9

Thermally resistant fibres

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9.1 Introduction (ARH)

Thermally resistant organic polymeric fibres include those that resist thermal degradation and some degree of chemical attack, notably oxidation, for acceptable periods during their service lives. As a consequence of their generally inert structures, like the chemically resistant fibres in the previous chapter, they may also be flame resistant and so address markets where that property is also desirable. Their thermal resistance derives from their possessing aromatic and/or ladder-like chain structures that offer a combination of both physical and chemical resistance and the former is quantified in terms of high second order temperatures, preferably above 200 °C or so, and very high (>350 °C) or absence of melting transitions.

Obviously, this group overlaps with the HM-HT polymer fibres described in Chapters 2 to 4, in which strength and stiffness are primary properties. In this chapter, reference will be made only to applications and characteristics of these fibres that enable them to be used in environments where thermal resistance is of prime importance. Some aspects of the meta-aramids, which are not HM-HT fibres, are included in Chapter 2. The only HM-HT fibres that do not have good thermal resistance are the polyethylene fibres described in Chapter 3 and Section 4.5. The inorganic fibres covered in Chapters 5 to 7 also have, in varying degrees, high thermal resistance. The fibres described in this chapter are those in which high strength is not a primary requirement, and includes some where lower stiffness is needed to give good textile properties in clothing and upholstery.

Fibres in this group tend, however, to see service in applications which are often differentiated only by the severity of thermal environments and their respective resistance to it and the degree of protection and/durability demanded by the end-user. For instance, and again like the chemically resistant fibres discussed previously in Chapter 8, hot gas and liquid filtration fabrics, braiding materials, gaskets, protective textiles, conveyer beltings and high-performance sewing threads are typical end-uses. The major difference here is that temperature upper limits extend often to service temperatures well above 400 °C, and higher if shorter times of heat exposure are evident. Protective clothing, for example, may be required to give protection to flame temperatures (>1000 °C) for a few minutes while hot-gas filtration fabrics may require continual service exposure temperatures of 120–150 °C or so and be expected to sustain these for days, weeks and even months.

9.2 **Thermosets** (HE and HS)

The thermoset polymeric fibres are sensitive to heat in that they continue to polymerise and even crosslink when heated. However, depending upon their respective reactivities and opportunities for crosslinking via reactive side groups, this may give rise to rapidly crosslinking polymers like the melamine–formaldehydes or relatively unreactive polymers like heat-cured novolac phenol–formaldehydes. Both these polymers, although not fibre-forming in the manner that linear polymers tend to be, can give rise to fibres that have acceptable textile properties, each of which reacts to heat in different ways. Both types on heating will continue to crosslink and eventually char, hence giving rise to high levels of fire resistance. Under controlled heating, novolac-derived fibres, or novoloids, can give rise to carbon fibres in their own right.

9.2.1 Melamine–formaldehyde fibres: *Basofil* (BASF) (HE)

Condensation products made from melamine are used in a wide range of applications in the textile, paper, leather and adhesive industries. *Basofil*®, a synthetic melamine fibre produced by BASF is the result of a condensation reaction between melamine, a melamine derivative and formaldehyde, which form a three-dimensional network typical of thermosetting resins. From its chemical structure, the fibre has inherited the characteristic properties of melamine/formaldehyde condensation resins such as high temperature and flame resistance, low flammability and chemical resistance. *Basofil* is the only commercial member of this recently generated class of melamine fibres.

Originally developed at BASF's central research laboratories in Ludwigshafen/Germany, the fibre is now produced in a 1500-tonnes capacity plant at Enka, North Carolina, USA.

9.2.1.1 Chemistry of condensation reaction

In general, one mole of melamine reacts with six moles of formaldehyde at pH 8.0–9.5 at elevated temperatures under general acid–base catalysis to form methylol compounds. In a slightly exothermic reaction, the reaction mixture turns into a clear solution whose viscosity strongly increases with temperature and reaction time. The initially formed methylol compounds then react with each other by oligocondensation and elimination of water and formaldehyde to form methylene ethers and methylene bridges. The ratio of methylene to dimethylene bridges is pH and temperature dependent.[1] During further processing, the reaction has to be interrupted at a certain viscosity when a curing step follows by pH reduction at elevated temperatures.

9.2.1.2 Resins and fibre manufacturing

Melamine–formaldehyde condensation resins can be extruded to filaments at high viscosity;[2] the high viscosity stabilises filament formation and also stabilises the fragile primary fibre. Depending on external conditions, melamine–formaldehyde resins can be spun into fibres within a viscosity range of 300 to 3000 P.[3]

For textile applications, the resulting fibre would, however, be far too brittle. To increase the elongation to a level required for processing the fibre in usual textile machinery, specially modified melamine derivatives have to be added. These derivatives are substituted melamines which act as an internal plasticiser by reducing the degree of crosslinking and hence improving mechanical properties such as elongation-at-break and tensile strength.[4]

The manufacturing process can be divided into two sections, the condensation section and the subsequent spinning as outlined above to produce the finished fibre.

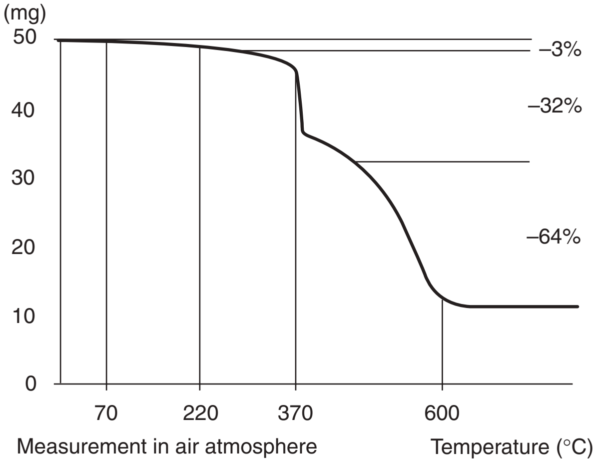
9.2.1.3 Properties of fibres

The property profile and the characteristics of *Basofil*® fibre are essentially related to its chemical building blocks and to its manufacturing process. The important physical properties are shown in Table 9.1. The most important properties of the *Basofil*® fibre are its high limiting oxygen index, LOI, low thermal conductivity and excellent heat dimensional stability. Thermogravimetric analysis (TGA) of *Basofil*® (see Fig. 9.1) shows that at 250 °C the residual mass of the fibre is reduced by only 3%. Under exposure to flames, the fibre does not melt and also does not produce burning drips.

In common with melamine condensation resins, the fibre shows good hydrolysis stability. Comparative tests on woven fabrics according to DIN 53 857 after storage under a standard atmosphere and after immersion in water for 12 hours show no change in tensile elongation and only a minimal reduction in tensile strength. The chemical resistance of a woven *Basofil*® fabric to various solvents, acids and bases in terms of tensile strength loss

Table 9.1 Physical properties of *Basofil*® fibres

Strength, cN/dtex	2–4
Modulus, nominal, N/tex	6
Elongation-at-break, %	15–20
Density, g/cm^3	1.4
Moisture regain, 23 °C & 65% RH, %	5
Limiting oxygen index, LOI, %	32
Hot air shrinkage, 1 hr @ 200 °C, %	<1
Continuous use temperature, °C	190



9.1 Thermogravimetric analysis of *Basofil*®.

after exposing to the test medium for 28 days at room temperature is shown in Table 9.2. The results indicate that, although the fibre is only moderately resistant to acids, it displays an excellent chemical resistance, especially with regard to organic and aromatic solvents and to bases.

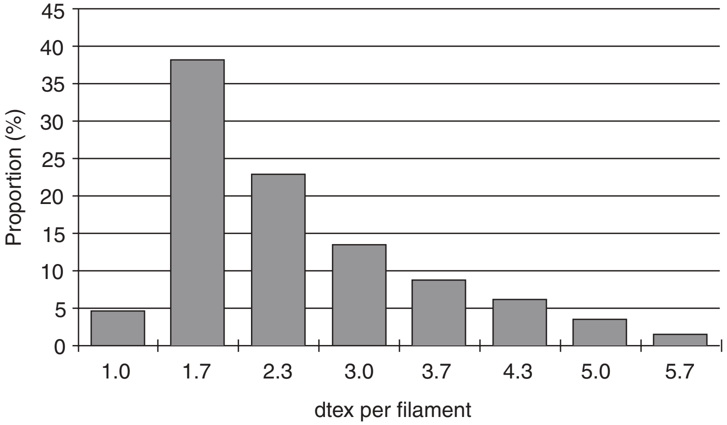
Within its recommended temperature use, the tensile strength of the fibre is hardly affected by exposing it to higher temperatures. Also, measurements of the tensile strength of *Basofil*® samples exposed to elevated temperatures indicate only minimal changes in tensile properties.

Because its manufacturing process is by spinning the condensation resin through a rotating disk, the fibre is produced as a staple fibre with some variation in staple length and also in diameter. Typical fibre diameter distribution and staple length distribution are shown in Figs. 9.2 and 9.3.

As shown in a scanning electron micrograph (SEM) (see Fig. 9.4), the cross-section of the fibre is variable, and to some extent elliptical, with a smooth fibre surface.

Table 9.2 Chemical resistance of *Basofil*® fibres after 28 days exposure at room temperature

Chemical	Strength loss (%)
Acetone	0
Butyl acetate	0
Gasoline	0
Methanol	0
Demineralized water	0
Sodium chloride solution, 5%	7
Sodium hydroxide solution, 20%	0
Hydrochloric acid, 20%	48
Sulphuric acid, 20%	48

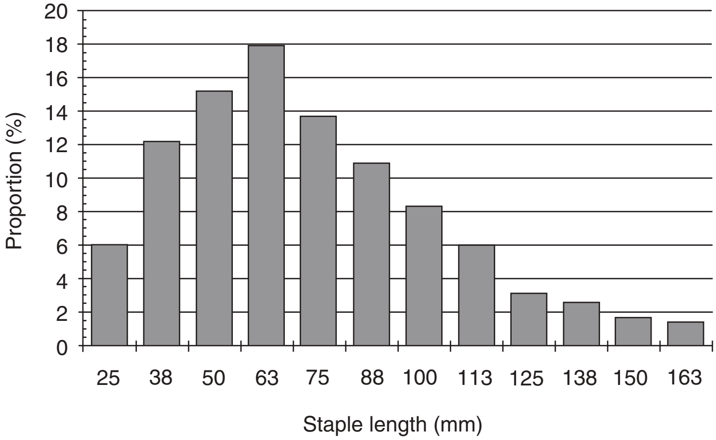


9.2 Diameter distribution of *Basofil*® fibres.

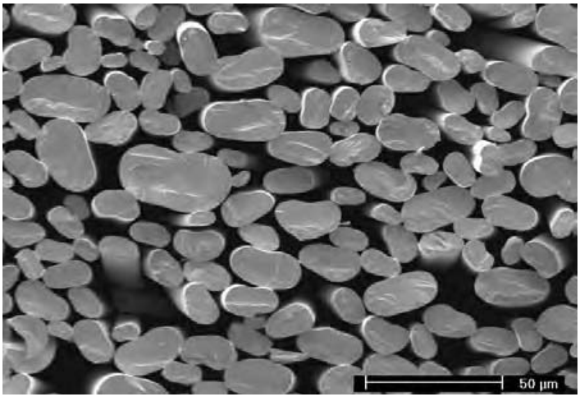
For fibres used in heat and flame protective applications, for instance in aircraft fire blocking, smoke toxicity in the event of a fire is an important characteristic. Analysis of smoke and gas samples taken according to ASTM E662-79/BSS 7239 after four minutes flaming of a *Basofil*® fabric are shown in Table 9.3. Results show the *Basofil*® fabric to be well under FAA requirements. The specific density of the smoke, according to the same test, is 25 (DS) after 4 minutes flaming. A DS value of less than 200 is required to pass FAA standard.

9.2.1.4 Processing

In common with other staple fibres, *Basofil*® can be processed into nonwovens and woven textiles. It can also be blended with other technical



9.3 Staple length distribution of *Basofil®* fibres.



9.4 Cross-sections of *Basofil®* fibres.

and natural fibres, depending on end-use applications. The property profile of the *Basofil*® fibre clearly indicates that the fibre can be used on its own wherever strength does not have to be the dominant characteristic. The breaking strength is equal to the level of natural fibres such as cotton. Likewise, *Basofil*® can be spun into yarns, woven into fabrics or processed into felts by common fibre and textile processing technology. If there are special requirements towards the tenacity of the yarn, fabric or nonwoven to be produced from *Basofil*, blending with other technical fibres is recommended. Other characteristics of the fibre, such as staple length distribution and diameter distribution are governed by the fibre production process and have therefore to be taken into account.

Table 9.3 Smoke toxicity of *Basofil*® fibres (ASTM E662-79/BSS 7239)

Toxic gas (4 min flaming)	Basofil fabric (ppm)	Boeing limit (ppm)	Airbus limit (ppm)
CO	100	3500	3500
NO*x*	12.5	100	100
HCN	62.5	150	150
HCl	0	500	150
HF	0	150	100
SO_2	0	100	100
Formaldehyde	0.35	—	—

In general, no processing problems should be encountered on producing needled felt and fleeces from *Basofil*®. It can also be spun in yarns, in particular in yarn counts up to Nm 60 (>17 tex), using state-of-the-art high-speed carding equipment. If yarns with counts less than Nm 10 (>100 tex) are to be produced, it is recommended that *Basofil* be blended with a higher tenacity fibre.

One important additional question relating to the end-use of *Basofil* concerns the dyeability of the fibre and its final products. *Basofil*® fibres can be dyed with best results only with selected small-molecular disperse dyes in a high-temperature process comparable to HT dyeing with disperse dyes on polyester.[5] Colour yields range from 60–80%, depending on the species and the amount of dye used. Lightfastness following xenon arc irradiation (DIN 54002) show ratings in the range of 4–6.

9.2.1.5 End-uses

Typical end-use applications of *Basofil*® can be found in all areas where heat and flame resistance properties and chemical resistance are required. Some examples include:

- high-temperature filtration
- fire blocking and heat insulating felts
- heat and flame protective apparel.

In high-temperature filtration applications, *Basofil* is used in a nonwoven felt based on an intimate blend of approximately 50% *Basofil*® with meta-aramid fibres. As seen in variable environmental simulation analysis (VESA) and also in baghouse applications, filter media from *Basofil* enhances filtration performance by simultaneously lowering particulate emission levels and reducing pressure drop compared to standard meta-aramid filtration media.[6]

Also in blends with other technical fibres, *Basofil*® enhances the fire blocking and heat insulating performance of needled felts and hydroentangled fleeces used for protective clothing and as fire blockers in transportation and furniture applications.[7]

In protective clothing, such as industrial workwear for the chemical, utility and automotive industries, and in fire fighting apparel, *Basofil*® is used in blends with meta- and para-aramids, FR (flame retardant) viscose or with cotton. The good heat insulation properties and low thermal conductivity of *Basofil*® allows construction of thinner fabrics with equal protection and good wear comfort due to the fibre's low stiffness and high moisture regain.

9.2.2 Novoloid fibres: *Kynol*® (HS)

9.2.2.1 Properties

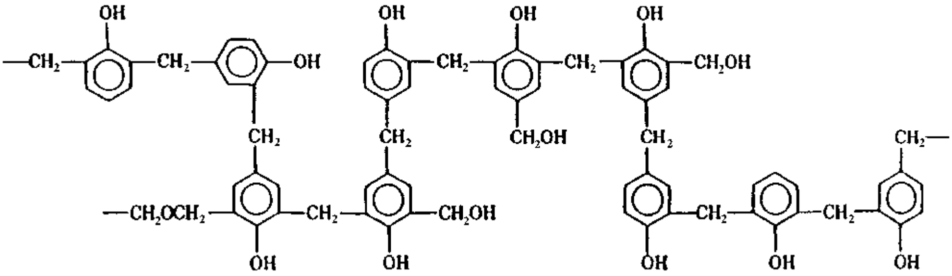
Kynol novoloid fibres are amorphous, crosslinked, phenol–aldehyde (novolac) fibres made by the Kynol Corporation of Japan. Chemically, the fibres contain approximately 76% carbon, 18% oxygen and 6% hydrogen (see Fig. 9.5). They embody many of the characteristics of the well-known phenolic resins, such as:

- excellent thermal/electrical insulation, because of low conductivity;
- retention of properties at low (even cryogenic) temperatures;
- outstanding resistance to acids, alkalis, solvents, fuels, steam;
- low specific gravity (1.27);
- high compatibility with resins, elastomers, adhesives; and
- being an excellent precursor for carbon and activated carbon fibres and textile materials;

and in the presence of heat or flame:

- high resistance: non-melting at any temperature;
- minimal smoke generation, little or no shrinkage;
- retention of textile integrity and no embrittlement or breakage; and
- practically no toxic off-gassing (no HCN, halogens, etc.).

Kynol fibres are generally elliptical in cross-section and are light gold in colour. The fibres feel soft and are available with or without crimp, in different lengths. They are highly flame resistant but are not high-temperature fibres in the usual sense of the term. For example, a 300 g/m^2 fabric withstands 2500 °C for 12 s or more without breaking, but the practical temperature limits for long-term application are 150 °C in air and 250 °C in the absence of oxygen. This is because the fibre is reactive above 150 °C and, in the absence of oxygen, crosslinks and slowly carbonises.



9.5 Polymer structure of *Kynol* novoloid fibre.

Table 9.4 Typical properties of Kynol fibres

Colour	gold
Standard diameter, μm	15, 18 (2 and 3 denier)
Standard fibre lengths, mm	standard 51 or 70
Specific gravity	1.27
Tensile strength, cN/tex	12–16
Elongation, %	30–50
Modulus, cN/tex	260–350
Loop strength, cN/tex	19–27
Knot strength, cN/tex	10–13
Elastic recovery, %	92–96
Moisture regain at 20 °C, 65% rh %	6
Limiting oxygen index, LOI %	30–34

The typical properties of *Kynol* fibres are listed in Table 9.4.

The chemical structure of these fibres includes only carbon, oxygen and hydrogen and so when *Kynol* products are exposed to flame, the products of combustion are principally water vapour, carbon dioxide and carbon char. There is no emission of HCN, HCl, bromine- and phosphorus-containing compounds and other toxic products of combustion typical of many other inherently flame-resistant and FR-treated organic fibres. Moreover, since the fibre chars without melting and produces few volatiles, smoke emission is also minimal and is less than that of virtually any other organic fibre.

These characteristics have led not only to their use as asbestos-replacement fibres and in safety-related textiles, but also to a number of other end-uses which will be explained briefly.

9.2.2.2 *Applications*

The applications of *Kynol* fibres and derived textile materials can be roughly divided in two groups: safety materials and industrial uses. In many industrial applications, safety is also a primary reason for the use of *Kynol* products. A more detailed breakdown may be given as follows:

- *Flame resistant safety products and smoke barriers:* Protective garments incorporating *Kynol* woven and nonwoven linings and waddings are used in a wide variety of flame, heat- and chemical-resistant fields where safety is required. Welders, racing drivers and fire fighters use not only regular *Kynol* garments, hoods and gloves, but also aluminised *Kynol* clothing. These are often more comfortable to wear than other aluminised materials and provide excellent heat insulation as well.

  Kynol materials have also replaced asbestos in protective curtains for flame, radiant heat and metal splash hazards, as well as in flame-resistant ventilation ducts, and insulation of roofs and walls.

  An important application of *Kynol* felts and fabrics are flame and smoke barriers and insulation in aeroplanes. The materials have been approved by leading aircraft producers such as Airbus Industries and Boeing. This is because of their low specific gravity and hence felt area densities, virtually no emission of toxic gases in flame (no HCN, etc.), extremely low smoke generation and high flame resistance.

  In addition to aircraft, such insulations and barriers are used in other transport, e.g. cars, trains, ships, ferries and submarines. In public facilities such as theatres, cinemas, hotels, discotheques, airports and hospitals, they are also of use as fire blockers, seat linings, smoke barriers, curtains, escape hoods, bed covers, emergency bags and aprons.
- *Applications requiring heat insulation and resistance to extremely low temperatures:* Certainly there are many other areas in which the combination of flame protection and thermal insulation is required by modern life and industry. *Kynol* materials are excellent thermal insulators thanks to their low thermal conductivity and retention of their textile properties at extremely low temperatures, even after immersion in liquid nitrogen. These factors have led to the use of *Kynol* felts in flexible insulation for liquid natural gas piping, as well as in military sleeping bags – two examples in which protection against both flame and cold extremes are required.
- *Industrial sealings and packings:* Asbestos-free sheet gaskets, both calender- and beater-processed, were among the first products to be produced with milled or short-cut *Kynol* fibres, in order to increase not only compressive strength and recovery but even more importantly, steam, heat and chemical resistance.

  Their outstanding resistance against acids, alkalis, solvents, fuels, steam and even hydrofluoric acid has led also to their highly successful use in braided packings of extremely high durability. For gaskets and packings, and certainly also for brake-bands and fabric-based seals, it is of great importance that fibre-to-matrix wetting and adhesion of *Kynol* fibres are excellent. In fact, an actual chemical crosslinking reaction occurs between the fibre and matrix resins and elastomers, in which the methylol groups formed during curing of the fibre play a key role, and this leads to improved characteristics in the final product.

- *Composites, including friction materials:* The crosslinking property mentioned above underlies the usefulness of *Kynol* fibres in composites. Frequently unexpected synergistic improvements in properties may be displayed in such composites; for example, *Kynol* fabrics coated with chlorinated polyethylene (CPE) or other elastomers and friction materials and similar moulded products with phenolic (resole) resin binders.

  Again, the low specific gravity of *Kynol* fibres often leads to a reduction in weight of such composites, while properties such as heat, steam and chemical resistance, impermeability, compressive strength, shock resistance, dimensional stability and hardness are improved. Similarly, lightweight friction materials have given rise to high-performance disc pads, clutch facings and textile-based industrial friction materials with reduced weight, more stable coefficients of friction, greatly reduced wear to mating surfaces and better noise absorption.

  The properties of many other materials based on thermoplastic and thermosetting resins can be improved by adding *Kynol* fibres in the same way.
- *Cables: Kynol* fibres are used in flame resistant and smoke-free filler yarns, wrapping tapes and coatings for communication and power cables where maximum circuit integrity must be maintained for safety reasons. They are found in highway and railway tunnels, underground concourses and subways, high-rise buildings and in industrial complexes. Because of good resistance to radioactive emissions, these fibres are extremely useful for cabling in nuclear power stations.
- *Carbon fibre products:* Since *Kynol* fibres are non-melting and have an inherently high carbon content of about 76 wt%, they are excellent precursors for carbon fibres and other carbon textile products. Carbonisation is a simple, one-step process, which is routinely performed on completed textile structures such as woven fabrics and needled felts. Yields are on the order of 55 to 60 wt%, with carbon contents up to 99.8%.

  The resulting carbon fibres are amorphous in structure and have a low modulus. They are soft, pliable, produce little dust or fly on processing, have good electrical conductivity and possess even higher resistance to heat and chemicals than the precursor fibre.

  Kynol-based carbon products perform even better than their *Kynol* precursors in a number of the applications mentioned previously, such as heat- and chemical-resistant braided packings. *Kynol* carbon fabrics are employed in significant quantity in composites for rocket motor exit nozzles. Other applications include brushes and similar products for static elimination in copying machines.

- *Activated carbon fibre products:* Again due to the high carbon content, *Kynol* fibres and products are used as a precursor for activated carbon materials. *Kynol* fibres and textiles are transformed into activated carbon by a one-step process and the effective surface area can approach 3000 m^2/g.

  The following important technical advantages can be obtained in comparison with granular activated carbon and other fibres:

  (i) highly efficient and cost-effective removal of very small amounts of impurities from large amounts of air or liquids;
  (ii) high fibre surface-to-volume ratio and direct connection of micropores to the fibre surface significantly shorten diffusion distance and increase speed of adsorption and desorption;
  (iii) pore dimensions and surface characteristics can be tailored to the application;
  (iv) depending on the target material, excellent rates of removal may be obtained even at ppb concentration levels;
  (v) fibres can be locked into textile structures, preventing 'channelling' and minimising loss and contamination due to interparticle abrasion;
  (vi) textile structures are often convenient for filter design and assembly, and compared to textiles impregnated with powdered carbon there is less shedding of particulates and no pore blockage by binders;
  (vii) shed particles tend to be fibre fragments with a minimum of 10 μm dimensions, easily trapped in particulate filter media;
  (viii) the strength of all activated *Kynol* products is superior to similar viscose products, especially when wet.

  Such technical considerations make activated carbon fibres highly useful in specialised filtration applications, such as air filtration, solvent recovery, radioactive iodine filtration, ozone elimination, medical and military (nuclear, biological and chemical [NBC] agent) applications, industrial safety and water treatment.

Kynol activated carbon products perform extremely well in electrical and electronic applications. Taking one example, the capacitance of a simple two-layer capacitor is linearly related to the surface area of its two electrodes. This means that even very small quantities of such fabrics achieve outstanding results in capacitors.

9.3 Aromatic polyamides and polyarimids (ARH)

Of all the inherently heat- and flame-resistant fibres developed since 1960, this group is perhaps the most well known and exploited. In the main, they are typified by having aromatic repeat units bonded together by amide—CONH—groups, the polyaramids, generally, shortered to ‘aramids’, imide—CON<groups, the polyarimids or arimids, or both in alternating manner, the poly(aramid-arimid)s. Their resistances to heat are dependent, therefore, on the weakest or most reactive bond present. In the polyaramids this is the single C—N bond in the amide group, whereas in polyarimids, this same C—N bond is strengthened by the presence of increased conjugation. Thus, polyaramids have inferior heat resistances to polyaramid analogues as will be shown below. All members of this group are typified by having thermal resistances in excess of 300 °C for short-term exposures and high levels of inherent flame resistance.

9.3.1 Aramid fibres

Perhaps the most well known of the thermally resistant fibres are the aromatic polyamides or aramids which originated with the commercial development of DuPont’s *Nomex* fibre in the early 1960s. While Chapter 2 reviews the aramid group of fibres in detail, it is useful to summarise some of their types and characteristics here in order to give an overall coherence to this chapter. In addition, their thermal and flame-resistant properties are often considered as benchmarks against which all other fibres in this group are measured.

For the purpose of this summary, a number of reviews describe the development of this group up to the mid-1970s,[8] more recently[9] and those produced in the former USSR.[10]

Commercially available fibres based on poly(*m*-phenylene isophthalamide), in addition to the well-established *Nomex*, are *Conex* (Teijin), *Apyeil* (Unitika) and *Fenilon* (former USSR) and variations having modifed tensile properties (e.g. *Inconex*, Teijin) and antistatic properties (*Apyeil*-α, Unitika). Most versions of these fibres have had improved dyeing properties, introduced during the last 10 years or so to enable them to compete effectively with flame-retardant versions of conventional fibres (e.g. flame-retardant cotton, viscose and wool), which are available in full colour ranges. However, their thermal resistances are very similar and defined by the physical and chemical features of the all-*meta* aromatic polymer chains. Their rigid structures and efficient intermolecular forces ensure that the fibres have minimal thermoplastic characteristics, with second order transition temperatures (T_g) of about 275 °C and an ill-defined melting point accompanied by thermal degradation starting at 375 °C. Together, these enable the fibres to be used in textiles where shrinkage should be minimal at temperatures of continuous use of 150–200 °C and to shorter exposures as high as 300 °C. Thus they are ideal for use in hot gas filtration and protective clothing applications respectively, although their resistance to acidic and basic environments is limited by the hydrolytic sensitivity of the amide links present in the polymer chains; however, continuous exposures up to 150 °C and higher are still possible.[9] Other important uses include their incorporation as very short fibres or flocs in papers and similar materials, from which a variety of heat and flame-resistant gaskets, tapes, honeycomb structures, insulation materials and similar products can be fabricated. Such has been the impact of the meta-aramids in certain industries such as aerospace, for example, that without the lightweight honeycomb board and composite structures available comprising them, modern aircraft development toward higher capacity and greater fuel efficiency could not have taken place.

Most commercial meta-aramid examples, typified by *Nomex* for example, are available in floc, short staple and continuous filament forms as well as a range of finesses and even cross-sections. *Nomex* Type 450, for example, has served the filtration industry for over 30 years, is available in 1.7 and 2.2 decitex and has a bean-shaped cross-section. However, as the desire for improved filtration has increased, so the tendency to reduce fibre fineness has given rise to fibres such as *Nomex Delta FF* and *Delta Micro*, with fineness values respectively of 1.1 and 0.78 decitex. While specific surface areas and hence filtration efficiencies of fabrics incorporating these fibres have increased, their fundamental thermal resistances have remained the same as all the other members of the *Nomex* family. It is merely the changes in physical dimensions that have enabled improvements in product performance and new applications for this fibre genus to be generated.

When heated above 400 °C or so, thermal decomposition proceeds via the formation of a tough, carbonaceous char that still provides a coherent heat-protective layer to underlying surfaces, thereby maintaining its protective character. This char formation ensures that all meta-aramid fibres have low flammabilities with limiting oxygen index values in the range 28–31%.[9] They, therefore, compete effectively with many other non-thermoplastic flame-retardant fibres such as flame-retarded cotton and wool, which have similar LOI values, although they are inferior to the highly crosslinked (e.g. *Kynol*) and ladder (e.g. semi-carbon and PBI) aromatic fibres.

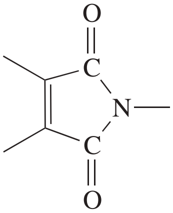
This combination of excellent thermal and flame resistance ensures that meta-aramids are used in both flexible (e.g. protective clothing) and inflexible (e.g. honeycomb-structured composites for the aircraft industry) protective materials which demand, in addition, little or no thermoplasticity and good tensile and other mechanical properties. However, in order to improve thermal properties further, blending with small amounts of para-aramid fibres (e.g. *Nomex III*) enables the thermal protective behaviour to increase, primarily through increasing the char tensile strength. Notwithstanding these advantageous features, all aramid fibres are expensive and, within the area of fire resistance, attempts to blend meta-aramids with lower cost flame-retardant fibres such as flame-retardant viscose, have given rise to protective fabrics such as *Karvin* (30% *Nomex*, 5% *Kevlar* para-aramid and 65% *Viscose FR* (Lenzing)) and similar blends (e.g. *Viscose FR/Twaron* (Acordis) para-aramid). These have similar flame retardancy to their respective parent single-aramid components, but their char structures are weaker and so do not offer sustained fire protection at high heat fluxes and temperatures as the 100% meta-aramid fabrics do.

The para-aramids, typified by *Kevlar* (DuPont) and *Twaron* (Acordis) and their modifications (see Chapter 2) which are based on poly(*p*-phenylene terephthalamide), while having enhanced tensile strengths and moduli as a consequence of the extreme symmetry of their polymer chains and hence order or crystallinity, also have enhanced thermal performance. The increased structural chain rigidity and order raises the second order transition temperature to about 340 °C and melting point to about 560 °C, before decomposing above 590 °C. Furthermore, higher continuous working temperatures of 180 °C and above are possible with resistance to short term exposures to temperatures as high as 450 °C being achievable. However, thermal degradation to carbonaceous char is similar to that occurring in the meta-aramids and so the LOI values are similar at 30–31%. However, as indicated above, the improved tensile properties coupled with this char-forming ability yield fabrics that can resist higher temperatures than the meta-aramid analogues to yield charred structures of superior tensile strength. Again, the higher cost, poorer textile processing properties and higher modulus of para-aramid fibres ensure that their use in applications such as protective textiles and filtration fabrics is limited to 100% contents only when performance demands are exceptional. As mentioned above, however, additions of small amounts of para-aramid to meta-aramid and indeed non-aramid fibres, can significantly add a combination of enhanced tensile and heat and flame resistance.

9.3.2 Arimid fibres

Arimid fibres were researched during the 1960–70 period as alternatives to the contemporaneous aramid fibre developments discussed above and in Chapter 2 of this book. Attempts to produce high-temperature resistant arimid fibres at this time focused on the aerospace industries and these have been reviewed up to 1976 by Hughes *et al.*[8] Not surprisingly, both the USA and former USSR research efforts produced similar products, under names such as *PRD-14* (Du Pont, similar to their *Kapton H* aromatic polyimide film) and *Arimid T*, respectively. These latter have been more fully reviewed by Duobinis.[10]

As stated previously, arimid fibres derive their extremely high heat resistance from the presence of the imide nitrogen, >N–, which not only lacks the active hydrogen present in the polyamide functional group, but also introduces the possibility of rigid and stable heterocyclic rings in the polymer chain, of the type:



Synthesis of these groups typically involves the condensation reaction of an aromatic tetracarboxylic dianhydride and an aromatic diamine, and Du Pont's original *PRD-14* fibre was considered to be based on pyromellitic anhydride and a diamine similar to *p*-phenylene diamine, 4,4′-diaminodiphenyl, 4,4′-diaminodiphenylether, substituted derivatives, or a mixture thereof. More recently, diisocyanates have been found to be more acceptable in place of the diamines. Thus, the number of single bonds per unit length of polymer chain is reduced compared to the aramids and this gives rise to high chain rigidity and hence high second order transition temperatures and greater resistance to pyrolytically induced chain scission reactions. Arimid polymers rarely start to break down below 500 °C under nitrogen and 450 °C in air, and this latter characteristic is complemented by a high degree of flame resistance.

Although Table 9.5 lists a selection of polyimide fibres reported to date, the major development has been by Lenzing of Austria, which introduced the polyarimid fibre *P84* during the mid-1980 period.[11] The development of arimids, and of this fibre in particular, has been reviewed.[12,13] *P84* fibres are now produced by Inspec Fibres (USA).

All polyimide polymers and fibres tend to be very intractable and so are often produced as reaction intermediate fibres, which although unstable, are soluble in appropriate solvents such as dimethylformamide (DMF) and dimethylsulphoxide (DMSO). Once extruded, the filaments are trans-

Table 9.5 Selected examples of polyarimid fibres[9–13]

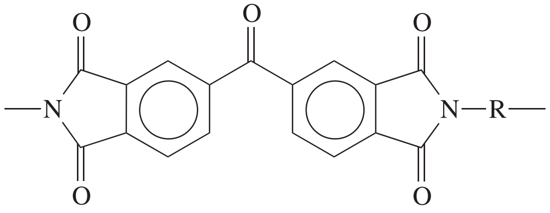
Fibre	Origin	Tenacity, N/tex
PRD-14	Du Pont, USA	>0.26
Polypyromellitimide (high strength)	Du Pont, USA	1.13–1.30
Arimid T	Russia	>0.35
Arimid T-TK 160	Russia	>0.50
P84	Lenzing, Austria (now Inspec Fibres, USA)	0.35–0.38

formed to fully reacted and imidised polymer chains by use of high temperatures (up to 300 °C) or chemically.[12] The properties of the resulting polymers are dependent upon the exact structure of the tetracarboxylic acid dianhydride and the diamine. For instance, physical properties such as tensile strength and modulus, and thermal stability, increase with the increasing simplicity and symmetry of the former, and for polyimides containing pyromellitic dianhydride (PMDA), 3,4,3′,4′-biphenyl tetracarboxylic acid dianhydride (BPDA) and benzophenone tetracarboxylic acid dianhydride (BTDA), the order of improving tensile behaviour and thermal stability generally is:

BTDA < BPDA < PMDA

which also reflects their order of increasing insolubility. Therefore, poly(pyromellitimide) filaments, initially produced as *PRD-14* by Du Pont, have also been produced as high strength and modulus forms.

Because of their high insolubility and hence need for a two-stage production method outlined above, successful commercialisation followed the development of the use of copolymeric polyimides which enabled directly soluble polymers and hence more easily and economically processible ones to be produced. *P84* is the major outcome of this development and is produced from benzophenone tetracarboxylic acid dianhydride and a mixture of aromatic tolylene and diphenylmethane diisocyanates. The *P84* polymer has the following structure representative of poly (4,4′-diphenylmethane-*co*-tolylene benzophenonetetracarboxylic imide):



where R= $C_6H_4.CH_2$ or $C_6H_4.CH_2.C_6H_4$

The fibre is produced by dry-spinning to yield typically gold-coloured fibres with lobed, irregular cross-sections. After drying and hot drawing, the fibres achieve moderate tenacities (see Tables 9.5 and 9.6). These fibres, as staple, continuous filament and with or without crimp, are produced solely for their thermal performance and their complete properties are presented in Table 9.6.

Their profiled cross-section and high specific surface area make *P84* fibres ideal candidates for hot gas filtration and thermal insulation. In addition, the TGA-derived onset of degradation in air at about 450 °C, coupled with an LOI value superior to those of the polyaramids (see Table 9.14,

Table 9.6 Properties of commercial polyimide and poly(amide-imide) fibres[8,11–15]

Property, unit	*P84* polyimide	*Kermel* poly(amide-imide)
Tensile		
Tenacity, N/tex	0.35–38	0.245–0.588
Breaking strain, %	33–38	8–20
Initial modulus, N/tex	3–4	4.9–9.4
General		
Boiling water shrinkage, %	<5	<0.5%
Thermal shrinkage, %	At 250 °C for 30 min, <1	At 200 °C <0.5%
Specific gravity	1.41	1.34
Moisture regain, 20 °C, 65% rh, %	3	3–5
Colour	Gold/yellow	Pale yellow
Second order temp., T_g, °C	315	<315
Maximum continuous temp., °C	160	150–180
Decomposition temp., °C	450	380
Limiting oxygen index, %	36–38	32

later) make *P84* fibres excellent candidates for high temperature end-uses in oxidative environments.

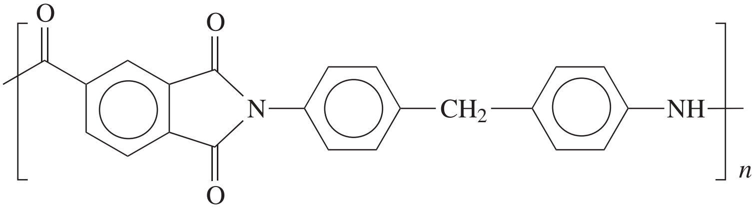
While the arimid fibres are not designed to be chemically resistant in the sense that the majority of fibres in Chapter 8 are, they do exhibit acceptable levels, even in the presence of strong acids and bases where hydrolysis of the imide linkages will be catalysed. Generally, the performance of *P84* is superior to that of the polyaramid fibres. For instance, immersion in the oxidising acids, sulphuric and nitric acids at 10–20% concentrations, can yield between 85–95% strength retentions after room temperature exposures of up to 100 hours. At elevated temperatures, retentions drop to, e.g. 75% after 20% sulphuric acid exposure at 50 °C. Resistance to hydrochloric acid is similar to that in these former acids at low concentrations and temperatures but is not so good at higher concentrations; only 45–55% retention is observed after 100 hours exposure to a 37% solution at room temperature.[12] On the other hand, resistance to dilute (5%) alkali at room temperature, even after 1000 hours exposure, is acceptable, with 85–95% strength retention. As might be expected of an all-aromatic structured polymer, solvents such as alcohols, ketones, chlorinated hydrocarbons and benzene have little, if any, adverse effect. However, aprotic solvents like DMF, DMSO, dimethylacetamide and *N*-methyl-pyrrolidone will swell and dissolve *P84* fibres.

The main arimid fibre applications exploit the high temperature and flame-resistant properties and are summarised as follows:

- *Protective clothing:* Outerwear, underwear and gloves may be made from 100% *P84* or blended with lower cost fibres such as flame retardant viscose (e.g. a 50/50 *P84/Viscose FR* (Lenzing) blend is used for knitted underwear with high moisture absorbency) or with high tenacity polyaramids to increase wear and tensile characteristics. Spun-dyeing of *P84* fibres enables their natural colour to be replaced by those demanded by customers who may, for instance, require more appropriate bright safety colours. The protective character of these arimid-containing fabrics is not only their tendency not to decompose at high temperatures but also to provide high levels of thermal insulation which may be improved by increasing fibre crimp levels.
- *Braided packings*: *P84* fibres are ideal candidates for high-temperature seals and packings, which may be impregnated with lubricants and PTFE dispersions when requiring higher levels of chemical resistance.
- *High temperature filtration:* Hot gas filter bags may be used up to 260 °C for prolonged periods; experience has shown that continuous use for periods of years is possible at temperatures as high as 160 °C with peaks up to 180 °C being permissable.
- *Aircraft and other transport interiors:* Three-dimensional components with structural rigidity may be fabricated from nonwoven fabrics following heating above the second order transition temperature (Table 9.6), which causes fibre contraction and consolidation of the structure with some fibre-to-fibre adhesion occurring. These low density, rigid and fire-resistant structures can replace conventional materials where low weight is at a premium, such as in aircraft and high-speed trains.

9.3.3 Poly(aramide-imide) fibres

If the tetracarboxylic acid dianhydride component in a polyimide is replaced by a tri- or even dicarboxylic acid, then reaction with a diisocyanate produces a poly(amide-imide), the prime example of which is the *Kermel* fibre, which has been produced by Rhone-Poulenc of France since 1971.[8] *Kermel* is now produced by Rhodia Performance Fibres. The chemical structure of *Kermel* is reported to be:[8]



and the diamino component is based on the diphenyl methane moeity. This chain segment is not very symmetrical and so the ability to crystallise is not high and hence the specific gravity is on the low side (see Table 9.6). However, this low order enables the polymer to be wet or dry spun from aprotic solvents such as dimethylacetamide, DMA. Furthermore, by incorporating isophthalate links in the chain, base dye affinity can be created.[9] In 1993, a so-called third-generation *Kermel* was announced, which claimed to have superior colouration properties.[15]

Properties are included in Table 9.6 and it is seen that a range of tensile properties are possible that are similar to those of conventional polyamides and the poly(meta-aramids) (see Chapter 2). Like the poly(meta-aramids), however, *Kermel* has poor UV stability, and so must be protected from intense radiation sources. Its lower second order and decomposition temperatures reflect the lower chain rigidity and the weaker polyamide bond structure; again, these properties are similar to those of the poly(meta-aramids). Its behaviour to chemical exposure is similar to that of the poly(meta-aramids), with good resistance to strong acids when cold, poor resistance when hot, but very good organic solvent resistance except for aprotic species as seen for *P84* previously.[14]

Flammability, measured as limiting oxygen index, (LOI = 32%) is lower than seen for the arimid fibres but comparable to the aramids (see Table 9.14, later, and Chapter 2). Like these same fibres, it competes for the same end-uses, although it has found a special market in protective clothing[9] where it is used as 100% *Kermel* or as blends with other fibres including FR viscose. The presence of the latter adds to the comfort and so is recommended for underwear like the similar *P84*/FR viscose blends outlined previously. Blends with wool have been shown to be ideal for uniforms, jerseys and pullovers. The years between 1971 and the present time have seen significant improvements in fibre quality and tensile properties, and these have been complemented by developments in colouration. As with the meta-aramids, this is usually carried out by spin or solution dope dyeing to yield bright, fast colours. A higher performance version, *Kermel Tech*, has been developed, with improved thermal resistance and designed for use in hot gas filtration where useful lifetimes of up to 20000 hours at 180°C are achievable.[15] Production of composite yarns with high modulus aromatic fibres such as the poly(para-aramids) (*Kermel HTA*) enables the strength and abrasion resistance of fabrics to be increased.

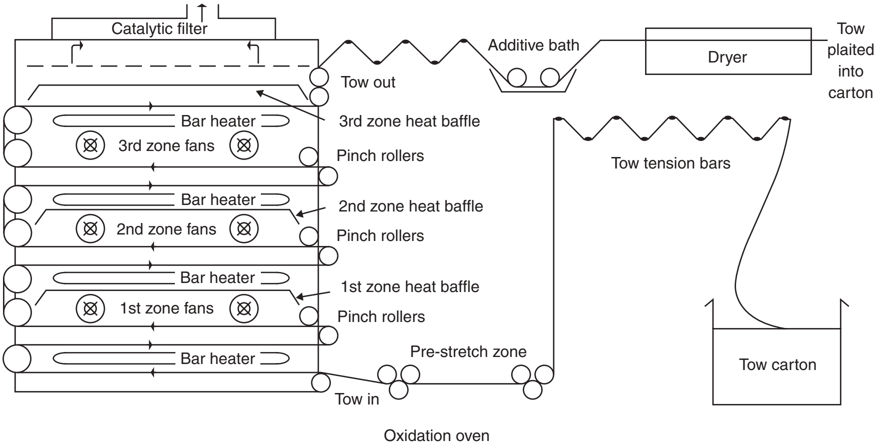
As an end-point to this group, while *Kermel* has been the only commercial example of a poly(aramide-imide) fibre to date, there is some interest being shown in the medical sector in hollow fibre membranes for blood purification.[16] Commercial exploitation, however, has yet to follow.

9.4 Semi-carbon fibres: oxidised acrylics (NS)

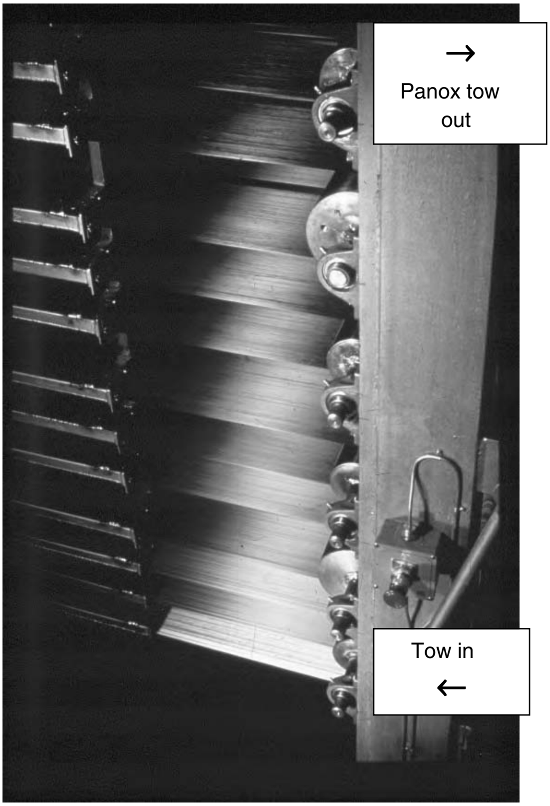
9.4.1 Development and manufacture

During the 1960–70 period, a number of carbonised or semi-carbon fibres were developed for high-temperature and flame-resistant end-uses. While these included carbonised viscose,[17] only those based on semi-carbonised or oxidised acrylics have survived and continue to be developed today. The oxidised acrylics represent a group of ladder polymer fibres that are produced following controlled high-temperature oxidation of acrylic fibres during the first stages of carbon fibre production (see Chapter 5 for full details). First reported about 1970 as '*Black Orlon*',[18] they became of commercial interest as potential high temperature-resistant fibres during the early 1980s. During this time a number of commercial versions were announced including *Celiox* (Celanese), *Grafil O* (Courtaulds), *Pyron* (Stackpole), *Sigrafil O* (Sigri Elektrographit, now SGL) and *Panox* (SGL UK Ltd., formerly R K Textiles). Other examples were produced, including one from Toho Rayon in Japan. There are presently large production plants for oxidised acrylics in North America, UK, France, Germany, Hungary, Israel, Korea, Taiwan and Japan. Oxidised polyacrylonitrile (PAN) yarns are in regular production in the USA, UK, France, Germany and Japan in 100% form and in blends with aramids and/or glass. More sophisticated blends can be obtained and a list of producers and products is available.[19]

All are produced by similar means to yield black fibres that, while retaining some of the fibre physical properties of their acrylic fibre precursors, have very high thermal resistances and inherent flame resistance because of their partially carbonised structures. For example, *Panox* fibre is manu-



9.6 Schematic diagram of acrylic tow oxidation.

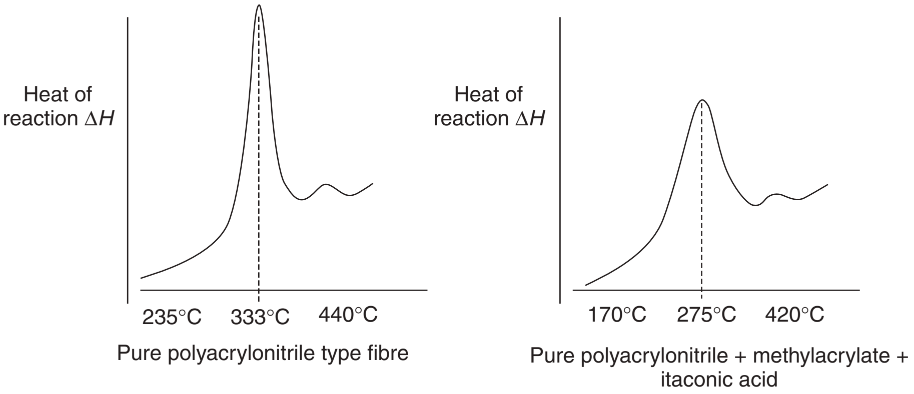


9.7 **Acrylic tow passing through an air oven at 200 °C.**

factured by the controlled oxidation of a *Courtelle* (Acordis) acrylic precursor textile fibre made specifically for the carbon fibre industry. The preferred acrylic precursor is a copolymer of the major monomer acrylonitrile, $CH_2{=}CHCN$ and methyl acrylate, $CH_2{=}CHCOOCH_3$ and the co-monomer originally introduced to promote base dye affinity, itaconic acid, $CH_2{=}C(COOH)\ (CH_2COOH)$. Conversion to oxidised fibres occurs in continuous form during slow passage through an oven at about 210–220 °C. Figures 9.6 and 9.7 show schematically and visually the passage of acrylic tows through an oven and, in the latter, the gradual change from a white acrylic to the black, fully oxidised acrylic fibres is clearly seen.

9.4.2 Theory of oxidation of polyacrylonitrile

The oxidation of PAN was first really studied by Hantz[20] in 1950, and since that time its role in the production of carbon fibres has been reviewed by

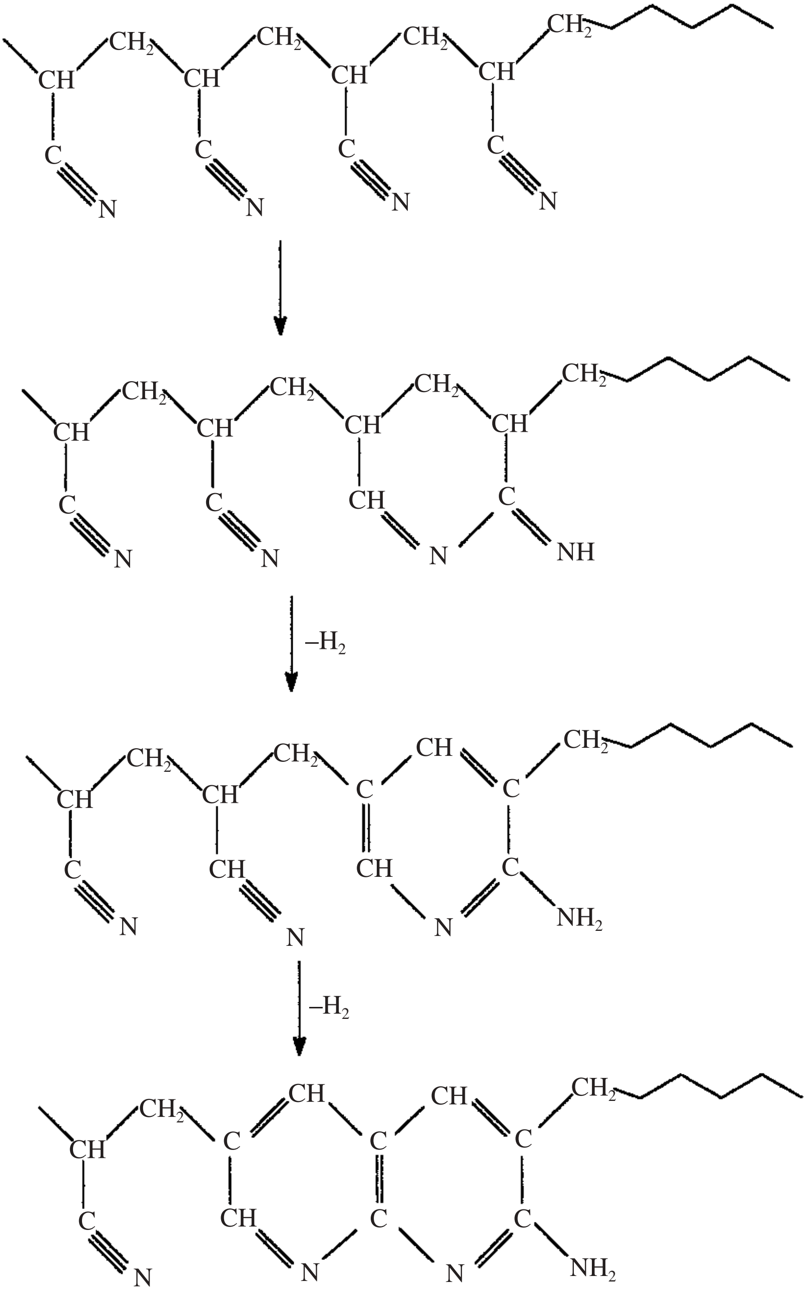


9.8 **Typical differential scanning calorimeter curves (heating rate 20 °C/min).[23]**

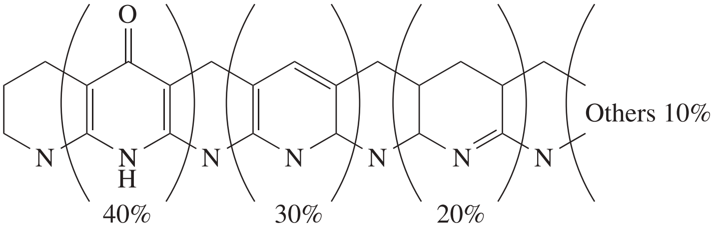
a number of authors.[21,22] Morgan[23] has described how pure PAN, when heated in air, has a sharp exothermic reaction, that is, a change in enthalpy by releasing heat from the tow's mass. This can be seen in Fig. 9.8, which shows how the temperature of the tow mass reacts to heat when examined in a differential scanning calorimeter. This clearly shows how the presence of itaconic acid comonomer helps to give a less pronounced exotherm peak, and at a lower temperature. This co-monomer also assists in promoting cyclisation of the pendant nitrile groups. If the acrylic fibre is heated in air too rapidly, a destructive exotherm occurs and there is a thermal run-away of the reaction inside the oven. Hence, the oxidation process must be very carefully controlled by a very sophisticated thermal control, or flash-over will occur in the oven, causing fire at worst or incorrect density of the threaded tow if mere overheating occurs.

Ammonia, water, carbon dioxide, carbon monoxide and hydrogen cyanide are evolved in the oxidation process and about 2.5 molecules of oxygen enter the fibre for every molecule of hydrogen cyanide evolved. Since the acrylonitrile repeat unit has a completely saturated hydrocarbon chain, the addition of oxygen will involve the elimination of hydrogen and nitrile groups. The hydrogen cyanide that is evolved can account for one half of an oxygen molecule of the 2.5 molecules entering the polymer, leaving four hydrogen atoms to be eliminated, possibly as water. The hydrogen loss, however, is greater than that due to removal by oxygen, and some crosslinking or hydrocarbon chain unsaturation must also occur. While the original mechanism of Hantz[20] shown in Fig. 9.9 is still considered to be correct, others have been published.[21,22]

After the oxidation process there is still about one third of the original hydrogen content remaining in the fibre product, which also retains half



9.9 The structure of polyacrylonitrile chain segments cyclising and transforming into a ladder-like, oxidised chain.[20–22] of its exothermicity. Carbon dioxide is both evolved and consumed and ammonia is known to inhibit the oxidation reaction. While there appears to be no generally accepted formula for oxidised fibre it is thought to be of the general form:[21,22]



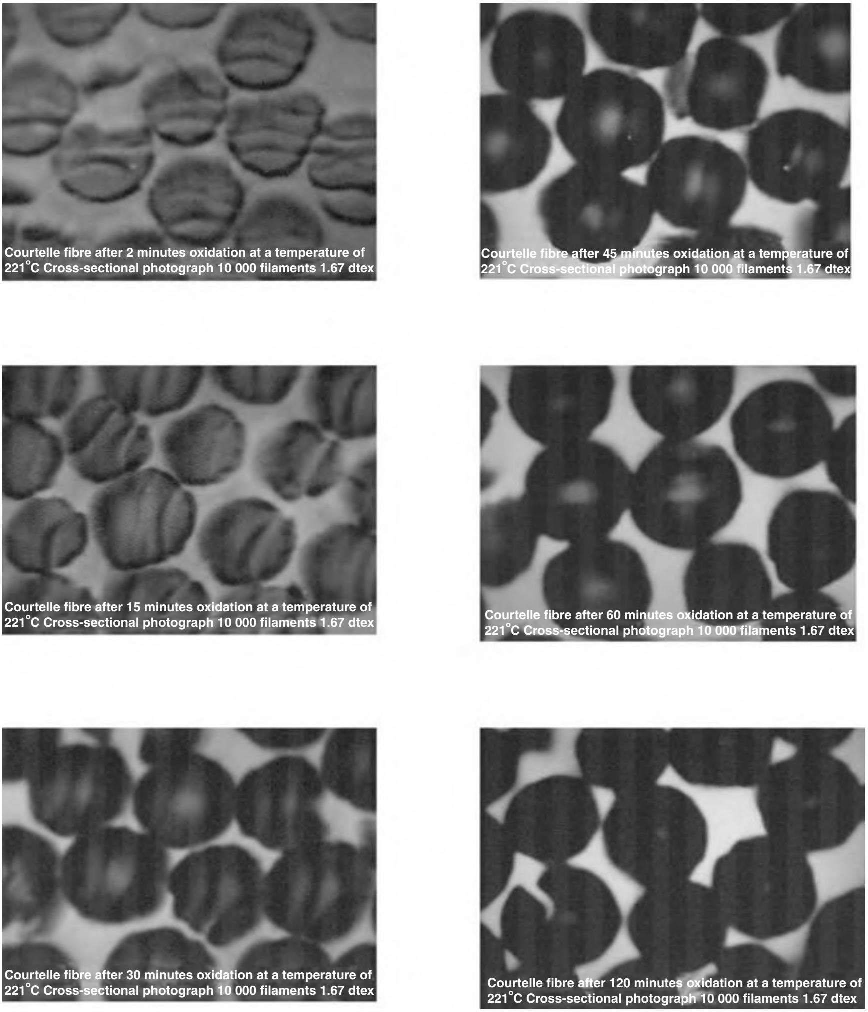
The cyclisation and oxidation processes are not considered to be separate reactions, but rather as progressing in parallel. In the oxidised form, hexagonal rings are believed to occur in groups of 7 to 10, which is probably due to co-monomer groups within the basic acrylic fibre structure interfering with the cyclisation along the chains. Subsequent carbonisation reactions involve the linking together of parallel chains of hexagonal groups, displacing oxygen and nitrogen atoms. The mechanism is best explained by reference to the photographs in Fig. 9.10 of the cross-sections of the polymer at different stages of oxidation.

The oxidation thus appears to occur in three stages:

(i) Oxygen rapidly diffuses into the outer zone of the fibre with resultant oxidation of the polymer.
(ii) A relatively slow cyclisation of the outer zone of the pre-oxidised polymer occurs without any observed progression of the zone boundary.
(iii) The final reaction occurs with the zone boundary moving towards the centre of the filament following a diffusion-controlled reaction obeying a 'square root of time' relationship. At the same time the outer zone darkens further to become black.

9.4.3 The oxidation process

The oxidation of the special *Courtelle* fibre is performed in an electrically heated oven shown previously in Figures 9.6 and 9.7. Figure 9.6 shows the passage of the tow through the oven. The tow is taken from the box and threaded over various tension bars to open it out to its full width (approximately 30 cm); the tow is then stretched by 8–10% prior to entering the oven. This will give an optimum extension of 11–13% in the oxidised tow. The tow then enters the oven at the bottom level and is fed backwards and forwards up through the oven, passing through three separate heater zones, set at gradually increasing air temperatures between 185 °C and 220 °C.



9.10 Cross-sectional micrographs of *Courtelle* fibres exposed to (a) 2 min, (b) 15 min, (c) 30 min, (d) 45 min, (e) 60 min, (f) 120 min oxidation at a temperature of 221°C, 10 000 filaments, 1.67 dtex.

The tow is driven through the oven and tensioned by ‘pinch’ rollers; these are rollers that can be moved horizontally to increase or decrease tension on the tow. It emerges from the oven at the top and is then passed through a bath to apply additives, dried and plaited back into a tow carton. A catalytic filter at the top of the oven removes the burnt tar and gases. The heating zones are heated by electric bar heaters. Fans and baffles keep the zones at uniform temperatures. All controls for the production process are incorporated in a data logger system that continuously monitors temperature distribution and tow speed.

Table 9.7 General properties of oxidised acrylic fibres

Property	Value
Tensile:	
Tenacity, GPa	0.2–0.3
Breaking strain, %	15–21
Modulus, GPa	7–11
General:	
Moisture regain, %	10
Specific gravity	1.35–1.40
Limiting oxygen index, %	55

9.4.4 Properties

After carbonisation, a major indicator of the overall fibre properties and suitability for end-use is the density. This is in spite of other physical and morphological characteristics being influenced by the degree of carbonisation achieved and shrinkage accommodated during the oxidation process.[24] The higher the density, the greater is the degree of carbonisation and the higher is the limiting oxygen index. Ideally, fibres having a LOI of 55% are considered to be acceptable. Table 9.7 shows the general properties of oxidised acrylic fibres, which may vary, of course, between manufacturers and types. Apart from continuous filament tows having individual fibre finenesses in the range 1.7 to 5 dtex, staple fibres are the more usual form with average lengths typically in the range 60 to 90mm. Fibre flocs with lengths of 4mm and below are also available.

As Table 9.7 shows, oxidised acrylic fibres have acceptable tensile properties for textile processing, a surprisingly high moisture regain and hence comfort factor of resulting fabrics, and a very high level of inherent flame resistance. Hence, they are used where a combination of acceptable physical properties and extreme heat and flame resistance are essential characteristics.

9.4.5 Applications

The fibres converted into fabrics satisfy the following end-uses: high temperature packings, anti-riot suits, tank suits, FR underwear, fire blockers for aircraft seats, heat-resistant felts (insulation), hoods and gloves, fire entry/fire proximity suits when aluminised, flexible hot air ducting, protection against phosphorus and sodium splash, welding blankets, components on aircraft side-walls and decorative double cloths for aircraft and ships.

The oxidised fibres/fabrics can be further carbonised by heat treatment and are then used as a valuable component in carbon–carbon composites that are essential components of aircraft brakes. They also find use as interface components for clutches and transmissions, reinforcement for plastics and composites, rocket motors, filters and electrical heating elements.

Oxidised PAN fibre-containing fabrics can be successfully printed and coated. They can also be flocked with fire-resistant coloured fibre for decorative FR end-uses. For molten sodium and phosphorus resistance, the fabric requires multiple fire-resistant coatings. Similar materials can be used for resistance against napalm. Special polymers can be impregnated to give strength and flexibility to the fabric after it has been burnt.

No one fibre has all the necessary properties for every fire-resistant application and, in the case of oxidised acrylic fibres, the best treatment is to blend them with other fibres to enhance colour and abrasion resistance, handling and wear characteristics.

Panox fibre is oxidatively degraded after prolonged periods at 210 °C and it is vulnerable to flexing, crushing and abrasion in 100% form for yarns finer than 90 tex. However, for non-apparel end-uses it may be spun to give yarns of about 38 tex and can be woven commercially. The fibre can be spun on a wide range of machinery but essential modifications have to be made to prevent fibre breakage and crushing.

9.4.6 Economic considerations

When comparing oxidised acrylics with competitive fibres such as PBI (Section 9.5), while their LOI values and carbon contents are very similar, the cost per kilo of the former is less than a tenth of the cost of PBI. *Panox* is also half to a quarter of the cost of a range of aramid fibres and double the cost of the modacrylics. One aspect of the true cost of a fibre is to consider the cost-advantages of using it during the product lifetime. Since a significant market for these fibres is their use in aircraft seat barrier fabrics, the weight and fuel savings may be calculated. Table 9.8 presents details for British Airways aircraft for 1986 which shows the weight and associated costs of seat fire-blocking fabrics in a range of commercial aircraft.

These figures show that in 1986 it cost around £45.00 per kilo of fabric per year in aircraft fuel charges. In terms of oxidised acrylic lightweight fire blockers for the seats, the cost of the fuel to fly the material over a four year period (= 4 × £808 870) is twice as much as the fabric price (£1.53 m). It is clear, therefore, that high carbon content fibres allow fire-blocking fabrics to be made at lower weights per square metre than fibres having lower carbon contents, which means they are more economic as well as more protective.

Table 9.8 Operational costs of fire-blocking fabrics fitted to passenger seats in selected British Airways aircraft in 1986 (reproduced with kind permission of British Airways)

Aircraft(A/C) type	No. of seats	No. of A/C	Fabric mass per A/C, kg	Cost of fabric mass: £/kg/yr	Cost per A/C £	Cost per fleet £
Selected aircraft:						
B737	114Y	35	68	26	1768	61880
B737 (Airtours)	130Y	8	78	26	2028	16224
B757	189Y	15	113	17	1921	28815
B757	195Y	9	117	17	1983	17847
B747	18F/90SC/262Y	28	267	57	15219	426132
B747 (Combi)	22F/92SC/220Y	2	250	57	14250	28500
Concorde	100F	7	100	65	6500	45500
Others	—	50	—	—	—	173972
Total aircraft		**154**	—	**~45 (ave)**	—	**808870**

Notes: F = first; SC = super club, Y = club and economy class seats.
Weight increase for fire blocking fabrics:
First Class seat: 1.1 kg per seat place
Super Club seat: 1.0 kg per seat place
Economy and Club seat: 0.6 kg per seat place
Concorde seat: 1.0 kg per seat place

9.4.7 Heat-treated oxidised acrylics

The Dow Chemical Company have shown that further heat treatment of oxidised acrylic fibres in an inert atmosphere promotes a further improvement in heat and flame resistance. One product, produced under licence from this technology, is *Curlon* (Orcon Corporation) whose properties have been reviewed recently.[25] The fibres have a crimp, hence the name, are circular and are available in diameters of 8 and 11 μm. While the tensile strength (0.5 GPa) and extensibility (4.5%) are closer to those values more typical of carbon fibres, and the specific gravity of 1.54 reflects this as well, the Limiting Oxygen Index has increased to 56%. Because of its increased degree of carbonisation, toxic gas emissions, particularly those of HCN, when heated to temperatures up to 1000 °C, are claimed to be less than for normal oxidised acrylics. The higher density improves the acoustic insulating qualities and so this fibre is finding application in thermal–acoustic, fire-blocking, nonwoven fabrics in aircraft and marine environments.

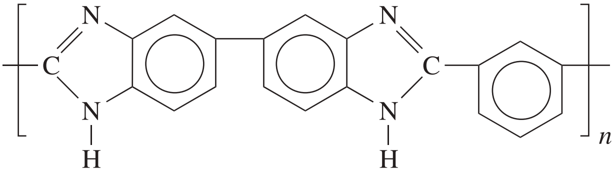
An even more recent version of this fibre is *Quiesse* (Quiescent Technologies, UK) which appears to have similar characteristics to *Curlon*.

9.5 **Polybenzimidazole, PBI** (CT)

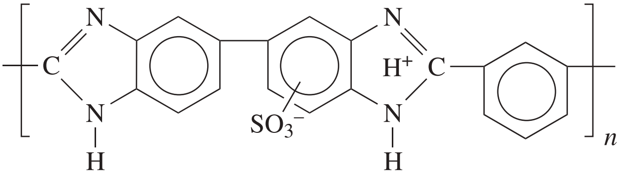
9.5.1 Develoment and structure

PBI fibre manufactured by Celanese Americas, USA, is a high-performance fibre recognized for its exceptional thermal stability and chemical resistance. These two qualities, along with its excellent textile processing characteristics, have secured *PBI* fibre a unique position in the high-performance fibre markets. Since around 1990, *PBI* fibre has found acceptance and is known as the premium product for many performance-based applications. These include fire protective fabrics for personnel, friction products, and fire-blocking substrates for aircraft. While *PBI* fibre is relatively new to the civilian market place, the story of *PBI* goes back to the early 1960s.[26,27] It was then that the US Air Force Materials Laboratory (AFML) contracted with the former Celanese Corporation to develop the polymerization and spinning processes for a high-temperature resistant fibre. Later, after the 1967 fire in the Apollo spacecraft, AFML and NASA examined PBI fibre as a non-flammable material for flight suits that would afford maximum protection to astronauts or pilots in oxygen-rich environments. After years of pilot scale manufacturing and use in highly specialized military and aerospace applications, Celanese, in 1983, built a full-scale manufacturing plant for the production of *PBI* polymer and fibre. It was then that Celanese began developing civilian markets for the various *PBI* products.

Polybenzimidazoles are a class of polymers that exhibit high thermal and chemical stability. The polybenzimidazole or PBI referred to in this report is poly (2,2′-(*m*-phenylene)-5,5′-dibenzimidazole) and it is the only commercially available polybenzimidazole. This particular PBI was commercialized because of its combination of excellent thermal stability and processability. PBI gains much of its thermal stability from the fact that it is a wholly aromatic, ladder-like polybenzimidazole structure.



Most PBI fibre sold today is treated with sulphuric acid to increase the flame stability of the fibre. Sulphonated PBI shrinks less than 10% when exposed to direct flame.

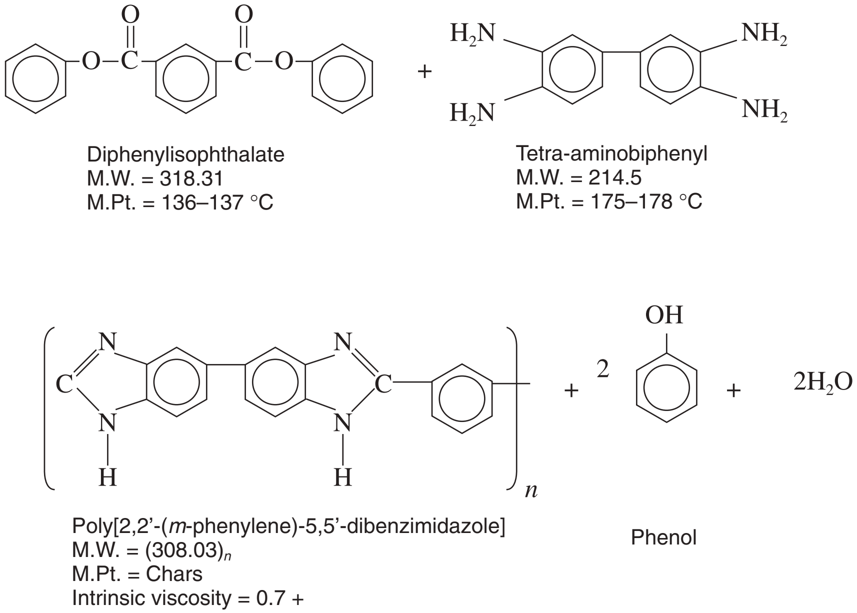


Even greater flame stability can be achieved by substituting the sulphuric acid treatment with a phosphoric acid treatment. Phosphonated PBI is available but it is only used in super critical applications.

9.5.2 Synthesis and fibre manufacture

PBI polymer is synthesized from tetra-aminobiphenyl (TAB) and diphenylisophthalate (DPIP) (see Fig. 9.11) in a two-stage reaction process.[23,28] In the first stage, equimolar amounts of the monomers are heated and melted in an inert atmosphere. As the monomers react and begin to build the PBI prepolymer, the by-products water and phenol evolve, causing the prepolymer to foam. After heating at 260 to 275 °C for 1–2 hours, the foam is allowed to cool and is then crushed into a fine powder. In the second stage, this PBI prepolymer is heated for an additional 2–3 hours at 375–400 °C to complete the polymerization process and provide the desired molecular weight for further processing. The resulting PBI polymer is in the form of a fine gold/brown powder.

Solutions of PBI dope are made by dissolving PBI polymer powder and lithium chloride under pressure and temperature in dimethylacetamide, DMAC, in an inert atmosphere. A typical dope solution contains 25% solid



9.11 PBI polymerisation.

PBI polymer by weight and has a viscosity of about 1500 P at room temperature. The lithium chloride is added to stabilize the solution, increasing the shelf life from days to several months. Before further processing, the PBI dope is filtered to remove particulates that could interfere with downstream processing.

Fibre forming involves the dry extrusion of the polymer solution through a fine-holed spinneret into a heated inert atmosphere. As the dope solution exits the spinneret, the DMAC evaporates and the solution begins to form into a semi-solid fibre. The resulting bundle of fibres (or 'ends') is drawn through a heated chamber to complete the fibre formation and remove most of the DMAC. The DMAC vapour is recovered through a vapour-recovery system. As individual fibre ends exit the heated chamber, they are combined with other ends to form a sub-tow. The sub-tows are laid and stored in a creel to await further processing.

After the required number of sub-tow creels are produced, they are brought together to form a heavy denier tow band for final processing. This final processing, known as tow finishing, consists of five major continuous steps:

(i) *Washing*: The tow band is run through a heated water bath to remove residual DMAC and lithium chloride left in the fibre from spinning.

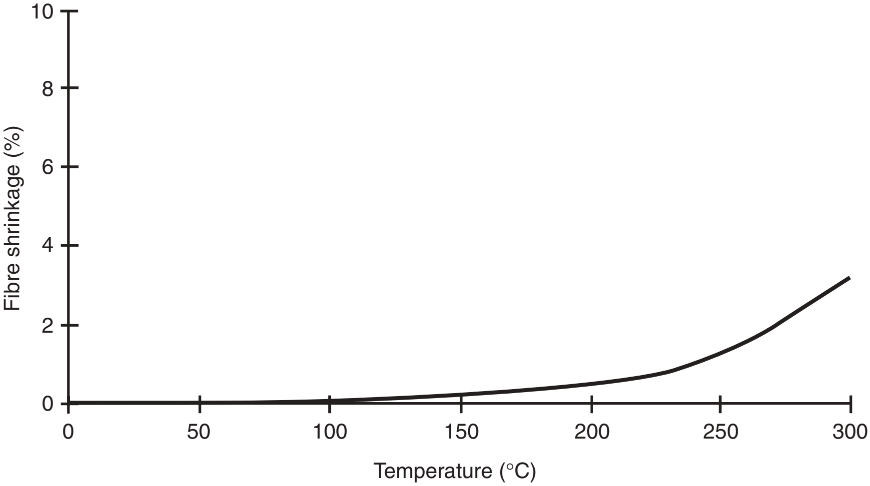
(ii) *Drawing*: After washing, the tow band is drawn and heated to orient the PBI fibre and produce a final fibre denier value of 1.5.
(iii) *Sulphonating*: The PBI tow band is submerged in a weak solution of sulphuric acid and subsequently heated at high temperature in an inert atmosphere to bond the sulphur chemically to the PBI molecule. Sulphonation reduces fibre flame shrinkage to less than 10%.
(iv) *Crimping, finishing, and cutting*: Depending on the customer requirements, the PBI has finish added, is crimped and is cut to various staple lengths, or is collected uncrimped and without finish for short-cut applications.
(v) *Packaging*: The finished product is packaged for delivery to the customer.

9.5.3 Fibre properties and applications

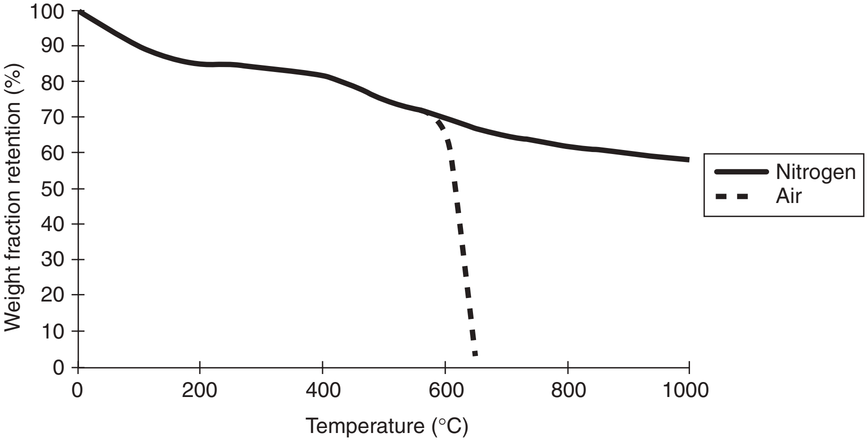
The full properties and fibre characteristics are fully described elsewhere but may be addressed with respect to the context of this particular discussion below.[27–30]

- *Flame and thermal stability:* PBI fibre will not undergo sustained burning in air, as demonstrated in the limited oxygen index test. The lowest concentration of oxygen that will sustain burning is 41%. Another standard test used to evaluate fire or flame resistance is the vertical flammability test (FSTM 191–5903). In this test, a fabric sample is exposed to a high flame temperature for a set time. Flammability performance is determined by measuring the after-flame time on the fabric and the length of fabric destroyed by the flame (char length). Fabric produced from PBI fibre exhibits no after-flame and minimal char length (10 mm or 0.4 inches), further confirming PBI's exceptional flame resistance.

  PBI fibre maintains its physical and mechanical integrity during and after exposure to a wide range of severe temperatures, and thermal stability has been examined in numerous high-temperature exposure tests. In these tests, where fibres are exposed to a range of temperatures for a predetermined duration followed by physical characterisation such as strength, mass and length retentions, PBI shows exceptional high-temperature stability. Figures 9.12 and 9.13 and Table 9.9 summarize some of these results. The thermogravimetric (TGA) analysis of PBI shown in Fig. 9.13 indicates that PBI retains integrity up to 450 °C (840 °F) in air and over 1000 °C (1830 °F) in nitrogen.
- *Heat release and smoke and gas generation:* Heat release is a measure of how much energy a material adds to pyrolysis and the burning reaction. In applications where a material is used to protect people and/or



9.12 **Thermal linear shrinkage of PBI fibre after 24-hours exposure.**

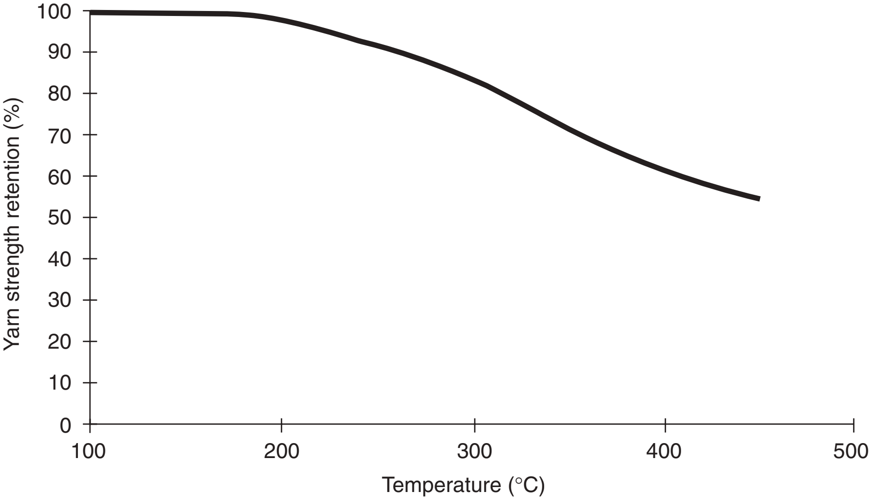


9.13 **Thermogravimetric analysis of PBI fibre in air and nitrogen.**

property from flame, it is important that the protecting material does not add to the danger by increasing the amount of available fuel. PBI fibre has negligible heat release as measured by the US Federal Aviation Administration (FAA) version of the Ohio State University heat release apparatus specified in FAA specification JAR 25.853 Part IV Appendix F(1). The two-minute average heat release is less than 10 kW/m^2 compared to the FAA's required maximum value of 65 kW/m^2.[31,32]

Table 9.9 Thermal stability of PBI fibre

Temperature, °F/°C	Useful life
1100/600	3–5 seconds
840/450	5 minutes
750/400	1 hour
625/330	24 hours



9.14 **Acid vapour resistance of PBI fibre after exposure to sulphuric acid vapour, 75% (w/v) concentration.**

Furthermore, because PBI fibre does not burn in air, it releases little or no smoke and off-gases up to its decomposition temperature. The specific optical smoke density (*ES* or D_s) of PBI is 2 compared to values of 3 to 8 for other common high-temperature fibres.[33]

- *Chemical resistance:* PBI fibre has excellent chemical resistance to a whole host of inorganic acids and bases, and organic chemicals. Chemical resistance is demonstrated by exposing PBI fibre to specific compounds and then measuring the strength retention of the fibre after the exposure. Results in Fig. 9.14 and Tables 9.10 and 9.11 show this resistance to some of the more common chemicals.
- *Physical properties:* PBI fibre has a large number of desirable physical properties that, along with the aforementioned thermal and chemical properties, make it the fibre of choice in many critical performance-based applications (see Table 9.12). In particular, its combination of high

Table 9.10 Tensile strength after immersion in inorganic acids and bases

Compound	Concentration, %	Temperature, °C/°F	Time, hr	Tensile strength retained, %
Sulphuric acid	50	30/85	144	90
Sulphuric acid	50	70/160	24	90
Hydrochloric acid	35	30/85	144	95
Hydrochloric acid	10	70/160	24	90
Nitric acid	70	30/85	144	100
Nitric acid	10	70/160	48	90
Sodium hydroxide	10	30/85	144	95
Sodium hydroxide	10	93/200	2	65
Potassium hydroxide	10	25/77	24	88

Table 9.11 Tensile strength after immersion in organic chemicals

Compound	Strength retention, %
Acetic acid	100
Methanol	100
Perchlorethylene	100
Dimethylacetamide	100
Dimethylformamide	100
Dimethylsulphoxide	100
Kerosene	100
Acetone	100
Gasoline	100

* All exposures at 30 °C (85 °F) for 168 hours.

moisture regain, low modulus, and good tensile strength makes it an excellent candidate for textile applications.

- *Textile properties:* PBI fibre has excellent textile properties and processes easily on conventional textile equipment. The properties of PBI fibre lend themselves to other fibres, making it an excellent candidate for blending. Products made from PBI and PBI blends are known for their superior flame resistance and soft hand and cotton-like feel. In many cases, PBI fibre will improve the processability of its partner fibre.

Table 9.13 lists the PBI fibre products that are available, along with the major applications and end-use. PBI fibre is available in a short-cut form for applications that require uncrimped, cut fibre. Short-cut PBI can be dis-

Table 9.12 Typical physical properties of PBI fibre

Property	English	Metric
Denier per filament (dpf)	1.5 denier	1.7 dtex
Tenacity	2.7 g/d	2.4 dN/tex
Breaking elongation	28.5%	28.5%
Initial modulus	32.0 g/d	28.0 g/d
Crimp (for crimped staple)	28.0%	28.0%
Finish	0.25%	0.25%
Specific gravity	1.43	1.43
Moisture regain, 20 °C, 65% rh	15.0%	15.0%
Boiling water shrinkage	<1.0%	<1.0%
Hot air shrinkage, 205 °C	<1.0%	<1.0%
Specific heat	0.3 BTU/lb °F	1.0 K/kg °C
Limited oxygen index (LOI)	>41.0%	>41.0%
Surface area resistivity, 21 °C, 65% rh		1×10^{10} ohms/cm
Colour	Gold	Gold
Standard cut lengths for crimped staple	$1\frac{1}{2}$, 2, 3 and 4 inch	38, 50, 76 and 102 mm
Thermal conductivity	0.022 BTU/hr.ft. °F	0.038 W/m °C

Table 9.13 PBI fibre available products

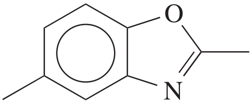
Product description	Availability	Applications	End-uses
Crimped cut staple	1.5, 2.0, 3.0 and 4.0 inch (38, 51, 76 and 102 mm)	1. Textile yarns and fabrics 2. Nonwovens	1. Fire-fighting turnout gear 2. Industrial flash-fire protective clothing 3. Aircraft fire blocking 4. Heat resistant thread
Short cut staple (uncrimped and unfinished)	0.125, 0.25 and 0.5 inch (3,6 and 12.5 mm)	1. Compounds 2. Nonwovens	1. Friction products 2. High-temperature paper products 3. Nonwoven insulative products
Phosphonated fibre	Same as above	Where increased thermal stability is required	Aerospace applications

persed and compounded with other materials, and is used in nonwoven insulative media, friction product formulations, and high-temperature paper products. A small percentage addition of PBI short-cut fibre can substantially improve the thermal performance of many products. PBI short-cut is available in $^1/_8$ (3 mm), $^1/_4$ (6 mm) and $^1/_2$ (12.5 mm) inch lengths.

PBI is also available in the raw polymer form and solution dope. For more information on the PBI products available, see the PBI website.[34]

9.6 Polybenzoxazoles, PBO (ARH)

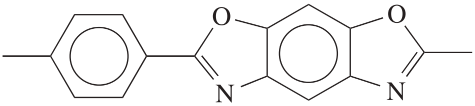
In the quest for improved polymer thermal and physical properties, introduction of the rigid benzoxazole segment:



within polymer chain backbones has been shown to improve significantly these characteristics, although problems of conversion to fibres have arisen, as they have for all linear aromatic-chain polymers.[8] Chapter 4 discusses this generic group of fibre-forming polymers in detail and so here they will be considered from the thermal property viewpoint only.

As early as 1973, Judge and Montgomery[35] had demonstrated that fibres derived from complex polybenzoxazole polymers synthesised earlier by Lindsey *et al.*, showed superior thermal degradative behaviour compared to the meta-aramid *Nomex*, with negligible mass loss occurring until above 500 °C when heated in a TGA instrument. Furthermore, these fibres showed good resistance when heated at temperatures up to 250 °C in terms of tenacity retention. This extreme temperature resistance has been referred to more recently where stabilities in air up to 650 °C and well above 700 °C in inert atmospheres have been reported.[36]

At the present time, there is one commercial example of a PBO fibre, poly(*p*-phenylene benzobisoxazole) or *Zylon*®, manufactured by Toyobo. It is evident from simple examination that the rigid and linearly symmetrical repeating aromatic structure



will have very high thermal stability and, because of the absence of aliphatic CH groups, excellent inherent flame resistance. The properties of this fibre discussed in Chapter 4 and published elsewhere[35–38] show that fibres do indeed exhibit the very high onset of thermal decomposition temperature of 650 °C and a LOI value of 68. While there are at least two variants of fibre, *Zylon-AS* and *Zylon-HM*, of which the latter has the higher modulus, they both have these same thermal and burning parameter values. These properties demonstrate that PBO fibre is the most thermally stable and flame resistant of all organic polymer fibres commercially available at the present time, as summarised in Table 9.14. This thermal stability is shown also by their greater strength retention when heated to temperatures above 200 °C, compared to the meta- and para-aramids.[38] Thus, when heated to 300, 400 and 500 °C, *Zylon-HM* retains about 65%, 50% and just below 40% respectively, of its normal ambient tenacity. In addition, when heated at temperatures as high as 400 °C for periods as long as 3 hours, the fibres lose only about 5% of their mass. Clearly, these properties, coupled with a very good resistance to hydrocarbon (e.g. gasoline), polar (e.g. dimethylformamide, methyl ethyl ketone) and hydrogen-bonding (e.g. methanol) solvents makes the fibre ideal for end-uses such as hot gas filtration.

The fibre is available in staple, filament and chopped forms and finds applications in the area of thermal and fire resistance products where a combination of these properties with high tenacity and modulus are required. Principal examples are heat-protective clothing including gloves, hot gas filtration media, high temperature conveyor beltings and reinforcements, and aircraft fragment/heat barriers.

9.7 Final comments (ARH)

This chapter has demonstrated that a significant number of fibres exist that have high levels of heat resistance and, usually, accompanying high levels of flame or fire resistance. Furthermore, as Table 9.14 shows, the range and level of fibre performances are considerable. Usually, however, the selection of a particular fibre for a specified use is governed by a balance of the overall properties, ease of processibility and, of course, cost. In the case where very high levels of thermal resistance, fire resistance, or both, are essential, then these respective fibre properties will be major selection criteria.

It should be mentioned at this point that, while the design and selection of flame and fire resistance of textiles comprising these fibres is made on data such as that presented in Table 9.14, there is now an increasing tendency to measure heat-release rates determined by calorimetric techniques. This has been driven by the recognition that fire spread is determined by the heat release of ignited component materials, and the definition of minimal heat-release values using standard calorimetric methods[31,32] has been enshrined in civil aviation authority regulations since the late 1980s.[40] The latter define values measured using the Ohio State University (OSU) calorimeter whereas the more recently developed cone calorimeter finds

Table 9.14 Summary of thermal and flammability parameters[39]

Fibre genus	Second order temperature, °C	Melting temperature, °C	Onset of decomposition, °C	Maximum, continuous use temperature, °C	LOI, %
Melamine –formaldehyde	NA	NA	370	190	32
Novoloid	NA	NA	>150	150/air; 250/inert	30–34
m-Aramid	275	375–430 (decomp)	425	150–200	28–31
p-Aramid	340	560 (decomp)	>590	180–300	29–31
Arimid (P84)	315	—	450	260	36–38
Aramid-arimid	<315	—	380	NA	32
Semicarbon	NA	NA	NA	~200/air	55
PBI	>400	NA	450/air;1000/inert	~300 (est)	>41
PBO	—	—	650; >700/inert	200–250 (est)	68

Notes: NA = not applicable; (decomp) = with decomposition; (est) = value estimated from data in cited references.

Table 9.15 Peak heat release (PHR) values for selected heat-resistant fibres and polymers[41–45]

Fibre/blend	PHR, kW m^{-2} (OSU; 35 kW m^{-2} incident flux)	PHR, kW m^{-2} (cone calorimeter, 50 kW m^{-2} incident flux)
Wool	—	286
63% oxidised acrylic/17% aramid/ 20% pvc	34	—
80% oxidised acrylic/ 20% aramid	38	—
33% modacrylic/ 35% FR viscose/ 32% aramid	47	—
Mixed m- and p- aramid	—	53
Oxidised acrylic	—	77
PBO (film)	47	—
PBO (carbon fibre (40%)/PBO(60%)) composite	—	50

greater acceptability in the wider fire science community.[31] Unfortunately, there is not very much published data regarding heat-release rates either as peak values (PHR) or average values available for the fibres discussed in this chapter. Such PHR values that are available are listed in Table 9.15 for incident heat flux values of 35 kW/m^2 [32,45] or 50 kW/m^2.[41–45] A value for wool is included merely to provide a reference PHR value more representative of a moderately flammable fibre.[44] The values for PBO are for film and composite variants. In order to pass civil aviation authority requirements, peak heat-release rates of samples subjected to 35 kW/m^2 incident heat flux must emit 65 kW/m^2 or less[32,40] and fabrics having the lowest values are those that comprise fibres having the highest degradation temperatures and LOI values (see Table 9.14).

An observation that is perhaps worthy of note is the very large number of speciality fibres reported in the literature and often patented since the 1960 period, of which only the fibres described in this chapter have survived as commercial examples. Furthermore, not until very recently has the general commercial availability of these fibres increased, as reductions in costs coupled with increasing performance demands have enabled them to displace the more conventional fibres. For example, before the 1960s, in high temperature uses such as hot gas filtration, because synthetic fibres were thermoplastic with only moderate to good thermal degradation resistance, their use was and still is limited to constant exposure temperatures of less than 120 °C or so. One exception, however, is the homopolymeric polyacrylic group by *Dralon T* from Bayer. This fibre type competed with the meta-aramids during the 1970–1990 period and could be used at constant temperatures as high as 150 °C in hot air atmospheres. This fibre genus seems not to be available today and, as shown in Table 9.13, the fibres discussed therein are clearly superior in terms of both temperature and fire resistance.

Another acrylic-related fibre which has recently ceased to be a commercial entity[46] is the polyacrylate *Inidex* (Acordis),[47] which is a zinc ion crosslinked acrylic polymer-based fibre often referred to generically as a polyacrylate. This non-thermoplastic, naturally pinkish-coloured fibre, unfortunately, while having a minimum LOI value of 31% with values as high as 41–45% being reported,[47] was relatively weak (0.12–0.15 N/tex) and so lent itself only to nonwoven fabric production methods. It has seen application in barrier products such as fire blankets, protective clothing and heat shields. However, a recent French development by Tecfibres SA is an improved polyacrylate, *Tecstar FR*, which is claimed to be available in a range of colours and have excellent processibility.[46]

Evidently, the improvements in thermal performance have been significant during the last 20 years and these have not only enabled longevity of many textile and related products to be increased but also higher limits of performance to be achieved. It will be interesting to see whether further improvements in performance will be forthcoming during the next 20 years and whether the performance limits expected of fibre-forming organic polymeric structures have already been reached in structures such as the semi-carbon oxidised acrylic, PBI and PBO fibres.

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