced by this process, shown in *Figure 1*.
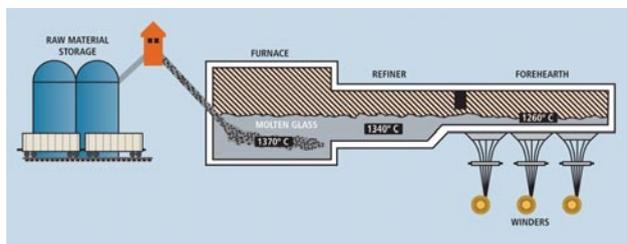

Figure 1: Typical Glass Fibre Manufacturing Process

The first step in the process is batching - precise quantities of the raw materials are measured and carefully blended together - then fed into a multi-stage natural-gas fired furnace for melting. The first area of the furnace is the hottest, at around 1370 ºC, where the materials become a uniform blend and bubbles are removed. Next, the glass flows to the refiner section where the temperature is lowered slightly, to around 1340 ºC, followed by the final section, the forehearth, where the temperature

drops to around 1260 ºC. The melt is fed into electrically heated bushings which contain an array of hundreds or thousands of holes through which the glass is extruded. The bushings are made from an erosion-resistant platinum/rhodium alloy and their temperature is controlled very precisely to ensure a constant viscosity of the glass as it exits the bushings where it is taken up by high-speed winders. These winders revolve much faster than the glass fibre is being extruded which causes the strands to be drawn into thin filaments. Water jets rapidly cool the filaments as they are drawn. Rapid cooling is necessary, as slow cooling will cause the material to form a crystalline structure rather than a glass which has a non-crystalline, amorphous structure. Glass fibres are typically produced at speeds of around 3 kilometers per minute, and a final processing step is often to apply a coating, known as sizing, which binds the filaments together into a strand and protects them from damage and moisture. The final product typically has a diameter of between 4 and 34 microns (10-6 meters).

Glass fibres are unique among the common high-strength structural fibres because they are isotropic; they have the same mechanical properties in the longitudinal direction as they do in the transverse direction.

The most important way in which different types of glass fibres differ from each other is in their chemical composition. The main ingredient in glass is silica, SiO_2, and it is possible to make glass fibres from pure silica; however, in practice other ingredients are always added to achieve various desirable properties.

E-Glass, so called because it was originally developed for electrical applications, is the most commonly used type of glass fibre. It includes significant amounts of Aluminum oxide, Magnesium oxide and Calcium oxide to achieve a very high electrical resistivity. It has a tensile strength of 1700-3500 MPa (megapascals, a unit of pressure or stress).

C-Glass, commonly used for storage tanks, includes significant amounts of Sodium Oxide and is formulated for better resistance to chemical corrosion. Its tensile strength ranges from 1700-2800 MPa.

S-glass contains high levels of Silica and Aluminum oxide is used for high-strength and high-temperature applications. It has a tensile strength of 2000-4500 MPa.

CARBON FIBRES

Carbon fibres have excellent mechanical properties and can be lighter, stronger, and much stiffer than glass fibres. They are widely used in the aerospace industry where their high cost can be justified by the weight savings.

Carbon fibres were first produced in 1958 by Roger Bacon. In his process, Bacon heated rayon fibres in an inert atmosphere until only the carbon remained. A few years later a similar process was developed using polyacrylonitrile (PAN) as a precursor and in the 1970s another method was developed that uses pitch as the starting point. These three processes are still the common way to produce carbon fibres today.

PAN: The process using PAN as a precursor is the most industrially important of the three and also the best understood chemically. The PAN precursor is a polymer in which the repeating unit is a vinyl group bonded to a nitrile group, as shown in *Figure 2.*
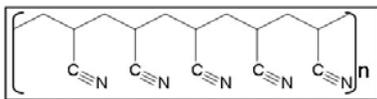
Figure 2: Structure of Polyacrylonitrile Precursor

The PAN is stretched to ensure proper alignment of the fibres and polymer molecules and then heated to approximately 700 °C in a nitrogen atmosphere. This causes the nitrile groups to bond together and the PAN becomes a ladder polymer, as shown in *Figure 3.*
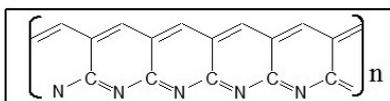
Figure 3: PAN Transformed into a Ladder Polymer.

This ladder polymer is now heated slowly from 400 °C to around 600 °C which causes the remaining hydrogen atoms to be driven off as the ladder polymers fuse together back-to-back into the ribbon-like structure shown in *Figure 4.*
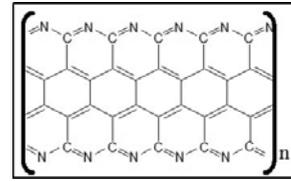
Figure 4: Fused Ladder Polymers

Finally, the polymer is heated to 1300 °C in an argon atmosphere which drives off the nitrogen, and the ribbon structures join together to form a sheet-like structure. These sheets are folded up on a small scale, but macroscopically remain approximately the same shape as the original precursor fibres, usually circular. *Figure 5* shows electron micrographs of a carbon fibre at three different magnifications, showing both the larger-scale circular fibres and the small scale graphite sheets. A final heat treatment is sometimes used with carbon, in which the fibres are briefly heated to 3000 °C to increase stiffness.
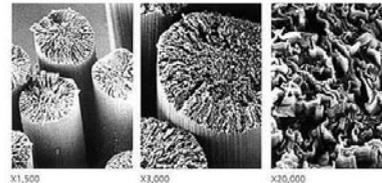
Figure 5: Microstructure of PAN-Based Carbon Fibres

The details of the chemical processes by which carbon fibres are produced by other precursors are less well understood, but they all share some similar features. They begin with an organic fibre that is able to withstand carbonizing temperatures without melting. The fibre is thermally or mechanically treated to orient its structure along the fibre axis. It is then heated to drive off most of the non-carbon elements. A final heat treatment is used to achieve the desired properties. As with glass fibres, a size is usually applied to the fibres to protect them and to hold the filaments together.

Rayon: Rayon-based fibres are mostly of interest because of the low cost of the rayon precursor. Rayon fibre is made from wood pulp and so is quite inexpensive, however the yield is low, only 15% to 30% compared with 50% for PAN. Initially rayon-based fibres had an advantage in that they could attain a higher stiffness than PAN-based fibres; however with the advent of higher strength PAN fibres, rayon is now becoming obsolete as a precursor.

Pitch: Pitch-based fibres fall into two categories, isotropic and mesophase pitch. Fibres produced from isotropic pitch have poor mechanical properties and are mostly used for insulation and fills. Mesophase pitch-based fibres, however, are able achieve the highest elastic modulus (stiffness) of any type of carbon fibre. To produce these fibres pitch is first maintained at a temperature of

350 ºC until it enters a highly-oriented liquid crystalline phase, the mesophase. This precursor is then melt spun into a fibre that is processed into carbon fibres by a series of heating cycles similar to the process for PAN fibres.

PAN/Pitch Comparison: Fibres produced from PAN (and rayon) exhibit a small-scale folded-up sheet like structure which does not have the ability to form large graphite grains. This limits the stiffness of these fibres. Mesophase pitch-based carbon fibres are able achieve a much greater stiffness because of their ability to form graphite grains with a high degree of orientation along the fibre direction. Small quantities of pitch-based fibres have even been produced with an elastic modulus (stiffness) as high as 990 GPa, which is very close to the theoretical limit of 1000 GPa, the stiffness of a single graphite crystal.

Fibre Type	Tensile Strength (MPa)	Tensile Stiffness (GPa)
PAN Precursor	1865 – 5200	228 - 400
Mesophase Pitch	1400 – 2200	500 - 720

Table 1: Typical Mechanical Properties of Carbon Fibres

  Conversely, the PAN-based fibres have the highest tensile strength *(see table 1)* because the final high-temperature heat treatment necessary for producing high stiffness fibres has a negative effect on the fibre's tensile strength. For this reason PAN-based fibres are usually used for high strength applications, whereas pitch-based fibres are more common in high-stiffness applications.
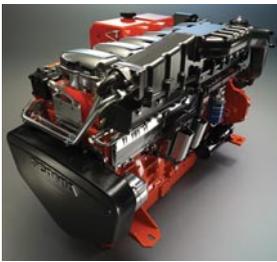
POLYMER FIBRES

Several polymers can also be made into high-performance fibres, with properties that are very desirable in some applications. The most important high-performance polymer fibres are aramid fibres, and ultra high molecular weight polyethylene fibres. These have strengths that can compete with glass and carbon fibres. Additionally, polymer fibres are also very light-weight, and able to absorb large amounts of energy before breaking.

Aramids: Aramid polymers are more commonly known by trade names such as Kevlar and Nomex (both Du Pont trademarks). The one used for high-strength fibres is poly-phenyleneterepthalamide, branded as Kevlar. These fibres commonly find use in bullet-resistant body armour, puncture-resistant tires, high-performance sails and watercraft. Because they are difficult to melt or dissolve, aramids were not able to be made into fibres until the 1960s, when Du Pont chemist Stephanie Kwolek invented a method which involves dissolving the polymer in concentrated sulphuric acid, spinning the solution into a

fibre, and then drying it. This is still the method used to produce aramid fibres today. Typical production rates in modern facilities are on the order of hundreds of meters per minute.
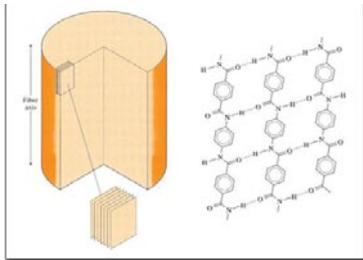

Figure 6: Microstructure of Aramid Fibres

The molecular structure of aramid is similar to Nylon, but the polymer chains are much straighter. This allows them to form into a highly crystalline polymer with the strongest molecular bonds oriented along the length of the fiber, which gives aramids their strength. In the fibres produced by this method the polymer chains join together side-by-side to form sheets. The fibres consist of these sheets, stacked radially as shown in *Figure 6*. The bonds between the chains are much weaker than the bonds within them, and the bonds between the sheets are even weaker. This makes the sheets vulnerable to buckling, and hence aramid fibres are much stronger in tension than in compression. Their tensile strength is similar to E-glass fibres or mesophase pitch-based carbon fibres. Their stiffness is similar to glass fibres, but less than carbon fibres; however, aramids are also have a lower density than either glass or carbon fibres and outperform both in strength per unit weight.

UHMWPE: Ultra-high-molecular-weight polyethylene fibres are more commonly known by trade names such as Dyneema and Spectra. Because of their combination of high strength and low density, UHMWPE fibres have the greatest strength-to-weight ratio of any of the commercialized high-performance fibres: 40% greater than aramid fibres and around 100 times greater than structural steel. They are produced by a gel-spinning process similar to the process used to produce aramid fibres.

Like aramids, their ability to absorb energy makes them extremely useful in applications such as bullet-resistant vests. They are also used in protective cut-resistant gloves and protective clothing because of their extremely good resistance to cutting and abrasion. UHMWPE fibres also find applications in marine ropes and nets, because they are not degraded by water and are also light enough to float.

The use of UHMWPE fibres in composite structures has been limited by several factors. Their use as a reinforcing fibre is made difficult because the fibres are extremely slippery, which can prevent them from forming good bonds with the materials surrounding them. For the same reason, special knots must be used with ropes made

from UHMWPE fibres to prevent the rope from slipping through the knots. Finally, under high loads they are susceptible to a phenomenon called creep, a slow stretching over time, which limits their use in applications where they must carry sustained loads for long periods of time.

The typical mechanical properties of several common types of polymer fibres are summarized in *Table 2,* below.

Fibre Type	Tensile Strength (MPa)	Tensile Stiffness (GPa)
Kevlar 29	2920	70.5
Kevlar 49	3000	112.4
Dyneema SK75	3300	109
Spectra 2000	3340	124

Table 2: Mechanical Properties of Polymer Fibres

CONCLUSION

Modern composite materials can have superlative mechanical properties. The incredible attributes of modern high-performance fibres has allowed the production of lighter, stronger, stiffer and more efficient structures than has ever been possible. ◄

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