Manufacturing Technologies and Scope of Advanced Fibres

Amal Chowdhury and S. Dhamija

1 Introduction

The evolution of fibre developments has gone through the phases of conventional, highly functional and advanced/high-performance fibres. The initial motivation for the development of high-performance fibres came from aerospace industry seeking fibres for light but stiff, strong and tough composite structural parts [1]. Later, constant pursuit for critical applications has enabled further evolution of advanced fibres with a wide spectrum. These advanced fibres are largely used in technical textiles––reaching to different application domains of vehicles, construction, agriculture, sports, health care, defense and security, electronics, power, environmental technologies, filter materials, protective clothing, reinforcement for tyres, rubber goods, composites and many more—thus providing new opportunities to the global textile industry.

For the production of advanced fibres, manufacturers need a comprehensive understanding of the fibre manufacturing technologies in the backdrop of the available fibre-forming polymers. Besides the introduction of new technologies such as gel- and microfiber spinning, there have been developments in melt- wet- and dry spinning. This paper is expected to provide an exposure to the manufacturing technologies of some revolutionary fibres.

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2 Aramid Fibres

These fibres are generally based on aromatic structures with well-oriented rigid chains which bestow excellent mechanical properties and thermal resistance. Aramids decompose before or during melting. Hence, they are spun from the solution. Over the period, a number of aramid fibres like Nomex, Kevlar, etc. have been developed.

2.1 Nomex

Nomex is synthesized by condensation process in which m-Phenylenediamine and Dichloride of m-isophthalic acid react to yield Poly (m-phenylene isophthalamide) or Nomex polymer. The polymer is dissolved in dimethylformamide (DMF) to make a dope solution of 20% polymer. 4.5% of Lithium Chloride (LiCl) is also added to improve its solvency by reducing the viscosity of the solution. The solution is then dry spun using hot air at 200–210 °C. Otherwise, it can also be wet spun by coagulating in water. The as-spun fibre is extracted in cold water with a bid to remove LiCl and lastly drawn. Drawing is carried out with a draw ratio of about 5.5 using steam.

Nomex has excellent thermal resistance [2], but poor mechanical properties. Poor mechanical properties can be attributed to the presence of meta-oriented aromatic rings, which disallow compact packing of molecules. Further, Nomex fibres show good chemical resistance and can also hinder radiation.

As far as applications of Nomex are concerned, it finds its applications in protective clothing in hostile environments having heat, chemicals, and radiation, spacesuit [3, 4], furnishings in public places, industrial fibres. It is also used to make hollow fibres for desalination by reverse osmosis.

Other variants of Nomex, viz., Nomex Delta FF and Nomex Delta Micro have also been developed for improved filtration efficiency.

2.2 Kevlar

The inherent weakness of Nomex fibre is its relatively poor mechanical property. This very fact became a motivation for the discovery of Kevlar fibre. Replacement of meta-oriented aromatic rings with para-oriented rings, perhaps, causes better intermolecular registration of amide groups and make it more crystallizable. This very thought opened a new space for the invention of Kevlar fibre.

Kevlar is synthesized by the condensation of terephthaloyl chloride (TCL) and p-phenylenediamine (PPD) in a mixture of hexamethyl phosphoramide (HMPD) and n-methyl pyrrolidone (NMP) solvents. This synthesis process produces poly (p-phenylene terephthalamide) fibre (PPTA). To avoid degradation and to minimize the side reactions, the polycondensation should be carried out at 10–20 °C. PPTA is dissolved in sulphuric acid. PPTA forms liquid crystal solution under suitable conditions of concentration, temperature, solvent and molecular weight. The liquid crystal form is akin to nematic-like structure. Maximum anisotropy occurs at a polymer concentration of 20% in 100% $H2SO_4$. At this stage, the 100% liquid crystalline phase is achieved. Liquid crystals are characterized by flowable, optically anisotropic structure. They essentially have insufficient energy for individual molecules. This restricts the freedom of rotation of the molecules and thereby assists with the formation of aggregated-parallel-arranged molecules [5].

The process of spinning Kevlar is dry-jet wet-spinning. The polymer is extruded at about 100 °C maintaining an air gap of 1.0 cm or 0.5 cm (Fig. 1). Subsequently, it is coagulated into cold water at the temperatures in the range of 0–5 °C. These conditions lead to bring about good molecular orientation along the spin-line.

During coagulation, the solution undergoes a relaxation effect resulting in a smectic-like structure, giving rise to skin-core super-molecular structure of Kevlar fibre. The properties of the fibre can be varied by introducing variation in the spin stretch factor (SSF). With the increase of SSF, tenacity and modulus both increase. However, these improvements are at the expense of extension to break. SSF is usually maintained less than 10 in a bid to control breakages of filaments. Kevlar, in general, is spun at a speed of around 50 m/min. After being spun, filaments are washed and dried. Subsequently, they are given heat treatment under tension in the range of 450–550 °C for a few seconds. This step helps in the improvement of the orientation of molecular chains to enhance fibre properties. It is important to mention here that Kevlar could also be wet spun. However, mechanical properties of wet spun Kevlar are inferior to those obtained from dry-jet wet-spinning.

Kevlar is accepted as high-performance fibre because of its outstanding modulus, strength, toughness, and temperature resistance. It is lighter in weight, durable and cheaper than steel.

Kevlar finds its best applications in belting in radial tyres and as cord in heavy-duty track tyres and aircraft tyres. These are also used for composite applications in

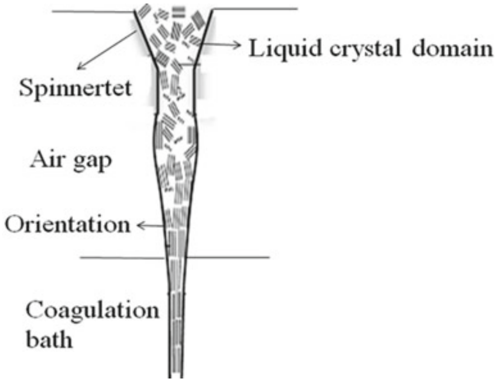

Fig. 1 Liquid crystalline domains in dry-jet wet spinning

civilian and military aircraft, helicopter parts, protective apparel, ropes and cables, industrial fabrics and pressure vessels.

Different grades of Kevlar, namely, Kevlar 29, Kevlar 49, Kevlar 149, Kevlar 981, etc. have been developed to suit various high-performance applications.

3 PBO

PBO [Poly (p-phenylene benzobisoxazole)] is called ‘ordered polymer’ because of its ability to form highly ordered structures in the solid state. The persistence length of PBO is around 640 Å, much higher than that of Kevlar (200 Å), which confers high rigidity to the former.

PBO is synthesized by the condensation of 4,6-diamino-1,3-benzenediol dihydrochloride (DABDO) and terephthalic acid (TA). The reaction is carried out in polyphosphoric acid (PPA) solvent, yielding PBO which has about 200–400 repeat units per chain, which translates into the molecular weight of 50,000–100,000. The dope exhibits liquid crystalline phase which is a function of various parameters such as concentration of polymer, solvent and temperature and is extruded through spinneret using dry-jet wet-spinning technique. Polymer is coagulated in water. Subsequently, filaments are washed and dried. At the next step, fibres are heat treated under tension in an inert atmosphere. The temperature during heat treatment is maintained in the range of 500–700 °C with a residence time of a few seconds to several minutes. Heat treatment causes stabilization of the structure, which may be attributed to post-crystallization and stress relaxation in the fibre.

PBO is known for its high mechanical properties [6] and thermal resistance. However, it possesses poor compressive strength. It is used as reinforcement in composites, multilayered circuit boards, athletic equipment, marine applications and cables. It is also used in fire protection fabrics. Fabrics made from these fibres are used for ballistic protection. As PBO has poor compressive strength, its uses are limited to those applications where axial compression loading does not occur.

4 Vectran

Vectran is made from wholly aromatic polyester. Normal polyester fibre is made from the condensation process of TPA and Glycol, which produces aliphatic-aromatic polymer. Aromatic terephthalic acid residue confers rigidity to the fibre while glycol residue is responsible for its flexibility. It has not been possible to make high-performance fibre of PET, even with high molecular weight. However, wholly aromatic polyesters overcome this shortcoming.

Vectran fibre is made from Vectra liquid crystal polymer [5, 7]. This polymer is made by the acetylation polymerization of p-hydroxybenzoic acid and 6-hydroxy-2-napthoic, which upon melting, attain liquid crystalline phase over a certain range of temperature. The spinning process is akin to melt spinning. The thermotropic liquid crystalline spinning melt is extruded at 280–350 °C through a spinneret. Spinning speed is about several thousand metres per minute. The as-spun fibres are given heat treatment at temperatures of 250–300 °C for several hours. During heat treatment, solid-sate polymerization occurs, which increases molecular weight (M_n) by three times, along with an increase in crystallinity by almost 20%. All these changes enhance fibre strength.

The fibres are largely used for ropes and cables because of their high strength, good abrasion resistance and negligible creep. As Vectran fibres have the excellent vibration-damping capability, they are used as bowstrings, bicycle frames and sailcloth.

5 Spectra

High-performance polyethylene fibres are commercially produced under the trade name ‘Spectra’ by Honeywell in the USA. The only flexible chain which has been commercialized as high-performance fibre is polyethylene. The flexibility of the backbone of chain may be accounted for by two reasons. First, there is a possibility of rotation around C–C bonds in its structure. Second, the presence of light hydrogen as the only other element confers flexibility.

Spectra is synthesized by polymerizing ethylene. Under specific conditions of polymerization, it yields a polymer of high molecular weight (approximate M_w 10^6). However, high molecular weight of polymer always associates high melt viscosity that hinders spinning of fibre from the melt. Furthermore, a flexible polymeric chain of high molecular weight leads to a very high degree of entanglement of the molecular chains—which restricts the drawing of a melt-processed UHMW-PE to a very limited extent.

However, the solution comes with the gelation/crystallization method, a well-known and powerful technique [8], to prepare ultra-high-molecular-weight polyethylene (UHMWPE) fibre. This innovative technique can produce fibres with high modulus and high strength as it offers the advantage for dry gel form of being drawn with a high draw ratio. The polymer is in a ‘gel’ state—only partially liquid—which keeps the polymer chains somewhat bound together. These bonds give rise to strong inter-chain forces in the fibre, which increase its tensile strength. While manufacturing through gel spinning, the polymer is dissolved in decalin or paraffin oil to make 5% solution at 130–140 °C. The solution is pressurized through the spinneret into a small air gap and then enters a water bath (Fig. 2) at room temperature to form a gel fibre.

The fibre is hot drawn with a draw ratio of 30–100 at temperatures of 130–140 °C.

Spectra has lightweight, high strength [9], high modulus, high toughness and high chemical resistance. However, the melting point is low as the chains are flexible. Thus, thermal resistance is a limitation of this type of fibre.

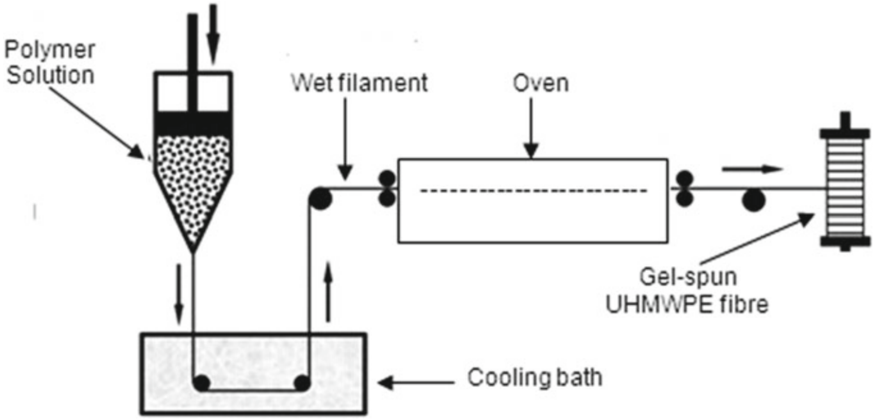

Fig. 2 Gel spinning process

One can find the applications of Spectra in marine ropes, cables, sailcloth, concrete reinforcement, fish netting, sports equipment and medical implants. The high modulus of Spectra permits its use in ballistic protection, cut-resistant gloves. Apart from these, Spectra is also used in space research as layers of polyethylene are supposed to protect astronauts. Polyethylene has a lot of hydrogen, which is a good radiation blocker, thus making it a promising material for spacesuit [10].

Further developments in manufacturing specialized UHMWPE has also been carried out by incorporating multi-walled nanotube [8]. Well-blended UHMWPE-MWNT composites prepared by gelation/crystallization provide characteristics of high modulus along with high electric conductivity.

6 Carbon Fibre

Unlike, other polymeric fibres, carbon fibres have planar graphite structure. The arrangement of the layer planes in the cross section of the fibre is important since it affects the transverse and shear properties of the fibre.

Among various precursors, evaluated for manufacturing carbon fibres, only three precursors, viz., Viscose rayon, Pitch and Polyacrylonitrile (PAN) are commercially successful. Out of these, viscose rayon (carbon yield ~30%) is losing its importance as it produces an inferior quality of carbon fibre. On the other hand, pitch-based precursors produce carbon fibres with a higher yield (80%) and relatively higher strength.

PAN-based carbon fibre is the best when mechanical properties are considered. The production of Viscose rayon and PAN-based carbon fibres involves three stages, viz., oxidative stabilization, carbonization, and graphitization. The temperature may be varied during each stage to produce the type of fibre required.

When it comes to pitch-based carbon fibre, the production route is somewhat different from PAN-based carbon fibre. There are two types of pitch: isotropic and anisotropic. Isotropic pitch goes through centrifugal spinning or melt blowing technique whereas, anisotropic pitch undergoes melt spinning giving liquid crystalline phase to produce carbon fibre. Mesophase pitch fibres can further be heat-treated to produce very high modulus carbon fibres.

Carbon fibre has high specific strength and stiffness. It also exhibits high temperature resistance, chemical and biological inertness, better electrical conductance, good vibration damping ability and fatigue resistance. Two main sectors of carbon fibre applications are the high technology sector that includes aerospace and nuclear engineering. Other applications include bearings, gears, cams, fan blades, automobile bodies and sports equipment.

Carbon fibre has a drawback that they are having an inert surface. So, they do not allow matrix material to make bonding with it. Surface treatment of fibres is one of the suggested methods to improve adhesion between the two [11]. There are various techniques for surface treatment, e.g. gaseous oxidation, liquid-phase oxidation, whiskerization or polymer grafting.

With the development of technology, it has been possible to produce carbon fibres with diameters in the range of 4–50 nm and lengths of several micrometers, using arc and laser ablation process and chemical vapour deposition process. The fibres have well-defined multiple or single wall. Correspondingly, these are known as multi-wall carbon nanotubes (MWCNT) and single-wall carbon nanotubes (SWCNT). These fibres have contributed a lot to high-performance applications.

7 Glass Fibre

Glass fibres come under the category of inorganic fibres. It is relatively inexpensive amongst other inorganic fibres. These fibres have three-dimensional structures in contrast to the uni-dimensional polymeric fibres and two-dimensional carbon fibres.

Glass fibres are produced by the melt-spinning route. It is a special processing technique which is different from those used for other polymeric fibres described earlier.

There are four steps involved in the manufacture of glass fibres. First, dry mixing of ingredients (SiO_2, Al_2O_3, CaO, etc.) is carried out. Second, melting is done in a refractory furnace at 1370 °C. Third, extrusion follows through orifices in an electrically heated platinum bushing and rapid attenuation occurs under gravity [5], accompanied by cooling. Fourth, after solidification, 0.5–2% by weight of size, a binder is applied to the strand. Glass fibres are produced in various forms, namely, strands, roving, chopped strands (3–2 mm), milled fibres (0.8–3.2 mm).

These fibres have moderate density, high strength and corrosion resistance. Applications of glass fibres can be divided into four basic categories: (a) insulations, (b) filtration media, (c) reinforcements and (d) optical fibres. One of the principle high-performance applications for these fibres is in their use as reinforcements for composite materials.

Various types of glass fibres have been developed such as soda-lime-, D-, E- and S- glass fibre, etc. It is worth pointing out that unlike soda-lime glass, the total alkali content in E- and S-glass fibre is kept below 2% to ensure good corrosion resistance and a high electrical surface resistivity. Among these, E-glass fibres are used in fire-resistant textiles, which can be coloured using dyeable sizing.

8 Conclusion

To meet the needs of the consumer, the fibre producer must have a good understanding of how the technologies control the fibre properties. Based on this understanding, the fibre can be engineered by a suitable choice of different variants. To add, far-reaching developments can take place in the growth of high-performance fibres through technological innovations. As the researchers are searching new classes of polymeric materials with unique applications, it is likely that new advanced fibres will be engineered in near future in positive and productive ways. Because of the phenomenal growth of high-performance applications, the future of advanced fibres appears to be very promising indeed. However, an in-depth research is still needed for their development and is poised for a revolutionary change.

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