4

Other high modulus-high tenacity (HM-HT) fibres from linear polymers

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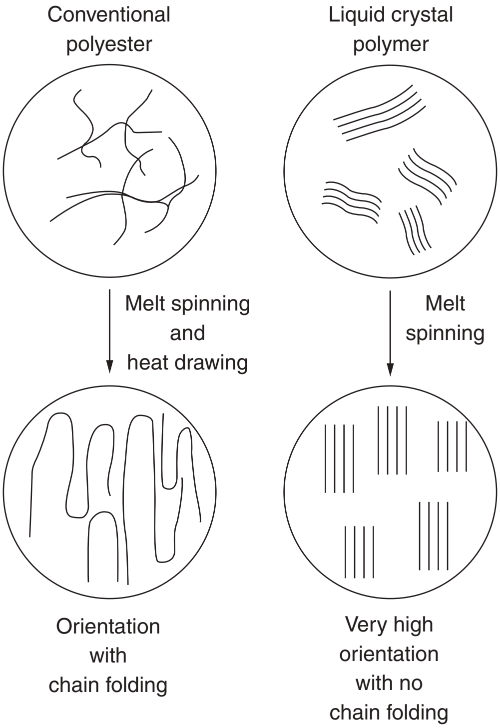
4.1 Melt-spun wholly aromatic polyester (DB)

4.1.1 Thermotropic liquid crystal polymers

Research into liquid crystal polymers dates back to the 1970s. This research has resulted in a commercially available melt-spun wholly aromatic polyester fibre called *Vectran*®. This high-performance fibre is used in numerous applications around the world that require its unique properties. Because of its relatively high cost, it remains a niche-market product driven by cost–performance benefits. Nevertheless, it significantly improves end-product performance when used properly. Much has been written about liquid crystal polymers (LCP) generally. This section focuses on the commercial fibre produced from thermotropic liquid crystal polymer (TLCP).

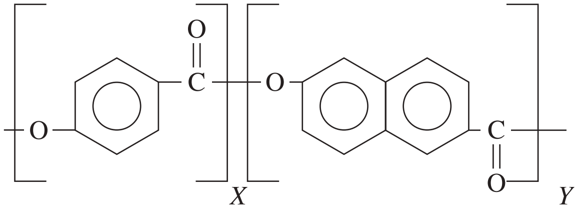
'Liquid crystal' is a term given to an organic polymer that exhibits order similar to an ordinary solid crystal. When viewed in the molten state on a hot stage microscope through polarising lenses, this polymer is called a 'thermotropic liquid crystal polymer'. The temperature range over which this phenomenon is observed depends on the chemical composition of the TLCP. These polymers consist of very rigid, chain-like molecules that position themselves into randomly oriented domains. When these domains are extruded through very small holes, the flow and accompanying shear aligns the domains parallel to each other in the direction of flow (Fig. 4.1). When cooled down, the extruded fibre has a highly oriented structure with high tensile strength and modulus. Because of this high orientation, drawing after spinning is not necessary. What is needed for high strength is to increase chain length. Solid-state polymerisation of the spun fibre, which raises the molecular weight, results in fibres with very high strength and modulus.



4.1 Schematic of molecular chain structure of fibres.

4.1.2 *Vectra* and *Vectran*

The commercially available TLCP fibre, *Vectran*, is produced from *Vectra LCP* polymer. This polymer is made by the acetylation polymerisation of *p*-hydroxybenzoic acid and 6-hydroxy-2-naphthoic (Fig. 4.2). It is one of a family of naphthalene-based thermotropic liquid crystal polymers developed by Celanese Corporation in the 1970s and discussed by Calundann *et al.*[1] No classical glass transition temperature is clearly observed in the polymer, although molecular transitions do occur with increasing temperatures. Research and development for the polymers and fibres were focused on tyre cord, to compete with para-aramids. When a cost advantage with these TLCP polymers could not be realised in tyre cord, emphasis shifted towards resin development for electronics parts. The excellent dielectric properties of the polymer and tight tolerances allowed during injection molding resulted in commercial success with the polymer and the start-up of the first commercial liquid crystal polymer manufacturing plant in 1989.



4.2 *Vectran* fibre chemical structure.

Celanese licensed its TLCP fibre technology to the Kuraray Company. Since the mid 1980s, both companies have pursued process and market development with a focus towards cost performance in niche markets. Kuraray produces significant volumes of TLCP fibre in Saijo, Japan. Celanese produces specialty products in the US for the US and European markets.

4.1.3 Fibre production

TLCP fibre is melt spun using conventional polyester extrusion practices. Attention to uniform polymer flow is essential. Wind-up speed is much lower, as is draw down, compared with PET processes. Some form of lubrication, either finish or water, is necessary for ease of processing, owing to the fibrillar nature of the fibre surface. Typical physical properties for the spun product are 10 g/denier tenacity (0.9 N/tex), 2% elongation, and 425 g/denier initial modulus (40 N/tex). This product represents a small percentage of the total TLCP fibre sales.

High strength, 23–28 g/denier tenacity (2–2.5 N/tex), is achieved in TLCP fibres by heat treating in an inert atmosphere. Again, some type of lubricant, normally water, is initially applied to ease processing. However, care must be taken to remove the water before the final heat-treatment temperatures are reached, to preserve the inert atmosphere required and thus achieve maximum physical properties. The fibre is produced as a continuous filament. Typical properties are given in Table 4.1. There are no significant environmental issues in the production of TLCP fibres.

TLCP fibres have been produced from polymers with varying chemical compositions to achieve an initial modulus in the range of 850–1000 g/denier (80–90 N/tex; 105–124 GPa). However, these fibres were not commercialised because of their lower tensile strength and flex fatigue when compared with commercial TLCP fibre products.

Long and short cut length TLCP fibres are produced by combining high denier continuous filament thread lines for cutting. The traditional economics of producing staple fibre from high denier tow are not realised with

Table 4.1 Properties for high-strength thermotropic LCP fibres

Physical forms:	
Yarn denier (continuous filament)	50–3750
Filament denier	5
diameter, μm	23
Density, gm/cm^3	1.4
Moisture regain, %	<0.1
Extractables ($MeCl_2$), %	<0.1
Mechanical properties*:	
Tenacity, g/denier	23–28
M/Pa	2850–3470
Elongation, %	≥3.3
Initial modulus, g/denier	525–700
GPa	65–87
Thermal properties:	
Melting point, °C	330
Boiling water shrinkage, %	≤0.5
Hot air shrinkage (177 °C), %	≤0.5
Limiting oxygen index	30
Coeff. of axial thermal expansion, m/m °C × 10^{-6}	–4.8 (20–145 °C) –14.8 (145–200 °C) –26.7 (200–290 °C)

* Test conditions – 25 cm gauge length, 10% strain rate, 98 tpm twist.
5 breaks/sample, ASTM D885 for I.M.

TLCP fibres because the high cut resistance of the material necessitates the use of low tow deniers. Paper products are also produced from short-cut fibre and pulp made from TLCP fibre.

4.1.4 Fibre properties

Essentially all high-performance fibres have high strength and modulus as well as low elongation, and these properties are very important for most TLCP fibre markets. However, the commercial applications for TLCP fibres also take advantage of one or more of the other unique properties of the fibre as well as high strength and low elongation.

Fibre-to-fibre abrasion resistance: A low level, generally <0.8% oil-on-yarn (OOY), weaving finish is applied to facilitate fibre processing during twisting, braiding, weaving, or knitting and for use in composite applications. This finish can be scoured off or removed with methanol. Processors topcoat over this finish with special coatings for improved UV resistance or to add colour, since TLCP fibre cannot be dyed. For dynamic applications requiring fibre-to-fibre abrasion resistance, silicone finishes are applied

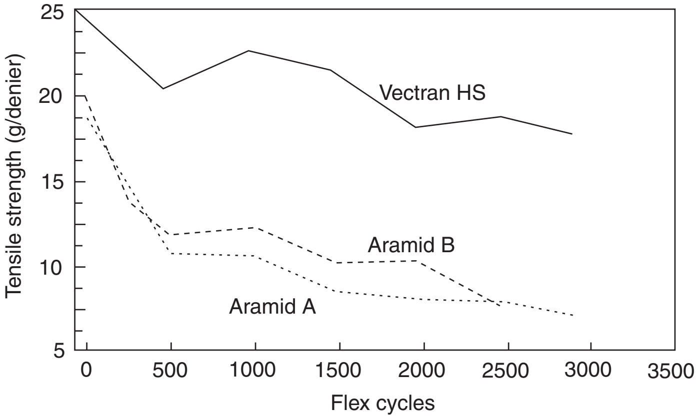
Table 4.2 Comparison of fibre-to-fibre abrasion resistance

Fibre	Average cycles-to-failure (CTF)	
	Dry	Wet
TLCP	16672	21924
Aramid (lowest CTF dry)	718	258
Aramid (highest CTF dry)	1773	758
UHMW-PE (lowest CTF dry)	8518	23619
UHMW-PE (highest CTF dry)	17761	78369

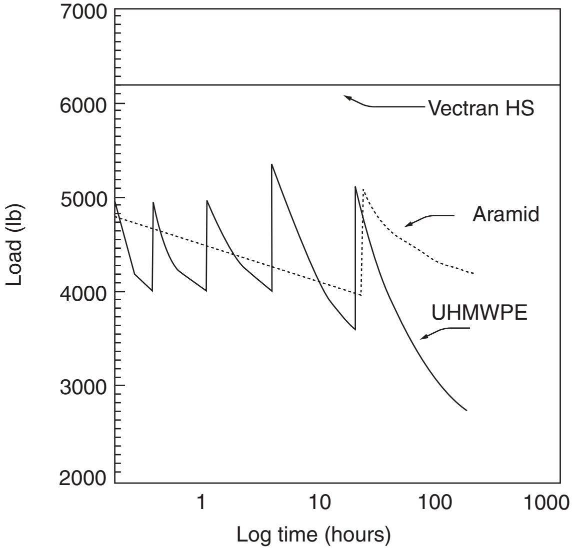
at a higher level, generally >4.0% OOY. These silicone finishes can be removed with hexane. TLCP fibre exhibits excellent fibre-to-fibre abrasion resistance when compared with other fibres in thread-line dynamic abrasion testing (Table 4.2). These relative values of abrasion resistance for the fibres listed are confirmed in tests of braided ropes. Wax or a combination of wax/silicone top-coated onto the fibre is also used to improve fibre-to-fibre abrasion resistance.

Bending properties: The high strength and modulus of both TLCP and aramid fibres are attributed to their highly oriented structure, although they are made by different processes and from different polymers. However, the flex fold characteristics of these fibres are very different. During flex fold testing, failure generally occurs by strain localization or energy absorption via the formation of kink bands, and also by fibrillation. Kink band formation has been studied by Dobb and McIntyre,[2] and Sawyer and co-workers.[3–5] The kink bands are believed to be dislocations caused by buckling and breaking of the stiff polymer chains. TLCP and aramid fibres both show kink band formation with increased flex cycles. However, more energy is absorbed in kink-band formation in TLCP than in aramid, and it is believed that this results in the significantly increased resistance to failure in flex folding of TLCP fibres compared with aramids (Fig. 4.3). This is further demonstrated in fabric testing. Specifically, in one test a heavy roller was passed over the crease of a folded strip of sample fabric and the specimen was folded back upon itself in the opposite direction and rolled again (the total constituting one cycle). After 100 cycles, the tensile strength of the TLCP fabric sample was reduced by 0.8% as compared to 22% tensile strength loss for an aramid fabric sample.

Creep: Tests at ambient temperature show that TLCP fibres in thread-line form exhibit no creep when loaded at <50% of the breaking strength. Stress relaxation studies on a nominal 13 mm diameter wire rope construction confirmed the lack of change in TLCP fibres under tension (Fig. 4.4). When tested at 80 °C, TLCP fibres exhibited some creep (0.8% after four days),



4.3 Tensile strength *vs* flexural fatigue of *Vectran HS* and aramids. Flex: Tinius Olsen/MIT, Modified ASTM D2176.



4.4 TLCP parallel strand rope stress relaxation. Whitehill Manufacturing Corporation WMCJETS/JETSTRAN 1-A VEC 1/2″ Rope.

but less than the aramid tested (1.2%) and significantly less than the ultra high molecular weight polyethylene (UHMW-PE) tested (>25%).

Thermal effects: TLCP fibres retain their strength for short periods at elevated temperatures, but gradually decrease in strength over extended time at elevated temperatures. For example, no strength loss was observed when the TLCP fibre was tested at ambient temperature following exposure to 195 °C for 30 eight-hour cycles. Aramid fibre tested simultaneously exhibited considerable strength loss. However, when exposed continuously to 195 °C for 30 days and subsequently tested at ambient temperature, TLCP fibre showed a 24% strength loss. TLCP fibres lose tensile strength when tested at elevated temperature. For example, when tested at 100 °C, the tenacity of these fibres is reduced by 35%. At the other end of the spectrum, tests on the polymer from which the fibre is produced indicate no tensile strength reduction after exposure to –196 °C (77 °K).

Cut resistance: TLCP fibres generally demonstrate excellent cut resistance, although this can be dependent upon the test used. Early tests measured the load necessary for a 5 cm diameter blade to begin cutting a tensioned knitted fabric. The relative cut resistance ranking using this test was:

High-strength TLCP	3.4
Aramid	1.1
UHMW-PE	1.0

Other test methods give different fibre rankings depending on the cutting method (slice or chop), test load and speed.

Chemical resistance: Tests have shown that the polymer from which commercial TLCP is produced is hydrolytically stable, resistant to organic solvents, and stable to acids at <90% concentration and bases at <30% concentration depending upon time and temperature of exposure.

Adhesion: Tests with an adhesive activated development finish resulted in very good TLCP fibre adhesion to rubber, provided the fibre is processed properly downstream. TLCP fibres are used in solid composites and in polyurethane systems.

Ultraviolet radiation (UV): Similar to other highly oriented fibres, TLCP fibres exhibit poor resistance to UV. The fibres must be protected when exposed to UV over extended periods of time. This protection can be a jacket over a TLCP fibre rope or a protective film over a fabric. UV inhibitors are not added to the TLCP polymers used for fibre because of the potential for reducing fibre strength.

4.1.4 Applications

A summary of commercial markets for TLCP fibres is given in Table 4.3. Ropes and cables for dynamic applications requiring fibre-to-fibre abrasion resistance and good bend-over-sheave is the largest single market for TLCP fibres. End-products include towed arrays/streamers for off-shore exploration, halyards for racing yachts, restraint lines for race cars, and long lines

Table 4.3 Commercial uses for TLCP fibres

Market	Examples	Reasons for using TLCP fibre
Ropes and cables	Yacht ropes Towed arrays Control cables Fishing gear	Abrasion resistance, flex/bend-over-sheave, no creep, small terminations possible in eye-splice, cut resistance
Protective materials	Gloves	Cut resistance, abrasion resistance, resistance to bleach and dryer heat
Industrial fabrics	Sailcloth Inflatable structures	Flex/fold, dimensional stability, tear strength
Sports	Bow strings Hockey sticks Bicycle forks Tennis rackets/strings	No creep, abrasion resistance, vibration damping, impact resistance
Medical	Catheters Control cables	Abrasion resistance, no creep, gamma sterilisation
Paper/non-wovens	Insulating papers Speaker cones	Dielectric properties, vibration damping, low moisture absorption, tear strength

for tuna fishing. Small TLCP braids (e.g. ~1.5 mm diameter) are terminated in an eye-splice with a pin diameter : braid diameter ratio down to 1 : 1, important for applications where space is critical, such as in ships or aircraft, and adding to the uniqueness of TLCP fibres.

TLCP fibres are used with other high-performance fibres in the sophisticated sail designs for the America's Cup sailboats. The relatively high cost of the fibre generally prevents it from being used by the weekend sailor. The air bags used to land the Jet Propulsion Laboratory Pathfinder on Mars in 1997 were produced with TLCP fibre because of the flex/fold characteristics and tear strength of composite fabrics made from the fibre. These properties are being utilized in a broad range of inflatable structures. In addition, TLCP fibres have thermal vacuum stability for space applications.

High-performance fibres are broadly used in composites for tensile strength reinforcement. TLCP fibre is used in composites when its additional properties provide unique performance or solutions to specific problems. For example, it improves vibration damping for bicycle forks, hockey sticks and tennis racket handles. Its low moisture absorption results in greatly reduced stress cracking when used as a sewing thread in an epoxy/fibre composite.

TLCP fibres are used in non-implant medical applications such as catheters and surgical device control cables. The material withstands gamma ray sterilization and is supplied in very low deniers for many of these applications. While there are no known health and safety issues related to the use of TLCP fibres, concern over the potential for litigation has prevented development of TLCP fibres for human implants. Nevertheless, its inertness, non-toxicity and bio-inactivity may bring significant potential for veterinary implants.

Recent developments in cutting and pulping technology allow the use of TLCP fibres for specialty insulating papers which take advantage of the excellent dielectric properties and low moisture absorption of the material for use in motors and printed circuit boards.

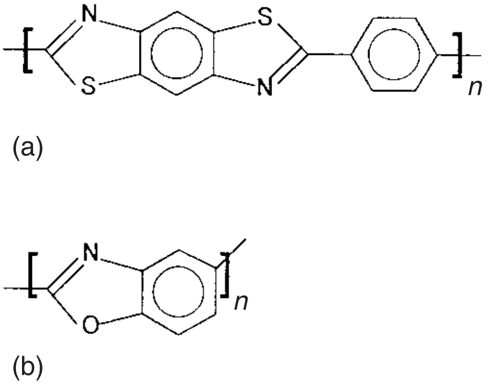
The market for TLCP fibres is growing in an expanding variety of specialty applications owing to the clear performance advantages achieved in end-use products because of the broad range of properties inherent in these fibres.

4.2 **PBO and related polymers** (RTY and CLS)

4.2.1 Introduction

Research at the Wright Research and Development Centre, Wright Patterson Air Force Base was directed in late 1960s and early 1970s toward the synthesis of highly fused aromatic heterocyclic polymers for high-temperature applications.[6] The initial polymers synthesised under this programme were the ladder polymers BBB and BBL, but difficulties in processing prevented further progress as has been reviewed by Arnold and Arnold.[7] In the 1970s, DuPont reported that extended chain, all para-aromatic polyamides ('aramids') gave high strength, high modulus fibres when processed from liquid crystalline solutions.[8] The ability greatly to increase the order in the liquid crystalline state, compared to conventional polymer solutions, offered an excellent opportunity to design and process new para-ordered polymer systems for fibre-reinforced composites. The synthetic effort at Wright laboratories began to focus on aromatic heterocyclic systems, other than ladder polymers, with a para-ordered geometry. One class of heterocyclic polymer system that could meet all the harsh requirements for advanced aircraft and aerospace applications and could be obtained in the form of fibres was the benzobisazole materials,[6] which have five-membered rings on either side of benzene rings. Poly(*p*-phenylene benzobisoxazole) (PBO) and poly(*p*-phenylene benzobisthiazole) (PBT) have received the most attention.

The molecules of PBO and related polymers are characterised by high rigidity and form highly ordered structures. The discovery of this highly ordered structure led to the term 'ordered polymers' for the aromatic



4.5 Chemical repeat units of related ordered polymers (a) PBT (b) ABPBO.

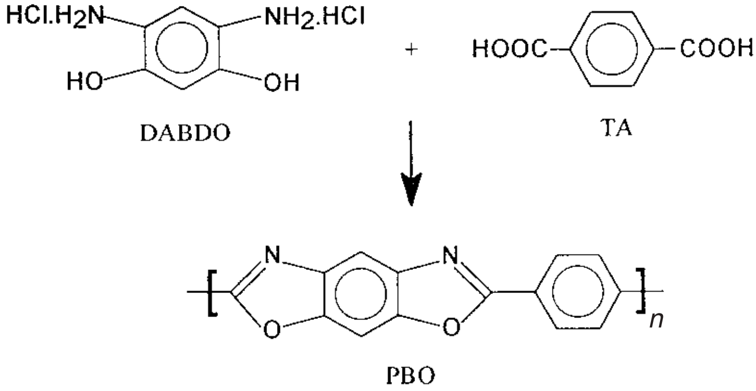
heterocyclic rigid rod polymers such as PBO and PBT. The term also includes some semi-rigid polymers such as poly(2,5(6)-benzoxazole) (ABPBO) and there have been a number of detailed reviews in the area of ordered polymer fibres.[6,7,9–12]

PBT is a rigid-rod polymer, shown in Fig. 4.5(a), in which sulphur replaces the oxygen in PBO, and its fibre manufacture is similar to that of PBO, as described below. PBT is synthesized by the polycondensation of 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) and terephthalic acid (TA), in a poly(phosphoric) acid (PPA) solution[6,7] and then spun into fibres via the dry-jet wet-spinning process. PBT fibre has excellent mechanical properties similar to those of PBO although not quite as good; this is mainly due to the slight differences in synthesis and processing. The high cost of manufacturing PBT has allowed the PBO fibre production to become more dominant.

ABPBO is a semi-rigid ordered polymer with high thermal stability, but the chain stiffness is much lower compared with PBT and PBO[10] owing to the presence of kinks in the main chain, Fig. 4.5(b), and thus it does not have the stiffness required for use as a reinforcing fibre. It does, however, have good thermal properties.

4.2.2 Manufacture of PBO fibres

PBO is manufactured via the monomer synthesis of 4,6-diamino-1,3-benzenediol dihydrochloride (DABDO), developed by Wolfe,[6] and a simplified synthetic route to PBO is shown in Fig. 4.6. This involves the condensation polymerisation of DABDO with terephthalic acid (TA) carried out in poly(phosphoric) acid (PPA). Stoichiometric amounts of amine and



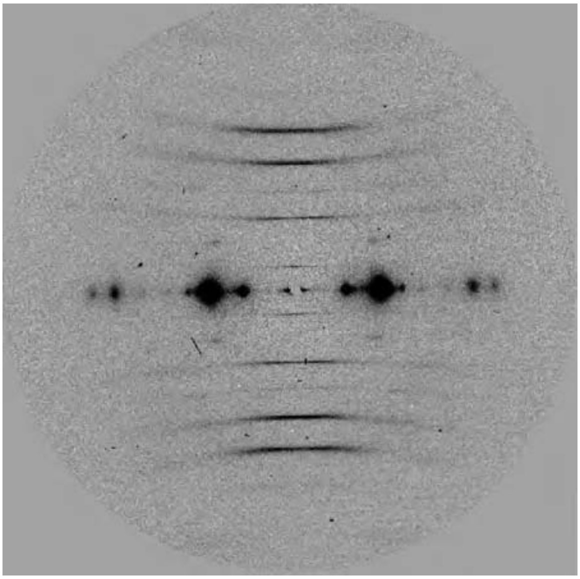
4.6 Simplified schematic of PBO polymerisation.

TA are heated in 77% PPA at 60–80 °C for the dehydrochlorination of the amine monomer. The temperature is lowered to 50 °C and P_2O_5 is added to obtain the high degree of polymerisation (between 82–84%) that is favoured for the dehydration of PPA and drives the polycondensation to completion.[6] A relatively more economic synthesis route for PBO monomer using 4,6-diaminoresorcinol has been produced at the Dow Chemical Company.[9]

Rigid rod polymers decompose at high temperatures without melting and can be dissolved in very few solvent systems owing to their aromatic structure and to their rigid molecular backbone. Conventional melt-spinning and solution-spinning technologies cannot therefore be used. These fibres, however, can be spun from solutions in PPA via the dry-jet wet-spinning technique,[9] as described in Chapter 2. This involves extrusion of polymer solution (liquid crystalline phase) under heat and pressure through an air gap into a coagulating bath (generally water at room temperature), followed by washing, drying, and finally heat treatment. Heat treatment is usually carried out in the 500–700 °C range under tension, in nitrogen, for between a few seconds and a few minutes. The structure formed during coagulation shows a network of oriented microfibrils. This network serves as a basis for the structure and properties of the final material.

4.2.3 Structure of PBO fibres

The degree of molecular alignment present in PBO fibres can be determined using wide-angle X-ray scattering (WAXS). Figure 4.7 shows a WAXS pattern obtained from a single PBO fibre using synchrotron radiation.[13] The sharp equatorial peaks indicate that the crystallites are well

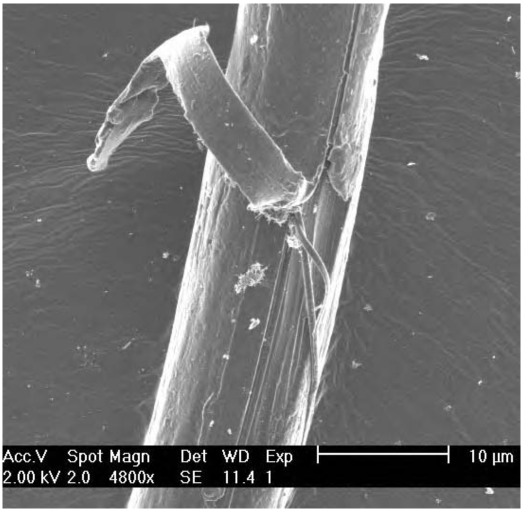


4.7 Wide-angle X-ray diffraction pattern of a single PBO fibre, showing the high degree of molecular orientation characteristic of rigid-rod polymer fibres. (The fibre axis is vertical).

aligned parallel to the fibre axis, whereas the streaks up the meridian are a result of scattering from the highly aligned PBO molecules.

A hierarchical microstructure for high-performance polymer fibres has been proposed by Sawyer *et al.*[14] A fibre is envisioned to comprise macrofibrils, fibrils, and microfibrils, with typical diameters of 5, 0.5 and 0.05 μm, respectively. The microfibrils consist of crystallites in combination with amorphous or disordered regions. Figure 4.8 shows a scanning electron micrograph (SEM) from a damaged PBO fibre revealing the underlying fibrillar structure. Although a fibril structure is the common feature of high-performance polymer fibres, the dimensions cannot always be discerned from the ratios indicated in this model, i.e. different high-performance polymer fibres have different fibril structures owing to the various molecular structures and processing conditions.[3] Kitagawa *et al.*[15] have proposed a similar structure for as-spun PBO fibre, where the microfibrils run parallel to the fibre axis with inherent voids between them. The fibrils consist of highly oriented PBO molecules parallel to the fibre axis, with the *a*-axes of the crystals aligned radially across the fibre.

Additionally, heat treatment results in fibres that have improvements in their overall axial orientation, crystal perfection and lateral order, leading to improved mechanical properties. The existence and magnitude of the



4.8 Scanning electron micrograph of a damaged PBO fibre, showing the surface skin and fibrillar structure.

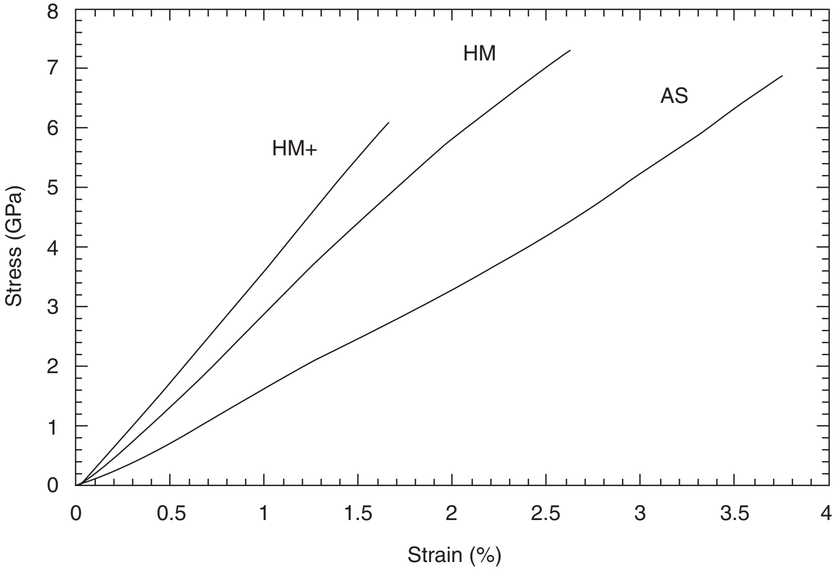
skin/core differences (Fig. 4.8) are believed to be the result of processing conditions, such as solvent diffusion and fibre coagulation.

4.2.4 Properties of PBO fibres

The excellent mechanical properties of PBO fibres compared with other high-performance fibres (Table 4.4) are accompanied by equally impressive thermal properties (Chapter 9). PBO fibres exhibit very high flame resistance and have exceptionally high thermal stability (onset of thermal

Table 4.4 Mechanical properties of a range of high-performance fibres[8–11,16,17]

Fibre	Density (g/cm^3)	Tensile modulus (GPa)	Tensile strength (GPa)	Compressive strength (GPa)
PBO	1.56	280	5.8	0.20
PBT	1.58	325	4.1	0.26–0.41
‘M5’	1.70	330	4.0	1.00
Kevlar 49	1.45	125	3.5	0.35–0.45
Twaron HM	1.45	115	3.2	0.45
P100	2.15	725	2.2	0.48
T300	1.80	230	3.2	2.70–3.20
Alumina	3.70	350	1.7	6.90
E-glass	2.58	76	3.4	4.20



4.9 Stress–strain curves for different PBO fibres. (After Kitagawa *et al.*[20])

degradation in the 600–700 °C range). PBO fibres also have very good resistance to creep, chemicals and abrasion. However, the poor compressive strength of these fibres restricts their use in composites (Table 4.4). Under compression, the failure of polymeric fibres is via kinking.[18] Unlike carbon and inorganic fibres, polymeric fibres do not exhibit a catastrophic failure in compression. The kinks in polymeric fibres develop at the yield point in compression. Attempts have been made to improve the compressive strength of ordered polymeric fibres via processing variation (fast and slow coagulation), crosslinking and structural disruption. None of these approaches has resulted in significant improvements in compressive strength.

Toyobo have recently succeeded in improving PBO fibres further in laboratory experiments by adopting a non-aqueous coagulation system and a new heat-treatment method.[19] It is important to implement a slow coagulation process during fibre production because the prestructure of the fibre induced before heat-treatment determines both the final fibre structure and its mechanical properties. The modulus of the improved PBO fibre thus obtained can be as high as 360 GPa. Figure 4.9 shows a series of single-fibre stress–strain curves for different PBO fibres.[20] The as-spun (AS) fibre has the lowest Young's modulus, which is improved by heat treatment in the HM fibre. The HM+ fibre produced using the non-aqueous coagulation system has the highest Young's modulus. It should also be noted from Fig. 4.9 that individual fibres can have very high values of strength, in excess of 7 GPa, although lower average values are normally quoted (Table 4.4).

The HM+ fibres also show an absence of the four-point small-angle X-ray scattering pattern that is characteristic of the morphology of heat-treated PBO fibre obtained using the normal (aqueous) coagulation process.[19] The apparent crystal size measured is almost the same as for the HM fibre and the molecular orientation is slightly higher for the improved HM+ fibre. This implies that factors other than just molecular orientation are concerned with improving moduli.

4.2.5 Applications of PBO fibres

The applications of PBO fibres are vast[21] owing to the excellent properties mentioned previously. Current PBO fibre composites, however, appear to be limited mainly to secondary structures and non-structural uses where axial compressive loading is minimised. Therefore, significant improvement in the compressive properties of PBO would be a major breakthrough.[10] Secondary structures that benefit from the excellent mechanical properties are found in such diverse areas as athletic equipment and high-fidelity speaker cones, in which good dielectric properties are important. Non-structural applications may take the form of woven fabrics and cables. PBO fabrics are light and flexible, providing improved comfort and mobility, and are ideal for heat and flame resistant work-wear such as for fire fighters. Motorcycle suits have particular areas, such as the knee and elbow regions, reinforced with PBO fabric, providing the required excellent heat, flame and abrasion resistance. As with aramids, PBO is ideal for ballistic-protection fabrics and panels owing to its high energy absorption and rapid dissipation of impact by the fibrillar morphology. Another application utilising the excellent thermal properties is heat-resistant felt, which is now being used by glass manufacturers as mats on which the hot, shaped-glass fabrications are placed for cooling. General applications for reinforcement include those for tyres, belts, cords, etc., as well as for optical fibre cables.

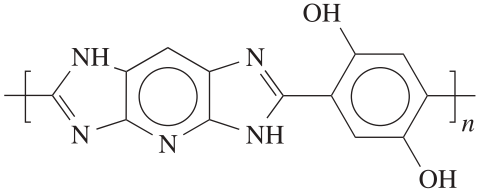
4.2.6 Conclusions

PBO fibres are the successful result of a research programme aimed at designing, synthesising and processing rigid-rod molecules into ordered polymer fibres with exceptional mechanical properties. The fibres are now being commercialised by Toyobo Co. Ltd of Japan under the trade name *Zylon*®. They are finding use in a number of applications where they have benefited somewhat from the development of a market for such materials through the exploitation of aramid fibres. PBO fibres have specific (per unit weight) values of strength and stiffness in excess of all other materials and their future appears to be very promising indeed.

4.3 PIPD or 'M5' rigid-rod polymer (DJS)

4.3.1 A new HM-HT fibre

As a result of research in Akzo-Nobel laboratories a new high-performance fibre, known as 'M5', has been produced. The polymer is poly{2,6-diimidazo[4,5-b:4′,5′-e]pyridinylene-1,4-(2,5-dihydroxy)phenylene} or PIPD, with the formula:



Two methods have proved effective in preparing high modulus, high tenacity (HM-HT) polymer fibres:

(a) perfecting the drawing technique of precursor fibres to attain draw ratios far above ten, as in the well-known polyethylene *Dyneema* and *Spectra* yarns[22] described in Chapter 3.
(b) manipulating rigid rod-like molecules into fibres that are already very highly oriented in the as-spun state, as in PPTA fibres,[23] described in Chapter 2.

Work has been directed at much stiffer rigid rod-like materials, culminating in the PBO fibre (Section 4.2) that is now becoming commercially available from Toyobo after much development at Wright-Patterson AFB, at SRI International and at Dow Chemical.[23a,24] Although PBO shows very impressive tensile properties, its performance under compression has been disappointing, and much work has been done in various ways to correct the problem, without making much headway. Various schemes have been tried to increase lateral strength in PBO after fibre formation,[25] often by crosslinking. One attempt at introducing hydrogen bonds in such a polymer did not afford the improved compression performance hoped for; its lack of success in attaining improved compression properties was attributed to the hydrogen bonds being formed intra- rather than inter-molecularly.[26]

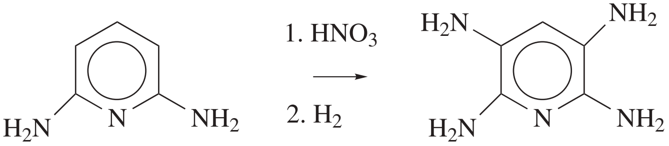
It has been the ambition of this author to create polymers as *rigid rod-like* as PBO, with *strong intermolecular hydrogen bonds*.

After much experimentation, some of which has been reported,[27] we turned our attention to the well-proven (albeit experimentally challenging, see

Ref. 25) polymerisation of one-ring aromatic tetrafunctional nucleophiles. An example of high merit appeared to be 2,3,5,6-tetraaminopyridine: 2,6-pyridinediamine, a commercial product, fairly simply accessible by Chichibabin amination,[28] and, importantly, nitration was expected to be highly selective to produce the 3,5-dinitro isomer. Literature reports existed on this nitration, albeit with low yield after purification,[29] as well as on polymerisation of the tetraamine HCl salt (along the USAF–SRI (US Air Force–Stanford Research Institute) lines[25] for PBO), with isophthalic acid to prepare a thermally stable polymer.[30]

4.3.2 Monomer selection and syntheses

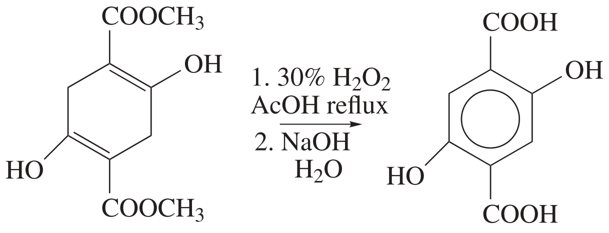
Synthesis of 2,3,5,6-tetraaminopyridine (TAP) along the lines of Gerber,[30] with low yield after nitration, and including reduction with tin/hydrochloric acid, afforded our early samples of TAP.



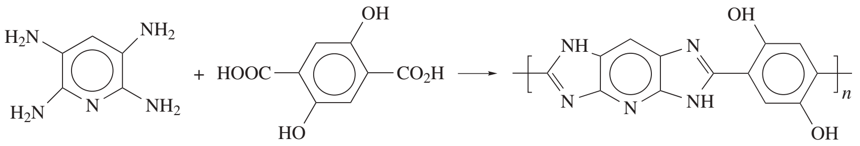
In early work, we isolated TAP as the hydrochloride salt and used it in the polymerisation, see Ref. 25. The nitration problems were soon corrected by modifying the nitration medium – changing from concentrated sulphuric acid[29] to oleum.[31] Thus, we could isolate high-purity products at 90–95% from the nitration and 85% yield of polymer grade purity crystal (TAP.3HCl.1H_2O) from the reduction with hydrogen. Having a sufficient supply of TAP in hand, we tackled the polymerisation. Reaction according to the method developed in Ref. 25 with terephthalic acid produced almost instantaneous precipitation of very low molecular weight (MW) oligomer.

Polymerisation with 2,5-dihydroxyterephthalic acid seemed desirable in itself because the hydroxyl groups could[32] contribute to the hydrogen bond network envisioned; the reaction led to high molecular weight products, in contrast to the results with unsubstituted terephthalic acid. Thus, not only an enhanced-polarity polymer proved accessible, in fact the analogue with fewer active protons could not be prepared in a usable form. Concentrations of almost 20 wt.% of polymer in solution in PPA could be attained. By contrast, 1,2,4,5-tetraaminobenzene[33] (which likewise gives insoluble, very low MW material with terephthalic acid)[34] proved to have a solubility limit in its high-MW polymer with 2,5-dihydroxyterephthalic acid of about 8.5%, in related work in our laboratory.[35]

2,5-Dihydroxyterephthalic acid (DHTA) is described in the literature as the product of bromine/sulphuric acid mediated aromatisation[36] of diethyl succinoylsuccinate, a commercial product, followed by hydrolysis. The aromatisation can also be effected with sulphur,[37] or with sulphur and a Pd/C catalyst.[27] We found a convenient and non-noxious procedure in aromatising the succinoylsuccinate in acetic acid at reflux with 30% aqueous hydrogen peroxide and a sodium iodide catalyst. After hydrolysis, >90% of polymer grade DHTA[38] from succinoylsuccinate can be isolated upon acidification. Alternatively, the sodium salt of DHTA can be crystallised from the hydrolysis reaction mixture in high purity and somewhat lower yield (*ca* 87%).



4.3.3 Polymerisation



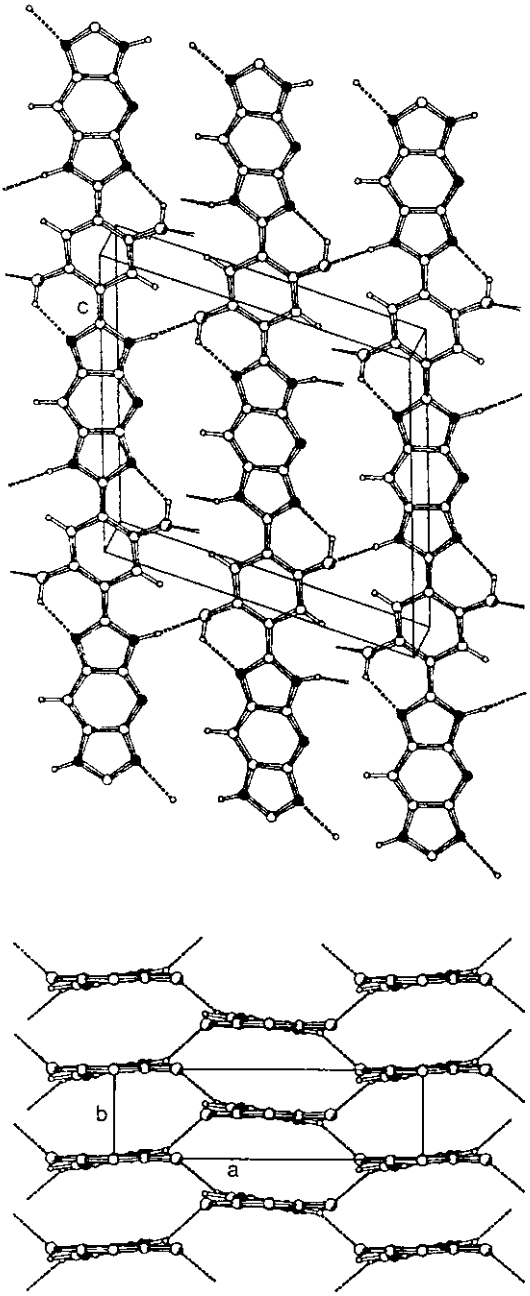
Right from the outset of our work with TAP hydrochloride and DHTA, we avoided the experimental difficulties inherent in the traditional[24] method of adding most of the phosphorus pentoxide and the organic diacid only after driving off the hydrochloric acid by heating in 'weak' polyphosphoric acid (PPA). When working at a small scale at least, we could add all ingredients at the outset of a heating cycle that involved (see Ref. 24) many hours of heating at about 100 °C while evacuating, to eliminate the hydrochloric acid. An important improvement was found in isolating TAP as its phosphoric acid salt, resulting not only in a much faster polymerisation cycle, but also eliminating the corrosion-type difficulties implicit in the earlier route. A much greater step forward was achieved by the synthesis of the TAP-DHTA 1:1 complex, or TD salt. This complex is significantly more stable against oxidation than TAP phosphate and it precipitates in a high yield from the combination of aqueous solutions of TAP HCl salt and DHTA Na or K salt. A fast polymerisation cycle (typically 4–5 h, rather than >24 h according to Ref. 24) now yields high MW polymer much more consistenly than in the case where amine and acid components are weighed separately: relative viscosities (0.25 g/dl in methane sulphonic acid) of 50 and above could be reached routinely. We did not succeed in preparing the terephthalic acid salt of TAP, which we attribute to the weaker acidity of terephthalic acid.[39] Thus, copolymers employing both DHTA and terephthalic acid (TPA) necessitated use of TAP phosphate and TPA next to TD salt. Such copolymers showed lower relative viscosities when more TPA was used as a comonomer, and became insoluble in the polymerisation medium when more than 50% of DHTA was substituted by TPA.

The polymerisation of homopolymer consists of taking TD salt, polyphosphoric acid and P_2O_5 with a trace of tin powder into the reactor, displacing air by nitrogen and raising the reaction temperature to 140 °C. Mixing for at least 1.5 h at that temperature before taking the mixture to 180 °C and stirring for another 1–2 h yields the spinning solution. The solution becomes liquid crystalline about 1 h after it reaches 140 °C. Work on the mechanism of PBO polymerisation has been reported.[40]

The P_2O_5 content of the solvent system controls the final molecular weight, and obviously only the highest purity TD salt will deliver the highest MW polymers. The solubility limit of high MW homopolymer in 80.5–83% PPA (i.e., a PPA consisting of 80.5–83% of P_2O_5, the balance being water) is 19 wt.%. At 180 °C, the solution (18 wt.% of polymer) is a nematic solution with long relaxation times of orientation; upon cooling, it crystallises at about 110 °C; the crystallised solution melts at about 140 °C. A further thermal transformation can be seen at about 80 °C by DMA (dynamic mechanical analysis). Crystallosolvate fibres of astoundingly high and perfect crystallinity could be prepared under special conditions.[41]

4.3.4 Spinning and fibre properties

Conventional air gap wet-spinning of the as-polymerised solutions of polymers with M_W 60 000–150 000 (Twaron aramid calibration SEC (size exclusion chromatography) in methane sulphonic acid) at 180 °C into a water or dilute phosphoric acid bath, proceeded readily; spin-draw ratios attainable depend on spinning orifice diameter and the result normally delivers filaments with a diameter of about 10 μm, which are further washed to a low phosphorus content and drawn (by a few percent at most) at high temperature (>400 °C) to produce the final, high modulus product. It is unclear whether the crystal solvate can form in this process characterised by very fast cooling. The coagulated and washed fibre is isolated as a crystal hydrate and the hot drawing process transforms this into the final high modulus 'M5' crystal structure.[41] The as-spun fibre already shows attractive mechanical properties, comparable to para-aramid fibres, although the modulus is higher (about 150 GPa). The as-spun fibre excels in fire resistance.[42] The crystal-to-crystal transformation during the hot drawing leads to a much



4.10 The crystal structure of M5-HT seen along the chain axis. Note the bidirectional hydrogen bonded network between the chains resembling a honeycomb and reinforcing the lateral chain–chain interaction. This leads to a high shear modulus and shear strength and thus to good compressive properties of the M5 fibre. We speculate that this honeycomb-like structure may be involved in the explanation of the impact and damage tolerance properties of M5 products.

higher modulus, owing to a more slender effective chain and much stronger interchain bonding, coupled with an improvement of the orientation.[41] Note that the fibre modulus depends on the shear modulus through non-perfect orientation of the molecules.[43]

Evolution of fibre structure and morphology, and its properties, during the manufacturing process is discussed in detail by Lammers *et al.*[41] The final crystal structure is analysed by Klop and Lammers[44] and illustrated in Fig. 4.10. The rod-like polymer molecules feature internal hydrogen bonds between –O–H groups and imidazole N atoms, and a *network in both directions perpendicular to the rod-like chains* between imidazole N–H atoms and the –O–H groups.[44] For the determination of this hydrogen-bond structure, it was not sufficient to ascertain the precise arrangement of the heavier atoms, but further measurements were needed. The fact that over a very large temperature range, both directions perpendicular to the polymer chain direction showed the same thermal expansion was the final lock on the proof of the three-dimensional (3D) network character of the hydrogen-bond system (as opposed to a sheet-like character),[44] as an independent observation in addition to the very high shear modulus determined from the relation[43] between molecular orientation and fibre properties.[41]

Even though much optimization remains to be done, we soon achieved promising mechanical properties and structure data in our new 'M5' fibres, even from bench scale operations using improvised machinery. Moduli well over 300 GPa, tenacities of over 2.3 N/tex (4 GPa), elongations at or above 1.5% and compressive strengths of 1.7 GPa (onset of plastic deformation) were recorded – the highest compressive yield strength by far shown by any polymer fibre.[41] Tensile and compressive deformation were investigated by micro-Raman spectroscopy, with qualitatively the same conclusions.[45] The good compressive properties are coupled to a very high internal shear modulus of 7 GPa.[41] The first composite test bars that were tested for longitudinal compressive strength confirmed the high compressive properties of the new fibre in composite form.[46] Three-point bending tests of composite bars pointed to a compressive yield stress of 1.75 GPa in the fibre.[46]

Ab initio calculations were performed on the M5 molecule and crystal.[47] A chain modulus of 553–578 GPa was concluded (depending upon details in the unit cell), in good agreement with the experimental chain modulus from WAXS measurements of 510 GPa.[41] The internal hydrogen bond contributes to this particularly high value.

Work is proceeding to spin fibres with properties exceeding the values given in Table 4.5 for early experimental samples of the new[48] fibre. Details of convenient laboratory-scale procedures for preparing the monomers and the polymer have been published;[49] alternative routes intended for scaling up were worked out also.[28,31,38]

Table 4.5 Provisional characterisation of M5 fibre, *spun at bench scale*, compared with commercial fibres

	Twaron HM	Carbon HS	PBO[b]	M5 experimental
	Filament averages, except carbon HS[a]			
Tenacity, GPa	3.2	3.5	5.5	5
Elongation, %	2.9	1.5	2.5	1.5
E-modulus, GPa	115	230	280	330
Compr. str., GPa[c]	0.58	2.1	0.4	1.6
Compr. strain, %[c]	0.5	0.9	0.15	0.5
Density, g/ml	1.45	1.8	1.56	1.7
Water regain, %	3.5	0	0.6	2
LOI, % O_2	29		68	>50
Onset of thermal degradn, air, °C	450	800	550	530
Electr. conduction	–	++	–	–
Impact resistance	++	––	++	++
Damage tolerance	+	––		++
Weaving props	+	–	+	+
Knot strength	+	––	0	0

[a] Mechanical properties of carbon are evaluated in resin-impregnated strands to protect the material against premature brittle failure in the tensile testing machine. (The organic fibres are tested as such: filament averages at 10 cm gauge length are presented.)

[b] Toyobo data.

[c] Measured in UD composite test bars, three-point bending test, onset of deflection for the organic fibre-reinforced composites; catastrophic failure for the carbon composites. M5 composites proved to be able to carry much higher loads than the load at onset of deflection in these tests, and to absorb much energy at high strains in a mode analogous to the ductile behaviour of steel structures being overloaded.

4.3.5 Applications and outlook

The mechanical properties of the new fibre make it competitive with carbon fibre in most applications – in light, slender, load-bearing *stiff* advanced composite components and structures. Very promising indications were obtained pointing to a *ductile* failure mode of (bending and compression) test pieces, notwithstanding the high stiffness. Similarly, such very stiff composite test pieces showed outstanding *impact* properties in scouting experiments. This suggests the possibility of designing, for instance, vehicle parts substantially lighter than can now be done on the basis of *brittle* reinforcing fibres. The ductile (as opposed to brittle) properties of the fibre under (bending; compression) overload conditions also explain the easy *processability* of the new fibre in textile-type operations (weaving, knitting, braiding, and so on). Exploratory evaluation of the *UV stability* of M5 indicated excellent performance in that field, unsurprising in view of its chemical similarity to existing commercial UV stabilisers. The high *electrical resistance* of the new fibre would enable it to perform in areas where carbon fibre presents problems (corrosion in metal contacts) or is unsuitable, such as in electrical and electronic contexts. The high polarity of M5 aids in easy *adhesion* to a variety of matrix materials, judging by bundle pull-out tests performed with various epoxy, unsaturated polyester and vinyl ester resins. These gratifying results were obtained without any optimisation, suggesting further possibilities of even higher or (if needed) specifically tailored adhesion levels, depending on the application.

Stepping up from the bench scale to semi-technical, and later technical scale manufacture of this fibre is being addressed by Magellan Systems International, with special emphasis on further optimisation of its properties.

4.3.6 Acknowledgements

In addition to my colleagues, then at Akzo Nobel Central Research, whose names are in the references to this paper, special thanks are due to Antoine Duindam for his indefatigable efforts in improving our syntheses and polymerisation procedures, and to Henk ter Maat, and Bert-Jan Lommerts for their pioneering work in spinning the new polymer. The expertise and professionalism of many further colleagues, especially Leo Busscher and Bart Janssen, made it possible for this study to progress from a laboratory-scale curiosity to a multigram venture producing fibre samples on a sufficient scale for a first and successful evaluation in filament winding and pultrusion. The invaluable help of Noor van Andel to make this project survive in the corporate environment is also gratefully acknowledged.

4.4 **Russian aromatic fibres** (KEP)

4.4.1 Monomers and polymers

The search for aromatic fibres with high strength and stiffness began in Russia (by Prof. Georgy I. Kudryavtsev, All-Russia Research Institute of Polymeric Fibres) in the 1970s. The research generated an extensive literature,[50–183] which is not well known by much of the world. The investigations concentrated on:

- polymers based on poly-(*p*-phenylene terephthalamide) (PPTA) and related copolymers
- heterocyclic para-polyamides and para-copolyamides – para-heteroarylenes (PHA), mainly poly-para-amidobenzimidazole, which

is used here as a contraction for poly(terephthaloyl-2-*p*-aminophenyl-5-aminobenzimidazole)
- other heterocyclic aromatic polymers – polyimides, polyoxazoles, separate semi-ladder polymers, etc.

The main reactants that were investigated are presented in Fig. 4.11 (indicated by their residues). This list includes raw materials for polymers of regular and irregular molecular structure and statistical copolymers.

The research led to the production of the following fibres:[50,51,60,61,67,68]

- *Terlon*® – PPTA copolymer including diamines selected from the left column of Fig. 4.11.
- *SVM*® (formerly *Vnivlon*®) – aromatic heterocyclic polyamide of principal chemical constitution:

$$—[NH—Ar_1—NH—CO—Ar_2—CO]—$$

- *Armos*® – aromatic heterocyclic copolyamide of principal chemical constitution:

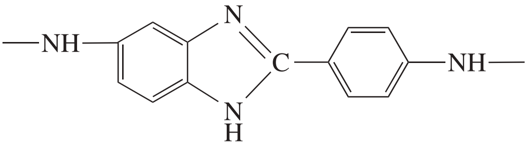
$$—[NH—Ar_1—NH—CO—Ar_2—CO]—$$

$$—[NH—Ar_3—NH—CO—Ar_2—CO]—$$

Terlon is an aramid copolymer fibre, based on PPTA with up to 10–15% comonomer content. Its manufacture, structure and properties are similar to other aramid fibres, which are described in Chapter 2, although the *Terlon* copolymer is not the same as the copolymer in *Technora*. This section concentrates on the *SVM* and *Armos* fibres.

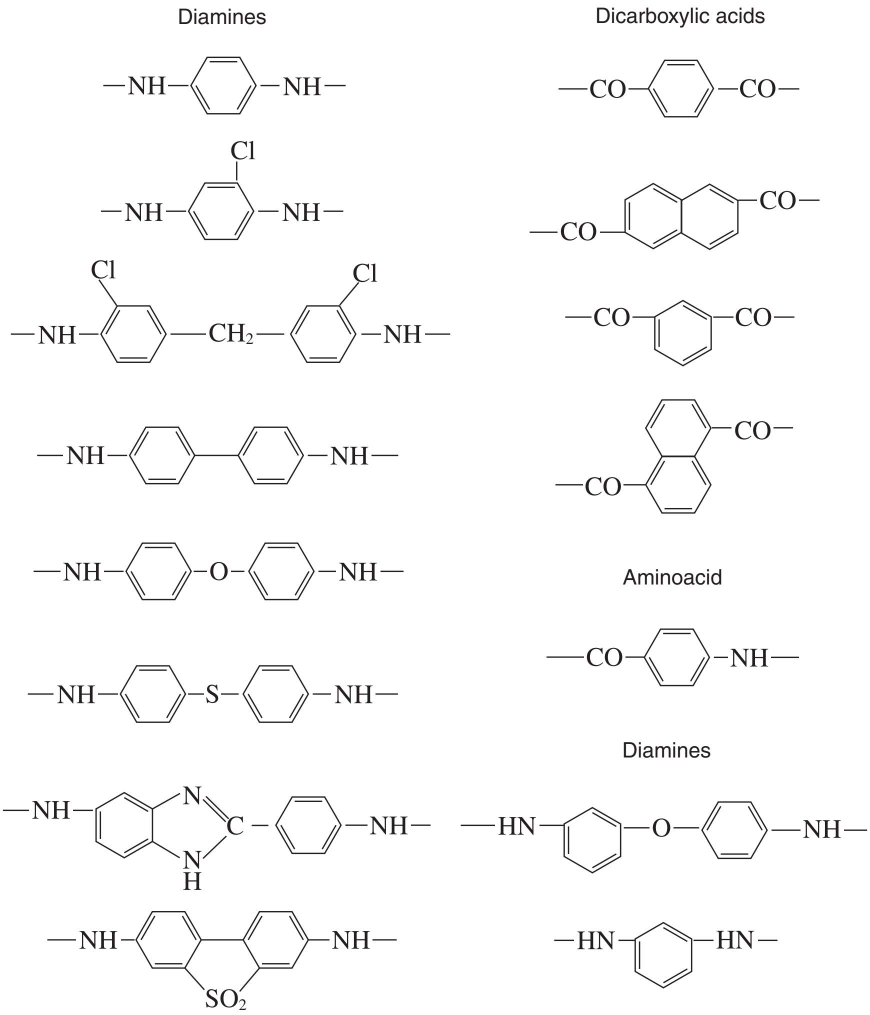
The aromatic groups that are shown in the above heterocyclic polyamide formulae are as follows:[68,168,169]

- $—[NH—Ar_1—NH]—$ is the heterocyclic diamine:



- $—[CO—Ar_2—CO]—$ is the residue of terephthalic acid shown at the top of the right column in Fig. 4.11
- $—[NH—Ar_3—NH]—$ is the residue of *p*-phenylenediamine shown at the top of the left column in Fig. 4.11

The first publication about the PHA fibre *Vnivlon*, now *SVM*, was written in the middle of 1969. *Armos* is a higher tenacity fibre and yarn that retains the high thermal and fire-resistant properties of *SVM*. Creation of *Armos* was the principal step after the elaboration of *SVM* fibres. This achievement



4.11 Structural units derived from reactants investigated in Russian HM-HT fibre research.

is the result of joint work (investigations and production) by the All-Russian Research Institute of Polymeric Fibres and the ‘Tverchimvolokno’ Joint-Stock Company.[54–61]

PPTA and the copolymer in *Terlon* form liquid crystals in solution, which are oriented in spinning. However, our view is that it is not necessary to have a liquid crystalline state as the initial state in the dope for making super-high tenacity fibres. The non-crystalline solutions of poly-*p*-heteroarylenes give higher tenacity fibres, but do not have the ability to crystallise in solutions or in the solid state. There is an opinion that PHA polymers transform to a liquid crystalline or quasi-crystalline state during the structure building process, but this transformation is not proven.

The high thermal properties of aramids are the result of their wholly aromatic structure, but heterocyclic units, such as those in PHA polymers, lead to increased thermal and fire resistance.

4.4.2 Polymer solutions and fibre formation

Heterocyclic para-polyamides and para-copolyamides (PHA) are soluble in highly polar aprotic amide solvents with addition of lyophilic salts (in particular dimethylacetamide with the addition of lithium chloride or calcium chloride).[50,58–60,62,74–76] They do not create a liquid crystalline state, owing to their irregular molecular chain structure. Their solutions are isotropic and therefore have high viscosity. For a suitable spinning viscosity, the dope concentration must be limited: 5–6% concentration gives a viscosity of 50–70 Pa s.[50,67,73–76] These solutions are structured and their rheological properties are classical for non-crystalline high polymers solutions of this type.

The spinning solutions are directly obtained from the synthesis of PHA polymers. They contain hydrogen chloride, which is ionically connected to tertiary nitrogen atoms.[73,83,84] The role of this complex is important both in viscosity regulation and in orienting effects during fibre formation, owing to neutralisation (discharging) of polar tertiary nitrogen groups and therefore increase of molecular chain rigidity. Both these effects lead to more ordered packing in structure building during fibre formation. It is interesting to note the same effects in the case of other rigid polymer solutions (for example, xanthogen groups neutralised by sodium hydroxide in viscose) and the pH dependence in concentrated protein solutions. Variation of the electrically charged ionised group leads to changes in molecular chain rigidity and therefore influences the process of fibre formation.

PHA fibres are produced by a normal wet-spinning process from solution into an organic or water bath. This method is used for the organic solvent solutions of heterocyclic para-polyamides (poly-*p*-amidobenzimidazole) and heterocyclic copolyamides. This process is carried out at low speed (12–25 m/min) with a long fibre-forming time. The fibre structure is thus built up by a ‘soft’ spinning bath action, which allows for simultaneous solidification over the whole cross-section. Coagulation is followed by wet drawing at a higher take-up speed. Fibre formation in a tube which has a spinning bath stream allows for an increased spinning velocity and leads to more uniform fibre bundle (yarn) formation. The molecular orientation of as-spun fibres results from the transverse velocity gradient flow in the spinneret orifices, which is due to the high ratio of orifice length to diameter, and after that from stretching the extruded fibres in a plasticised state. The formed fibres are washed to remove solvent and dried. Simultaneous structure building in the cross-section of fibres is necessary to create a homogenous macrostructure. The as-spun fibres have a gel structure that includes a large amount of immobilised solvent. Cross-section contraction during fibre drying leads to additional structure orientation.[94,95] After drying, the fibres from this wet method of formation have a deformation modulus of 50–70 GPa and a tenacity of 0.8–2.0 GPa. The fibre-formation process has been extensively researched.[50,62,67,75,76,86,88–95]

Thermal treatment is the next stage of processing. This occurs in a temperature range approximately 100 °C higher than the glass transition temperature, and leads to spontaneous structure ordering in the fibres.[50,62,67,75] The thermal treatment at 350–450 °C may be either uninterrupted or interrupted, with or without a small loading. The additional drawing (2.5–5.0% only) is applied in order to increase mechanical properties.[50,96] The self-ordering, orientation and number of stress-holding molecular chains increase, and hence there is an improvement in mechanical properties into the range for dynamic modulus of 130–160 GPa and for tenacity of 4.0–5.5 GPa.

The conventional view, which applies to the aramid fibres described in Chapter 2 of this book and to the Russian fibre *Terlon* produced in a similar way, is that in order to obtain the right structure, it is necessary to start with a liquid crystalline state in the polymer solution. This is right, but is not the only possibility. Limited aggregation in solution also gives the possibility of high orientation and chain extension. This may be a thermodynamically more advantageous state of 3D order for homopolymers in conflict with kinetic peculiarities for creation of maximal high-ordered fibre structure. The new polymers and copolymers with controlled molecular regularity and rigidity were optimal for improving fibre properties. Our experience shows that better results will be obtained if the initial solution is not liquid-crystalline, but is isotropic, and the transition to a liquid crystalline state is during the time of structure building by fibre formation. The rapid crystallisation of para-aramids prevents attainment of high orientation order, owing to reduced molecular mobility during the stages of fibre structure formation by spinning and of thermal treatment.[67] The progression from *Terlon* (PPTA copolymer, liquid crystalline in solution) to *SVM* and *Armos* (hetero-aromatic polymer and copolymer fibres, non-crystalline in solution) illustrates this situation.

4.4.3 Fibre production

The scheme for production of *Terlon* fibre is similar to that for other aramid fibres. PHA fibres and yarns, on the other hand, are produced from ‘direct’ solutions immediately after their formation during polymer synthesis. The principal scheme of this process is shown in Fig. 4.12.[59,105,179,183] Homopolymer and copolymer synthesis (poly-*p*-benzimidazole type) is based on polycondensation in solution (dimethylacetamide with addition of lithium chloride) of terephthaloyl chloride with heterocyclic diamine and, for the copolymer, *p*-phenylenediamine. There is a possibility of either a one-stage or a two-stage polymer synthesis process, the first stage being oligomer synthesis and the second further polycondensation. The solutions are isotropic and their concentration is limited to 5–6% by viscosity value. Polymer solutions are made by a classical scheme: mixing, filtration and degassing. Of great importance for spinning dope is careful removal of impurities and gel particles by filtration. Therefore, there are two filtration operations, first of oligomer solution and then of polymer solution, before the stages of degassing and subsequent transport of the solution to fibre extrusion.[58,59]

The fibre formation process is by a wet method into a water–organic spinning bath, or, in some cases, to an organic–organic spinning bath, such as dimethylacetamide plus isobutanol. The as-spun yarns then go to wet-drawing, washing to remove residual solvent, drying and winding. Countercurrent flow of water and yarn is important for controlling the increase of solvent concentration and aiding solvent recycling or waste purification. All these above-mentioned operations are carried out in a step-by-step uninterrupted process on equipment similar to that used for production of viscose or polyacrylonitrile yarns.[175,176]

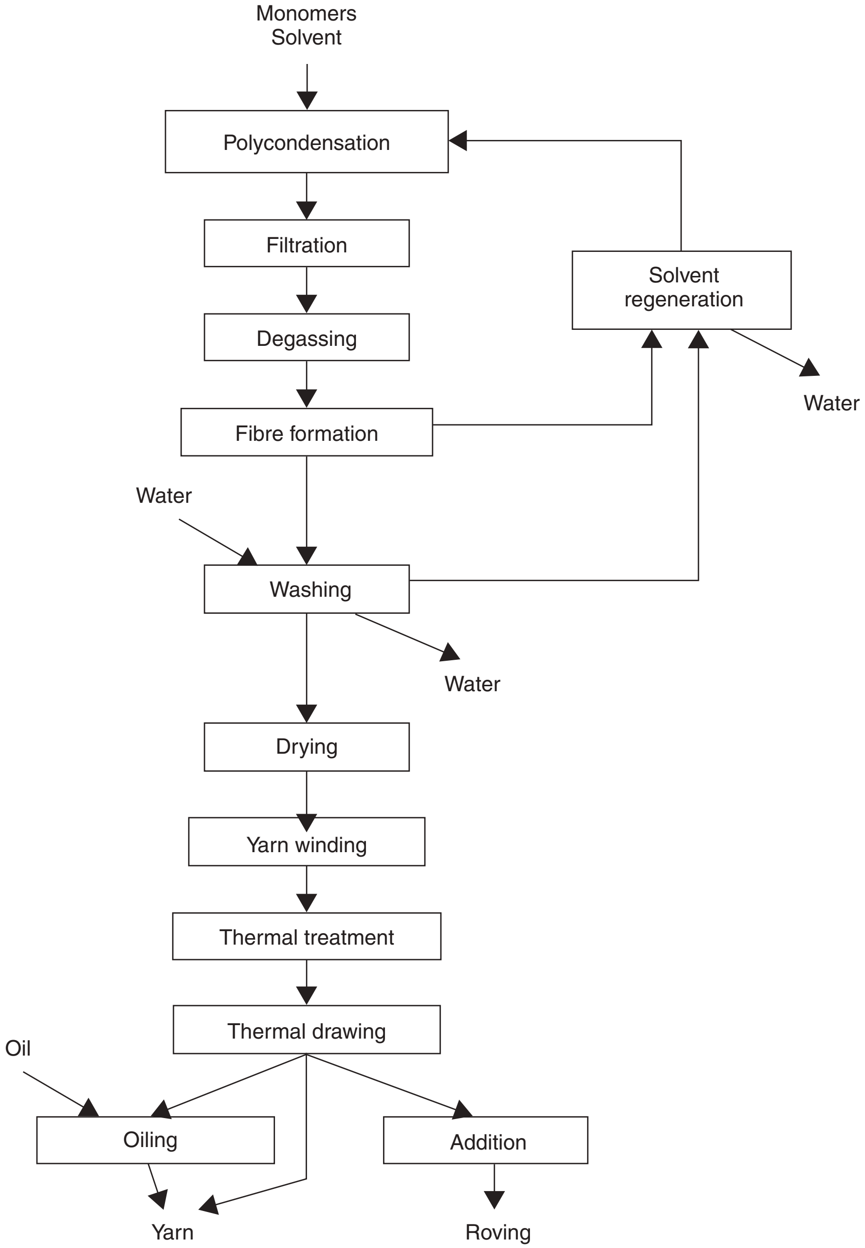
The spun yarns go to thermal treatment or to thermal treatment plus drawing, which may be either continuous or periodic (interrupted). At this stage there is a small self-elongation of the yarns and increased orientation. Owing to these phenomena, the modulus and strength are increased to their final values. The final operations are, for yarn production, winding, and for roving production, a combination of yarns and winding.

There is maximal recycling of chemicals and water for improved economics and waste elimination. Part of the washing water goes to spin bath dilution. The main part of the after-spinning bath and the washing water, which contain dimethylacetamide and lithium chloride, go to regeneration. The solvent is rectified, lithium chloride is crystallised, centrifugally separated and dried, and both are returned to the technological cycle.

4.4.4 Fibre structure

The fibre structures differ on all three levels (molecular, super-molecular and micro) from the usual fibre structure of flexible and semi-rigid polymers.[50,63,76,106–112] The main structural features are shown in Table 4.6.

SVM and *Armos* fibres contain heterocyclic links and two kinds of polar



4.12 Principal scheme for fibre production based on heterocyclic polyamides and copolyamides.

Table 4.6 Para-aramid and PHA fibre structure features

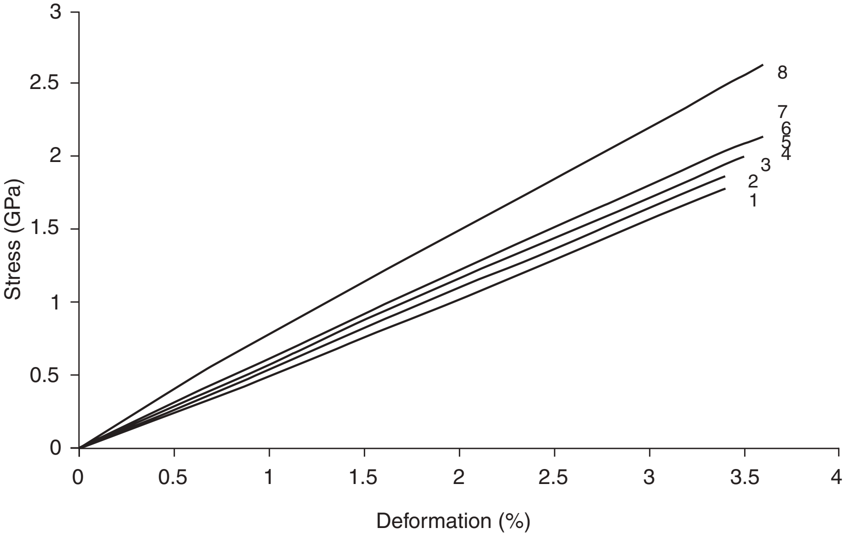
Structural levels	*Terlon*	*SVM*	*Armos*
Molecular level	PPTA and copolymers; statistical segment 30–50 nm; main polar group: —CONH—	Heterocyclic para-aramid; statistical segment 20–40 nm; polar groups: —CONH—; =N—	Heterocyclic para-aramid copolymer; statistical segment 20–40 nm; polar groups: —CONH—; =N—
Super-molecular level	Extended chain 3D crystalline order; fibrillar; highly oriented.	Extended chain 1D crystalline order; fibrillar; highly oriented.	Extended chain non-crystalline; fibrillar; highly oriented.
	Stress-holding molecular chains proportion 0.6–0.75		
Micro level (fibre)	Round cross-section, low heterogeneity		

group, amide links and tertiary nitrogen atoms. The structure of these polymers and copolymers is characterised by less regularity and less rigidity than PPTA. The absence of liquid crystalline domains in solution makes it possible to regulate structure building at the fibre forming and thermal treatment stages to give maximal orientation order. Owing to the lack of a plane of symmetry in the heterocyclic groups and to the mixed linking of monomers (head-to-head, tail-to-tail and head-to-tail), the extended chain conformations are irregular and lead to minimal crystalline order, with a consequent reduction in the possibility of axial movement. The less regular molecular chain structure leads to a higher proportion of stress-holding molecular chains and therefore to mechanical properties that are superior in *SVM* and especially in *Armos* fibre to those of aramid fibres such as *Terlon*, which is similar to *Kevlar* and *Twaron*.

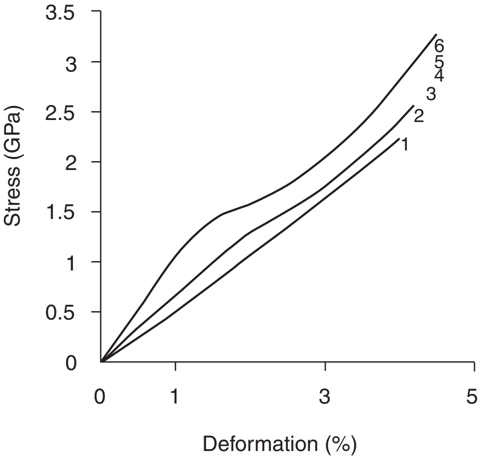
4.4.5 Mechanical properties

SVM and *Armos* fibres have mechanical properties superior to those of *Terlon* as shown by the data in Table 4.7. Stress–strain curves at different temperatures for *Terlon*, *SVM* and *Armos* yarns are presented in Figs. 4.13–4.15.[178] An interesting feature is that the high strength of *SVM* and *Armos* fibres is due to a higher breaking elongation, not to a higher modulus. The energy to break is therefore greater.

The data that are shown in Table 4.7 are determined by different

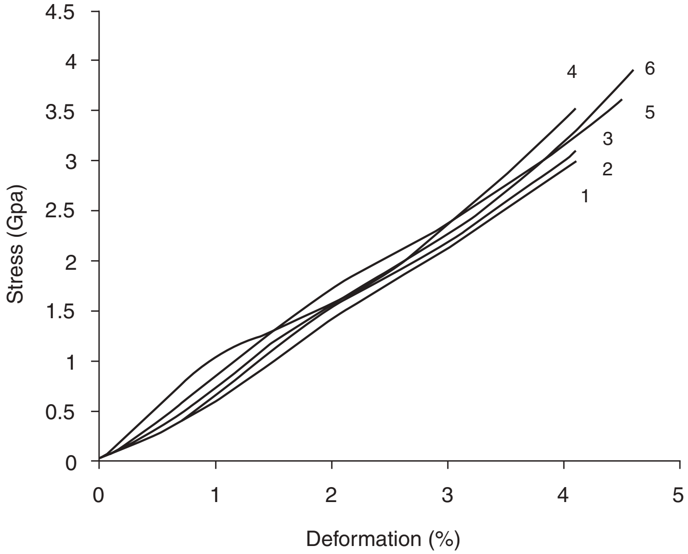


4.13 Stress–strain plots for *Terlon* yarns: 1, 220 °C; 2, 180 °C; 3, 140 °C; 4, 100 °C; 5, 80 °C; 6, 60 °C; 7, 40 °C; 8, 20 °C.



4.14 Stress–strain plots for *SVM* yarns: 1, 220 °C; 2, 180 °C; 3, 140 °C; 4, 100 °C; 5, 60 °C; 6, 20 °C.

methods. The deformation modulus is determined by three methods: mechanical (from the initial slope of the stretching diagram), dynamic and acoustic. Breaking characteristics are determined by single-fibre testing and a microplastic method; the results are approximately the same. There are differences in mechanical properties in literature data, resulting from



4.15 Stress–strain plots for *Armos* yarns: 1, 220 °C; 2, 180 °C; 3, 140 °C; 4, 100 °C; 5, 60 °C; 6, 20 °C.

Table 4.7 Fibre mechanical properties

Fibre (yarn) types	Density, g/cm^3	Deformation modulus, GPa*		Tenacity, GPa*	Elongation at break, %	Standard moisture content, %
		Dynamic	Static			
Armos	1.45–1.46	140–160	100–120	4.5–5.5	3.5–4	3–3.5
SVM	1.45–1.46	135–150	95–115	4–4.5	3–3.5	3.5–4.5
*Terlon**	1.45–1.47	130–160	95–120	2.5–3.5	2.5–3	2–3

* The tenacity data are based on different testing methods for separate fibres or epoxide microplastic; modulus data for yarns.

different and often unrecorded testing methods, that make objective comparison difficult.

Fibre tenacity depends on moisture content owing to two influences – the plasticisation effect and the intermolecular interactions caused by hydrogen bond bridges, which are created by water molecules. These two influences lead to tenacity increasing to some extent with increasing moisture content up to a maximum value and then falling when wet to 90–95% of the dry value.

High orientational, structural and energy anisotropy of the fibres lead to

Table 4.8 Anisotropy of mechanical properties

Fibres	Modulus, GPa		Strength, GPa	
	Axial	Across	Axial	Across
Terlon	100–105	3.5–5.5	3.0–3.5	0.025–0.055
SVM, Armos	100–110	4.0–6.0	4.0–5.0	0.035–0.055

anisotropy of their mechanical properties.[63,108,110] The moduli across the fibre axis were determined by two methods: fibre compression and calculation based on data from one-dimensional (1-D) composites. Tenacity across the fibre axis was determined for the first time by stretching of an epoxide film containing a single fibre.[60] The results of mechanical anisotropy determinations are presented in Table 4.8.

The calculated theoretical modulus, based on perfect crystals, for the PHA fibre is slightly less than for PPTA fibres, and the strength is about 30% less. The modulus realisation is between 60 and 70% for both types, but the strength realisation is about 15% for *Terlon* aramid fibre with higher values of 24% for *SVM* and 30% for *Armos*.

4.4.6 Thermal properties

All three para-aramide types are characterised by high glass transition temperatures, high thermal and thermal-oxidative resistance, high ignition and self-ignition temperatures, and high limiting oxygen indexes.[50,55–57,108,114,120–125,180] All three, especially *SVM* and *Armos*, are dimensionally stable on long heating. The tendency to spontaneous elongation in technological heat treatment ('self-ordering effect') leads to the same effect in the first stage of heating – slight elongation or very small shrinkage with rise in temperature. The data show that change in dimensions is practically absent up to 300 °C. There is a small shrinkage of *SVM* and *Armos* yarns by 350 °C; the shrinkage at 400–450 °C is not more than 2–3%.

It is known theoretically and practically that thermo-oxidative degradation includes three main reactions – separation of substances with low molecular weight, molecular chain destruction by oxidation or hydrolysis, and intermolecular bridge creation. From this point of view, carbocyclic aromatic polyamides are more stable than heterocyclic ones.[123] If chain degradation leads to loss of mechanical properties, on the other hand, the intermolecular bridges lead to tenacity preservation. Therefore the resultant effect of all three kinds of reaction is indefinite in terms of change in mechanical properties.

Table 4.9 Effect of ageing on mechanical properties

Fibres	Ageing conditions		Properties retention, %	
	Temperature, °C	Time, hours	Tenacity	Elongation at break
Terlon	300	100	27	33
	250	325	47	45
	225	500	60.4	54.8
	200	1500	63.7	57.1
Armos	300	100	27.5	39.2
	250	325	60.6	80.4
	225	500	61.5	76.3
	200	1000	82.9	109.8*

*The result of relaxation processes

Table 4.10 Fire resistance and thermal characteristics

	Terlon	*SVM*	*Armos*
Ignition temperature, °C	450–500	500–600	500–600
Self-ignition temperature, °C	500–600	550–650	550–650
Limiting oxygen index, %	27–30	41–43	39–42
Glass transition temperature, °C	345–360	270–280	220–240
Exploitation temperature (limited), °C	200–250 (250–270)	250–270 (300–330)	250–270 (300–330)
Destruction temperature, °C	450–550	450–550	450–550

The comparative thermal-ageing characteristics of *Terlon* and *Armos* fibres at 200–300 °C are presented in Table 4.9.[120–122] At higher temperatures, the loss of strength is greater. For *Armos*, the retention of tensile properties (strength and elongation at break) is slightly higher than for *Terlon*. These data give calculated activation energies of 52.5 kJ/mol for *Terlon* and 55 kJ/mol for *Armos*.

The high glass transition temperature and practically zero shrinkage for para-aromatic fibres give thermoresistant goods made from them important advantages in high temperature media, in comparison with meta-aramid fibres. *SVM* and *Armos* fibres are highly fire resistant and superior to PPTA fibres, owing to the nitrogen-containing heterocyclic structure and the presence of hydrogen chloride, which is a good fireproofing compound. The main thermal characteristics and fire resistance indices are shown in Table 4.10.

4.4.7 *Armos* fibres and applications

At present, *Armos* fibres and yarns have the highest mechanical properties among aramids and related fibres. *Armos* yarns are produced by the Tverchimvolokno Joint-Stock Company in Tver city, not far from Moscow. The linear density of yarns is in the range of 29.8–167 tex; and rovings of 600 tex or 1000 tex are made by combining 100 tex or 150 tex yarns.[54,56–59,105,126,179,180,183] The main types of *Armos* yarns are:

- high-modulus reinforcement yarns and roving (*Armos HMR*)
- high-modulus yarns for technical textiles (*Armos HMT*)
- highly thermally stable yarns for textiles (*Armos HTS*).

The properties of these yarns are listed in Tables 4.11 and 4.12. All values were measured by Russian standard methods. The yarn tests were done on the base of State Standard 6611 at clamp length 250 mm, microplastic tests by State Standard 28007 at clamp length 100 mm. Dynamical elastic

Table 4.11 Properties of high-modulus reinforcement and technical yarns

Properties	*Armos HMR*		*Armos HMT*	
Linear density, tex	100	600	58.8	100
Load at break, N	208–221	>1225–1324	>116	>206
Elongation at break, %	—		3.5–4.5	
Dynamical elasticity modulus, GPa	>14 200		>14 200	
Breaking stress by microplastic method, MPa	>4 905		>4 412	
Yarn twist, twist/m	—		50 ± 15	
Oiling agent content	none		on agreement	

Table 4.12 Properties of highly thermally stable yarns

Properties	*Armos HTS*	
Linear density, tex	58	100
Specific tenacity, cN/tex	>127	160–170
Elongation at break, %	3.5–4.5	
Yarn twist, twist/m	50 ± 15	50 ± 15 (or <15*)
Oiling agent content	on agreement	

*To order.

modulus was determined by the impulse dynamical method of State Standard 28007 at clamp length 100 mm. Yarn moisture content was 3.5% under standard conditions.

4.4.8 Modified fibres

New chemically and physically modified fibres based on heterocyclic polymers and copolymers have been produced with properties depending on the modification method:

- use of different monomers for new polymer or copolymer synthesis at the stage of polycondensation (see Fig. 4.11)
- polymeric mixtures
- additives to polymer solution
- surface modification.

One way is to include meta-links or other non-para-links in polymeric chains. This leads to increased chain flexibility and therefore lower fibre modulus. These copolymers have better solubility and their solutions are isotropic. The principles of fibre formation are approximately the same as for traditional flexible chain polymer processingr – wet-spinning, stretching for orientation, and additional thermal treatment to fix fibre structure. The fibre properties are characterised by modulus and tenacity, which are similar to general purpose fibres, of the type required for some kinds of technical textiles and reinforcement of rubber goods.

Changing up to 50% of the terephthalic links in the heterocyclic polymer to isophthalic links at the polycondensation stage leads to decrease of fibre rigidity and increase of elongation to normal textile values. This kind of fibre, named *Togilen*®, has good thermal and fire resistance (high oxygen index),[73,129,130,172,173,183] but it has the disadvantage of water action on mechanical properties – the tenacity in the wet state is only 70% of that in the conditioned state.

Another possibility is to change up to 30% of heterocyclic diamine to *m*-phenylenediamine in the polycondensation stage. This polymer also gives fibres, named *Tverlana*®, with good thermal properties.[169–171,183] The properties of these two fibres are presented in Table 4.13 in comparison with the ‘mother-fibres’ – *SVM* and *Armos*.

New analogues of *Armos* yarns have been produced on the basis of a copolymer with chlorinated aromatic links based on a chlorine-containing *p*-diamine – *Diamet-X* (chemical name 3,3′-dichloro-4,4′-diaminodiphenylmethane).[67,127,131] The mechanical properties are approximately the same, but this way gives a simplified fibre production process owing to a change from organic solvent to sulphuric acid. Therefore the production technology of these fibres is similar to *Terlon* and other aramid fibres.[87,132,133]

Table 4.13 Property comparison of heterocyclic polymer fibers – 'mother fibres' and modified fibres

Properties Composition	*SVM* Heterocyclic *p*-polyamide	*Armos* Heterocyclic *p*-copolyamide	*Togilen* *m*(25%)-*p*(75%)-copolyamide	*Tverlana* *m*(15%)-*p*(85%)-copolyamide
Assembly	Yarn, roving	Yarn, roving	Yarn, staple fibre	Yarn, staple fibre
Density, g/cm^3	1.45–1.46	1.45–1.46	1.43–1.44	1.40–1.41
Tenacity of yarn (fibre)	Yarn 3–3.5 GPa	Yarn 3.5–4 GPa	30–45 cN/tex	35–50 cN/tex
Deformation modulus, GPa	Dynamic 140–160 (Static 95–120)		Static 8–12	Static 10–14
Elongation at break, %	3–3.5	3.5–4	15–30	12–17
Yarn tenacity (as epoxide microplastic), kg/mm^2	400–450	450–550	—	—
Shrinkage onset temperature, °C	350–370		320–370	320–370
Boiling water shrinkage, %	—	—	2–2.5	2–2.5
Limiting oxygen Index, %	41–43	39–42	42–44	35–36
Moisture content (at standard climatic conditions), %	3.5–4	3–3.5	13–15	11–12

Modified aramid fibres, created by adding different polymers in the spinning solution,[60,134–136] lead to new application possibilities. The best result was obtained by adding flexible-chain polymers to the solution of PPTA in sulphuric acid. A modified *Terlon* yarn with 10% addition of polycaproamide (nylon 6) had improved adhesion to rubber in tyres or other elastomeric manufactured goods.[50,137,138] At the same time this polymer addition led to an increase in mechanical properties. These practically important effects may be due to formation of intermolecular bonds and increase in super-molecular structural order. Addition of rigid-chain polymers did not have a positive effect.

The inclusion of disperse fillers in fibres may be useful in obtaining special physical properties. There is experimental research on the addition of different dispersed oxides and ceramic powders to the spinning solution.[139–141] One aim of such additions is to make super-conducting fibres. The fibre mechanical properties are decreased by a small amount of additives.

Surface modification is useful for barrier creation against water and protection against external influences. Surface treatment of *SVM* and other fibres by silicon–organic substances as emulsions in water leads to higher moisture resistance.[142] Surface grafting of polytetrafluorethylene decreases wettability and water sorption.[143]

4.4.9 Conclusions

The fibres described in this section may be regarded as part of the 'aramid family', although they may not fall within the strict definition of aramids. They have a wide spectrum of characteristics and the raw materials, production processes, structure and properties are different for each member of this 'family'.[180] All the fibres and yarns are thermal and fire resistant and they can be divided into two main groups:

- high mechanical properties (high tenacity and high modulus) plus thermal resistance
- normal mechanical properties with thermal resistance.

Comparative data have been given earlier, but it is informative also to review mechanical properties on a mass basis. These quantities are presented in Table 4.14 and show that the tenacity of *Armos* yarn is 20–50% higher than that of other aramid and related yarns and glass yarns. The thermal characteristics show the advantages of heterocyclic polymers (*SVM*, *Armos*, *Togilen*, *Tverlana*) in comparison with aramid fibres based on PPTA (*Terlon*, *Twaron*, *Kevlar*) and meta-aramid fibres (*Fenilon*, *Nomex*), especially to open fire resistance.

Table 4.14 Specific mechanical properties

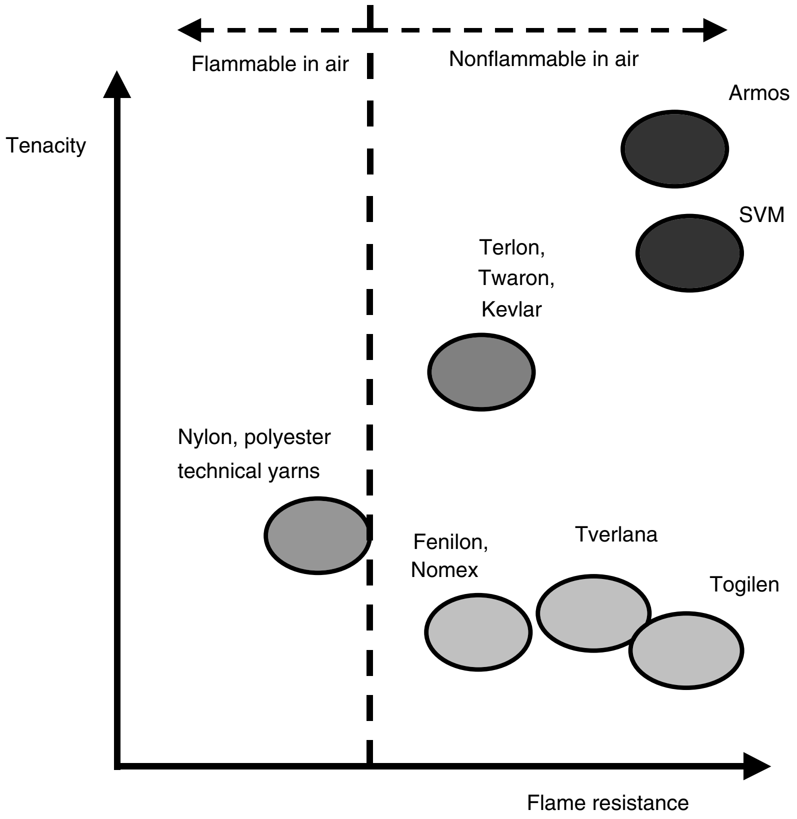
Yarns	Specific modulus, km	Specific strength, km
Armos	7600	350
SVM	7000	295
Terlon	7000	215
*Glass yarn S-type**	3450	170

* Data for glass yarn S-type are following: density 2.52–2.55 g/cm^3; elasticity modulus 85–90 GPa; tenacity 4–4.6 GPa.

It is important to compare fibres and yarns in terms of the two above mentioned characteristics – mechanical and thermal properties. The main peculiarities of different fibre types are presented in the scheme of Fig. 4.16.[126,180–182] Properties of high-tenacity technical yarns (nylon and polyester) are shown on this diagram for comparison. *Armos* fibres and yarns are the best in two qualities simultaneously – tenacity and open fire resistance.

The applications found for the Russian aromatic HM-HT fibres are similar to those found elsewhere and reported for aramids in Chapter 2 – high-strength and high-stiffness technical textiles loaded in the axial direction. This includes high-strength composites, ropes, conveyor belts, hoses, protective clothing and a host of similar uses.[144–167]

The creation of para-aramid and related fibres was an important step in the field of fibres and yarns for high-performance technical textiles and composites. The newer Russian aramid-related fibres – production principles, structure, properties, modification and application areas – are described in this chapter. The methods of fibre modification and property improvement for different applications are discussed. New super properties of heterocyclic PHA fibres (*SVM* and, even more, *Armos*) were found by the All-Russian Institute of Polymeric Fibres using advanced methods and these fibres are produced today with mechanical and thermal property values that exceed those of PPTA and other conventional aramid fibres. At present the Russian Tverchimvolokno joint-stock company is producing reinforcing *Armos* yarns with tencsity as high as 5.0–5.5 GPa and dynamic deformation modulus more than 145 GPa. This yarn is highly thermoresistant in conditions of use up to about 330 °C and flame resistant (oxygen index about 39–43% – see Tables 4.10 and Figure 4.16). There is a possibility of further advances in fibre properties by means of structure building and technology optimisation.



4.16 Comparison of tenacity and fire resistance of various aramid and other fibres.

4.5 Solid-state extrusion high-molecular weight polyethylene fibres (GW)

4.5.1 Background

As has been described in Chapter 3, ultra-high molecular weight polyethylene (UHMW-PE) is an ideal candidate for the production of fibres of exceptional strength. The molecular conformation and chemical structure lend themselves to the achievement of very high specific strength and moduli, provided that the molecule can be fully oriented. For ultra-high molecular weight polyethylene it was believed that the molecular chain needed to be in either the molten state or solution in order to facilitate orientation. In these situations, however, the process must be carefully controlled or the molecule can freely rotate and entangle, thus contravening the original purpose.

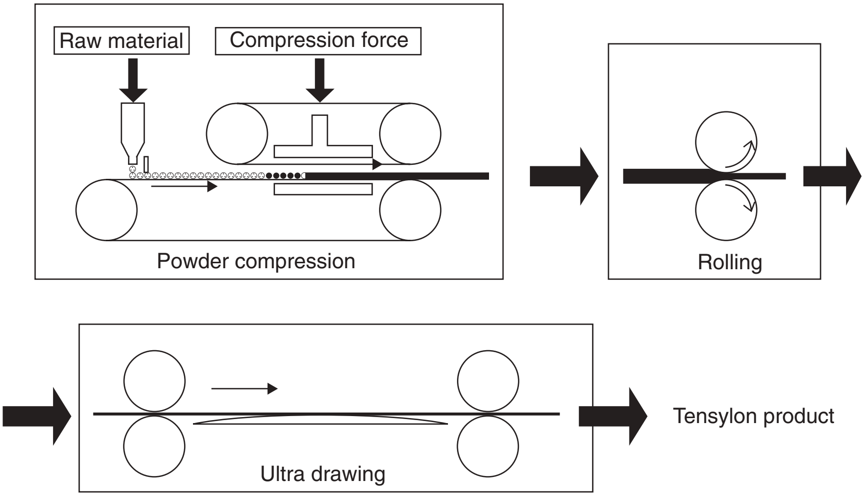
Several approaches have been developed to unfold these long chains or to draw the polymer in such a way that the entanglements are not exacerbated. The most notable commercial technologies for accomplishing this orientation are gel-spinning, solid-state extrusion (SSE), and special high-stress spinning and tensile drawing (using conventional molecular weight polyethylene).

The details of gel-spinning are described in Chapter 3, and the process and properties are repeated here only as comparisons arise. The special drawing technology developed by Ian Ward (Leeds) was licensed by the British Technology Group to Snia Fibre (Italy) and Hoechst-Celanese (USA).[184,185] The commercially produced fibres were known as *Tenfor*™ and *Certran*™, respectively. These fibres enjoyed only limited commercial success and both companies ceased production of these fibres in the 1990s.

In the late 1970s, A E Zachariades, T Kanamoto, and R S Porter reported that they had succeeded in orienting ultra-high molecular weight polyethylene powder by solid-state extrusion.[186] Subsequently, in 1986, the Nippon Oil Company (NOC), (now the Nippon Mitsubishi Oil Corporation – April 1999), began an extensive research project on developing the solid-state extrusion process for commercial applications. This process was envisioned as a low-cost alternative to gel-spinning for the production of high-modulus polyethylene fibres. NOC ultimately commercialised a pilot plant in Japan in 1994. For a limited period, they produced and sold the SSE fibre, *Milite*™, through a subsidiary, the Nippon Petrochemicals Company (NPCC),[187] which was already a major manufacturer of low and high density polyethylene. In 1999, NOC licensed the solid state technology for fibre production in the USA[188] to Synthetic Industries (SI), who worked with Integrated Textile Systems (ITS). This product is being produced and sold in North America under the *Tensylon*™ trademark. Subsequently, Synthetic Industries withdrew and the enterprise is now run solely by ITS.

4.5.2 Process description

Like gel-spinning, the starting material for the solid-state extrusion (SSE) process begins with a conventional ultra-high molecular weight polyethylene (UHMW-PE) polymer having a molecular weight range of three to five million. Because of the nature of the solid-state process however, it is important that the starting UHMW-PE polymer has low inherent chain entanglements in the nascent powder. In this respect, polymers produced at low polymerisation temperatures are more desirable. It is also important that the powder is not exposed to melting temperatures prior to processing. Such exposure could cause an undesirable increase in chain entanglements. Polymer powder containing a high level of chain entanglement cannot be used for SSE.



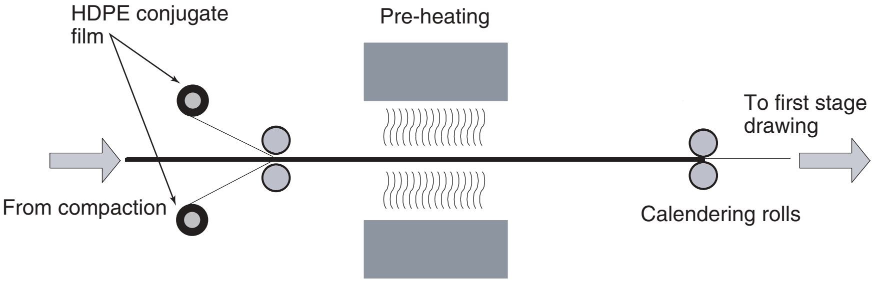
4.17 The SSE process. (Reproduced by courtesy of Synthetic Industries.)

Unlike gel-spinning, solid-state extrusion uses no solvents, processing aids, or adjuvants to facilitate processing of the powder into a drawn fibre. Additionally, all of the operations in the process are carried out below the melting point of the polymer. These rather remarkable features of the process give rise to an operation that avoids the high costs and environmental difficulties of handling large amounts of solvents common to many high-performance fibres. This process simplicity also significantly reduces the need for large support utilities.

The solid-state extrusion process consists of three basic unit operations: powder compression and compaction, rolling, and ultra-drawing (see Fig. 4.17). In the first step (compaction), the polymer powder is fed between two endless, heated, counter-rotating steel belts. A compression force is applied through each of the belts by a series of rollers which cause the powder to be compressed into a cohesive sheet capable of being handled and processed further. During this process, the density of the UHMW-PE powder is increased more than two-fold, from about 0.4 to 0.95 g/cm^3. This precompression step is necessary because it is extremely difficult to calender (roll) the powder directly into a cohesive, oriented film in a single operation.

In the next step (rolling), the compressed sheet is fed into a pair of heated, counter-rotating rolls. The compressed sheet is calendered to about one-seventh of its original thickness, slit to the desired width and taken up on conventional low-speed winders.

In the final step (ultra-drawing), the tapes are drawn at a draw ratio of



4.18 Schematic view of conjugating process. (Reproduced by courtesy of Synthetic Industries.)

about 12 to 13 using very long hot plates. The temperature of the hot plates must be carefully controlled to maintain the temperatures below the melting point of the polymer. Long draw zones also are required in order to reduce the high drawing stress generated during solid-state drawing. If desired, split (fibrillated) yarns can be produced during the ultra-drawing step for products requiring a softer 'hand.'

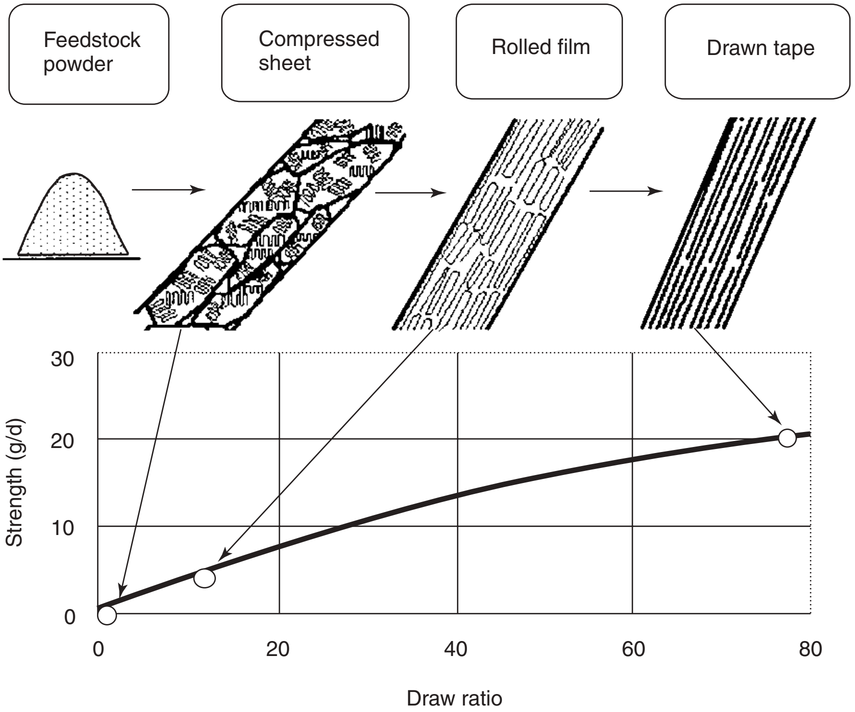
The total draw ratio (TDR) of the finished product is defined by the product of the rolling shear stress effect multiplied by the ultra-draw ratio, i.e. TDR = (rolling ratio) × (ultra-draw ratio). A TDR of 85 to 100 is typical for the SSE process. A standard 720d drawn tape is about 2 mm wide and 45 μm thick.[189]

The most important feature of the solid-state extrusion process, however, is the on-line capability to laminate coloured, heat stabilised, UV stabilised, adhesion promoting, or other modified films to the compacted sheet (Fig. 4.18). This 'conjugating' film technology allows the manufacturer to provide a wide variety of specialised products from the same production line without making any major alterations to the feedstock or the process.[190] For many applications, such as specialty ropes, fishing lines, and composites, this unique feature of the solid-state process is often the major determinant for its use versus gel-spun UHMW-PE yarns.

The fully drawn tapes and yarns from the SSE process have tensile strengths of ~1.9 GPa (18–20 g/denier; 1.6–1.8 N/tex), a Young's modulus of ~120 GPa (1000–1400 g/denier; 90–130 N/tex) and an elongation of about 2.6%.

4.5.3 Structure

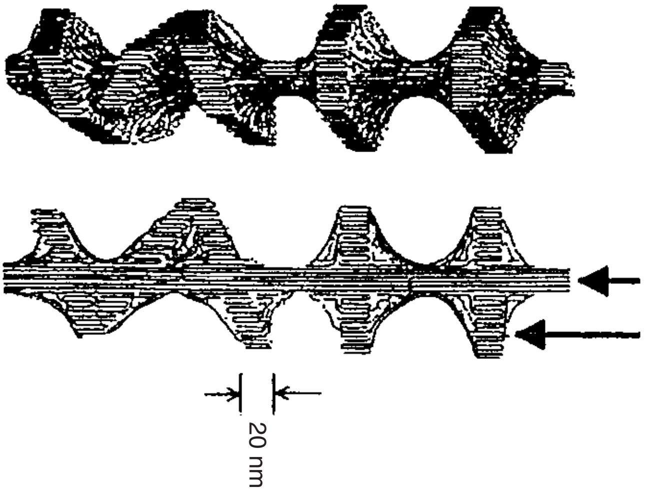
Generally, polyethylene is considered to consist of a crystalline phase, an amorphous phase in which the molecular chain is entangled and cannot grow into a crystal, and an intermediate phase. As noted earlier, in the solid-



4.19 Structural changes during SSE. (Reproduced by courtesy of Nippon Oil Co.)

state process it is imperative that the starting UHMW-PE powder has minimal chain entanglements in the amorphous phase. In practice, the suitability of a particular polymer can be determined by measuring the thermal characteristics of the material. Measurements of the melting point, heat of fusion, and crystallinity in the powder give an early indication of the suitability of a particular feedstock. It is these initial morphological properties that will control the ultimate performance of the particular UHMW-PE being used in the process. Obviously, other parameters such as particle size, particle size distribution, bulk density, and flow times are important to overall processing, but they have no direct effect on the ultimate tensile properties achieved.

The structural changes that occur in the UHMW-PE during compaction, rolling, and ultra-drawing are illustrated in Fig. 4.19. As heat and pressure are applied to the feed powder, the powder is compacted. As a result, the air between the particles is expelled and the polymer particles stick together. The internal crystal structure is not destroyed, however, because



4.20 Structure of the final solid-state extruded product.

the powder surface is only slightly melted. At this stage the compacted sheet still can be easily broken into powder. The process is similar in some respects to compressing snow to make a snowball. The material is cohesive, but still frangible.

As the shearing force is applied to the sheet in the rolling stage, the crystals are literally broken into pieces, increasing the number of terminal chains. In addition, because these crystals are oriented in the drawing direction by the shearing force, the crystals can be easily drawn. Moreover, because the folded molecular chains are slightly drawn during this process, the fragility of the compacted sheet decreases. At this stage, the film can be easily torn in the machine (longitudinal) direction, but not in the cross-machine orientation.

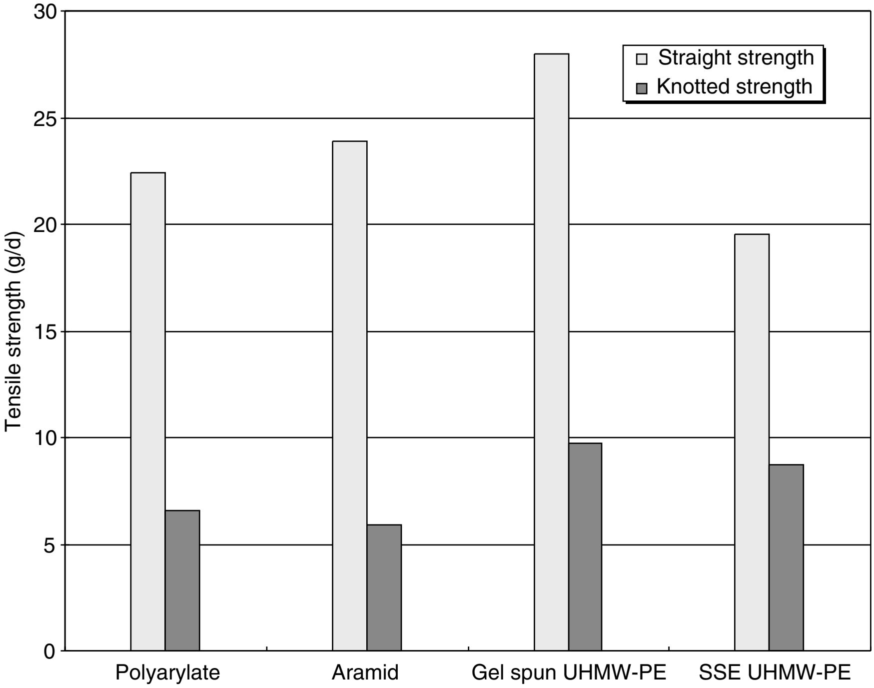
The changes in the internal organization of the material during processing also can be confirmed by X-ray diffraction patterns. As expected, the compacted sheet X-ray pattern is ring shaped, indicating no major orientation. As the processing proceeds to rolling and drawing, the X-ray pattern clearly transitions from a hemispherical pattern to the characteristic X-ray pinpoints of a highly oriented structure.

Although the molecular structure after SSE ultra-drawing is well ordered, the polymer chains are not as perfectly aligned as is the case with gel-spun fibre. SEM photomicrographs clearly show a ‘shish-kebab’ structure in the final SSE product. As illustrated in Fig. 4.20, there are a significant number of residual lamellae. For this reason, the tensile strength of fibres produced by SSE is lower than from gel-spinning.

4.5.4 Properties

Tapes and yarns produced from solid state extruded polyethylene, for example *Tensylon*™, possess many of the same useful features as those from gel-spinning. Both have low shrinkage, high abrasion resistance, high strength and modulus, and excellent chemical resistance. The major property differences between the two technologies lie in creep resistance, translation efficiency, and ease of surface modification for improved adhesion, increased UV stability, or the addition of colour.

Yarn strength comparisons between *Tensylon*™ and other high strength yarns are shown in Fig. 4.21. In general, the breaking strength of polyethylene yarn from SSE is about 65%–75% of that achieved with gel-spinning. However, in practice, this differential is offset somewhat by the higher translational efficiency for the SSE product. As shown in Fig. 4.21, the knot strength for *Tensylon*™ is about 50% of the original yarn strength. For gel-spun yarns, the knot strength is about 35% of the original yarn. Therefore, the two yarn knot strengths are nearly equal. This phenomenon also is observed in some rope constructions and twisted yarn applications, in which



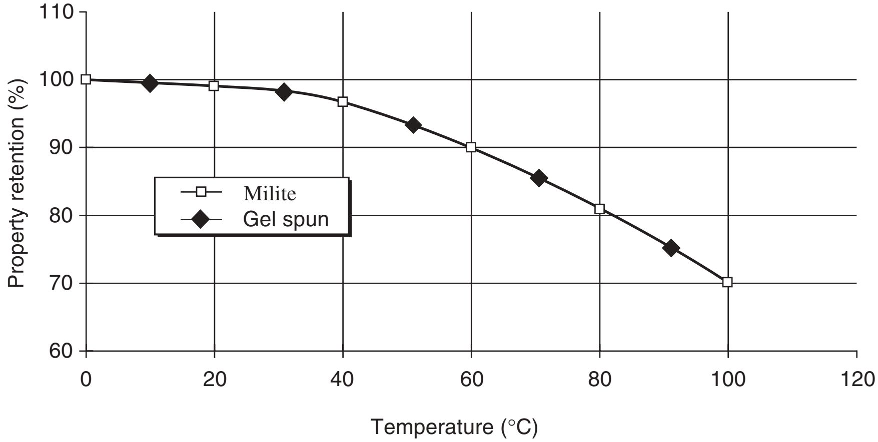
4.21 Strength comparison of various yarns. (Reproduced by courtesy of Nippon Oil Co.)

the finished products have comparable strengths in spite of the strength differences in the starting yarns. It is probable that the physical structure of the SSE yarn, that is, fibrillated tape versus multifilament, contributes to this effect.

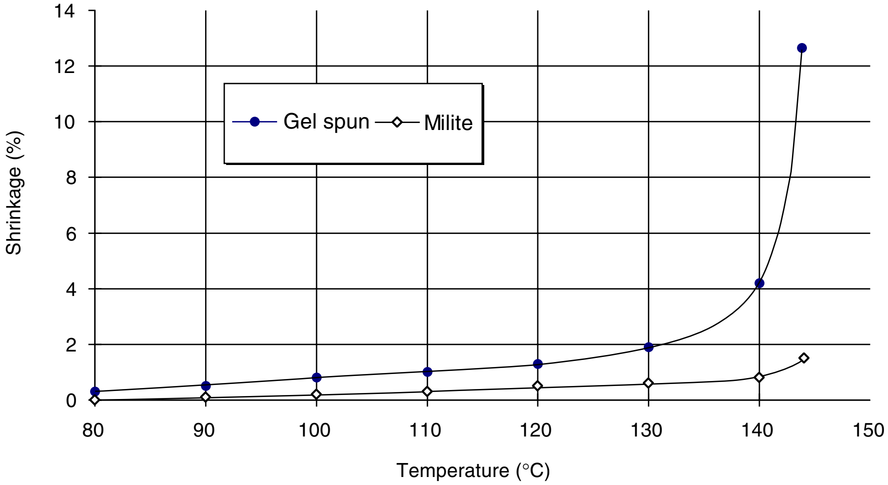
The effect of temperature on the strength and heat shrinkage of *Tensylon*™ versus gel-spun yarn is shown in Figures 4.22 and 4.23. As shown in the plot, the tensile responses of SSE and gel-spun yarns to temperature are identical. This is to be expected since the melting behaviour of both products is dependent primarily upon the physical nature of polyethylene. In the case of shrinkage, however, yarn subjected to solid-state processing exhibits substantially less shrinkage near its melting point. This response is somewhat unexpected because of the 'shish-kebab' structure of SSE yarn and the very high shearing forces in SSE.

Although both gel-spinning and SSE may start with similar molecular weight UHMW-PE polymers, the polymers in gel-spinning are necessarily subjected to a higher degree of thermal degradation during the process and, consequently, the final yarns have much lower molecular weights. Because SSE is carried out under relatively mild conditions, the molecular weight of the polymer is essentially unchanged during the process. As a result, there is a significant difference between the two yarns in terms of abrasion resistance and creep properties that can be attributed to the higher molecular weight of SSE yarn.

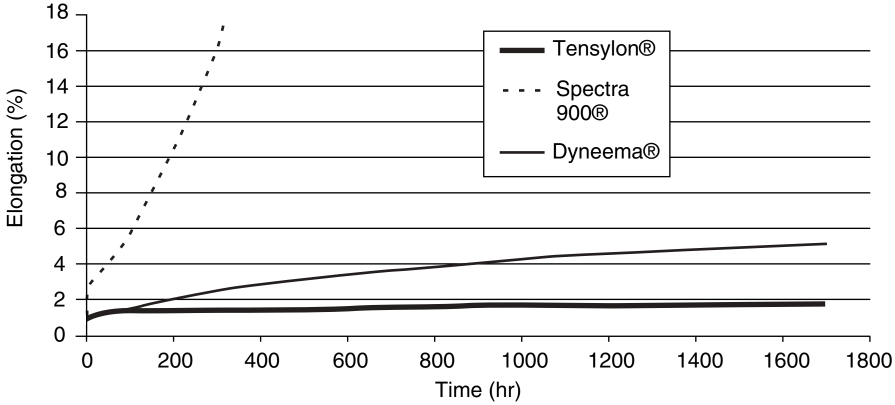
Although some of the improvements in the abrasion resistance of SSE yarn also can be attributed to its physical form (tape), the degree of improvement in this property is very dependent upon the construction of



4.22 Effect of temperature on thermal strength. (Reproduced by courtesy of Nippon Oil Co.)



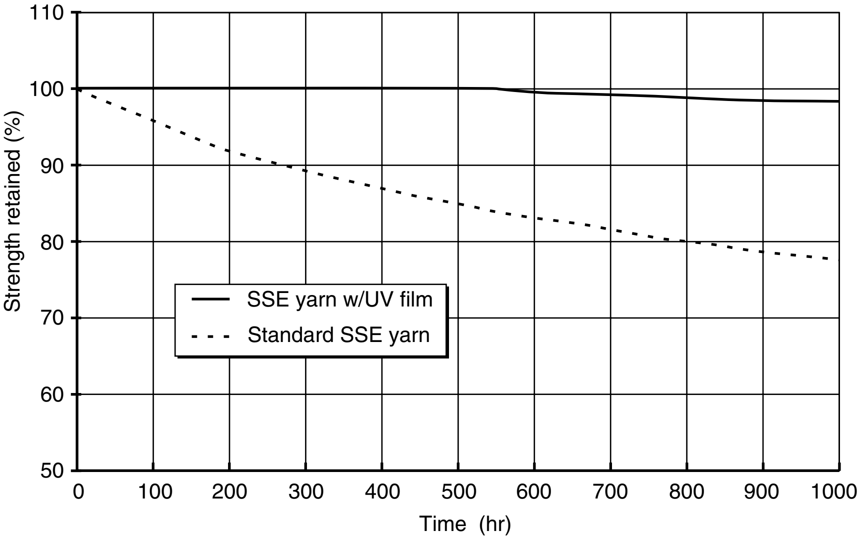
4.23 Effect of temperature on heat shrinkage. (Reproduced by courtesy of Nippon Oil Co.)



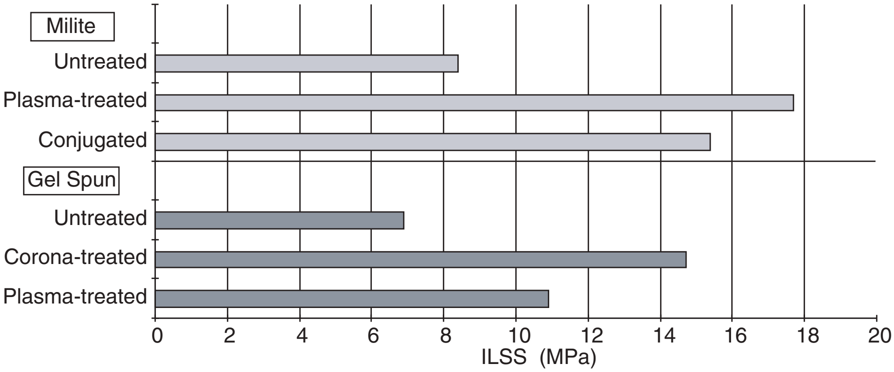
4.24 Creep elongation at 20% breaking load. (Reproduced by courtesy of Synthetic Industries.)

the fabricated article and the particular abrasion test being used. With respect to creep resistance, both the lack of residual solvent and the higher molecular weight of the polyethylene in SSE yarns probably contribute to its improved creep performance (See Fig. 4.24).

As mentioned earlier, it is possible to laminate coloured, stabilised, or adhesive films to the compressed sheet during processing. By using pigmented films it is possible to make coloured yarn for ropes and other applications where a colour is desired or needed. Since colouring of gel spun



4.25 UV-resistance (light and water exposure test based on JIS B 7754). (Reproduced by courtesy of Nippon Oil Co.)



4.26 Effect of surface treatments on interlaminar shear stress (ILSS). (Reproduced by courtesy of Nippon Oil Co.)

polyethylene yarns is usually very difficult, this is a distinct advantage for the SSE process.

The UV resistance of SSE yarns also can be improved by application of films containing UV stabilisers, as illustrated in Fig. 4.25. By using high density polyethylene copolymer films containing reactive groups it is also possible to create long-lived active bonding sites on the yarn to improve adhesion in composites. This technique gives interlaminar shear strengths comparable to conventional corona and plasma treatment of gel-spun yarns (Fig. 4.26).

4.5.5 Applications

The fields of application for SSE yarns are the same as those for gel-spun polyethylene (see Chapter 3). As noted earlier, this is not surprising since yarns from both processes share many similarities. In applications where very high strength or stiffness, high flexibility, exceptional ballistic protection, or very small deniers are required, gel-spun yarn will have an advantage. In applications where low cost, low creep, colour, UV stability, or exceptional abrasion resistance is required, SSE yarn generally will have an advantage. Because the commercial production of *Tensylon*™ SSE fibre started only in August 1999, there were few announced commercial applications at the time this text was written.

Specialty ropes, cordage, and fishing line are the largest identified markets for SSE yarns. It is in these applications that all of the attributes of the SSE product are utilised: good translational efficiency (offsetting its lower initial strength), the ability to be coloured or UV stabilised, and significantly lower creep. It is the combination of these features that make the product a strong candidate in these areas.

Like gel-spun fibres, the toughness and low friction properties inherent in UHMW-PE also translate into the finished SSE yarn. Both properties are important in the production of cut-resistant gloves and aprons. The tape form of the SSE product enhances the high cut resistance because of the benefit of a monolithic form versus a multifilament, but this bulk also reduces fabric flexibility (hand). In most constructions, however, fibrillating the yarn mitigates the harsher hand. Since it is common to use high modulus yarns in combination with other materials, such as steel wire or glass fibres, to create very highly cut-resistant yarns, the tape form is advantageous because it facilitates complete encapsulation of the secondary component. The ability to colour SSE yarn also is an advantage in this market.

As announced by Synthetic Industries, the new markets being explored for SSE fibres are those of geotextiles and building materials for reinforcement, repair and retrofit.[188] The high specific strength, potentially low cost, and the ability to modify the fibres for increased UV stability and adhesion offer great promise in this area.

As the data in Fig. 4.26 suggests, it is possible to produce low cost, surface modified SSE yarns for composite applications. The low dielectric properties of polyethylene coupled with the improvements provided by an adhesive film would suggest that radar enclosures such as radomes are a natural area for SSE yarn development. Other composite structures where high modulus, low cost, high impact resistance, and colour or UV stability are important also would be likely candidates.

The major area where SSE yarns currently do not compete with gel-spun polyethylene fibres is in the area of ballistic protection. Although SSE fibres have high moduli (1000–1400 g/d), a critical requirement for good ballistic protection, these moduli are significantly lower than those of gel-spun polyethylene. Nevertheless, preliminary ballistic tests have indicated that there is a strong potential for SSE yarns to compete in areas where less than maximum ballistic protection is required. However, because a high level of technology is involved in producing ballistic-resistant articles and the production of SSE yarns is only just beginning, it may be several years before there is any significant penetration of SSE yarn into this area.

There are several potential medical applications for SSE yarns, such as dental floss, sutures, and reinforcement for *in vitro* devices. These products tend to be low volume, specialty end-uses and, although evaluations are underway in several of these areas, no commercial applications have been announced.

4.5.6 Economics

The announced capacity for the *Tensylon*™ semi-works is 80–100 metric tons per year.[188] Therefore, it is difficult to compare the economics of this initial SSE process directly with the older, more established ones for gel-spinning. A general estimation of the relative production costs can be made, however, by examination of the general elements of the two processes.

Both processes use UHMW polyethylene as a feed stock, so raw material costs in this regard will be similar. Both processes involve relatively low-speed multiple-stage drawing equipment. Again, the capital and operating costs in this area should be similar. General staffing for labour and supervision for the yarn processing are probably equivalent. The major difference in production costs, therefore, lies in the costs for conversion of the powder into the intermediate yarn product (xerogel versus compressed sheet).

Regardless of the gel-spinning technology used, a large solvent recovery plant is needed to recover, purify, and recycle the spinning solvent(s). The capital costs for this recovery plant, the special spinning equipment, the associated labour and supporting utilities constitute a major additional cost for gel-spinning. By comparison, the SSE process requires only a compaction extruder and rolling unit.

On this basis, one would estimate that the production costs for SSE should be approximately 40–50% of those of gel-spinning. Long term, at similar production levels, one would expect the selling prices of SSE yarns also to be about half those of gel-spun yarns.

The future of SSE yarns will depend upon both the general price/performance factors as well as the market's need for the unique features that the solid-state process/products provide. Although the product features appear to offer clear benefits in several important high-performance fibre areas, it is much too early in the commercialisation process to predict the outcome. The initial predictions on markets and costs, however, have proved accurate. The sales have been in areas where colour and low creep are important: rope, fabric stabilisation (geotextiles), and luggage. Cut protection is currently the biggest market, in addition, the product line has been broadened to include 350 and 1000 denier yarn and unfibrillated full width tape (21 800 denier) with a breaking strength of 800 lb. The ITS pilot plant is now being run at its full design rate and there are plans for a larger (225 metric tons/year) unit.

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