Manufacturing Technologies and Scope of Advanced Fibres

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Abstract

Fibres form the basic identity of textiles. These are not confined merely to apparel and household textiles (traditional uses) these days; rather have been recognized as advanced fibres in the field of technical textiles. Different sectors of technical textiles viz. automotive, medical, geo-textiles, agro textiles and protective clothing etc. need specific properties for functionality purposes in textile fibres. To cater to the stringent requirements for these specialized applications and the quest to produce sustainable innovative products in respective fields, the world has seen paradigm shift in the technology and growth of advanced fibres. However, these advanced fibres come with several advantages and disadvantages - defining their scope and limitations – and therefore, provide a room for further research in technological developments pertaining to their manufacturing technologies. This paper focuses on the details of the scope of these advanced fibres and related technological advancements/innovations, which will be worthwhile to provide a window to carry out further research in this area.

Keywords: Nomex, Kevlar, PBO, Vectran, Spectra, Carbon

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 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 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 about the fibre manufacturing technologies in the backdrop of the available fibre-forming polymers. Beside 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.

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 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*-Phenylene diamine and Dichloride of *m*-isophthalic acid react to yield Poly (*m*-phenylene isophthalamide) or Nomex polymer. The polymer is dissolved in dimethyl formamide (DMF) to make a dope solution of 20% polymer. 4.5% of Lithium Chloride (LiCl) is also added to improve its solvency. The solution is then dry spun into hot air at 200 – 210^{0}C. Alternatively, it can also be wet spun by coagulating in water. The as-spun fibre is extracted in cold water to remove LiCl and finally drawn with a draw ratio of about 5.5 in 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 have good chemical resistance and can also inhibit radiation.

As far as applications of Nomex are concerned, it finds its applications in protective clothing in hostile environments having heat, chemical 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 (relatively poor mechanical property) of Nomex fibre became a motivation for the discovery of Kevlar fibre. Replacement of meta-oriented aromatic rings with para-oriented rings is expected to allow better intermolecular registration of amide groups and make it more crystallizable. This very thought initiated the invention of Kevlar fibre.

Kevlar is synthesized by the condensation of terephthaloyl chloride (TCL) and *p*-phenylene diamine (PPD) in a mixture of hexamethyl phosphoramide (HMPD) and *n*-methyl pyrrolidone (NMP) solvents. These synthesis process yields a produce named poly (*p*-phenylene terephthalamide) fibre (PPTA). The polycondensation is carried out at 10-20^{0}C to avoid degradation and to minimize the side reactions. PPTA is dissolved in sulphuric acid. PPTA forms liquid crystal solution (nematic-like structure) under certain conditions of concentration, temperature, solvent and molecular weight. The 100% liquid crystalline state is achieved at a polymer concentration of 20% in 100% H_2SO_4, when maximum anisotropy occurs. Liquid crystals have flow-able, optically anisotropic structure and lack sufficient energy for individual molecules to rotate freely in the liquid and therefore form aggregated-parallel-arranged molecules [5].

The process of spinning involved is dry-jet wet-spinning. The polymer is extruded at about 100^{0}C through about 1.0 cm or 0.5 cm of air gap (Figure 1) into cold water maintained between 0 and 5^{0}C, leading to good molecular orientation along the spinline.

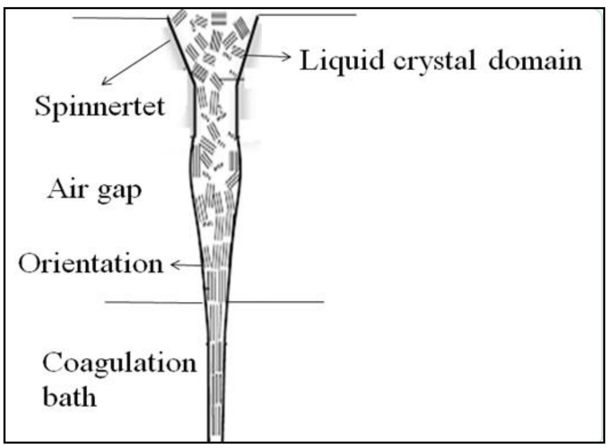

Figure 1: Liquid crystalline domains in dry-jet wet spinning

During coagulation, solution is rearranged under a relaxation effect into a smectic-like structure, giving rise to skin-core supermolecular structure of Kevlar fibre. The properties of the fibre can be diversified by variation in the spin stretch factor (SSF). As the SSF increases, tenacity and modulus both increase at the expense of extension to break. However, it is usually less than 10 to control filament breakages. Spinning speed is around 50m/min. Following washing and drying, filaments are given heat treatment under tension in the range of 450 – 550^{0}C for a few seconds to enhance fibre properties. Kevlar could also be wet spun. However, mechanical properties of wet spun Kevlar are poorer that 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 civilian and military air-craft, helicopter parts, protective apparel, ropes and cables, industrial fabrics and pressure vessels.

Different grades of Kevlar, namely, Kevlar 29, Kevlar 49, Kevlar 149 and 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). Reaction is carried out in polyphosphoric acid (PPA) solvent and PBO of molecular weight of 50000 -100000 is obtained, that corresponds to about 200-400 repeat units per chain. This polymer in liquid crystal solution form is spun through dry-jet wet-spinning technique. Water is used as coagulant. Following washing and drying, the fibres are heat treated under tension in an inert atmosphere. The temperature during heat treatment is maintained in the range of 500 -700^{0}C with a residence time of a few seconds to several minutes. Stabilization that occurs during heat-setting is due 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, multi-layered circuit boards, athletic equipment and for marine applications and cables. It is also used in fire protection fabrics. Fabrics made from these fibres are also used for ballistic protection. However, poor compressive strength limits their use 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 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 produced 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 temperature range. The spinning process is similar to melt spinning. The thermotropic liquid crystalline spinning melt is extruded at 280 – 350^{0}C through spinneret with winding speed several thousand metres per minute. The as-spun fibres are heat treated at temperatures of 250 – 300^{0}C for several hours during which solid sate polymerization occurs (M_n increases by three times), crystallinity increases by almost 20%, enhancing fibre strength.

The fibres are principally used for ropes and cables because of their high strength, good abrasion resistance and negligible creep. Other applications are as bow strings, bicycle frames and sail cloth mainly because of excellent vibration-damping capability.

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 backbone of chain is highly flexible because of the possibility of rotation around C-C bonds and the presence of light hydrogen as the only other element.

Spectra is synthesized by polymerizing ethylene to obtain a polymer of high molecular weight (approximate M_w 10^6). The problem with this polymer is its extremely high melt viscosity that makes the spinning of fibre almost impossible from the melt. Furthermore, the drawing of a melt-processed UHMW-PE is only possible to a very limited extent owing to the very high degree of entanglement of the molecular chains. However, the solution comes with the gelation/crystallization method, a well-known and powerful technique [8], to prepare ultra-high-molecular-weight polyethylene (UHMWPE) with high modulus and high strength arising from the great drawability of the resultant dry gel form, The polymer is in a ‘gel’ state, only partially liquid, which keeps the polymer chains somewhat bound together. These bonds produce strong inter-chain forces in the fiber, 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^{0}C. The solution is pressurized through the spinneret into a small air gap before entering a water bath (Figure 2) at room temperature to form a gel fibre.

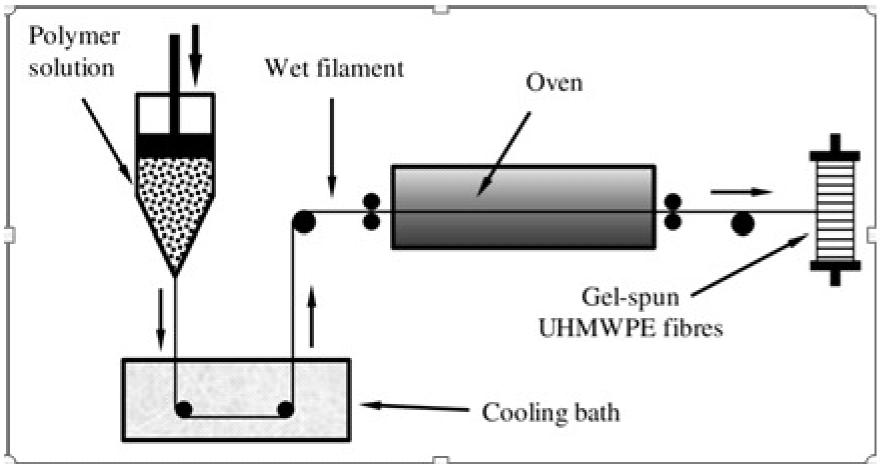

Figure 2: Gel spinning process

The fibre is hot drawn with draw ratio of 30 – 100 at 130 – 140^{0}C.

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

One can find the applications of Spectra in marine ropes, cables, sail cloth, 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. Layers of polyethylene are supposed to protect astronauts because polyethylene contains 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 nano-tube [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 due to inferior quality of carbon fibre. On the other hand, pitch based precursors produce carbon fibres with 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 involve three stages viz. oxidative stabilization, carbonization and graphitization. The temperature may be varied during each stage to produce 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 inert surface and do not allow matrix material to make bonding with it. Surface treatment of fibers is one of the suggested methods to improve adhesion between the two [11]. Hence, after manufacturing of carbon fibre, suitable surface treatment e.g. gaseous oxidation, liquid phase oxidation, whiskerization or polymer grafting is necessary.

With development of technology, it has been possible to produce carbon fibres with diameters in the range of 4 to 50 nanometers 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. Amongst other inorganic fibres, glass fibre is relatively inexpensive. 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, special processing techniques, which are different from those used for other polymeric fibres described earlier. There are four steps involved in the manufacture of glass fibres: Dry mixing of ingredients (SiO_2, Al_2O_3, CaO etc); melting in a refractory furnace at 1370^0C; extrusion through orifices in an electrically heated platinum bushing and rapid attenuation under gravity [5], accompanied by cooling. After solidification, 0.5 – 2% by weight of size, a binder is also applied to the strand. Glass fibres are produced in various forms, namely, strands, roving, chopped strands (3 -12 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 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, 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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