

Novel high performance fibres

PUSHPA BAJAJ

Department of Textile Technology, Indian Institute of Technology, New Delhi 110016, India

Abstract. The need for high performance materials for aerospace and other structural engineering applications has led to the development of carbon fibres. At IIT Delhi, an attempt is being made to develop acrylic precursor fibres for manufacturing carbon fibres indigenously. The present study deals with the structural regulation of acrylic precursors during thermo-oxidative stabilization and subsequent carbonization. A new microporous acrylic fibre-acrysolb has also been developed which has high water imbibition and moisture sorption properties. Production of X-ray opaque and antistatic polyester fibres has also been highlighted.

Keywords. Carbon fibres; fibre-acrysolb; water imbibition; antistatic polyester fibres; acrylic precursors or fibres.

1. Introduction

During the last decade, advanced composites based on continuous carbon fibres are being used in the aerospace industry, viz. commercial and military air crafts, in reentry components, rocket nozzles which demand higher operating temperatures. Metals creep at such high temperatures and polymeric materials decompose. Carbon fibres on the other hand, if provided protection from oxidation, are shown to retain their properties to temperatures well above 2000°C.

In addition to space applications, carbon fibres are being used extensively in marine structures, nuclear reactors, biomedical applications etc.

Precursors for carbon fibres are polyacrylonitrile (PAN) based fibres, mesophase pitch or cellulosic fibres. However, PAN based precursors to carbon fibres are selected on the basis of a fairly high degree of C–C orientation within the polymer chain (Balasubramanian *et al* 1992).

Production of carbon fibres from PAN based precursors involve the following as shown in figure 1:

- formation of oriented fibres, usually through solution spinning and a combination of drawing in the gel state and plastic deformation of dried fibres.
- low temperature (200–270°C) thermo-oxidative stabilization of the oriented precursor fibre to yield a structure that can maintain its cohesion during subsequent carbonization.
- carbonization (800–1500°C) in an inert atmosphere to drive off non-carbon elements.
- an optional graphitization (> 2000°C) in an inert atmosphere for producing high modulus carbon fibres.

As the structure of precursor plays an important role in the development of carbon fibres, it is beneficial to do certain modifications of the precursor prior or during thermo-oxidative stabilization for accomplishing high performance carbon fibres. The various factors which influence the thermo-oxidative stabilization are: furnace temperature, rate of heating, time of stabilization, the tension application on the tow, furnace

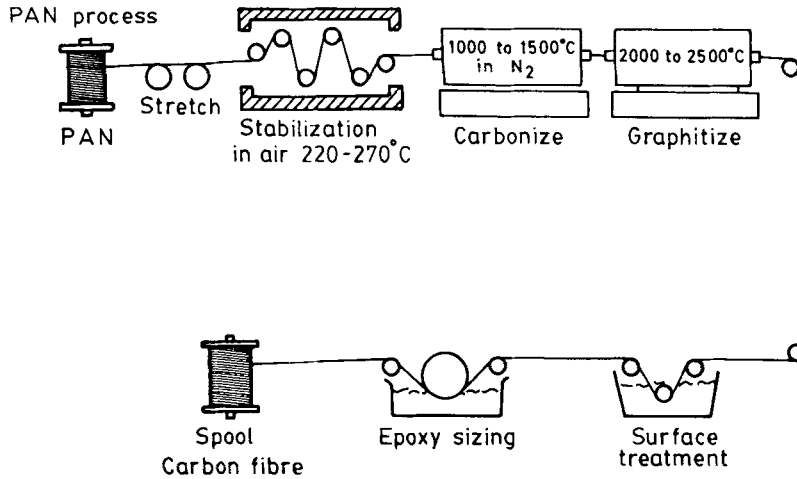


Figure 1. The process of PAN stabilization and subsequent carbonization.

environment and the chemical structure of the precursor (Bashir 1991; Dunham and Edie 1992). In the present study, an attempt has been made to understand the structure development of acrylic precursor during heat treatment in stabilization and carbonization furnace (Roopnwal 1993).

Other speciality acrylic fibres are microporous hydrophilic fibres. Use of additive or polymeric materials have been widely used to improve the hydrophilicity and water retention capacity of acrylic fibres. When an acrylic fibre is solution spun from a dope containing a blend of two incompatible polymers and the content of second polymer exceeds to a certain critical value, phase separation occurs in the resulting fibre, yielding voids in the fibre structure. Such voids if allowed to remain in the final product, may act as capillary conduits for transferring water in or out of the fibre. Following this principle, microporous hydrophilic acrylic fibres have been developed and commercially produced by Pasupati Acrylon (Soni and Gupta 1994).

Hydrophilic, antistatic and X-ray opaque polyester fibres have also been developed by using BaSO_4 as the filler in the melt. BaSO_4 filled PET fibres were subsequently saponified for improving the antistatic and comfort properties of PET fibres (Koul 1994).

Following is the brief summary of the various processes developed at IIT Delhi.

2. Acrylic precursors to carbon fibres

The thermo-oxidative stabilization of the precursor fibres (M and C) was carried out at 230°C for 30 min to 2 h with an air flow rate of 3 l/min. The changes taking place during heat treatment are given below:

(i) Change in weight: Both the precursor fibres, M and C show significant changes in weight during isothermal heat treatment at 230°C for 30 min to 2 h.

Precursor M (AN/MAA) shows a weight gain of 14.2% during first hour of heat treatment which reduced to about 7% in the subsequent heat treatment cycle. On the contrary, precursor C (AN/MA/IA), shows a weight loss from initial stages of heating cycle which gradually increases to 4.8% in 2 h. The weight gain in precursor M may be

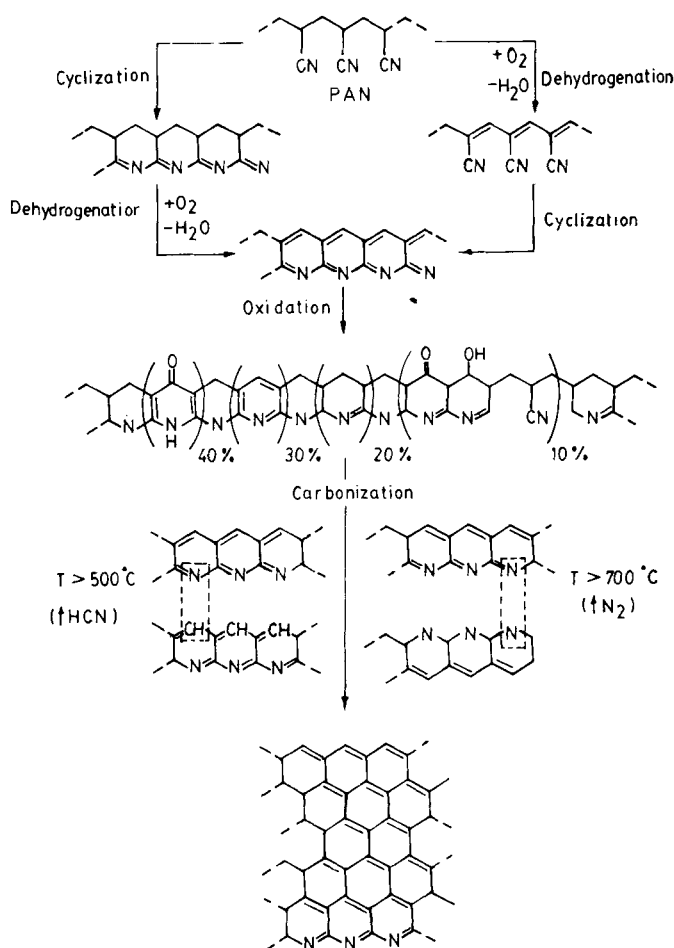


Figure 2. Structure development during stabilization and carbonization.

attributed to the higher amount of oxygen pick up along with the liberation of some volatiles during thermo-oxidative stabilization which results in the formation of oxygen containing groups (such as $-\text{OH}$, $>\text{C}=\text{O}$, $-\text{COOH}$) in the polymer. The loss in weight in precursor C is due to the removal of volatiles such as NH_3 , HCN , CO and H_2 during stabilization much more than M. Differential behaviour in terms of weight gain/loss of the two fibres may be explained as: during heat treatment in air, the precursor fibres do pick up oxygen which facilitates the cyclization and intermolecular crosslinking reaction. At the same time, some volatiles are also produced during dehydrogenation and cyclization reaction (figure 2). Since both the processes, viz. oxygen pick up and liberation of volatiles, are occurring simultaneously, the change in weight amongst the two fibres could be attributed to their different chemical structure and oxygen pick up.

Elemental analysis of heat treated samples further confirms the greater oxygen pick up in case of precursor M which is in accordance with the changes in weight of two precursors during stabilization.

It has been demonstrated by Fitzer *et al* (1986) that oxygen acts in two opposite ways during stabilization. On the one hand, it initiates the formation of active centres for cyclization, while on the other hand, it retards the reactions by increasing the activation energy. Thermal stabilization in air is therefore preferred as it results in the formation of some oxygen containing groups ($-\text{OH}$, $>\text{C}=\text{O}$, $-\text{COOH}$) in the backbone of ladder polymer, which subsequently help in fusion of the ladder chains during carbonization (figure 2).

(ii) Density: The density of the acrylic precursors increases during heat treatment perhaps due to the closer packing of molecules because of the ladder polymer

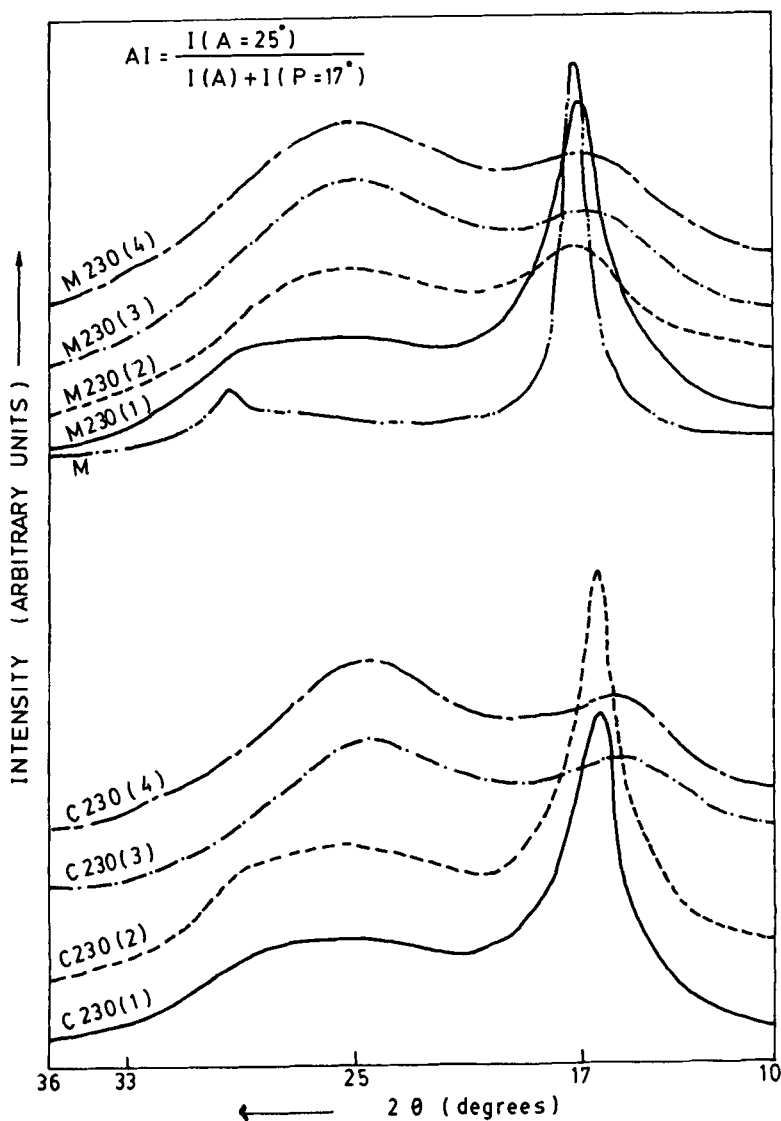


Figure 3. Wide angle X-ray diffraction pattern of precursors C and M stabilized at different temperatures and time.

formation and incorporation of oxygen in the polymer. From the data, it may be seen that precursor M(AN/MAA) has higher density values than precursor C(AN/MA/IA) during thermal stabilization for different times. The higher density values of precursor M suggest higher degree of cyclization during thermo-oxidative stabilization and/or higher oxygen pick-up during stabilization as reported by Mathur *et al* (1994).

(iii) Wide angle X-ray diffraction (WAXD): Wide angle X-ray diffractograms of acrylic and stabilized fibres for varying time (0.5 to 2 h) are shown in figure 3. The X-ray scans of the precursor fibres show only one intense and one weak equatorial reflections at $2\theta = 17^\circ$ and $2\theta = 29^\circ$ respectively. The equatorial reflections corresponding to Bragg spacing of approximately 0.52 nm ($2\theta = 17^\circ$) due to (100) planes of pseudo hexagonal lattice or due to (200) planes of the orthorhombic unit cell, and one corresponding to a Bragg spacing of 0.3 nm ($2\theta = 29^\circ$) due to (201) planes of orthorhombic structure or (101) planes of pseudo hexagonal cell are obtained. Off equatorial reflections are generally absent. This observation has led to the inference of a lack of periodicity in the direction along the fibre axis and the presence of only lateral order. Energetically favourable conformation of the PAN molecule is a helix, with the pendant nitrile groups having no specific orientation with respect to the helix axis. The large dipole moment of the nitrile groups together with their close proximity in space leads to a very large intramolecular dipolar and steric repulsion which compel the individual macromolecules into a somewhat helical conformation. Thus, the structural units in PAN may be assumed to be helices placed 0.6 nm apart on hexagonal array. The parallel rods constitute the major part of the ordered phase in a fibril. The rods are not in perfect alignment with respect to rod ends, but rather exhibit some misalignment. The disoriented regions connecting the rods consist of loops, folds, entangled chains, defects, comonomer sequences etc. The lateral dimensions (L_c) of the ordered domains as estimated from WAXD data, are in the range of 5 to 20 nm, depending on the thermal

Table 1. Wide angle X-ray diffraction data of precursors M and C stabilized at 230°C.

| Sample code | Density (gcm^{-3}) | Crystallinity (%) | Size of lateral order (crystal size L_c (nm)) | AI (%) | Orientation (%) |
|-----------------------------|-------------------------------|-------------------|---|--------|-----------------|
| M(AN/MAA) 98:2 wt% | 1.184 | 51 | 6.62 | — | 86.1 |
| $M_{(230)(0.5)}$ | 1.29 | 40.2 | 4.40 | 11.1 | 85.4 |
| $M_{(230)(1.0)}$ | 1.32 | 32.6 | 3.61 | 21.6 | 81.9 |
| $M_{(230)(1.5)}$ | 1.345 | 22.5 | 2.09 | 33.9 | 71.1 |
| $M_{(230)(2.0)}$ | 1.345 | 17.6 | 1.53 | 46.6 | 65.0 |
| C(AN/MA/IA) (93:6:1 wt%) | 1.182 | 41.2 | 5.67 | — | 83.2 |
| $C_{(230)(0.5)}$ | 1.29 | 39.6 | 4.40 | 8.1 | 81.0 |
| $C_{(230)(1.0)}$ | 1.296 | 36.2 | 3.78 | 16.8 | 72.0 |
| $C_{(230)(1.5)}$ | 1.305 | 29.7 | 2.94 | 30.6 | 66.3 |
| $C_{(230)(2.0)}$ | 1.313 | 22.76 | 2.27 | 42.4 | 55.0 |

FWHM, Full width at half maximum intensity; AI, aromatization index; AM, acrylonitrile; MAA, methacrylic acid; MA, methyl acrylate, IA, itaconic acid; M or $C_{230(0.5)}$, stabilized at 230°C for 30 min.

history of precursor fibres. The length of these domains is of the order of 8 to 10 nm, roughly twice that of disordered regions (Gupta *et al* 1991; Balasubramanian *et al* 1992).

In the present study, average lateral size (L_c) and crystallinity calculated from the equatorial scans are higher for precursor M (51% and 6.62 nm) as compared to precursor C (41.2% and 5.67 nm). The orientation values obtained (table 1) are also in the same order. Wide angle X-ray diffraction patterns of stabilized fibres show that the main reflection at $2\theta = 17^\circ$ due to (100) planes of ordered domains diminishes with the heat treatment and spread of these reflections indicate a decrease in crystallinity and crystal size (table 1).

On stabilization, a new diffuse scattering at $2\theta = 25.5^\circ$ which according to Pinghua *et al* (1992) will sharpen into (002) spacings on carbonization, is developed. The appearance of this scattering is due to the formation of cyclized aromatic structures in the polymer (figure 3).

Structural parameters (crystallinity %, lateral size and orientation) obtained from WAXD measurements show a sharp decrease with stabilization. The decrease in structural parameters is more in sample M due to the loss of ordered region with the progress in the cyclization reaction. The crystallinity after 2 h of heat treatment in stabilized samples M and C were found to be 17.6 and 22.76% and lateral size 1.53 and 2.26 nm respectively. This shows total collapse of ordered domains during stabilization resulting in a amorphous structure which later develops into stacks of graphite structure during carbonization.

The aromatization index (AI) which is a measure of degree of cyclization, was calculated from relative intensities at $2\theta = 17^\circ$ and $2\theta = 25.5^\circ$ peaks. A gradual increase in AI values suggest a steady progress of cyclization reaction (table 1). At every stage of stabilization, precursor C shows lower value of AI than precursor M. After 2 h of heat treatment precursor M showed an AI value of 46.6% and precursor C a value of 42.4%. This is also supported by higher ΔH values of precursor M in DSC. By KMnO_4 and CoCl_2 treatment the process of cyclization appears to be delayed as supported by aromatization index. However, with boric acid treatment, AI of the stabilized precursor M was similar, viz. 45% in $MB_{230(2)}$.

The tensile strength of the fibres shows a continuous decrease during the stabilization due to decrease in cohesive energy between the molecular chains as the $-\text{C}\equiv\text{N}$ are converted into $-\text{C}=\text{N}-$ groups during cyclization. It is observed that precursor M retained higher strength than precursor C (table 2). Interestingly, for an equivalent aromatization index boric acid treated precursor showed higher TM in $MB_{230(2)}$ as compared to $M_{230(2)}$.

The elongation-at-break also shows an increase due to deterioration in the morphological order and cohesive energy density between the molecular chains.

2.1 Carbonization in a furnace

Original and chemically treated precursor fibres M and C stabilized at 230°C were subsequently carbonized in a furnace up to 1000°C in an inert atmosphere in low temperature and high temperature furnaces. In LT furnace, the fibres were heated between 300 to 600°C under tension, then in HT furnace between 600 to 1000°C . The changes taking place during carbonization are discussed below:

(i) Density: The density of the carbon fibres varies in the range of 1.749 to 1.815 g cm^{-3}

Table 2. Properties of chemically pretreated precursor fibres stabilized at 230°C.

| Sample | AI (%) | TS (GPa) | TM (GPa) | Strength retention (%) | Elongation-at-break (%) |
|---------------------------------|--------|----------|----------|------------------------|-------------------------|
| M | — | 0.68 | 12.2 | — | 10.5 |
| AN/MAA (98:2 wt%) | | | | | |
| M ₂₃₀₍₂₎ | 46.6 | 0.32 | 9.7 | 46.0 | 11.1 |
| MK _{230(0.5)} | 10.2 | 0.64 | 12.24 | 94.0 | 12.3 |
| MK ₂₃₀₍₂₎ | 35.0 | 0.45 | 11.6 | 66.0 | 16.1 |
| MC _{230(0.5)} | 10.8 | 0.58 | 12.5 | 85.5 | 10.1 |
| MC ₂₃₀₍₂₎ | 40.0 | 0.34 | 12.2 | 50.0 | 12.6 |
| MB _{230(0.5)} | 11.0 | 0.58 | 12.0 | 85.0 | 13.5 |
| MB ₂₃₀₍₂₎ | 45.0 | 0.28 | 12.8 | 40.1 | 9.8 |
| C (AN/MA/IA) (93:6:1 wt%) | — | 0.66 | 8.25 | — | 16.3 |
| C ₂₃₀₍₂₎ | 42.4 | 0.30 | 11.9 | 41.0 | 18.7 |
| CK _{230(0.5)} | 9.6 | 0.64 | 9.0 | 96.0 | 15.2 |
| CK ₂₃₀₍₂₎ | 34.0 | 0.34 | 11.6 | 51.5 | 18.48 |
| CC _{230(0.5)} | 10.2 | 0.59 | 9.1 | 89.2 | 14.4 |
| CC _{230(2.0)} | 33.3 | 0.33 | 10.7 | 50.0 | 21.2 |
| CB _{230(0.5)} | 9.9 | 0.52 | 9.9 | 78.8 | 16.1 |
| CB ₂₃₀₍₂₎ | 42.0 | 0.29 | 10.0 | 44.0 | 17.1 |

(table 3). The density of the carbon fibres increases due to packing of fibre structure in graphite form during carbonization. The variation in density values may be attributed to the following factors:

- Varying degree of carbonization due to difference in the chemical nature of the precursors and chemical pretreatments.
- Varying density values of stabilized fibres used for carbonization.
- A number of voids or cavities produced during carbonization.

The variation in density would also depend upon aromatization index of stabilized fibres, oxygen pick up and packing of molecules during stabilization.

(ii) Mechanical properties: The mechanical properties of the carbon fibres are dependent on the preferred orientation of the carbon basal planes and the flaws present. The modulus of the fibres depend upon the preferred axial orientation while the strength will be a function not only of preferred orientation, but also on the extent of flaws present.

It is observed that the carbon fibres obtained from precursors M and C have similar tensile strength (1.9–2.0 GPa). However, the carbon fibres from precursor C (AN/MA/IA) showed higher modulus (89.5 GPa) as compared to the carbon fibres obtained from precursor M (69.9 GPa). This suggests that MA/IA comonomers in precursor C help in the development of more regulated structure in stabilized fibres, and subsequent carbon fibres.

Table 3. Mechanical properties of the carbon fibres.

| Sample code | Dia. (μm) | Density (g/cm^3) | Filament (d_{pf}) | T.M. (GPa) | Elongation at break (%) | T.S. (GPa) |
|-------------|------------------------|------------------------------------|-----------------------|------------|-------------------------|------------|
| M | 8.1 | 1.761 | 0.82 | 69.9 | 2.8 | 1.9 |
| MK | 7.5 | 1.752 | 0.70 | 102.7 | 2.4 | 2.3 |
| MC | 6.9 | 1.749 | 0.60 | 109.4 | 2.4 | 2.6 |
| MB | 6.3 | 1.764 | 0.50 | 116.2 | 2.2 | 2.5 |
| C | 7.2 | 1.770 | 0.65 | 89.9 | 2.2 | 2.0 |
| CK | 6.6 | 1.815 | 0.56 | 71.7 | 2.4 | 1.7 |
| CC | 6.3 | 1.803 | 0.554 | 120.1 | 2.2 | 2.6 |
| CB | 6.2 | 1.782 | 0.50 | 151.8 | 2.4 | 3.6 |

CK, MK, KMnO_4 treated; MC, CC, cobaltous chloride treated; MB, CB, boric acid treated precursor.

The tensile strength and modulus of the carbon fibres improved by the chemical treatments except with KMnO_4 in precursor C. This suggests that the chemical treatments like COCl_2 and boric acid accelerate the process of cyclization and subsequent formation of graphitic carbon. The boric acid treatment exhibited the best performance in both the precursors (CB, TS = 3.6 GPa and TM = 151.8).

2.2 Wide angle X-ray diffraction

X-ray diffractograms show a sharp equatorial reflection at $2\theta = 25.5^\circ$ corresponding to d-spacing of 0.343–0.345 nm due to (002) planes of turbostratic carbon and one diffused reflection at $2\theta = 43^\circ$ due to (100) planes.

The wide angle X-ray measurements show that the crystal size (L_c), and the mean number of layer planes (L_c/d) are higher in carbon fibres produced from precursor M ($L_c/d = 3.54$) as compared to precursor C ($L_c/d = 3.21$). Higher mean number of layer planes, (L_c/d) in case of M, indicates higher number of crystalline carbon basal planes.

The crystal size or stack height (L_c) and mean number of layer planes (L_c/d) further improve in chemically treated fibres in both the precursors, M and C (table 3).

3. Microporous acrylic fibres

The hydrophilic fibre made at Pasupati has a microporous structure which is obtained by conjugate spinning of polyacrylonitrile with a cellulose derivative. The cellulose acetate gets distributed in an elongated form having its longest dimension parallel to the fibre axis. The resulting phase separation in the two leads to development of voids. These micro voids are distributed both in core and sheath. This provides the fibre with enhanced water absorption and rapid capillary action and thereby faster moisture transport. Properties of hydrophilic acrylic fibres produced by blending with acrylonitrile–vinyl acetate (AN–VA), AN–acrylic acid (AN–AA) and P_6B_8 blend with 10% cellulose acetate are given in table 4.

Although the fibre has a microporous structure it has depicted good tensile properties. Table 5 gives the characteristics of hydrophilic acrylic fibre along with normal acrylic fibre and cotton.

Table 4. Properties of hydrophilic acrylic fibres.

| Sample | Void content | | | | Water retention (%) |
|---|------------------------------|------------------------|-------------------------|-------------------------------|---------------------|
| | Density (gcm ⁻³) | Mercury density method | Water absorption method | Porosity (cm ³ /g) | |
| P ₀ (AN-MA-SAMPS) 92:7.2:0.8 wt% | 1.19 | 0.05 | 0.06 | 0.04 | 6.24 |
| P ₂ B ₂ (AN-VA blend) 4.2% VA | 1.188 | 0.18 | 0.19 | 0.18 | 14.5 |
| P ₅ B ₀ (AN-AA blend) 2% AA | 1.182 | 0.31 | 0.33 | 0.38 | 29.73 |
| P ₀ B ₈ (10% C A blend) | 1.175 | 0.45 | 0.53 | 0.69 | 46.62 |

Table 5. Comparison of different fibres.

| Characteristics | Normal acrylic fibre | Hydrophilic acrylic fibre | Cotton |
|------------------------------|----------------------|---------------------------|---------|
| Denier | 1.5 | 1.5 | 1.5 |
| Tenacity (g/d) | 3.0-3.5 | 2.8-3.0 | 2.1-3.0 |
| Elongation at break (%) | 35-40 | 26-30 | 3-10 |
| Water imbibition (%) | 3-5 | 25-35 | 35-45 |
| Density (gcm ⁻³) | 1.17 | 1.19 | 1.54 |
| Capillary action | Poor | Excellent | Good |
| Drying capacity | Excellent | Very good | Good |
| Dyeing properties | Very good | Very good | Good |

Extensive work has been done by the company in the production of towels and knitted fabrics out of the hydrophilic acrylic fibres. The test results are given in table 6. It was established that these towels have an excellent absorption, and in addition to that it can dry very quickly. They are extremely durable and have excellent colour fastness. These towels unlike cotton towels remain soft in repeated washes. Tests conducted on knitted fabrics have also yielded equally good results.

This new hydrophilic acrylic fibre introduced is most appropriate for the climatic conditions prevailing in tropical countries like India.

4. Production of BaSO₄ filled X-ray opaque PET fibres

In the medical applications, the polyester fibre sutures coated with polytetrafluoroethylene, silicones or polytetramethylene adipate are known for their excellent stability in the biological environment. Dacron tube treated with CH₂Cl₂ and NO₂ can be used as prostheses for repair or replacement of damaged ligaments or tendons. Isotropic

Table 6. Comparison of hydrophilic acrylic and cotton towels.

| Property | Acrylic hydrophilic towels | Cotton towels |
|--|----------------------------|---------------|
| Water retention (%) | 768 | 525 |
| Comparative drying | | |
| (a) Water retained on soaking for 30 sec and squeezing (%) | 169 | 243 |
| (b) Water retained in sample a after 1 h drying in ambient temperature (%) | 6 | 62 |
| (c) Residual water in sample a after 2.5 h drying in ambient temperature (%) | 6 | 65 |
| No. of cycles required to rupture the towel | 1035 | 469 |
| Washing fastness | | |
| (a) Change in shade | 4/5 | 4 |
| (b) Staining on white cloth | 4/5 | 4 |
| Crock fastness | | |
| (a) Dry | 5 | 5 |
| (b) Wet | 4/5 | 4/5 |

Table 7. Mechanical properties of drawn BaSO₄ filled PET fibres (D.R. = 5.2).

| Sample | Tex | Tenacity (cN/tex) | Strength retention (%) | Breaking elongation (%) | Modulus (N/tex) | Density (g cm ⁻³) | Boiling water shrinkage (%) |
|---|-----|-------------------|------------------------|-------------------------|-----------------|-------------------------------|-----------------------------|
| P ₀ (PET) | 2.0 | 39.38 | 100 | 24 | 10.0 | 1.370 | 7.5 |
| P ₀ Si | 1.9 | 39.0 | 99 | 26 | 9.0 | 1.370 | 7.2 |
| P ₀ C ₁ | 2 | 39.0 | 99 | 27.5 | 9.2 | 1.369 | 7.0 |
| P ₀ C ₂ | 1.9 | 37.0 | 94 | 24 | 10.5 | 1.369 | 7.1 |
| P ₀ SiF ₅ | 2.1 | 37.1 | 94.2 | 22 | 12.5 | 1.401 | 5.1 |
| P ₀ SiF ₁₀ | 2.3 | 31.0 | 78.7 | 20 | 10.0 | 1.441 | 4.9 |
| P ₀ SiF ₂₀ | 2.7 | 22.1 | 56.1 | 20 | 8.5 | 1.582 | 4.1 |
| P ₀ SiF ₅ C ₁ | 2.4 | 38.04 | 96.6 | 23 | 13.7 | 1.399 | 6.0 |
| P ₀ SiF ₁₀ C ₁ | 2.5 | 35.5 | 90.1 | 23 | 12.0 | 1.440 | 5.5 |
| P ₀ SiF ₂₀ C ₁ | 2.6 | 26.0 | 66.02 | 21 | 10.0 | 1.582 | 5.2 |
| P ₀ SiF ₅ C ₂ | 2.2 | 34.0 | 86.3 | 23 | 13.2 | 1.400 | 5.1 |
| P ₀ SiF ₁₀ C ₂ | 2.3 | 32.0 | 81.2 | 19 | 10.4 | 1.442 | 4.8 |
| P ₀ SiF ₂₀ C ₂ | 2.5 | 23.2 | 58.9 | 18 | 8.9 | 1.584 | 4.3 |

P₀Si, Silicone oil coated; P₀C₁, titanate coated; P₀C₂, titanate coated; P₀SiF₅, 5% BaSO₄ filled.

carbon coated strand of polyester fibres are used as artificial tendon prostheses. X-ray opaque PP fibres containing 55 to 70% barium sulphate and a titanate coupling agent (isopropyl-*tri*-isostearyl titanate) have been found suitable for surgical swabs and dressings.

In the present study, an attempt has been made to produce X-ray opaque and antistatic polyester fibres from BaSO₄ (5–20 wt%) filled PET. Influence of titanate

coupling agents and silicone oil used for blending, on the spinnability of BaSO₄ filled PET has also been highlighted.

Breaking strength and breaking elongation of X-ray opaque fibres decreases with the increase in BaSO₄ filler (5 to 20 wt%) (table 7). The initial modulus also decreases with the increase in filler content. The breaking strength decreases from 39.38 cN/Tex for unfilled polyester to 22.1 cN/Tex for 20% BaSO₄ filled polyester fibre. The increase in initial modulus was from 10.0 N/Tex (for unfilled polyester) to 12.5 N/Tex (for 5% BaSO₄ filled polyester). The increase in initial modulus is attributed to reinforcing effect of rigid fillers into an elastomeric matrix. The lowering of tensile properties may be due to (i) poor matrix–filler adhesion, (ii) poor dispersion of filler particles in the polyester matrix and (iii) formation of voids in the filled fibres.

Further, it was observed that with the use of titanates, neoalkoxy *tri*(dioctyl phosphato) titanate, C₁ and C₂ neoalkoxy *tri*(dioctyl) pyrophosphato titanate coated BaSO₄ (5 to 20 wt%), the breaking strength and elongation-at-break showed a decrease over unfilled polyester fibre, though the improvement was observed over uncoated BaSO₄ filled fibre at 20% filler level for C₁ coated filler. The breaking strength improved from 22.1 cN/Tex (20% uncoated BaSO₄) to 26.0 cN/Tex (20% C₁ coated BaSO₄).

The analysis made from scanning electron microscopy (SEM) showed that dispersion is more uniform in case of polyester fibre containing C₁ and C₂ coated BaSO₄ filler. Agglomeration can be distinctly seen for 20% uncoated BaSO₄ filled fibre.

4.1 Shrinkage behaviour

The data obtained from boiling water shrinkage and TMA shrinkage experiments of PET (unfilled) and BaSO₄ filled fibres showed noteworthy results—the shrinkage values as expected decreased with the addition of BaSO₄. The presence of filler particles act as heterogeneous nuclei and promote rapid crystallization, in particular at higher molecular mobility, and thus retard the shrinkage process substantially. The reduction in the shrinkage values was further supported by the orientation values which decrease for the filled samples.

4.2 Differential scanning calorimetry

From melting endotherms of BaSO₄ filled and unfilled fibres, it was seen that the onset of melting, T_i (initial melting temperature), and T_m (peak melting temperature), shifts to the lower side for all the BaSO₄ filled fibres. This can be attributed to the smaller and less perfect crystals indicating the nucleating ability of BaSO₄. The crystallinity values increase for the barium sulphate filled sample over control PET sample.

4.3 WAXD

The wide angle X-ray diffraction (WAXD) patterns obtained for unfilled polyester and BaSO₄ filled polyester fibres showed that the reflections were more sharp for filled samples which further improved with annealing.

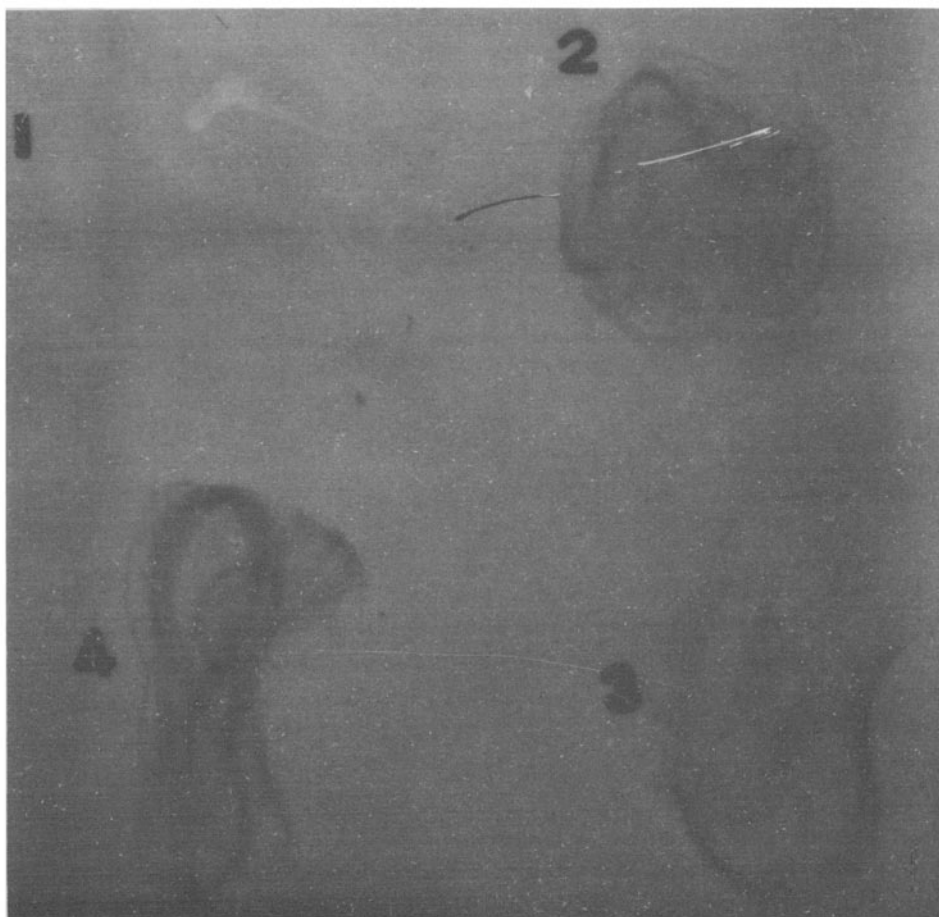


Figure 4. X-ray opaque PET fibres.

4.4 *X-ray opacity of BaSO₄ filled polyester fibres*

It was possible to obtain X-ray opaque fibres with a loading of 10 to 20% BaSO₄, however, at 20% loading, opacity was better which further improved with the addition of titanate (figure 4).

4.5 *Antistatic property*

Samples filled with BaSO₄ were tested for antistatic properties. It was observed that by the addition of BaSO₄ the decay time reduced from 460 sec (unfilled) to 145 sec (filled with 5% BaSO₄), whereas saponified samples also showed an improvement in antistatic properties. The decay time decreased from 250 sec (unfilled) to 125 sec (filled). Even in case of unfilled PET, the saponified sample showed better antistatic properties.

References

- Bashir Z 1991 *Carbon* **29** 1081
- Balasubramanian M, Jain M K, Bhattacharya S K and Abhiraman A S 1987 *J. Mater. Sci.* **22** 3864
- Dunham M G and Edie D D 1992 *Carbon* **30** 435
- Fitzer E, Frohs W and Heine M 1986 *Carbon* **24** 387
- Gupta A K, Paliwal D K and Bajaj P 1991 *Rev. Macromol. Chem. Phys.* **C31** 1
- Koul R 1994 *Synthesis, characterization and production of X-ray opaque and antistatic polyester fibres*, Ph D Thesis, Indian Institute of Technology, New Delhi
- Mathur R B, Mittal J, Bahl O P and Sandle N K 1994 *Carbon* **32** 71
- Pinghua W, Jie Lin, Zhongren Yue and Rengyuan Li 1992 *Carbon* **30** 113
- Roopanwal A K 1993 *Effect of comonomers and chemical pretreatments on the thermo-oxidative stabilization of acrylic precursors and resulting carbon fibres*, Ph D Thesis, Indian Institute of Technology, New Delhi
- Soni Bhavna and Gupta V 1994 *AATCC Book of Papers, International Conf. and exhibition* (NC, USA: Am. Assoc. of Textile Chemists and Colorists) p. 24