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Fibre Reinforcements for Composites

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ABSTRACT

The paper describes some important aspects concerning the most widely used reinforcing fibres namely, glass, carbon and aramid fibres. An attempt has been made to highlight the factors governing the mechanical properties of these fibres with an emphasis on understanding the factors which determine the properties of the fibres. A brief account of the work carried out at National Aeronautical Laboratory on the development of aramid fibres (NALAR fibres) is presented.

1. INTRODUCTION

Fibres, in general, possess higher tensile strengths compared to the tensile strengths of the same material in the bulk form which is due to one or more of the following reasons[1-3].

(a) Absence of defects of a critical size,
(b) Non-equilibrium structures obtained during preparation of fibres,
(c) Orientation of molecules along the fibre direction in the case of molecularly anisotropic materials like polymers, and
(d) Favourable residual stresses introduced during the fibre manufacturing process.

Out of the four reasons, (a) and (c) are the most important reasons for the higher strengths achieved when a material is converted into fibres. The strength of glass fibres depends on the number of the defects of critical sizes which are less frequent in them compared to bulk glass. In carbon and all polymeric fibres, the higher strength is due to the alignment of graphitic planes or polymer molecules along the fibre direction. When high tensile strengths are derived by an orientation process (as in carbon and polymeric fibres) there is also an increase in the Young's modulus of the fibres. In isotropic fibres like glass fibres, the Young's modulus is essentially the same, both in fibres and in bulk forms.

The higher strength of materials when they are converted to fibres has been the main driving force behind the development of composites. For example, by using glass fibre mats and a polymeric matrix like epoxy or polyester resin it is possible to prepare composite materials with a tensile strength of 200 MPa, where as the tensile strength of sheet glass is only of the order of 120 MPa. Further the glass fibre composites will also have other desirable properties like greater resistance to impact damage. The fibres can be converted into many different forms like fabrics, braided forms, knitted forms, etc which facilitate fabrication of components having complicated geometries in fewer number of fabrication steps.

2. GLASS FIBRES

There are basically five varieties of glass fibres used in composites[4]. These are E-glass, S-glass, R-glass, AR-glass and Z-glass (zirconia containing glass fibres). E-glass fibres are by far the most widely used glass fibres. These are used in resin matrix composite for structural and electrical applications. S-glass and R-glass fibres have superior mechanical properties than E-glass

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fibres. They are generally used in Defence and aeronautical applications. AR- and Z-glass fibres possess good resistance to alkaline environments and are generally used as reinforcements in cement matrix composites.

In India only E-glass fibres are manufactured on a commercial scale. The other varieties are to be imported. S-glass and R-glass fibres may be needed only in small quantities and hence, it may not be economically viable to produce them in the country. However, serious efforts to produce AR-glass fibres in the country should be made since glass fibre reinforced cement will become an extremely imrortent material when the asbestos fibres that are presently being used become unavailable (asbestos fibres are also imported by the users).

Though E-glass is being manufactured in the country in sufficient quantities, the forms in which these are available are as rovings, chopped strand mat and woven fabrics. Rovings are being used for filament winding and making unidirectional pre-impregnated tapes. The major forms in which the fibres are used are the chopped strand mat and woven fabrics. These forms are structurally inefficient forms. Unidirectional tapes, though structurally more efficient, are difficult to handle and are also beset with shelf life and storage problems as they are generally pre-impregnated with a resin. In recent years some novel forms of reinforcements have been developed in developed countries. These new forms are structurally efficient, easy to handle and do not have storage problems associated with impregnated tapes. These forms include non-woven bidirectional fabrics, unidirectional knitted fabrics, veiled tapes, etc. The use of these structurally efficient forms of reinforcement can give about 20 per cent increase in strength and about 60 per cent increase in stiffness over comparable woven reinforcements. Thus it is necessary to develop structurally efficient forms of reinforcements like knitted unidirectional and bidirectional fabrics to increase the cost competitiveness of composite materials.

3. CARBON FIBRES

Carbon fibres are prepared by carbonisation of a precursor fibre in inert atmospheres at high temperatures (1600 to 2200 °C). The precursor can be an organic polymer fibre like rayon or polyacrylonitrile, or it can be petroleum or coal tar pitch fibre[5,6]. The structure and properties of carbon fibres depend on the nature of the precursor and the conditions of carbonisation.

Carbon fibres from rayon precursors do not possess high strength. The tensile strength of these fibres can be improved by employing a high temperature stretch graphitisation. This is mainly due to the fact that cellulose materials yield lower percentage of carbon on heat treatment resulting in higher porosity. The carbon obtained on heat treatment of cellulose is glassy carbon which is difficult to graphitise[5].

Pitch-based carbon fibres have structures very close to that of graphite[6]. Pitch being a mixture of a variety of high molecular weight compounds made up of fused benzene rings, yields soft carbons which graphitise readily at high temperatures. The highly graphitised structure of pitch-based carbon fibres results in high tensile modulus of the fibres. Because of the high modulus, the fibres become extremely sensitive to the presence of defects. Thus the strength of the pitch-based fibres are primarily determined by the number and criticality (size) of the flaws. The critical size of the flaw in high modulus pitch-based fibres is estimated to be around 45 to 60 nm.

Polyacrylonitrile (PAN) precursors on heat treatment gives carbon residue which has a structure which is intermediate between those of rayon and pitch derived carabons[7]. Unlike carbon fibres derived from rayons, carbon fibres from PAN precursors have fairly well developed graphitic sheets but the graphitic sheets have large number of bends and are not as regularly packed as in pitch-based fibres. Consequently PAN based carbon fibres have higher strength than rayon based fibres[8]. The relatively imperfect graphite structure of PAN-based fibres make them less sensitive to defects compared to pitch-based carbon fibres. The critical flaw size of PAN-based fibres are in the range 500 to 600 nm compared to 125 to 150 nm in pitch-based fibres of comparable tensile modulus. Hence higher tensile strengths are more easily achieved in PAN-based carbon fibres than in pitch-based carbon fibres. As a matter of fact by proper choice of precursor and carbonisation conditions it is possible to prepare carbon fibres from PAN precursors having a number of combinations of tensile strength and tensile modulus. Basically the following three grades of fibres are available commercially.

Low modulus carbon fibres: Tensile strength - 3.5 GPa, tensile modulus - 230 GPa.

Intermediate modulus fibres: Tensile strength - 5.5 GPa, tensile modulus - 300 GPa.

High modulus fibres: Tensile strength - 2.5 GPa, tensile modulus - 350 GPa.

Carbon fibres of the first grade are being manufactured in India by IPCL, Baroda. However, the precursor fibres for these fibres are still being imported. The thrust of developmental activity in the area of carbon fibres should be directed towards the development of PAN precursor fibres. Efforts are also needed to gain an understanding of various scientific and technological aspects related to the entire process of manufacture of carbon fibres; from the precursor to the final carbon fibres. Development of intermediate modulus carbon fibres with a tensile strength of 5 GPa and a strain to fracture of 2.0 per cent will be important for aeronautical and Defence applications. Success of such efforts will depend on (i) a complete understanding of scientific aspects of the process like the relationship between precursor structure and the structure of the carbon fibres as a function of processing conditions, and (ii) the development of the technology required to minimise the number of critical defects.

4. ARAMID FIBRES

Aramid fibres are synthetic organic fibres prepared from aromatic polyamides. These are high strength and high modulus fibres with properties suitable for use in composite materials[9]. There are three grades of aramid fibres:

Low modulus fibres with a tensile strength of 3.2 GPa and tensile modulus 60 GPa. These are generally used for reinforcement of rubber.

Intermediate modulus fibres with tensile strength 3.2 GPa and tensile modulus 130 GPa. These are used in reinforced plastics.

High modulus fibres with tensile strength 2.2 GPa and tensile modulus 170 GPa. These are also used in reinforced plastics.

Aramid fibres are prepared by spinning the polymer poly (*p*-phenylene-terephthalamide) (PPTA)[9,10]. The polymer PPTA is synthesised through low temperature polycondensation of *p*-phenylene diamine and terephthaloyl chloride.

PPTA molecules have very rigid backbones due to the presence of aromatic groups in the main chain and due to the absence of flexible linkages between these rigid moities. Because of this, when PPTA is dissolved in suitable solvents, the solutions become liquid crystals in certain concentration and temperature regimes. PPTA dissolves only in strong acids like concentrated H_2SO_4 and HF. In concentrated H_2SO_4, liquid crystalline solutions are formed when the concentration of PPTA in the acid is above 10 per cent by weight. The liquid crystalline solution transforms to an isotropic state above 120 °C.

In the liquid crystalline state the PPTA molecules are highly ordered and are aligned parallel to each other. Spinning fibres from such solutions yield fibres with a high degree of molecular orientation and hence very high tensile strengths and moduli. The important factors which determine the properties of aramid fibres are the molecular weight of the polymer, and the degree of molecular orientation in the fibres. The tensile strength of aramid fibres are determined by the number of hydrogen bonds formed by the amide hydrogen atoms with the amide oxygen which depends on the molecular weight of PPTA. The average molecular weight should be atleast about 45,000 for the formation of enough number of interchain hydrogen bonds and to minimise segregation of chain ends to obtain fibres with tensile strength greater than 3.0 GPa. The fibre spinning conditions should be such that the orientation angle of the PPTA molecules with respect to fibre axis is less than about 10° to get high strength and high modulus fibres.

4.1. Development of Aramid Fibres (NALAR) at NAL

The polymer poly (*p*-phenylene terephthalamide) with molecular weight (weight average) 45,000 has been synthesised at the National Aeronautical Laboratory (NAL) using a specially designed polymerisation reactor. The monomer terephthaloyl chloride of the required purity has also been prepared in the Laboratory. The second monomer *p*-phenylene diamine was purified to obtain polymerisation grade monomer. The synthesis of poly (*p*-phenylene terephthalamide) was carried out on a 1 kg per batch level. The synthesis procedure including preperation and purification of terephthaloyl chloride, purification of paraphenylene diamine and the solvent, *N*-methyl-2-pyrolidone has been standardised.

Fibres were spun from poly (*p*-phenylene terephthalamide) using a solution of the polymer in 100 per cent concentrated sulfuric acid. This solution was extruded through a platinum spinnerette having 200 holes of 60 micrometres each into an air gap of 6 to 10 mm. The liquid jets were coagulated into fibres in water and subsequently neutralised and washed free of sulfuric acid. The washed fibres were then dried at 125 °C under nominal tension. The physical and mechanical properties of the fibres were measured.

The properties of the NALAR fibres are given in Table 1. These properties compare very well with commercial aramid fibres like Kevlar and Twaron.

Table 1. The properties of the NALAR fibres

Colour	golden yellow
Density	1.44 g/ml
Filament dia.	10 to 11 μm
Filament denier	1.3
Filament mechanical properties	
Tensile strength	3.5 GPa (27 gpd)
Tensile modulus	120 GPa (940 gpd)
Elongation to failure	3.5 %

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