Some recent advances in the production of acrylic fibres for specific end uses

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Since the introduction of acrylic fibres as a wool-like apparel fibre to the textile market in the early 1950s, their applications have greatly diversified. Substantial modifications of the acrylic fibres are now possible at several points in the manufacturing route. These range from the selection of comonomers through changes in spinning conditions to specific thermal and chemical modifications. In this paper, some of the developments which have taken place in the recent past to tailor the properties of acrylic fibres for specific applications have been highlighted.

Keywords: Acrylic fibre, Antibacterial fibre, Carbon fibre precursor, High-performance fibres, Solution spinning, Spinning additives

1 Introduction

Acrylic fibre has replaced wool in many major applications, particularly in hand-knitted and hosiery garments. Blankets and carpets are the other applications where acrylic fibre competes with wool because of its high elasticity, colour brilliance, voluminosity, resistance to pilling, and colour fastness properties.

Acrylic fibre for textile or technical uses has always been valued for its resistance to UV radiation, mildew, bacteria, etc. Its low specific mass and adequate elasticity make it an ideal material for the production of textiles with excellent thermal insulating properties.

In the past decade, as a result of a number of physical and chemical modifications, it has been possible to produce a variety of acrylic fibres for specific end uses. The modified acrylic fibres produced include high-shrinkage flame-retardant, antistatic, acid-dyeable, germ-resistant, ion-exchange, profile and microdenier fibres. Polyacrylonitrile (PAN) fibres have also proved to be excellent precursors for carbon fibres.

In Japan, modified acrylic fibres, as described above, account for one third of the total acrylic fibre production, and even more than one half in some companies. The range of acrylic fibres being offered includes wet- and dry-spun, spun-dyed, shining, matt and flame-retardant and other industrial-grade fibres. Acrylic fibres are available in various deniers and cut lengths, and with different shrinkage and crimp properties.

This paper deals with some of the recent developments in the modification of acrylic fibres at various stages of its manufacture.

2 Advances in the Spinning of Acrylic Fibres

2.1 Wet Spinning

The process of wet spinning is very versatile as it enables a wide range of properties to be achieved. The principal parameters that influence the fibre structure and properties at this stage are: polymer composition, dope formation and its viscosity, coagulation bath composition and its temperature, spinnerette dimensions, drying, steaming, nature of the finish applied, and crimping. These factors have a predominant influence on the internal morphology, surface characteristics, cross-sectional shape, and tensile and frictional properties of the fibre. Studies on the inter-relationship between spinning parameters and fibre properties enhance our understanding of how structure develops during spinning; consequently, fibres for specific applications can be tailor-made.

In conventional wet spinning of acrylic fibres, the occurrence of voids, particularly large voids, has an adverse effect on fibre properties and has, therefore, been the subject of investigation by a number of research workers. These studies suggested that void formation is a diffusion-related problem. The coagulation of fine dope stream involves the diffusion of solvent from the interior of the coagulating fibre into the bath and the diffusion of water in the reverse direction. The surface cuticle of the coagu-
ating fibre thus plays a decisive role in the diffusion of solvent and water. The important features of the coagulated fibre structure can be determined by examining the cross-sections of the filaments with the help of electron microscope. Large tear-shaped voids, known as macrovoids, that begin near the outer edge of the filament and extend to the centre are generally observed.

A number of investigations have been made to optimize the microvoid structure of protofibres, i.e. the fibre as it emerges from the spin bath, by varying the coagulation bath composition and its temperature. Coagulation baths consisting of polyalkylene glycol and solvent produce dense fibre with very fine fibrils and the desired microvoid structure. The high molecular weight glycols diffuse into the fibre very slowly and a fine microvoid structure is formed as the solvent diffuses out. The use of hexanetriol, low molecular weight alcohols and cumene-paraffin mixtures in the spinning bath has also been reported.

When the spin bath temperature is increased from 10 to 70°C, the cross-sectional shape of the freeze-dried protofibres undergoes a transition from kidney bean to round, and macrovoids begin to appear at the higher bath temperatures. In a recent paper, Catoire et al. have reported the structures of acrylic protofibres, produced at 5, 20 and 40°C spinning bath temperatures, as observed through spectroscopic techniques [electron spin resonance (ESR), infrared (IR) and electron microscopy]. Their production unit is shown schematically in Fig. 1. The fibres were extruded into a spinning bath which contained a mixture of DMF (48%) and water (42%). After coagulation, the unwashed gel was drawn to a draw ratio of 1.33 at 25°C. The washed gel fibre was subsequently heated in water at 98°C allowing 25% shrinkage and then drawn in the same bath to a draw ratio of 5.5. Fibre samples were collected at five locations along the production line for characterization.

It was observed that a decrease in spin bath temperature resulted in densification of the protofibre structure (collected at the first step). The fibre coagulated at 40°C had relatively larger voids than the fibre coagulated at 20°C. IR data showed that at the coagulation step, the nitrile orientation factor (as deduced from the dichroic ratio) does not show any significant difference in the protofibres on account of coagulation bath temperature. However, as a result of the air drawing step (3rd step in Fig. 1), the orientation factor increases and becomes sensitive to the spin bath temperature (40°C < 20°C < 5°C). After the water-boiling step (the fifth step of the process), the authors observed a significant difference in the orientation values of the fibres coagulated at 5°C and 40°C; the orientation value for the 40°C coagulated fibres was considerably lower.

ESR studies using the spin probe technique indicated that at the coagulation bath step, the bulk of the structure was accessible. However, after the boiling-water shrinkage step, a relatively more compact macromolecular structure (pore-matrix composite), characteristic of acrylic finished fibres, was found to develop.

We have studied the effect of spinning dope additives and spin bath temperatures on the structure and properties of wet-spin acrylic fibres. At a higher coagulation bath temperature, coagulation takes place by counter diffusion of solvent and nonsolvent in approximately equal volumes across the fibre surface. As the coagulation temperatures are lowered, the outward diffusion of solvent predominates, resulting in non-round sections, higher fibre density and low pore size. Consequently, the fibres produced at high coagulation bath temperature (60°C) scattered less light, when examined on the optical microscope, and appeared brighter. Further,
addition of 5% secondary cellulose acetate as an additive in the spinning dope resulted in fibres with relatively low density, high moisture regain (2.6% against 1.6% of the parent fibre), and a three-to-four fold increase in water retention values. Dye uptake values are also enhanced by the use of spinning dope additives.

Zuguang and Anding varied the coagulation bath temperature from 7 to 16°C using 8% NaSCN as a coagulator. As shown in Table 1, an increase in the coagulation bath temperature accelerates the formation of tow, and reduces the formation of sticky fibres and fibre defects. However, tenacity is reported to decrease if the spinning bath temperature is higher than 16°C.

In another interesting study, Gupta et al. have demonstrated the effect of hot-wet draw ratio on the coefficient of friction of wet-spun acrylic fibres using dimethylacetamide-water mixture in the coagulation bath. The fibres were produced with different cascade stretches, keeping the final denier constant by adjusting the cascade and the jet stretches; the overall draw ratio was also kept constant at 5. The measurement of friction by both the line and the point contact methods was carried out on an Instron machine using a traverse rate of 0.5 in/min. Table 2 lists the average values of the coefficient of friction for the two levels of the initial tensions and also the values of the sonic modulus orientation factor. The value of the orientation factor increased with cascade stretch but the rate of increase gradually dropped with increase in stretch ratio. A linear correlation has been found between the molecular orientation and the interfibre coefficient of friction in wet-spun and hot-wet-drawn acrylic fibres. From scanning electron microscopy of acrylic fibre surfaces, it was postulated that the smoothing out of the surface leads to a more intimate or greater area of contact with increased draw ratio, which is responsible for higher interfibre coefficient of friction.

### 2.2 Gel Dyeing

Recently, efforts have been made to dye acrylic fibres in the gel state during wet spinning. The protofibre has fibrillar and porous structure with a network of fibrils. This loose structure of protofibre has adequate permeability for dye molecules and is exploited to develop the process of gel dyeing. The gel dyeing may be carried out at any of the following stages during wet spinning: (i) coagulation, (ii) washing and stretching and (iii) after stretching.

Gel dyeing in coagulation bath is also known as Neochrome dyeing. In this process, the dope is extruded into a dye bath having coagulating reagent. The dye molecules enter the protofibre and a dyed tow emerges out of the coagulation bath. The fibres dyed by this technique have a tendency to release the dye during subsequent washing and stretching and this is known as bleeding. The other shortcoming of the fibres dyed by this technique is their poor fastness property.

The tow of protofibre may also be dyed during the washing and stretching stages. The fibre is treated with a solution of the dye at the time of washing or stretching. Due to the open structure of undried fibre, the diffusion of the dye into the fibre is very quick even at low temperatures. The equipment needed for dyeing consists of two pairs of squeeze rollers, guide rollers and airing device. Uniform and

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cascade stretch</th>
<th>Sonic modulus orientation factor</th>
<th>Average coefficient of friction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>108mN</td>
<td>245mN</td>
</tr>
<tr>
<td>1</td>
<td>2x</td>
<td>0.6949</td>
<td>0.186</td>
</tr>
<tr>
<td>2</td>
<td>3x</td>
<td>0.7316</td>
<td>0.221</td>
</tr>
<tr>
<td>3</td>
<td>4x</td>
<td>0.7556</td>
<td>0.230</td>
</tr>
<tr>
<td>4</td>
<td>5x</td>
<td>0.7715</td>
<td>0.235</td>
</tr>
<tr>
<td>5</td>
<td>6x</td>
<td>0.7847</td>
<td>0.238</td>
</tr>
<tr>
<td>6</td>
<td>7x</td>
<td>0.7918</td>
<td>0.243</td>
</tr>
</tbody>
</table>
constant concentration of dye in the liquor results in uniform shade. The dye concentration is continuously monitored by an on-line spectrophotometer interfaced with a metering pump.

The problem of bleeding, which is due to the presence of solvent in the fibre, is reduced if the tow of acrylic fibre is dyed after stretching but before drying since on drying, the porous and fibrillar structure collapse and causes hindrance to the diffusion of dye.

Gel dying is advantageous because it reduces the cost of production of a dyed fibre by saving energy and time. Moreover, it is not necessary to establish and maintain a separate dye house. However, there are some limitations, viz. problem of bleeding, poor fastness properties and contamination of solvent recovery area with colourants, which have to be overcome to make this process a success.

Monsanto, USA, has also developed a spun-coloured acrylic staple fibre with high light fastness. This fibre called Du-Rel is considered to be suitable for the industrial vehicle trade.

2.3 Dry Spinning

The story of acrylic fibres started with dry spinning, but the production facilities set up during the last ten years are dominated by the wet spinning technique.

Owing to the different physical conditions that prevail during the formation of primary filaments, wet- and dry-spun acrylic fibres are easy to distinguish. There are significant differences in the cross-section and surface structure. Some new developments in the production of dry-spun acrylic fibres have been described by Wagner of Bayer AG. The aim of these is to improve process economics, minimize solvent losses, control pollution, and to stabilize the quality of the product.

Dry spinning involves the extrusion of spinnable dope into a hot chamber in which hot gases are circulated to evaporate the solvent from the extruded fibres. The spinning speeds are much higher (500-1000 m/min) than the speeds commonly used in the wet spinning process.

Compared to wet-spun fibres, dry-spun acrylic fibres have higher cover because of dog-bone shape. In addition, the dry-spun fibres have softer feel, better whiteness and whiteness retention after repeated washings. However, the dyeability of the dry-spun acrylic fibres is inferior to that of wet-spun products.

In India, there are two manufacturers of acrylic fibres, viz. J.K. Synthetics, Kota, and Indian Petrochemicals Corporation Ltd (IPCL), Baroda. The production of acrylic fibres in India started in 1979 when IPCL commenced the production of 'Indacryl' fibre using wet spinning technology of Asahi Chemicals Industries, Japan. They have recently commissioned another production plant based on DuPont's dry spinning technology.

J.K. Synthetics is producing acrylic fibre 'Jaykryl' using the wet spinning process based on the technology of Montefibre, Italy.

2.4 Dry-Jet-Wet Spinning

A new spinning process, namely dry-jet-wet spinning, has been introduced to avoid the formation of big voids which adversely affect the properties of fibres. This process is characterized by the fact that small streams of dope extruded from the die are allowed to pass first through a short air gap before entering the spinning bath for complete coagulation. This process clearly combines the advantages of dry spinning with those of wet spinning.

Dry-jet-wet spinning possesses the advantages of high speed of fibre formation, high concentration of dope and high degree of jet stretch that usually characterize the dry spinning method, but still retains the capability of controlling the structure of as-spun fibres by adjustment of spinning bath parameters.

During dry-jet spinning, a thin, dense, hydrophobic cuticle is formed which decreases the rate of diffusion of water into the fibre. As a result of this, no big voids are formed irrespective of the change in coagulating conditions. At high jet stretch this is particularly marked, in agreement with the increase of $D_n / D_s$ (ratio of diffusion coefficients in solvent and non-solvent) as is clear from an examination of Figs 2(a) and 2(b). The jet stretch in the air gap and inside the bath tends to enhance the formation of a dense cuticle and a dense, coherent gel in case of dry-jet spinning, and prevents the formation of big voids. This results in a fibre of high transparency.

Fig. 2a—Effects of dope concentration on the ratio of diffusion coefficients in immersion-jet (wet) spinning at different temperatures: (1) 50°C, (2) 30°C, and (3) 10°C. The symbol D denotes diffusion coefficient and subscript 's' and 'n' denote solvent and non-solvent respectively.
Fig. 2b—Effects of dope concentration on the ratio of diffusion coefficients in dry-jet spinning at different temperatures [(1) 50°C, (2) 30°C, and (3) 10°C] (ref. 10).

2.5 Melt Spinning

Acrylic fibres could not be produced by the melt spinning technique in the early days as they tended to degrade well below their melting point. However, by the addition of water or plasticizers, it is now possible to decrease the melting point. As a result, melt spinning of acrylonitrile polymers has been possible. Frushour has reported the depression of melting temperature of polyacrylonitrile (PAN) from 320°C to 185°C. Similarly, the addition of polyethylene glycol reduces the melting point of the acrylic polymer and makes it melt spinnable.

Asahi Chemical Co. Ltd. have melt-spun acrylic fibres from acrylic polymer containing water and a water-soluble polymer (PEG); the fibres had a tenacity of 0.38 GPa (4.3 gpd). In another patent, the production of heat-resistant acrylic fibre is described by melt spinning of acrylic polymer at 230°C to give heat-resistant fibres of tenacity 0.25 GPa (2.9 gpd).

Mitsubishi Rayon Co. Ltd., in its patent, disclosed the process for melt spinning of acrylic fibres of tenacity 0.42 GPa (4.8 gpd). The acrylic copolymer was blended with another copolymer (of similar constitution) of low molecular weight (Mw = 4800) and extruded through a 72 hole spinnerette at 215°C.

Grove et al. investigated the structure and mechanical properties of melt-spun water-plasticized PAN fibres. The morphology of these fibres is reported to be similar to that of wet- and dry-spun acrylic fibres; however, surface defects and internal voids are more in the melt-spun water-plasticized fibres than in the wet- or dry-spun ones.

3 Chemical Modification of Acrylic Fibres

3.1 Acrylic Fibres with Enhanced Hydrophilicity and Dyeability

Small amounts of certain comonomers may be added to acrylonitrile to enhance the mobility of polymer segments and thereby improve dye diffusion. Most commercial acrylic fibres contain 5-10% of methyl acrylate, methyl methacrylate or vinyl acetate as plasticizing molecules. In addition, use is made of acid comonomers such as methallyl sulphonate or styrene sulphonate acid as dye accepting molecules.

With plasticizing molecules in the main chain, the rigid coherency of the polyacrylonitrile chain is disturbed. They loosen up the overall structure. The second-order transition temperature, at which the chain molecules become mobile in relation to one another, is lowered. Basic dyes can now diffuse unhindered from the dye bath into the fibre at boiling temperature.

Attempts have been made to produce hydrophilic acrylic fibres by copolymerization of acrylonitrile with vinyl monomers containing functional groups, i.e. hydroxy-, ester-, carboxyl, amide and substituted amides

\[- \text{H}_2 \text{C}-\text{CH}-(\text{OH})_m-\text{CH}_2-\text{CH}-(\text{OH})_n-\text{CN} X\]

where X = OH, COOH or COOR

Acrylonitrile copolymers containing 1-4.8 mol% of hydroxyalkylmethacrylate comonomer were found to give hygroscopic fibres with good dyeability. Poly(acrylonitrile-2-hydroxymethyl methacrylate) copolymer fibres with 4.26 mol% of the comonomer had a moisture regain of 2.4% at 65% RH. The dye uptake of Astrazon Yellow of the same copolymer fibre was 6-7 times higher than that of the corresponding PAN homopolymer fibres.

Grafting of AN-methylacrylate copolymer with fibroin was found to improve the hydrophilicity and dyeability of the resulting fibres. Addition of fibroin and collagen to the spin bath has also been reported. Addition of ≤20% of these compounds increases the strength of PAN fibres, particularly its resistance to repeated deformations. These fibres have a uniform structural network and morphology.

Toyobo Co. has reported the use of milk casein as the amorphous portion and polyacrylonitrile for the crystalline portion for developing Chinon silk-like fibres. Table 3 shows the chemical composition and properties of Chinon and silk fibroin. The manufacturers of Chinon and silk fibroin. The manufacture of Chinon can be divided into three steps: (i) polymerization, (ii) solution spinning, and (iii) recovery of solvents. An outstanding characteristic of
3-oxohydrid... 3.2 High Water-Absorbent Acrylic Fibres

This type of high water-absorbent acrylic fibre normal acrylic fibres. sages are formed. This promotes capillary action which absorbs water quickly and this effect remains unchanged during drying and dyeing processes. This type of high water-absorbent acrylic fibre maintains the physical and mechanical properties of normal acrylic fibres.

In a Japanese patent, acrylic fibres with 54% water retention have been reported. These fibres were obtained by wet spinning a mixture of regular polyacrylonitrile and acrylonitrile-styrene copolymer. To obtain a porous acrylic fibre, the polyacrylonitrile and the added copolymer must be incompatible. The criterion of incompatibility is the difference of solubility parameter of the blend components. The composition of the copolymer, the sequence distribution of segments in the copolymer and the spinning bath temperature influence the void structure. Since there are a large number of small holes in the fibre, and its specific gravity is about 25% less than that of normal acrylic fibre, light and warm wearing comfort is experienced.

3.3 Antistatic and Conductive Acrylic Fibres

Acrylic fibre is made of non-ionizing hydrophobic polymer with a high resistance of $10^{13}$ ohm/cm, which can easily accumulate an electrostatic charge. This can cause dust adherence and also a spark discharge. In order to solve the problem of static generation, a lot of research has been done which may be considered under the following categories.

(i) Copolymerization of PAN with poly(ethylene oxide) is reported to confer characteristics to antistatic acrylic fibres. Copolymerization of N-3-oxohydrocarbon substituted acrylamide and poly(ethylene glycol) acrylates or methacrylates was also reported to provide another route to antistatic fibre production.

(ii) Permanent anti-electrostatic acrylic fibres were obtained by the addition of block copolyether ester to PAN spinning solutions. The permanency of the antistatic effect was influenced by the conditions of coagulation. It was found that poly(ethylene oxide) exerted the greatest influence over the lowering of electrical resistance (Table 4).

In an excellent review by Brown and Pailthorpe, a number of formulations have been listed for the production of antistatic acrylic fibres. Acrylic fibres can be made conductive by spinning from mixtures containing electroconductive fillers such as carbon black, antimony oxide, tin oxide, titanium dioxide, ammonium or metal salts, or copper ions. Polymeric additives in the fibre spinning dope include polyester/polyether block copolymers, diacrylic ester of poly(ethylene glycol) and sulphur containing polyethers. Addition of nylon 6 (5% by weight) to AN-methylacrylate-sodium methallylsulphonate, and 5-10% poly(ethylene adipate) to AN-methyl styrene-vinyl acetate copolymer gave antistatic fibres.

Electrically conducting acrylic fibres based on treatment with zinc oxide have been reported by Kanebo. Another approach is provided by the Exlan process, in which a copolymer of 86% acrylonitrile, 11% vinyl acetate and 3% dimethyl amino

| Table 3—Chemical constitution of Chinon fibre and silk fibre |
|-----------------|-----------------|
|                  | Crystalline part | Amorphous part |
| Chinon           | Polyacrylonitrile | Milk casein     |
|                  | 70              | 30              |
| Silk fibre       | Fibroin         | Platin          |
|                  | 80              | 20              |

Chinon fibre is its dyeability. It has an affinity for various classes of dyes (acid, premetalized, mordant, direct and basic) and exceptional build-up properties.

Addition of glycerol or tetraethylene glycol in the spinning dope of an AN-methylacrylate-sodium methallylsulphonate terpolymer is reported to have given fibres with 10% water retentivity.

Fibres having 7% moisture absorption (65% RH at 21°C) and water retention capacity of at least 25% were produced by dry spinning of AN copolymer containing more than the specified amount of carboxyl groups from a solvent containing 5-50% (w/o) of an additive having a boiling point higher than that of the spinning solvent. However, the production of porous acrylic fibres by adding some soluble material into the fibres during formation processes and then removing it by washing after treatment is inefficient and expensive.

3.2 High Water-Absorbent Acrylic Fibres

For certain applications, acrylic fibres of porous structure with high water retention and warmth and good insulating and dyeing properties are required. Bayer Co. in West Germany successfully introduced high water-absorbent acrylic fibre “Dumova” in 1976. Later, similar products were developed by Japanese companies. Researchers at China Textile Univ. developed water-absorbent fibres with a total water content of 20-35% of the fibre weight. The principle is to add another copolymer, which is soluble in dimethyl sulphoxide but insoluble in polyacrylonitrile molecule, and yet remain as a macro-molecule in the dope. Due to its shrinkage during coagulation, many small pores with connecting passages are formed. This promotes capillary action which absorbs water quickly and this effect remains unchanged during drying and dyeing processes. This type of high water-absorbent acrylic fibre maintains the physical and mechanical properties of normal acrylic fibres.

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|                  | 80              | 20              |
Table 4—Effect of spinning bath additives on some physical properties of polyacrylonitrile fibres

<table>
<thead>
<tr>
<th>Additive</th>
<th>Gauge dtex</th>
<th>Tensile strength cN/tex</th>
<th>Elongation at break %</th>
<th>Loop tenacity cN/tex</th>
<th>Temp. of glass transition °C</th>
<th>Hygroscopicity %</th>
<th>Dyeability mg dye/100 g fibre</th>
<th>Electrical resistance ohm/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without additive</td>
<td>11.26</td>
<td>24.2</td>
<td>35.0</td>
<td>11.1</td>
<td>75</td>
<td>10.1</td>
<td>18.8</td>
<td>$5 \times 10^{11}$</td>
</tr>
<tr>
<td>Poly(ethylene oxide)</td>
<td>11.24</td>
<td>27.8</td>
<td>33.6</td>
<td>13.2</td>
<td>88</td>
<td>13.8</td>
<td>7.2</td>
<td>$6 \times 10^{04}$</td>
</tr>
<tr>
<td>Salts</td>
<td>11.27</td>
<td>24.6</td>
<td>33.3</td>
<td>11.6</td>
<td>80</td>
<td>21.0</td>
<td>19.0</td>
<td>$1 \times 10^{11}$</td>
</tr>
</tbody>
</table>

Ethylmethacrylate is spun into fibres and then treated in a solution containing copper sulphate and $\text{(NH}_2\text{OH})_2\text{H}_2\text{SO}_4$. The resulting fibres were reduced in a solution containing $\text{Zn(HSO}_4\text{CH}_2\text{O)}_2$ to give fibres rich in copper ions with a specific resistance of only $33 \text{ ohms/cm}$ compared to $10^{10} \text{ ohms/cm}$ without this treatment.

It has also been demonstrated that partial saponification of acrylic fibre fabrics with 2% NaOH improves the dissipation of static charge significantly (Fig. 3).

### 3.4 Ion-Exchange Fibres

Fibres possessing ion-exchange properties have been spun from a copolymer comprising acrylonitrile and the quaternary salt of 1,2-dimethyl-5-vinyl pyridine methyl sulphate or 2-methyl-5-vinyl pyridine and also from poly(acrylonitrile-methyl vinyl pyridine) copolymers. Attempts have been made to produce ion-exchange fibres from mixtures of polyacrylonitrile and poly(ethylene imine). The various routes used for the production of ion-exchange fibres along with some of the fibre properties and applications are listed below.

#### Production Routes

- Reaction with hydroxyl amine
- Reaction with hydrazine
- Hydrolysis with NaOH
- Grafting onto acrylic fibres
- Copolymerization

#### Properties

- Large surface area
- Electrically conductive
- Catalytically active
- Improved heat stability
- Improved fire resistance

#### Applications

- Recovery of rare metals
- Removal of heavy metals

Through partial saponification with NaOH and reaction with hydrazine, it is possible to obtain ion exchangers which can bind metal ions both ionically and in complexes. The capacity and selectivity of the exchange fibres can be influenced by the reaction conditions, concentration, time and temperature.

The large surface area of the fibres controls their ion-exchange property. Simanova has reported the use of ion-exchange fibres for the selective exchange of rare metals such as ruthenium, osmium, uranium and with waste water treatment through the adsorption of cadmium or zinc.

In another study, a fibre exchanger has been used as a second downstream ion-exchange unit for the removal of zinc ions from industrial effluent.
3.5 Flame-Resistant Acrylic Fibres

Acrylic fibres have an oxygen index (OI) of 18%, which is the lowest among all textile fibres. Attempts have been made to impart flame retardancy to acrylic fibres through incorporation of halogen- or phosphorous-containing vinyl comonomers.

Self-extinguishing modacrylic fibres have been produced from a terpolymer containing AN (35-85%), vinylidene chloride (5-30%) and Me[Et]P(O)CH₂CH₂OOCCH = CH₂ (5-30%). Main examples are Teklan (Courtaulds) and Monsanto SEF. The latter is used in the USA for tents, awnings and upholstery, but the possible workwear uses must be restricted to those in which radiant heat is not encountered. Moreover, the low softening point of chlorofibre discourages its use in several types of workwear for flame protection.

In another study, AN copolymers containing 2-9 mol% halalkyl acrylate and/or methacrylate have been used for producing hygroscopic and flame-retardant acrylic fibres.

By far the cheapest of the fire blocking fibres, and the most persistent under flame, are oxidized acrylic fibres like Panox. A blend of Panox, Kermel (polyamide-imide) and wool represents a very useful combination for producing comfortable fibres to wear when the going gets hot.

R.K. Textiles is one of the world's largest manufacturers of oxidized polyacrylonitrile fibres which are used in advanced carbon/carbon brake aircraft systems and fire-resistant barrier fabrics.

3.6 Acrylic Antimicrobial Fibres

A range of acrylic fibres has been produced through chemical modification to fix bacteriostats. Included in this group are fibres described as having antimicrobial activity, antibacterial or as being bactericidal. Many patents claim fibres which incorporate phenol derivatives such as 3-methyl-4-isoproponylphenol and 2,4,4’trichlorohydroxydiphenyl ether.

A new high performance acrylic fibre, known as Courtek M, which can prevent the build up of hazardous bacteria in cloth furnishings and medical equipment, has been developed by Courtaulds, U.K. The fibre contains a combination of antimicrobial compounds, based on metallic salts. These compounds are bound into the fibre matrix, which means their effectiveness is not minimized by wear and washing. Courtaulds predict that the fibre will find many applications in industry and clothsings required in hospitals, food processing or intimate apparel, where the build up of dangerous bacteria can be unpleasant or a hazard to health.

<table>
<thead>
<tr>
<th>Tensile properties of Courtek M are listed below:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Property</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>Tenacity, cN/tex</td>
</tr>
<tr>
<td>Relative wet strength, %</td>
</tr>
<tr>
<td>Breaking elongation (dry &amp; wet), %</td>
</tr>
<tr>
<td>Moisture regain at 20°C, 65% RH</td>
</tr>
<tr>
<td>Sp. gravity, g/cm³</td>
</tr>
<tr>
<td>Heat resistance under constant exposure (moist &amp; dry), °C</td>
</tr>
</tbody>
</table>

4 Technical Applications of Acrylic Fibres

4.1 Acrylics in Filtration

Due to their excellent resistance towards acids, acrylonitrile homopolymer fibres are recommended for wet filtration under acidic conditions. Acrylic woven fabrics have, therefore, been used in chemical, galvanic, petroleum and mining industry. The advantages of such filter media are:

(i) No rotting under constant moist conditions,
(ii) Easy removal of filter cake, and
(iii) Scouring/cleaning at large intervals.

Further, the low swelling capacity ensures that fabrics made of this fibre retain their air permeability in a moist atmosphere.

In the form of filter hose and filter bags, it is used for dry filtration, e.g. in the separation of fly ash in coal fired power stations. Table 5 shows the physical properties of Dralon T fibres used in filtration.

Nonwoven fabrics produced from blends of antibacterial acrylic fibre and polypropylene can be used as air filters. Such fabrics have been noted for their high air permeability, low bulk and high efficiency.

Hollow fibres have also been recommended for reverse osmosis, gas separation, ion-exchange, ultrafiltration and dialysis. Courtaulds has developed a porous acrylic fibre, Courtek D, which has a structure similar to that of a conventional wet-spun acrylic fibre but with considerably increased porosity. These fibres can be used as a carrier system for the controlled release of pharmaceuticals, bactericides, fungicides, pesticides, horticultural nutrients, and acid-alkali absorbents.
4.2 High Tenacity Acrylic Fibres as a Substitute for Asbestos

Attempts were made to develop a synthetic fibre that could replace asbestos in fibre-reinforced cement products, e.g., in flat roof sheets and facing slabs, corrugated sheets, and discharge and vent pipes. Polycrylonitrile would appear to be a likely candidate for replacing asbestos because of its good chemical resistance in alkaline media. Hoechst AG has recently developed Dolanit fibres (type 10, 12, 15) by varying certain process parameters in spinning and aftertreatment. Fig. 4 shows the stress-strain behaviour of the different industrial-grade acrylic fibres compared with a textile-grade acrylic, Dolan 37. The breaking strength of Dolanit 10 is about 980 N/mm². Fibre-reinforced cement sheets containing 2% (by wt) Dolanit 10 and 4% (by wt) cellulose were tested for flammability and in all the tests the material met the requirements for Building Material Class A₁ of DIN Standard 4102, Part 1, and may be classified as a non-flammable building material that develops no toxic gases.

In sprayable concrete, used for embankment stabilization, tunnel linings, etc., shrinkage cracks are significantly reduced by Dolanit VF 11. In comparison to steel fibre-reinforced sprayable concrete, no corrosion occurs. Montefibre has also produced a high-modulus polycrylonitrile fibre, RICEM, which can be used as a reinforcing medium for cement matrices, as an alternative to asbestos, or in eliminating cracks in mortar or concrete in the curing stage.

RICEM has been made from homopolymer of polycrylonitrile of high molecular weight (Mw = 500,000), spun using conditions which impart a high degree of orientation to the amorphous phase.

The extrusion is through jets into a coagulation bath of water and solvents. The resulting void-free fibre undergoes the following operations in sequence: washing → stretching in boiling water → drying stretching at 200°C → cooling → winding under tension. The total draw ratio of the fibre is greater than 12 which results in a high degree of orientation.

The flat sheets made with 2% RICEM and 3.5% pulp fibres showed the same bending strength as sheets produced with 15% asbestos. In addition, boards produced with RICEM are less brittle and are able to absorb a greater breaking force (Fig. 5).

4.3 Acrylic as a Precursor for Carbon Fibres

Among the various precursors for carbon fibre, PAN has a wide acceptability due to high carbon yield and flexibility for tailoring to a desired product. The weight loss at 1000°C in helium is quite low for PAN fibres compared to that for various other precursors of carbon fibres.

To produce good quality carbon fibres, special acrylic fibres (SAF) are required. SAF forming polymers should possess the following properties:

(i) High molecular weight in the range of 10⁵.

(ii) Moderate molecular weight distribution with dispersion 2-3, and

(iii) Minimum molecular defects at the polymerization stage.

The precursor fibre should have:

(i) Fine denier (10-12 μm diameter).
Table 6—Effect of acid and alkali on mechanical properties of RICEM

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Tenacity cN/tex</th>
<th>Elongation %</th>
<th>Modulus cN/tex</th>
<th>Residual tenacity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>77.0</td>
<td>9.4</td>
<td>2154</td>
<td>—</td>
</tr>
<tr>
<td>In 50% H₂SO₄ at 20°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>after 7 days</td>
<td>76.3</td>
<td>9.4</td>
<td>2088</td>
<td>99</td>
</tr>
<tr>
<td>after 30 days</td>
<td>76.0</td>
<td>9.4</td>
<td>2070</td>
<td>99</td>
</tr>
<tr>
<td>after 60 days</td>
<td>75.2</td>
<td>9.4</td>
<td>2069</td>
<td>98</td>
</tr>
<tr>
<td>In 30% HNO₃ at 20°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>after 7 days</td>
<td>77.3</td>
<td>9.8</td>
<td>2133</td>
<td>100</td>
</tr>
<tr>
<td>after 30 days</td>
<td>77.6</td>
<td>9.2</td>
<td>2231</td>
<td></td>
</tr>
<tr>
<td>after 60 days</td>
<td>76.9</td>
<td>9.6</td>
<td>2123</td>
<td></td>
</tr>
<tr>
<td>After soaking in NaOH (pH 13)</td>
<td>69.3</td>
<td>9.8</td>
<td>1721</td>
<td>90</td>
</tr>
</tbody>
</table>

(iii) High strength and modulus,

(ii) During heating, the exothermic peak due to nitrile group oligomerization should be broader and the threshold temperature should also be low, and

(iv) High carbon yield (> 50%).

High molecular weight and a moderate MWD are the essential requirements for producing high-strength precursor fibres. Acrylonitrile copolymer of intrinsic viscosity > 2.36 is not recommended owing to poor spinnability and filtration ability, while the copolymers with intrinsic viscosity values < 1.25 yield fibres with poor mechanical properties.

Amongst the various comonomers used for the production of acrylonitrile copolymer, itaconic acid (0.5-2%) seems to be superior. It has been established that its carboxylic group comes in the vicinity of nitrile group and initiates the exothermic cyclization reaction at lower temperature. The propagation step in the thermal cyclization is also slowed down in comparison to the PAN homopolymer.

The heat evolved in PAN is quite high during the propagation reaction; it might be detrimental to the properties of carbon fibre if not dissipated efficiently. Hence, acrylonitrile copolymers with low percentage of acidic comonomer are better candidates for producing precursors for carbon fibres.

Mikolajczyk and Krucinska have shown the effect of the intrinsic viscosity of acrylonitrile-methyl methacrylate copolymer on the mechanical properties of PAN carbon fibre precursor.

In addition to the modifications made during the polymerization stage, extensive work has been carried out in the area of spinning of acrylonitrile fibres for producing high-strength precursors for carbon fibres. Attempts have been made to produce void-free acrylic fibres by wet spinning technique. Acrylic precursor fibres, in their gel state, are obtained by spinning the polymer solution into a coagulation bath having higher percentage of solvent at low temperature. Subsequent stretching of the gel fibres results in the unfolding of polymer chains and in the formation of oriented network morphology with relatively homogeneous distribution of pores and void size.

The void content in acrylic fibres may be reduced by increasing the solid contents in the dope. Siami Carbon has reported improvement in the mechanical properties of acrylic fibres spun from solution containing Zn²⁺.

Japan Exlan, in a patent, disclosed the method for the production of high-strength (2.20 GPa or 25.1 gpd) acrylic fibres by spinning a 5% polymer solution in 50% aqueous NaSCN and stretching the fibre in different media to a total draw ratio of 14.4.

The dry-jet-wet spinning for the production of acrylic precursor fibres is becoming more popular because of its following advantages over wet spinning:

(i) Higher spinning speed than in ordinary wet spinning.

(ii) Fibres of very fine linear density (< 1 tex) can be produced.

(iii) Dope can be spun at a higher temperature. Therefore, solutions of higher solid contents may be used for spinning.

(iv) Production of filaments of controlled non-circular cross-section is claimed by this technique.

Superior mechanical properties are achieved in this technique because the fibres are extruded in air above the coagulation bath, thereby leading to better molecular orientation prior to coagulation.
Acrylic fibres with high tenacity of 1.65 GPa (18.8 gpd) and modulus of 32 GPa (365.7 gpd) were produced by Japan Etxan by stretching the fibres in ethylene glycol and glycerol.

Superior mechanical properties of acrylic fibres have also been obtained by drawing the fibres at 185°C. Using 80% of the tension force at this temperature, it is possible to obtain fibres with maximum tensile strength amounting to 646.0 MPa and Young's modulus of 5.64 GPa.

The acrylic precursor fibres produced by wet spinning and dry spinning have circular and dogbone shaped cross-section depending on the rate of coagulation. However, melt spinning of acrylic precursors can produce trilobal and multilobal fibres which are considered to be better for the composites because they possess greater surface area for providing better reinforcement with the matrix.

References: