2

Aramids

SERGE REBOUILLAT

2.1 Introduction

Aromatic polyamides became breakthrough materials in commercial applications as early as the 1960s, with the market launch of the meta-aramid fibre *Nomex*® (Nomex® is a DuPont Registered Trademark), which opened up new horizons in the field of thermal and electrical insulation. A much higher tenacity and modulus fibre was developed and commercialised, also by DuPont, under the trade name *Kevlar*® (Kevlar® is a DuPont Registered Trademark) in 1971. Scientists in the fields of liquid crystals, polymers, rheology and fibre processing, as well as process and system engineers, spent several years prior and during the early stage of its market introduction establishing the basics and fundamental understanding necessary to take full advantage of this new class of high-performance materials. Their outstanding potential derived mostly from the anisotropy of their superimposed substructures presenting pleated, crystalline, fibrillar and skin-core characteristics. This achievement is due in part to DuPont science and technology excellence brought into this field by Kwolek,[1–4] Blades,[5,6] Tanner and co-workers,[7–9] Gabara and co-workers,[10] Yang,[11,12] and many others who took an active part in this enterprise, starting with the inception of the aramids. Among a rather scattered literature on the matter, paramount contributions appeared relatively early in four books entitled *High modulus wholly aromatic fibers*, Black and Preston[13] (1973), *The strength and stiffness of polymers*, Schaefgen[14] (1983), *High performance aramid fibers*, Jones and Jaffe[15] (1985), and *Aromatic high-strength fibers*, Yang[11] (1989).

Another para-aramid, *Twaron*® (Twaron® is a registered product of Teijin), similar to *Kevlar*®, and an aromatic copolyamide, appeared on the market towards the end of the 1980s. The aromatic copolyamide derived from a good fundamental understanding of the earlier work done with rather stiff para-aramid chains and the new space created for more flexible, high tenacity fibres. Teijin, after a remarkable scientific interpretation of the prior art by Ozawa and Matsuda,[16] who pioneered the development of the aromatic copolyamide fibre, commercialised the *Technora*® (Technora® is a registered product of Teijin) fibre.

In the last 15 years, tremendous scientific contributions have been made towards establishing the structure–property relationships. Dobb and co-workers,[17,18] Morgan *et al.*,[19] Termonia,[20,21] Roche *et al.*,[22] Northolt and co-workers[23–26] and Jackson *et al.*,[27] were part of the scientific community who brought analytical, theoretical and modelling tools to approach these rather complex relationships revealing important characteristics which go beyond the traditional mechanical and chemical interpretations – such as the role which the micro-morphology plays in the biological accessibility of the internal structures.

For the sake of completeness, in the 1970s, based on an aromatic polyamide–hydrazine composition, Monsanto developed an aromatic copolyamide fibre under the code *X500* which almost reached the market.

In this chapter we will focus on the synthesis, fibre processing, structure–property relationships and applications of the commercial aramids. We will use the word para-aramid for both the *Kevlar*® and the *Twaron*® fibres.

2.2 Polymer preparation

2.2.1 Basic synthesis

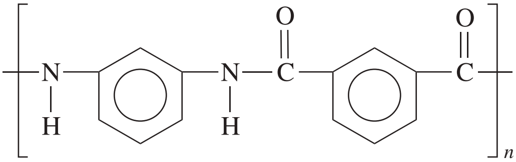
The following designation was adopted in 1974 by the United States Federal Trade Commission to describe aromatic polyamide-based fibres under the generic term aramid: ‘a manufactured fibre in which the fibre-forming substance is a long chain synthetic polyamide in which at least 85% of the amide (—CO—NH—) linkages are attached directly to two aromatic rings’.

Aramids are prepared by the generic reaction between an amine group and a carboxylic acid halide group. Simple AB homopolymers may be synthesised according to the scheme below:

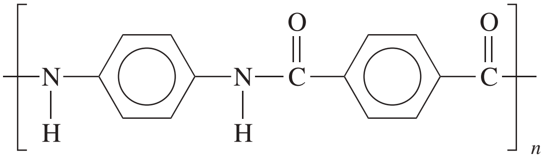
$$n\mathrm{NH_2{-}Ar{-}COCl} \longrightarrow \mathrm{{-}[\underset{A}{NH{-}Ar}{-}\underset{B}{CO}]{-}}_n + n\mathrm{HCl}$$

A similar reaction scheme also yields AABB homopolymers. For these reactions several methods[28–30] of preparation can be used, such as interfacial polymerisation and low-temperature polycondensation, which remains the most frequently encountered synthesis. Melt or vapour-phase polymerisation reactions should also be mentioned.

AABB aromatic polyamides are prepared from various aromatic diamines and diacids or diacid chlorides. This facilitates the generation of aromatic polyamides with extensive variations in molecular structure. The early AABB polymers contained predominantly meta-orientated linkages. The earliest representative of this class is poly-*m*-phenyleneisophthalamide, which was commercialised by DuPont in 1967 as *Nomex*® aramid fibre. Its chemical formula is:



The discovery in 1965 of high modulus, high tenacity (HM-HT) fibres from liquid crystalline solutions of synthetic para-aromatic polyamides led to the commercial production of *Kevlar*® aramid fibre by DuPont in 1971;[1] the corresponding chemical formula is given below:



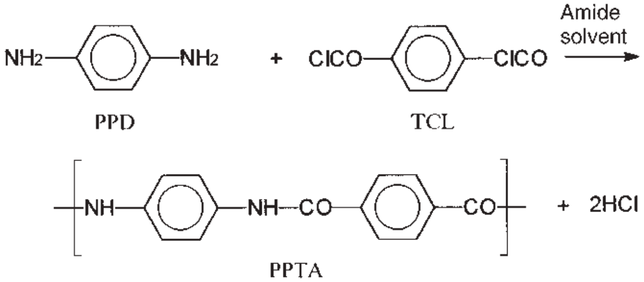
Kevlar® fibres are poly (*p*-phenylene terephthalamide) (PPTA),[31] the simplest form of AABB para-orientated polyamide.

2.2.2 The aromatic polyamide polymerisation process

Many examples of low-temperature polymerisation for aromatic polyamides and copolyamides can be found in seminal work by Kwolek.[2] Morgan[32] pointed out several pertinent factors affecting polymer characteristics in low-temperature polycondensation reactions. The most critical ones are:

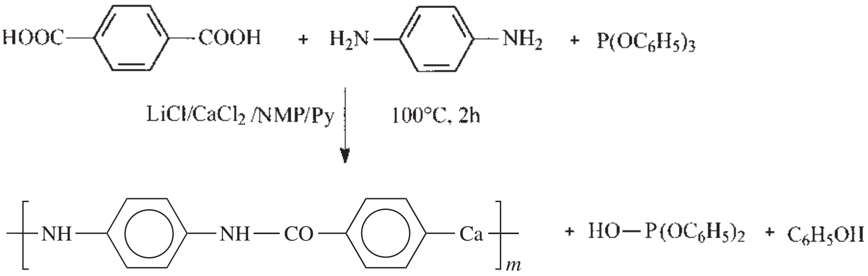
- the solubility–concentration–temperature relationships, which make the choice of solvent critical, and
- the salt concentration at constant polymer concentration, which partly governs the degree of polymerisation and polymer inherent viscosity (η_{inh}).

Rather than detailing generic, mostly empirical, rules governing the polycondensation to achieve the optimum and narrowest molecular weight distribution, we propose below a more specific description of a process based on patent examples and related literature.

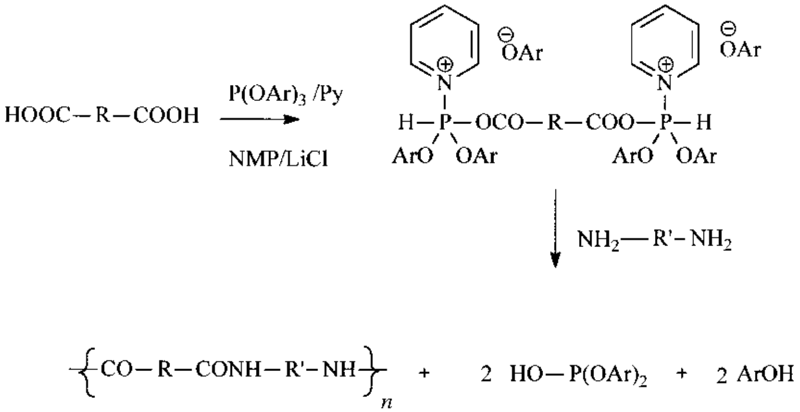


2.1 PPTA synthesised by low-temperature polycondensation of *p*-phenylene diamine (PPD) and terephthaloyl chloride (TCl).

Aromatic polyamides of the PPTA type are usually synthesised via a low-temperature polycondensation reaction based on *p*-phenylene diamine (PPD) and terephthaloyl chloride (TCl), according to Fig. 2.1. The specifics of the process have been reported by Bair and Morgan,[33,34] Kwolek[2] and Blades.[5,6] One methodology involves the dissolution of appropriate quantities of PPD in a mixture of hexamethylphosphoramide (HMPA) and *N*-methylpyrrolidone (NMP), cooling in an ice/acetone bath to 258 K (–15 °C) in a nitrogen atmosphere, and then adding TCl accompanied by rapid stirring. The resulting product is a thick, paste-like gel. Stirring is discontinued and the reaction mixture is allowed to stand overnight with gradual warming to room temperature. Work-up of the reaction mixture is accomplished by agitating it with water in a blender to wash away solvent and HCl. The polymer is collected by filtration. The stoichiometry of the solvent and reactant mixture is important in determining the molar mass of the final product. For instance, Bair and Morgan[33,34] report that a 2:1 ratio by volume of HMPA: NMP produced PPTA product with the highest inherent viscosity (and hence largest molar mass). An optimum reactant (PPD and TCl) concentration was *ca* 0.25 M. The inherent viscosity was shown to decrease quite rapidly if reactant concentrations less than 0.25 M. were used. A similar behaviour was observed for reactant concentrations greater than 0.3 M, although the fall-off in inherent viscosity was observed to be more gradual in this case. The viscosity fall-off at low reactant concentrations can be ascribed to the occurrence of competitive side-reactions of the type described by Herlinger *et al.*,[35] who examined the solution polymerisation of aromatic diamines and aromatic dicarboxylic acid chlorides in *N*,*N*-dimethylacetamide (DMAc). The drop-off in inherent viscosity at higher values of the reactant concentration could well be ascribed to a decrease in reactant mobility due to the onset of gelation before a high value of inherent viscosity could be attained. Of course, the polymerisation reaction is exothermic and a greater quantity of heat will be generated if higher



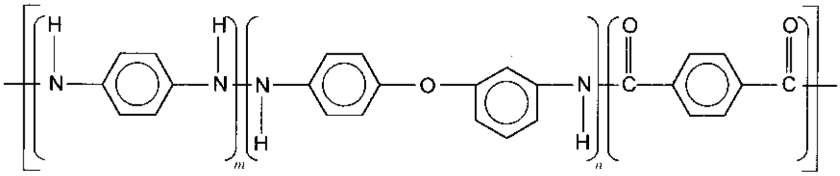
2.2 The Higashi synthesis: polycondensation of terephthalic acid and *p*-phenylene diamine.[11]



2.3 The Higashi triaryl phosphite reaction: note the generation of the *N*-phosphonium salt of pyridine, which subsequently undergoes aminolysis.

reactant concentrations are used. This could lead to an increased rate in side-reactions, which would also depress the value of inherent viscosity attainable.

Alternative synthetic pathways have been reported. In particular, reactions between aromatic dicarboxylic acids and diamines have been investigated since the diacids are reasonably cheap starting materials. The work of Higashi and co-workers is of note in this respect.[36–38] Solvent mixture/salt systems are utilised. In the Higashi approach[37] PPTA of high molecular mass was obtained when the polycondensation of terephthalic acid (TPA) and PPD was carried out in NMP which contained dissolved $CaCl_2$ and LiCl in the presence of pyridine. The synthetic strategy is illustrated in Fig. 2.2.



2.4 Polymer chemical structure of *Technora*®.[43]

In earlier work, Higashi *et al.*[36] explored the direct polycondensation reactions of aromatic dicarboxylic acids and diamines by using diphenyl and triaryl phosphates in NMP/pyridine solvent mixtures containing LiCl. The reaction with triaryl phosphates was assumed to proceed via a mechanism outlined in Fig. 2.3. This development arose from earlier work of a fundamental organic chemistry nature reported by Yamazaki and Higashi.[39,40]

The work of Preston and Hofferbert[41,42] is also relevant to the synthetic strategy under discussion. However the latter strategy was unsuccessful when terephthalic acid and diamines were used as polycondensation reagents, since high molar mass aromatic polyamide product was not obtained. This difficulty was subsequently overcome by substituting poly(4-vinylpyridine) in lieu of pyridine.

2.2.3 Copolyamides

The search for aramid copolymers was largely driven by scientific observations made early on by Ozawa and Matsuda.[16] In the pursuit of an ideal synthetic fibre with improved processability, it was recognised that the incorporation of diamines with wider distances between the two amino groups would be favourable to a lower spatial density of hydrogen bonding and rate of crystallisation. Furthermore, the incorporation of comonomers in which two phenylene groups are connected with a single atom unit generally improves the fibre drawability.

The resultant species, prepared via the copolymerization of several aromatic diamines and diacid halides, are referred to as copolymers. The use of copolymers in fibre production is a common technique with aromatic polyamides. These wholly or partially aromatic copolyamides contain alkylaryl groups, and other cyclic and heterocyclic groups. Some also contain pivotal substitutions and some pendent groups.

Teijin has commercialised an aromatic copolyamide, Technora®, Fig. 2.4, which exhibits high tensile stress properties as well as high resistance to hydrolysis. The manufacturing process of *Technora*®[43,44] reacts PPD and 3,4′-diaminodiphenylether (3,4′-ODA) (each at 25 mole %) with terephthaloyl chloride, in an amide solvent such as *N*-methyl-2-pyrrolidone/$CaCl_2$

(10% concentration), to complete the polycondensation. The reaction mixture is neutralised and subjected to spinning into an aqueous coagulation bath. The as-spun fibre is then brought to extraction of solvent, superdrawn at high temperature, and passed through finishing to give the final product. The whole process is very simple and straightforward since only a single solvent is used throughout. This greatly simplifies the solvent recovery process and also makes *Technora*® completely free of residual acid, which avoids later difficulties in the spinning process. Unlike the stiff chain *Kevlar*® aramid that is spun from a liquid crystalline solution directly to orientated HM-HT fibres, *Technora*® is spun from an isotropic solution. Its fibres have tensile stress properties similar to *Kevlar*® *29*. This semi-stiff chain copolymer has a homogeneous morphology, which leads to very good hydrolytic stability, while its greater molecular flexibility results in limited modulus.

2.2.4 Other aromatic polyamides

There are many aromatic polyamides not mentioned in this brief overview. They are extensively covered in the monograph by Yang.[11]

2.3 Spinning

2.3.1 Solution properties

Rigid chain macromolecules such as the aromatic polyaramids exhibit low solubility in many common solvent systems utilised in polymer technology. This is due to the fact that the entropy term in the Gibbs energy of solvation makes a very small contribution because of the rigidity. Consequently, the dissolution of such polymer materials is attained because of an extensive interaction of the polymer chains with solvent molecules, which is manifest in the enthalpy contribution to the solvation free energy.

The conformation adopted by macromolecules in solution is a well-established area of macromolecular science, but a somewhat general discussion of the possible states adopted by macromolecules in solution may be presented at this stage with some profit. A number of common scenarios may be envisaged. A common situation is that of randomly coiled polymer chains. The statistical analysis of such ensembles is well established.[45] However, if the chains are relatively stiff and are linked to extend the chain in one direction, then they are ideally described in terms of a random distribution of rods. Of course, association with the solvent may contribute to rigidity and also to the volume occupied by each polymer molecule. Now, as the concentration of rod-like macromolecules is increased and the saturation level for a random array of rods is attained, the system will simply become a saturated solution with excess polymer; or more interestingly, if the solvent/polymer relationships are right, additional polymer may be dissolved by forming regions in which the solvated polymer chains approach a parallel arrangement. These ordered regions define a mesomorphic or liquid crystalline state and form a phase incompatible with the isotropic phase. Continued addition and dissolution of polymer forces more polymer into the ordered state. If the rod-like chains are arranged in an approximately parallel array but are not otherwise organised, then the ordered phase is termed 'nematic'. Usually, a polymer sample will be polydisperse and the ordered phase will be organised in microscopic domains of varying size and direction of orientation. Aromatic polyamides form liquid crystal solutions on account of their extended chain structure.

It is clear that orientational order appears in solutions of rigid chain polymers because a random arrangement of the macromolecule assembly will be possible only up to a certain solution concentration. To retain a minimal volume, and indeed a minimal free energy, above a certain critical concentration, asymmetric macromolecules must acquire an ordered mutual arrangement that corresponds to a transition to the state typical for liquid crystals. In this case the solution becomes anisotropic. The degree of this anisotropy will be less than the strict three-dimensional ordering typical of a crystalline system, but at the same time it will differ significantly from an isotropic state characteristic of amorphous systems. The concentration threshold defining the transition to the liquid crystalline state will depend on the degree of shape asymmetry of the macromolecules, which will be determined as the ratio of their equilibrium length to their diameter, termed the 'axial ratio'. It should also be noted that liquid crystallinity can arise from anisotropy of intermolecular forces. But the latter are usually prominent in liquid crystal materials of low molar mass, although they could also be important in polymers that contain groups such as *p*-phenylene, whose polarizabilities are highly anisotropic.

Flory and co-workers[46–49] have described theoretically the behaviour of 'hard' rod-like polymers in solution and considered, in particular, the conditions under which the latter macromolecules would produce anisotropic phases. The Flory approach utilised a lattice model. This work followed on from the initial models developed by Onsager[50] and Ishihara,[51] which were relatively complex. These approaches rely on analysis of the second virial coefficient for very long, rod-like particles. Indeed, the Onsager paper[50] was the first to show that a solution of hard, asymmetric particles should separate into two phases above a threshold concentration that depends on the axial ratio of the particles. The paper also indicated that the phase separation was due to shape asymmetry alone, and that recourse to intermolecular attractive forces was not necessary. However, an approach based on the virial expansion suffers from the difficulty of evaluating higher virial coefficients for highly shape-asymmetric particles and, indeed, from the non-convergence of the virial series at the concentration required for the formation of a stable, anisotropic, liquid crystalline phase. The simple Flory lattice theory has been extended to consider polydisperse systems,[52] mixtures of rod-like particles with random coils,[53] and three-component systems consisting of a solvent and two solutes, the latter consisting of rod-like molecules with different axial ratios.[54] The problem of biphasic equilibria involving rod-like macromolecules has also been described.[55] Finally, the statistical mechanical analysis has been extended to mixtures of rod-like particles in which flexible joints connect the rods.[56]

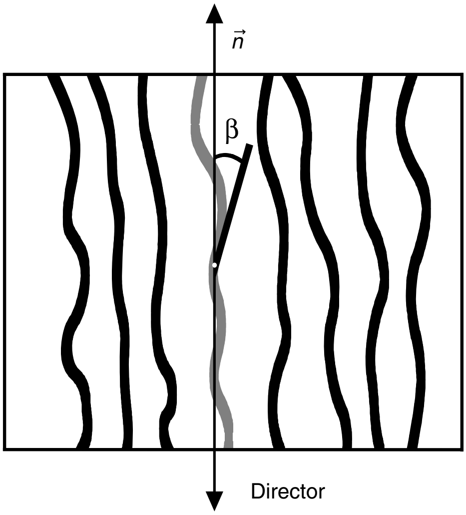
The behaviour of para-aromatic polyamides in solution has attracted considerable attention, especially with respect to their liquid crystalline behaviour. Both poly(*p*-benzamide) and poly(*p*-phenylene terephthalamide) have received particular attention in this respect. Papkov[57] has provided a useful review of this area. The topic has been discussed in a general way by Morgan.[32] The latter macromolecules are characterised by a stable *trans* configuration of the amide bond and by a high barrier to rotation around the stable aryl carbon bond.

Bair *et al.*[58] examined the behaviour of poly(1,4-phenyleneterephthalamide), PPTA, in solutions of HMPA/NMP. A strong dependence between the inherent viscosity attained by the polymer solution and the reactant concentration used was found. When dissolved in high strength sulphuric acid or HMPA/NMP/LiCl solvents, PPTA was found to form an interesting liquid crystalline solution composed of liquid isotropic and anisotropic (mesomorphic) phases at some critical concentration. The effect of polymer intrinsic viscosity on the critical concentration needed to form the anisotropic phase was determined. In the same paper it was shown that liquid crystalline solutions were formed from poly(chloro-1,4-phenyleneterephthalamide) (Cl-PPTA) in DMAc/LiCl solvents. In the latter case, the liquid crystalline solutions were readily separated into the component isotropic and anisotropic phases. Analysis of the polymer distribution in the respective phases indicated that the distribution depended on polymer concentration, polymer intrinsic viscosity and LiCl content. It was shown that the anisotropic phase always contained a greater amount of polymer than the isotropic phase. Furthermore, the intrinsic viscosity of the polymer present in the anisotropic phase was greater than that found in the isotropic phase. Hence, one could conclude that formation of an anisotropic phase occurred by the highest molar mass polymer chains packing into the ordered more dense fluid. It was also noted that by proper selection of polymer and solvent variables, the extent of anisotropic phase relative to isotropic phase could be varied from zero to essentially 100%.

2.3.2 Spinning of fibres

Production of fibres initially involves heating the spinning solution up to a suitable processing temperature, which is of the order of 80 °C for the highly concentrated solutions in 100% (water-free)[87] sulphuric acid. At this temperature, above a polymer concentration of about 10 wt% the solution state corresponds to a nematic liquid crystalline phase. The concentration limit for the polymer in spinning solution is 20 wt%. If concentrations above this critical limit are used, spinnability is affected due to undissolved material; therefore the resulting fibre has inferior mechanical properties. Because these rod-like polymers are rigid, they orientate themselves with respect to each other, forming a nematic phase as illustrated in Fig. 2.5 which shows the orientation angle β with respect to the director $\vec{n}$. This phase is dominated by liquid crystalline domains that contain aligned polymer chains. The degree of orientation of these polymer chains depends on solution temperature and polymer concentration.

Polymer spinning solutions are extruded through spinning holes and are subjected to elongational stretch across a small air gap, as illustrated in Fig. 2.6. The spinning holes fulfil an important function. Under shear, the crystal domains become elongated and orientated in the direction of the deformation.[3,32,58] Once in the air gap, elongational stretching takes place. This is effected by making the velocity of the fibre as it leaves the coagulating bath higher than the velocity of the polymer as it emerges from the spinning

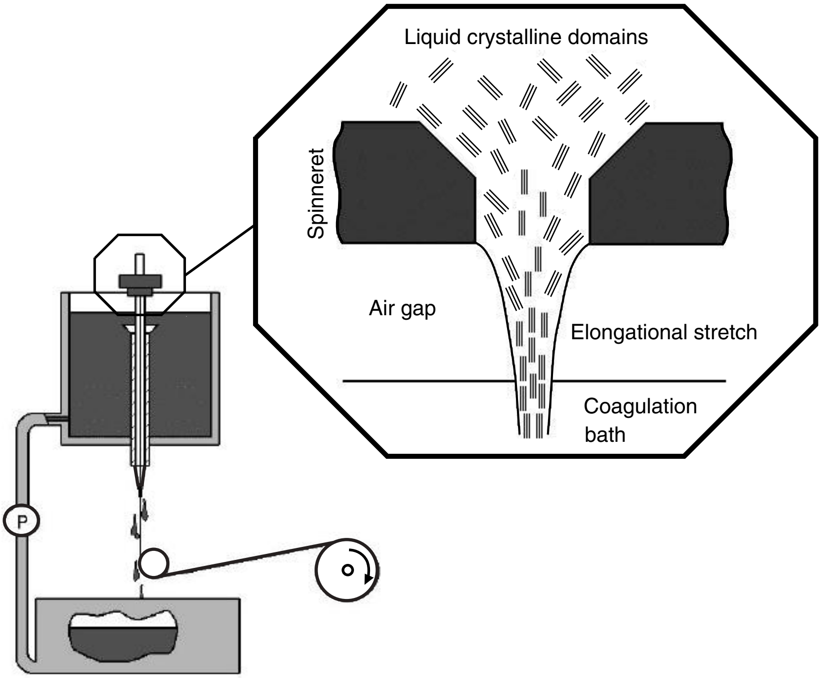


PPTA molecules are indicated by the thick lines

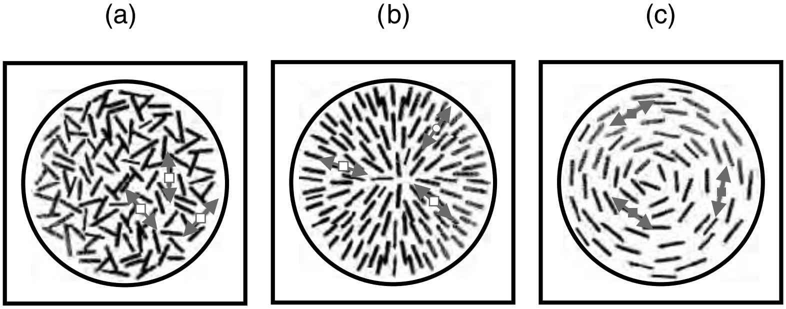
2.5 Schematic representation of the liquid crystalline solution.

holes. This ratio is often referred to as the ‘draw ratio’ and can be fine-tuned to obtain higher tenacities and moduli with lower elongations and denier. The resulting stretch in the air gap further perfects the respective alignment of the liquid crystal domains. Overall, a higher polymer orientation in the coagulation medium corresponds to higher mechanical properties of the fibre. Because of the slower relaxation time of these liquid crystal systems, the high as-spun fibre orientation can be attained and retained via coagulation with cold water.[4] Essentially, the crystallinity and orientation of the solution are translated to the fibre. These factors allow the production of high strength, high modulus, as-spun fibres. Fibres can exhibit three possible lateral or transverse crystalline arrangements and these are illustrated in Fig. 2.7. Figure 2.7(a) represents a fibre with random crystal orientation, Fig. 2.7(b) radial crystal orientation and Fig. 2.7(c) tangential crystal orientation. Interestingly, the radial crystalline orientation can only be brought about using the dry-jet wet-spinning process used for para-aramid fibres. This had never been observed before in a synthetic organic fibre.

Present para-aramid products have need of a very high molecular



2.6 Schematical representation of the extrusion of the liquid crystalline solution in the dry-jet wet-spinning process.



2.7 Crystal orientation of para-aramid fibre: (a) random; (b) radial; (c) tangential.

orientation (less than 12°), which has an almost directly proportional relationship to fibre modulus. The tenacity of a particular fibre material is also, but not only, governed by this molecular orientation angle. The modulus of the as-spun yarn can be greatly affected by the drying conditions, temperature and tension. Additional orientation inside the solid phase occurs during drying.

Fibres prepared by a dry-jet wet-spun process have a noteworthy response to very brief heat treatment (seconds) under tension.[59] These fibres will not undergo drawing in the conventional sense, showing an extension of less than 5% even at temperatures above 500 °C, but the crystalline orientation and fibre modulus is increased by this short-term heating under tension. As-spun fibre has an orientation angle of 12–15°; this decreases to about 9° or less after heat treatment, with the fibre modulus increasing from 64 GPa to over 150 GPa. The applications of these principles led to development of rigid polymer systems forming lyotropic liquids.[60] Molecular orientation, structure, and spinning method all affect how aramid fibres respond to this heat treatment. A recent study[61] of the mechanical change during heat treatment provides a comprehensive set of data regarding the relationships between the annealing time, the final crystallite size, the orientation angle, and the tensile modulus. Thermally induced changes in para-aramid fibre surface were evidenced by inverse gas chromatography. Rebouillat and co-workers[62–64] reported quite extensively on the use of this technique for fibre surface characterisation.

In order to circumvent the insolubility of rigid molecules in most solvent media, a significant amount of research has gone into semi-rigid molecules and their use in fibre production. For example, Black and Preston[13] worked on polymers based on aromatic polyamide hydrazine structures. The best-known semi-rigid rod aramid copolymer fibre in use is *Technora*®, developed from the work of Ozawa.[65] The copolymer is soluble in its polymerisation solvent, allowing the reaction mixture to be wet- or dry-jet wet-spun from an isotropic solution directly into filaments. The presence of solvent in a reasonably concentrated solution and the inherent rigidity of the molecules avoid molecular entanglement. The spun filaments are washed, neutralised, drawn at a high ratio (10 at 490 °C), and dried. As before, the hot drawing process helps to develop their strength further and to give them their high properties. The fibres have moderate crystallinity, with a random distribution of amorphous regions through their fine structure, with their high strength and modulus attributed to their extended chain structure.

Ozawa and Matsuda[16] provide more details regarding the effect of draw ratio and the associated mechanism in the case of aramid copolymer processing. They refer to three modes of drawing. An ordinary draw mechanism would prevail in the case of a low draw ratio (below 2 for *Technora*®), which is characterised by improved crystal size and uniformity, and better orientation of the chains. An intermediate draw mechanism, for a medium draw ratio (2 to 14 for *Technora*® fibre), is dominated by shearing, which yields to chain slips, reduction of the imperfections and therewith higher tenacity, elongation, and modulus (TEM) properties. Finally, an excessive draw mechanism (above 15 in the case of *Technora*®), is associated with the formation of microvoids and microfibrils, and therefore the beginning of decreasing TEM.

A fairly large coverage of spinning variants is proposed in the compilation on aromatic high-strength fibres written by Yang.[11]

2.3.3 Aramid types

The properties of aramid fibres depend on the particular spinning and post-treating conditions. Table 2.1 lists the forms that are commercially available, together with their TEM properties.

Table 2.1 Aramid types*

Type	Tenacity (mN/tex)	Initial modulus (N/tex)	Elongation at break (%)
Kevlar® 29	2030	49	3.6
Kevlar® 49	2080	78	2.4
Kevlar® 149	1680	115	1.3
Nomex®	485	7.5	35
Twaron®	2100	60	3.6
Twaron® High Modulus	2100	75	2.5
Technora®	2200	50	4.4

*From the manufacturers' leaflets and references.[3,15,87]

2.4 Structure and properties

2.4.1 Characteristics of aramid fibres

Aramid fibres have unique properties that set them apart from other fibres. Aramid fibre tensile strength and modulus are significantly higher than those of earlier organic fibres, and fibre elongation is lower. Aramid fibres can be woven on fabric looms more easily than brittle fibres such as glass, carbon or ceramic. They also exhibit inherent resistance to organic solvents, fuels, lubricants and exposure to flame.

Each type of aromatic polymer gives certain characteristic fibre properties because of its fibre and intrinsic polymer structure. Rather than going through an encyclopaedic description of the properties of the aromatic polyamides, we propose in the following section to review some of the predominant studies that we believe are important in order to understand the unique properties of this class of fibre materials. The superimposed structures, such as the crystallites, the fibrils and the skin-core boundaries, are definitely unique attributes that can be partially tailored through the fibre process engineering. This is worth examining in more detail. It is equally important to provide more insights into the pleated structure and the formation of the hydrogen bonds acting as zippers between the chains. Finally, the mechanical models and the related mathematical analysis are tremendous tools for both the scientist and the engineer to gain fundamental understanding through useful engineering parameters. We propose to focus on these aspects in the following sections.

2.4.2 Structure

It is a truism that the physical properties of macromolecules are determined by their structural characteristics at a molecular level. This is particularly cogent when aromatic polyamides are considered. For instance, as noted by Dobb and McIntyre,[68] the tensile modulus of a fibre will be largely determined by the details of the molecular orientation about the fibre axis, and the effective cross-sectional area occupied by single chains, which will, of course, be related to the degree of chain linearity. For instance, in poly(*p*-phenylene terephthalamide), the polymer chains are very stiff, brought about by bonding of rigid phenylene rings in the *para* position. In contrast, for *Nomex*® fibres, the phenylene and amide units are linked in the *meta* position, which results in an irregular chain conformation and a correspondingly lower tensile modulus. Also in PPTA, the presence of amide groups at regular intervals along the linear macromolecular backbone facilitates extensive hydrogen bonding in a lateral direction between adjacent chains. This, in turn, leads to efficient chain packing and high crystallinity.

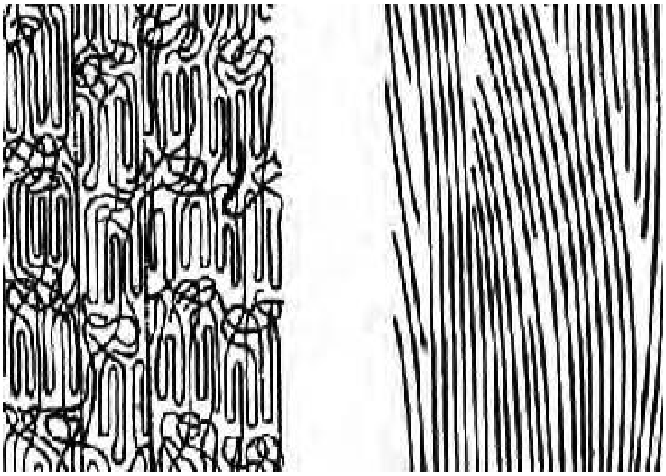
A similar situation is encountered for non-aromatic polyamides such as nylon. In the latter material (nylon 6.6 for example), the molecules present in the form of extended planar zigzags joined together in hydrogen bonded sheets.

Structural studies on PPTA fibres have been described by Northolt,[23] Haraguchi *et al.*[66] and Yabuki *et al.*[67] The supermolecular structure of the high-modulus aramid fibres which are essentially of the PPTA type have been reported by Dobb and co-workers.[17,18] A useful review discussing the relationship between the microstructure and the mechanical properties of aramid fibres has been presented by Northolt and Chapoy.[24]

Haraguchi *et al.*[66] have noted that two crystal modifications of PPTA are observed. Northolt and Chapoy[24] have reported on an X-ray diffraction analysis of PPTA fibres and proposed a model for the crystal and molecular structure of the PPTA. When the polymer is spun from a highly concentrated anisotropic solution, the chains form an essentially monoclinic[24] (pseudo-orthorhombic) unit cell with associated parameters a = 0.787 nm, b = 0.518 nm, c (defining the fibre axis) = 1.29 nm. There are two molecular chains per unit cell, one through the centre, the other through a corner, and two monomeric units in the axial repeat. Approximate values for the orientation angles between the phenylene planes and the amide planes are 38° for the *p*-phenylene diamine segment and –30° for the terephthalic segment. However, fibres formed from anisotropic solutions of lower concentration exhibit a different packing arrangement that is equivalent to a lateral displacement (b/2) of chains along alternate 200 planes. It should be noted that both crystallographic forms coexist in fibres spun from solutions of intermediate concentration. Northolt and Chapoy[24] proposed that hydrogen bonds are formed between adjacent chains lying in the 100 plane. They argued that the chain conformation is primarily governed by competitive intramolecular interactions between the conjugated groups in the chain. Similar interactions are also found for the conformation of benzamide, acetanilide and the terephthalamide molecules. These interactions arise from the operation of a resonance effect, which results from an attempt to stabilise coplanarity of the amide groups and the phenylene groups. A counteracting steric hindrance is also found between the oxygen and the ortho-hydrogen of the *p*-phenylene diamine segment, and between the amide hydrogen and the ortho-hydrogen of the terephthalic segment.

The regularly positioned amide segments allow reasonably strong hydrogen bonds, which facilitate a proper load transfer between the chains, as found, for example, in a zipper. The hydrogen bonded chains form sheets, which are stacked parallel into crystallites. Between adjacent hydrogen bonded planes, the interaction largely takes place by van der Waals' forces, with some pi-bond overlap of the phenylene segments. This causes the hydrogen bonded planes to function as slip-planes in a manner analogous to close-packed planes in metals. Note also that bond rotation and hence molecular flexibility is inhibited by the presence both of the aromatic rings and the double bond nature of the amide group arising from resonance effects.

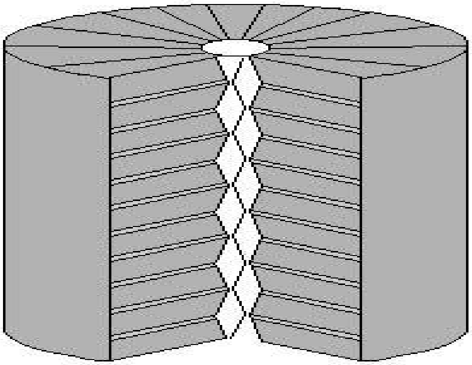
It should be appreciated that the microscopic chain structure and chain properties dictate the manner of fibre production. Northolt and Chapoy[24] have stated that the aromatic polyamides are manufactured in a wet-spinning process in which the chains are given a narrow orientation distribution around the filament axis. This optimises the tensile modulus. Dobb and McIntyre[68] have stated that no evidence has been found for small-angle two or four point meridional reflections, which would be traditionally associated with chain folding in polyamide and polyester fibres. The latter observation supports the proposal of an extended chain conformation. A schematic representation of the microstructure of (a) a semicrystalline polymer such as nylon 6 and (b) PPTA is outlined in Fig. 2.8. In each case the fibre axis is vertical. It should also be noted that PPTA fibres are generally characterised by intense but diffuse small-angle scattering features on the equator of the X-ray diffraction (XRD) patterns. This effect can be ascribed to the presence of microvoids. Electron microscopy and X-ray data indicate that the voids are rod shaped, with their long axis almost parallel to the fibre axis, having typical widths in the range 5–10 nm and length about 25 nm. The influence of microvoids in para-aramid fibres has been explored


(a) (b)

2.8 Schematic representation of the microstructure of: (a) semi-crystalline polymers such as nylon 6 and (b) PPTA (fibre axis vertical).

by Dobb *et al.*,[69] using a test method originally described by Allen.[70] The surface microstructure of an aramid fibre was also observed directly by atomic force microscopy.[71,72] The unit cell parameters *b* and *c* of the crystalline structures and the coplanar-like rotation of benzene rings are similar to the reported results but the registration angle is not constant. This discrepancy is explained as the difference between surface and bulk crystalline structure. At the surface of the polymer, chains tend to be arranged less perfectly and the surface crystalline structure can be influenced by several parameters such as the fibre manufacturing conditions and post treatment, adsorbed water, and even the possible friction of the atomic force microscopy (AFM) scanning tip.

The supermolecular structure of a high modulus polyaromatic material such as *Kevlar® 49* has been reported by Dobb *et al.*[69] In this work, a combination of electron diffraction and electron microscope dark field image techniques was utilised. The dark field images derived using selected meridional or off-meridional reflections from longitudinal sections, exhibited banding of two main types having periodicities of 500 and 250 nm. The former periodic band spacing is associated with the off-meridional reflections whereas the latter is assigned to meridional reflections. Detailed analysis conducted by the authors led to the assignment that there was a uniform distribution of ordered crystalline material throughout the fibre and that the dark field banding observed was a manifestation of changes in crystalline orientation and not of crystalline order. The results reported by Dobb *et al.*[69] provide strong evidence for a regular pleated structure with the alternating components of each sheet arranged at approximately equal but opposite angles to the plane of the section, as illustrated in Fig. 2.9.



2.9 Radial pleated structure model of PPTA fibre.

Experimental measurements indicate that the angle between adjacent components of the pleat is about 170°.

2.4.3 Analysis of mechanical properties

The mechanical properties of aramid materials underlie their significant commercial utilisation in many areas. For instance, the as-spun *Kevlar®* aramid fibre exhibits over twice the tenacity and nine times the modulus of high strength nylon.[73] On a weight basis it is stronger than steel wire and stiffer than glass. Both creep and the linear coefficient of thermal expansion are low and the thermal stability is high. The latter properties resemble those of inorganic fibres and, of course, can be attributed to the extended chain morphology, high molar mass and excellent orientation in a thermally stable structure that does not melt. Para-aramid fibres have utility due to a combination of superior properties allied with features usually associated with organic fibres such as low density, easy processibility and rather good fatigue and abrasion resistance.

The macroscopic mechanical properties of a polymer are determined by the molecular structure of the chain. Northolt[23] has described a polymer chain as a one-dimensional load-bearing conformation. He notes that a material such as polyethylene can be processed to exhibit a high tensile modulus and tensile strength (gel spinning followed by hot drawing of polyethylene afforded a fibre of tensile strength 3 GPa and modulus 200 GPa). The downside is that extremely long chains are required to ensure optimum load transfer between adjacent polymer chains due to the fact that intermolecular adhesion in the fibre arises only due to van der Waals' forces. Also, polyethylene has a very low melting point, which limits practical application. The latter disadvantages are removed if stiff polymer chains linked by hydrogen bonds are used. As previously noted in this chapter, chain stiffness is achieved when free rotation around interatomic bonds is not allowed and, by necessity, the chain will adopt the linearly extended conformation. Of course, the latter idea is manifested in the aromatic aramid materials. As noted by Northolt,[23] regularly positioned amide segments in the latter materials allow for medium to strong intermolecular hydrogen bonds that ensure a proper load transfer between the chains as, indeed, is found in a zipper. However, the chain properties exhibited by aromatic polyaramids are mainly due to the alignment of chains in one direction, which limits the macroscopic shape of the material to filaments and films. The aromatic polyamides are manufactured in a dry-jet wet-spinning process in which the chains are given a narrow orientation distribution around the filament axis. This procedure leads to an initial modulus of *ca* 70 GPa, which is subsequently increased by short-term heating under tension to *ca* 140 GPa. Typically, the filament strength for a gauge length of 2.5 cm is 4 GPa, with an elongation at break of about 4% and a fracture energy of *ca* 80 MJ/m^3.

An excellent theoretical approach by Termonia[20,21] led to the calculation, based on the molecular weight of commercial para-aramid fibres, of the ultimate tensile strength of PPTA filaments being 10 GPa. Another estimation can be calculated from the weakest chemical bond of the PPTA chain divided by the surface area of a cross-section of the chain in the crystal lattice. In the later case, a tensile strength of 29 GPa is found. These calculations, for a hypothetical ideal molecular structure and molecular alignment, take into account the weakest bond dissociation energy of the polymer molecule in its most elongated conformation, which, as we have emphasised in a previous section, is a difficult target to attain in view of the solution properties and the spinning conditions. Mechanical modelling further helps to appreciate the attainable improvement from the observable tenacity.

A detailed mathematical model to adequately describe the mechanical properties of an aromatic polyamide fibre such as PPTA has been developed by Northolt and van Aartsen[25] and by Northolt.[26] This model was based on knowledge gained of the polymer microstructure, and the analysis rests on the adoption of a single-phase paracrystalline model of the latter. The analysis is based on earlier work reported by Bartenev and Valishin[74] in which a theory describing the orientational dependence of the compliance for completely crystalline fibres was developed. The model adopted by Northolt is in good accord with XRD studies. On the basis of the mathematical model developed, and if we assume a uniform stress distribution along the fibre, it is possible to show[25,26] that the elastic extension of the aramid fibre is governed by the following expression:

$$S_{33} = \frac{1}{e_3} + A\langle \sin^2 \phi \rangle \qquad [2.1]$$

In this expression, S_{33} denotes the fibre compliance, e_3 is the modulus of elasticity of the chain parallel to its axis of symmetry, and the factor $\langle \sin^2 \phi \rangle$ represents the orientation distribution parameter of the crystallites with respect to the fibre axis. The latter quantity will be zero if the orientation is perfect and $\frac{2}{3}$ if the orientation is random. The factor A represents a measure of the mechanical anisotropy of the crystallite and is given by:

$$A = \frac{1}{2g} - \frac{2(1+\nu_{13})}{e_3} \qquad [2.2]$$

where g denotes the shear modulus in the plane containing the chain axis and ν_{13} represents the Poisson ratio for a stress along this axis. Equation [2.1] has been confirmed experimentally by Northolt[26] for PPTA fibres using dynamic moduli and crystallite orientation measurements. He has shown that the dynamic compliance S_{33} ($S_{33} = 1/E$, where E represents the dynamic tensile modulus) varies linearly with $\langle \sin^2 \phi \rangle$ for three different fibre samples. Very little scatter is obtained over the entire measurement range. Indeed, the expression is valid up to rupture. From least squares analysis of the data, $A = 0.26 \pm 0.01\,\mathrm{m^2/GN}$. Typically, $e_3 = 240\,\mathrm{GPa}$ and $g = 2\,\mathrm{GPa}$. It was determined that, up to a stress of *ca* 1.5 GPa, the extension of the fibre (the strain) is brought about mainly by elastic rotation, by some retarded as well as plastic rotation of the crystallites towards the fibre axis, and by elastic extension of the polymer chain itself.

Northolt also derived a relation between the stress σ and the orientation parameter as follows:

$$\langle \sin^2 \phi \rangle = \langle \sin^2 \phi \rangle_0 \exp[-(2A + \lambda)\sigma] \qquad [2.3]$$

where the parameter λ represents both the permanent and the retarded elastic rotation of the crystallites and $\langle \sin^2 \phi \rangle_0$ denotes the initial value of the orientation parameter. The relation expressed in Equation [2.3] has been confirmed experimentally. Typical values for λ lie in the range 0.15 to $0.28\,\mathrm{m^2/GN}$ for the aramid fibres examined (four samples). It was noted that λ values tend to be larger for less oriented fibres.

Northolt also determined that, for $\sigma > 1.5\,\mathrm{GPa}$, the fibre extension increases by axial flow that would, in principle, be caused by slip between adjacent chains. The work of Northolt[26] resulted in the generation of an approximate analytical expression for the tensile curve of a fibre, which consists of a linear arrangements of crystallites that have a narrow orientation distribution $\langle \sin^2 \phi \rangle_0$ with respect to the fibril axis. The stress(σ)/strain(ε) relation is given by:

$$\varepsilon = \frac{\sigma}{e_3} + \frac{\langle \sin^2 \phi \rangle_0}{2}[1 - \exp(-C\sigma)] \qquad [2.4]$$

where $C = 2A + \lambda$. Hence we can conclude that the ductility of the fibres is primarily determined by the initial orientation distribution of the crystallites and by the ability of the crystallites to rotate their symmetry axis towards the stress direction as a result of the relatively low value of the shear modulus g. During fibre extension, the latter distribution contracts and at near rupture the chains are oriented almost parallel to the stress direction.

Northolt[26] has also noted that because of the crystallite orienting mechanism governing the entire tensile deformation process, the presence of structural irregularities may hamper the alignment of the crystallites along the stress direction. This could give rise to premature rupture of the fibre. However, local slip of hydrogen bonded planes may serve to mitigate the effect of the presence of inhomogeneities.

2.4.4 Some useful comparisons between aromatic polyamides and copolyamides

The levels of tensile properties and thermal stability of *Technora*® are comparable to those of highly crystalline para-aramid fibres over standard practical temperature ranges. *Technora*® has a comparatively high fatigue resistance, which is the direct result of the flexibility of the copolymer chain and loose crystal structure in the copolymer; this has been confirmed using wide-angle X-ray studies.[3]

Most of the differences between these two families, the para-aramid and the meta/para copolymers, seem to have been anticipated at the design stage as described by Ozawa and Matsuda[16] in Table 2.2.

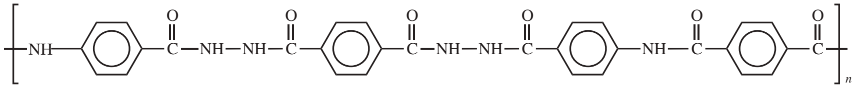
Although mainly derived from hypotheses partly validated through analytical methods, there are several mechanical failure modes, morphology characteristics and chemical accessibility properties which have been proposed by Morgan *et al.*,[19] Panar *et al.*,[75] Jackson *et al.*,[27] Lee *et al.*,[61] Li *et al.*,[76] Fukuda *et al.*,[77] Roche *et al.*,[78] Rao and Farris,[79] Young,[80] and Mooney and MacElroy.[81]

Regarding, more specifically, fibre failure modes and related morphologies, the atlas of fracture, fatigue and durability compiled and commented on by Hearle *et al.*,[82] constitutes a unique piece of literature in which a comparative series of scanning electron microscopy (SEM) pictures speak for themselves. Supplemented by the necessary information on how breaks occurred, this outstanding collection of data provides quite relevant information that sets the aramids apart from most man-made fibres owing to the

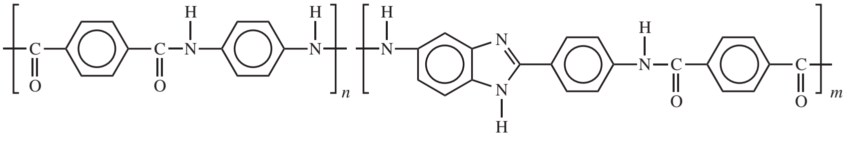
Table 2.2 Molecular requirements for improved characteristics of HM-HT aromatic fibres[16]

Improvement	Polymeric composition
Thermal resistance	Wholly aromatic polyamide Absence of unstable linkage (urethane, urea, alkylene, etc.)
Solubility	Copolymer with dissymmetrical units Inclusion of —O—, —CO—, —SO_2—, etc. Amides rather than esters
Drawing potential	High molecular weight Enhanced chain flexibility by incorporating —O—, —CO—, —SO_2—, etc. into polymer chain
Dimensional stability	Rigid molecular chain Crystallinity

multiple and long axial splits in the filaments, observable when the material is fractured by tensile testing. This mode of failure, which is also observed in the case of high-modulus polyethylene (HMPE) fibres, is easily distinguishable from the brittle tensile fracture of glass, ceramic, carbon and elastomeric fibres, the ductile tensile fracture of nylon, polyester and polypropylene fibres, and the granular fracture typical of polybenzimidazole (PBI) or alumina fibres for example. Finally, the fibrillar failure of cotton may, to a certain extent, show some similarities with the aramids owing to the microfibril assembly found in this type of natural fibres, although the very high strength nature of the para-aramids largely limits this kind of analogy. Hearle and Wong[83] also provide more insight into the flex fatigue and abrasion resistance of high modulus fibres. Although never commercialised, the experimental *X500* series of aromatic copolyamide fibres developed by Monsanto has been subject to detailed research work, the major findings of which have been disclosed in the extensive technical compilation done by Black and Preston[13] in 1973. The chemical formula of *X500*,[13] which is provided below, underlines the larger number of amide functions which shall increase significantly the amount of intermolecular chain bonding. This material remains very attractive as a comparative research model to help the understanding of the rather complex behaviours of para-aramids.



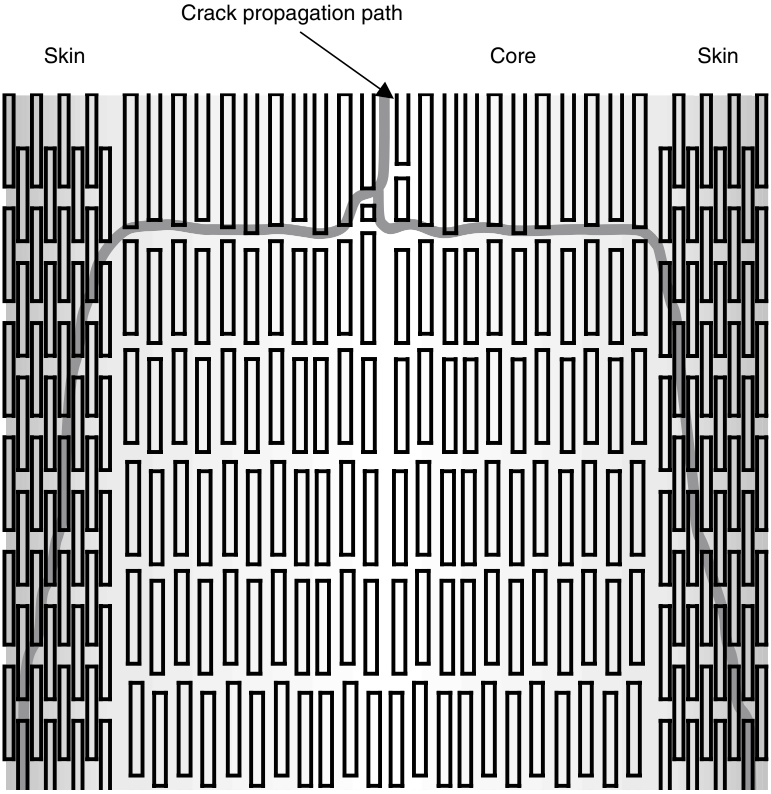
A more recent initiative from a Russian research organisation[84] (see also 4.4) led to the experimental development of the fibre *Armos*® (*p*-phenylene-benzimidazole-terephthalamide – co-*p*-phenylene-terephthalamide), based on a copolyamide consisting of para-substituted phenylene and benzimidazole whose fibre shows encouraging mechanical properties. Its chemical formula[84] is:



The comparative analysis[84] of the structure and the mechanical behaviour of regular para-aramid and the *Armos*® (Armos® is a registered product) remains a unique research work, outlining the analogies between these two materials although they differ significantly in terms of crystallinity. It is hoped that more studies will confirm the surprising presence of smectic structure as well as nematic mesophase in the non-crystalline phase of the copolyamide.

Although not always being unanimously accepted, the conclusions presented in these studies offer tremendous opportunities to gain fundamental understanding of structure–property relationships associated with fibre formation and consolidation, as well as fibre usage and biological accessibility and degradation.

The skin–core supermolecular structure of the PPTA fibre is probably the most broadly accepted feature. The difference in orientation and alignment of the skin chains versus the core microfibrils, which are substructured by crystallites, has been often used to support the hypothetical fracture model shown in Fig. 2.10. An explanation of this type of propagation can be associated with the fact that the nematic-like structure observable in the spinning solution is rearranged under a relaxation effect into a smectic-like structure during the fibre coagulation. The smectic alignment is parallel and



2.10 Schematic representation of a fracture model of PPTA fibre.

stratified like a two-dimensional order, with a very limited number of liaisons across the transverse boundaries like the ones depicted in the central part of Fig. 2.10, while the nematic order corresponds to molecules showing a parallel one-dimensional order with overlaps which resemble the skin representation of Fig. 2.10. The type of periodic alignment observed in the core part is promoted by the concentration of chain ends in transverse connecting zones, which are mechanically and chemically vulnerable.

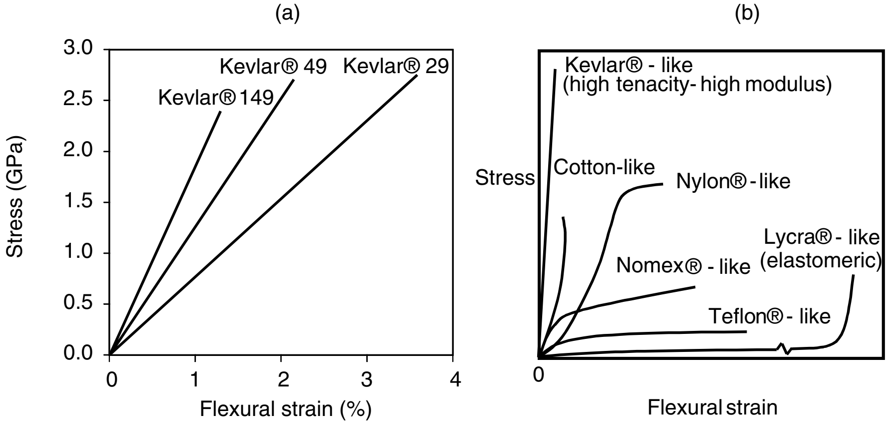
Ozawa and Matsuda[16] suggest that aromatic copolyamides are less susceptible to the formation of smectic structures, therefore offering different mechanical and chemical properties. In the case of *Technora*® fibres, they attribute this tendency to the fact that the chains are much more flexible than PPTA chains and the crystallites are looser; furthermore, the process allows more stress dissipation to occur. SEM and X-ray analysis support this position.

There are rather significant differences between PPTA fibres and the aromatic copolyamide *Technora*® in terms of moisture absorption, permeability of small entities and the related mechanisms. The moisture absorption relative to the unit weight of fibre is about half for the latter (2% *vs* 4–6% for para-aramids), which Ozawa and Matsuda[16] explain by the density of the hydrophilic amide groups at the surface and the degree of crystallinity. This further supports the observed difference in terms of chemical resistance and higher fatigue performance of the copolyamide fibre, whose level of chain extension and orientation caused by the super-drawing tends to retard the migration of small molecules, contributing to a higher apparent chemical resistance. Additional studies regarding the moisture transport phenomena and aqueous accessibility of PPTA crystallites are available.[27,85] These all tend to support and complement, using different approaches, the structure and mechanical properties described previously.

The stiffness of the PPTA chain is partly associated with the limited rotation of the carbon–nitrogen bond, itself due to the resonance-conjugation existing between the amide and the aromatic groups. This situation does not exist in the case of the meta configuration of the *Nomex*® fibre; therefore the fibre is white in contrast to the golden yellow colour of the para-aramid. The *Technora*® copolyamide, with a meta and a para molecular configuration, presents a golden brown coloration. The conjugated patterns provide a predominantly double bond character to the carbon–nitrogen liaison in the para-configuration, whose rotational energy is approximately ten fold greater than for a single bond.

2.4.5 A selection of observed mechanical properties

Typical stress–strain curves of different *Kevlar*® fibres are provided in Fig. 2.11(a), which clearly outlines the modulus increase from *Kevlar*® *29* to



2.11 Typical stress–strain curves of: (a) *Kevlar* fibres; (b) other commercially representative industrial yarns.

Kevlar® 149. The respective moduli, brought by various spinning conditions and post-treatments performed on para-aramid precursors, are generally considered as intermediate between those of graphite, boron and glass fibres. The typical linear stress–strain behaviour of para-aramids is typical compared to most man-made fibres, whose tensile behaviours are depicted in Fig. 2.11(b).

Creep is measured either by the length variation under tension or by the stress decrease at constant gauge length. Para-aramids, which exhibit little creep, differ significantly from other highly oriented polymeric fibres, such as HMPE fibres, which can break after several days under intermediate load due to their high creep properties associated with a stress slip of molecules (compared to a structure-tightening in the case of para-aramids). Creep is affected by the temperature, the load relative to the fibre ultimate strength, the water content and other parameters. There are differences between *Kevlar® 49* and *Kevlar® 29*. The latter tends to show no dependency of the creep amplitude as a function of temperature and load if the load is below 50% of the fibre breaking strength.

Compressive and shear properties tend to relate very well with the degree of axial orientation and radial intermolecular bonding. It is therefore not too surprising to find that HMPE fibres have been reported[70] to exhibit lower compressive yield stresses than para-aramids. Sikkema[86] gave a compressive strength of 0.6 GPa for the *Twaron®* fibres, which is about one-fifth of the tensile strength mentioned by Yang.[11] Greater than those of conventional man-made fibres, the shear moduli of para-aramids are lower than

Table 2.3 Properties of commercially representative reinforcement fibres*

Material	Density (g/m^3)	Decomposition melt (°C)	Tenacity (mN/tex)	Initial modulus (N/tex)
Para-aramid standard	1.44	550	2065	55
Para-aramid high-modulus	1.45	550	2090	77
Nomex®	1.46	415	485	7.5
Technora®	1.39	500	2200	50.3
PA 66	1.14	255	830	5
Steel cord	7.85	1600	330	20
Carbon HT	1.78	3700	1910	134
Carbon HM	1.83	3700	1230	256
E-Glass	2.58	825	780	28

* From the manufacturers' leaflets and references.[3,15,16,87]

their compressive moduli, which to a certain extent is due to the degree of anisotropy of their radial structure.

Like other polymers, aromatic polyamides are sensitive to radiations,[11,87] especially in the range between about 300 (nm) and 450 (nm). For outdoor applications proper protection from these radiations is necessary to maintain good mechanical properties.

The preceding discussions of structural and mechanical relationships provide a more precise and complete picture of the properties of the related polymers. Of the very large number of reports on the subject, general tendencies are broadly, although not unanimously, accepted amongst scientists. This situation is largely favourable to fruitful scientific debates, which support the uniqueness of the aromatic polyamides. One may see an opportunity, as a future direction, for translating this immense knowledge into end-use science that could help the fundamental understanding of the design parameters and the properties of items manufactured from these polymers in various forms. In order to offer comparative basic data, some of the most frequently encountered materials used in advanced technologies are compared in Table 2.3.

2.5 Applications

2.5.1 Systems engineering

The previous section of this chapter illustrated the role of molecular chain extension, orientation and structure in the fibre characteristics. The transition from the chemical structure to a physical structure, such as a polymer, can be considered as being part of *molecular engineering* as described by

Tanner *et al.*[7] A further step is the transition from the given physical structure to a product form, such as a fibre, and can be defined as part of *process engineering*. A later step encompasses the integration of the product, such as the aramid fibre, into an advanced structure or an advanced technology, which according to the definition of Tanner *et al.*[7] is part of *system engineering*.

The present section takes into consideration a selected, mostly commercially dominant, range of applications of the aramids with an attempt to emphasize some of the system engineering aspects. This approach may provide not only a better understanding of the major reasons for these fibres contributing to the best balanced performance of the system, but also may stimulate new ideas in the way these fibres are used in the considered system or how they could be used in a new one. As an example, the understanding of how a para-aramid fibre can be shaped into an optimised fabric pattern to resist a fragment impact, can provoke new ideas regarding the engineering of these fibres to offer cut and heat protection in other sectors, where the kinetics may be much closer to static conditions.

This is a system approach, which forces clarity of rationale to utilise the advantageous properties of the fibre. These can be used to minimise the effect of some features of the fibre, as well as finding possible synergistic combinations of properties of the other system components. Such approaches have led to the development of some of the aramid fibre applications to be outlined in this section, illustrated in Table 2.4.[87]

2.5.2 Ballistic and life protection

The dynamic mechanical properties of the aromatic polyamide fibres, as well as their viscoelastic behaviour, which can be tailored via suitable resin reinforcement, are perfectly adapted to their use in impact-resistant systems for low or high velocities. As early as the 1970s, this opportunity was rapidly recognised and translated into concrete applications such as protecting the lives of military personnel and then of civilians, and the protection of vital strategic equipment.

This type of application implies the use of a fairly large variety of materials, reinforced or not, in various forms, exposed to a fairly wide range of threats with different geometrical shapes being directed at the target, with variable dynamic impact profiles in terms of energy and velocity.

The diversity of components and parameters renders the task of the scientists, the designers and the engineers extremely complex and furthermore, multidisciplinary. Rather than giving descriptive detail regarding how aramids are used in this area, we want to pursue a more scientific approach, favouring the comprehension of some selected physical phenomena related to the fibre structure–property relationships and the dynamics involved. Therefore, our approach does not pretend to be exhaustive but should

Table 2.4 Aramid market segments and key attributes[87]

End-use	End-use systems	Key attributes
Composites	Fabrics for aircraft & containers Pressure vessels Ship building Sport goods Plastics additive Civil engineering	Light weight High strength High modulus Good impact strength Wear resistance
Protective apparels	Heat resistance workwear Fire blankets Flame retardant textiles Cut protective gloves Cut protective seat cover layers	Heat resistance Flame retardation Cut resistance
Tyres	Truck and aircraft tyres High speed tyres Motorcycle tyres Bicycle tyres	Low density Weight saving High tenacity Dimensional stability Low shrinkage Puncture resistance
Mechanical rubber goods	Conveyor belts Transmission belts Hoses for automotive Hydraulic hoses Hoses in off-shore Umbilicals	High strength High modulus Dimensional stability Thermal resistance Chemical resistance
Friction products and gaskets	Brake linings Clutch facings Gaskets Thixotropic additive Industrial paper	Fibre fibrillation Heat resistance Chemical resistance Low flammability Mechanical performance
Ropes and cables	Aerial optical fibre cable Traditional optical fibre cable Electrocable Mechanical construction cable Mooring ropes	High strength High modulus Dimensional stability Low density Corrosion resistance Good dielectric properties Heat resistance
Life protection	Bullet proof vests Helmets Property protection panels Vehicle protection Strategic equipment shielding	High tenacity High energy dissipation Low density and weight reduction Comfort

stimulate a reflection mode rather than an empirical guessing methodology. One needs nonetheless, to remain humble in front of the enormous challenge, which is yet to be faced to enhance further the ever-evolving life protection requirements and associated fundamental understanding.

Armour systems are generally classified in two groups, that is, soft and quite rigid composite structures. For the sake of conciseness, associated with the risk of possibly oversimplifying, we propose a single approach to summarise the rather complex dynamics of ballistic impact and relevant fibre property relationships. The absorption of the kinetic energy of the projectile is related to the wave propagation, transversely and longitudinally, and the penetration stress/strain profile which largely depends on the frictional energy dissipation.

Although there exist separate basic concepts and approaches for fibre and textile fabrics, and their interpretation in the case of embedded textile and/or fibres, it is generally admitted that the crossover tightness for the textile, the delaminating effect obtainable by adhesion-tailoring in the composite armour, and the looseness of the yarn ends at the boundaries are key elements in terms of the wave propagation, both longitudinally and transversely. A simplified physical explanation relates to the reflection of the wave at the boundaries, which, if they are too tight or compact, tend to promote a series of multiple reverberations back to the impact region, amplifying the local stresses and further helping the projectile penetration.

For the textile designer and engineer there are some practical consequences that can be deduced from the above. As long as the reverberation effect can be optimised by means of uniform tension, fabric density and crossover compactness, one can consider that the number of overlapping entangled zones and the number of yarns are the key variables affecting the ballistic performance of the textile structure. As a point of reference, it is generally accepted that up to 50% of the impact energy can be absorbed through wave propagation in the secondary yarn networks, which are the ones neighbouring the fibre bundles directly impacted by the projectile.

Regarding the fibre, a dominating selection parameter lies with the fact that the velocity of the wave propagation is directly proportional to the square root of the modulus and inversely proportional to the square root of the fibre density. This, of course, is quite favourable to the aramid fibres in general since, as an example, the velocity of propagation in the para-aramids is about 8000 m/s, that is four folds higher than for nylon.[88] This relates directly to the volume of matter that can participate in the wave propagation and energy dissipation. In this example, up to four times the volume of para-aramid can be involved in this process compared to nylon. One can easily conceive that the trivial approach of energy potential, based on the stress–strain curve integral, is far underpredictive of such phenomena, especially in the case of nylon, which would be superior to the para-aramid if such a limited approach was used. This is, today, not even a matter of comparison since the aramids are predominantly used in ballistic protection.

Transverse and longitudinal wave propagations have common physics, although the former more directly affects the local deformation and penetration of the matter being impacted at the ballistic strain rate. A debate still prevails within the community of ballistic experts, associated physicists, mathematicians and more and more rheologists and tribologists. This debate lies in the necessity to associate a rate-dependent or independent effect in the analysis of the impact effectiveness. By rate-independent effect one has to understand that the fibrous structure would deform and respond to the impact variable rate of stress and strain as if the governing parameters were the ones corresponding to their static properties. One can easily agree with the fact that all materials, including fibres, exhibit rate-dependent properties. Then, should the dynamic viscoelastic properties of the fibre, and of its direct neighbouring environment, be taken into account? Undoubtedly, yes. To what extent? Attempts[89] have been reported and reveal extreme complexities in their interpretations. In this discussion, which may generate opportunities for fundamental understanding of end-use science programmes, it appears clear that high modulus fibres with oriented molecular structures, in which internal process stresses have been dissipated by relaxation and/or drawing with the minimum boundary stress gradients, are by far the ones least affected by variable strain rate. Nylons are known to have tensile properties that are highly dependent on strain rate. On the other side, a superior dynamic modulus, which may contribute to a higher wave propagation speed, is not by itself always the answer. The brittleness of carbon fibres is detrimental to their ballistic performance.

Finally, once the maximum energy allowable by a given structure has been extracted from the incoming projectile, there are still numerous aspects to be considered to assess the probability of total penetration. Among these, the deformation mode and the frictional characteristics of both the matter and the projectile itself have attracted the most attention. Beyond and during the initial contact, the protective layers deform, depending in part on their respective shapes and geometry. Here again, scenarios are multiple and one should not oversimplify. For example, the well-known deformation cones are rarely conical but pyramidal in the case of woven fabrics. This anisotropy has to be integrated right away at the design level and on assembly blueprints of the armour structure being developed. Similarly, idealised projectiles, mostly seen as blunt curve shapes, by definition, are too ideal and may be misleading in view of the more complex multifacetted shapes encountered.[90] Self-explanatory fracture descriptions, such as brittle, radial, fragmenting or spalling, plugging and petaling or the blends of, correspond to given modes of penetration, whose descriptions are beyond the scope of this study. In these later cases, more semi-empirical analyses based on fractals coupled with finite element computing are probably the most predictive and are of reasonable help in detecting the impact characteristics and their relationships with the armour system's strengths and weaknesses.

Prior to the eventual penetration of the impacting threat, and after the cone has been extended to its maximum strain, which is dictated by the fibre elongation and/or the fabric distortion and/or eventually the fibre-reinforced matrix delamination, the projectile further loses energy in order to surpass the boundary frictional forces at the fabric–projectile interface. Many components are to be considered in the frictional force balance, such as the impacting velocity and the morphology of the penetrating fragment or bullet, the fabric pattern and its volume density, the fibre surface characteristics, and the tribological properties of all these elements. Once the maximum energy dissipation has occurred, either the projectile energy has been overcome and the threat is stopped, or the projectile reaches the target if the residual kinetic energy is still sufficient. Of course, during this ballistic event considerable heat has been generated at the impact zone. In this case para-aramids are more suitable, owing to their intrinsic thermal resistance compared to fusible polymers such as nylon and polyethylene. Furthermore, the formation of a glassy layer associated with the polymer melting can facilitate penetration at lower speeds. Such aspects may put into the spotlight the advantages of certain categories of fibres that offer tremendous frictional resistance, such as the para-aramids, compared to others that may present better potential for wave propagation than for frictional dissipation, such as nylons.

For obvious reasons, the theoretical physics of a ballistic event can only be simplistic, regardless of the degree of mathematical sophistication brought into the modelling steps. Reality checks against well-designed experiments are more than recommended in view of the ever-growing complexity and changing nature of the ballistic threats and related dynamics. The rather well-known V50 ballistic velocity limit is accepted as the performance parameter. V50 is defined as the statistical minimum velocity at which 50% of the projectiles will pass through the tested structure while the other 50% will be stopped by this ballistic barrier. Three books[91–93] should be mentioned, to cover in more detail impact dynamics and penetration mechanics.

In concluding this section, one should note that para-aramids are quite suitable in this domain of application where, for a number of years, multilayered jackets have been produced and successfully used, saving numerous lives. Helmets, tank panels and other military devices are reinforced with para-aramids, which have also been the fibres of choice in these applications for several decades.

2.5.3 Protective clothing with a focus on fire protection

It is well established that aramid polymers, particularly meta-aramids, exhibit high temperature resistance and stability. This gave a strong incentive to develop these materials for specific industrial heat-resistant applications. Poly-m-phenyleneisophthalamide (*Nomex*®) was the first aramid fibre developed with good thermal stability at exposure temperatures as high as 500 °C, and long-term stability in environmental temperatures as high as 220 °C.

One of the attributes among these that has further promoted this type of application is associated with a peculiar physical behaviour initially described by Tanner *et al.*[7] as follows. When meta-aramid fabrics are rapidly heated in a flash fire, the vaporised moisture and degradation gases expand the 'softened' polymer. This expanded material forms a carbonaceous insulating foam up to ten times the thickness of the original layer. When the flame is removed from the fibre, it self-extinguishes. Initially, these fibres seemed ideal for use in clothing, which can benefit from this intumescence. However, extensive studies showed that the fibre would shrink when heated to temperatures above its glass-transition threshold, causing tearing. This would expose the wearer to direct flames, leading to serious injuries. Further work led to the development of a material using intimate staple blends of the meta-aramid fibre *Nomex*® with the para-aramid *Kevlar*®. The para-aramid fibre maintains a strong structural integrity while the meta-aramid provides the insulating, foam-like barrier, which also contributes to the stress translation of the reinforcing network.

A specific piece of equipment, the *Thermoman*® (Thermoman is a DuPont Registered Trademark), initially developed for this very purpose and now more widely used for protective clothing flame-resistance testing, has been and remains very instrumental to the evaluation of newly engineered blends and designs. The corresponding instrumented *Thermoman*® manikin is equipped with a large number of thermo-sensors (>100) connected to a computer that delivers a comprehensive mapping of the burn level profiles, outlining the sensitive zones which can then be further engineered to meet more and more stringent specifications. This type of technology has found uses for *Nomex*®, *Kevlar*® and 'spunnized' yarns of *Technora*® in protective garments such as flight and industrial coveralls, fire fighters' turnout coats, and welders and race car drivers' apparel.

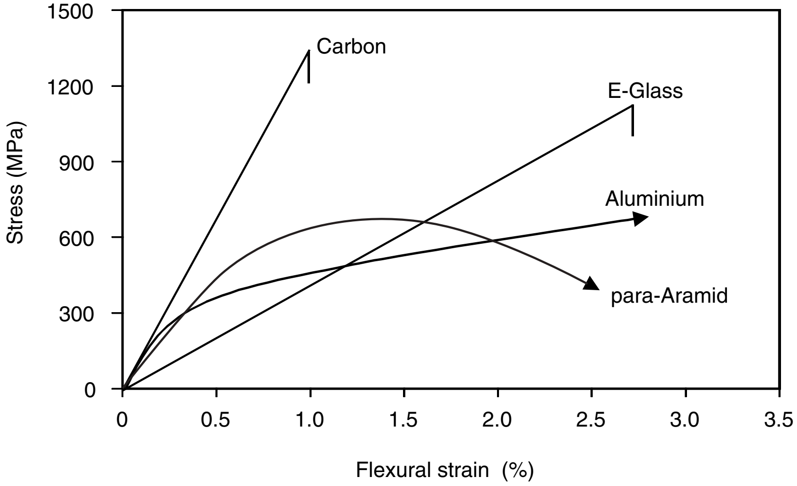
Hand injuries count heavily in the safety statistics. Metal-sheet forming, glass manufacturing and handling, and food processing are but a few areas where hand protection is a standard. Formerly made of cotton, synthetic commodity fibres, metal and other basic materials, gloves are now more and more manufactured from aramids, mostly para-aramid, either alone or in blends. The advantages are several, including the cut and puncture resistance through adequate coating, the abrasion resistance, the inherent thermal and insulating properties against heat and cold, and the tremendous weight saving which is part of better comfort properties. In this application area, the synergism gain from the association of various materials is a typical system engineering approach where the benefits are highly visible. A mitt designed for high-temperature protection is made of multiple layers, such as a para-aramid in knitted or woven form as a framework, an aluminium reflective foil and a meta-aramid or fibreglass woven or felt. The best balance of performance offered by the intrinsic properties of the aramids, as described in the more fundamental sections, can be reached without major compromise and most of the time with added comfort, associated with light weight and breathability of fibre structures, and dexterity.

2.5.4 Advanced composites

Advanced composites reinforced with aramid fibres have found significant applications in areas where the strength-to-weight and stiffness-to-weight ratio of these composites makes them more attractive for use than conventional materials such as aluminium and steel. This has been particularly evident where systems engineering has been used to incorporate fibres with high properties into structural components of aircraft. Not only must these components sustain the full spectrum of stresses and strains incurred in flight and remain structurally sound, they must also survive a catastrophic impact. Carbon fibres are not perfectly suitable since they are unyielding and undergo brittle fracture, despite their stiffness and compressive strength. This brittle behaviour is attributed to their rigid coplanar ring structure.

The usually expected significant reduction in composite compressive strength with the increase of the modulus has not been observed in para-aramid fibres.[94] Such fibres in a resin mix have structural features that provide excellent damage tolerance. Under compressive strain (0.5%), para-aramid molecules tend to buckle rather than fracture. This is, in part, due to the molecular rotation of the amide carbon-to-nitrogen bonds, which allows configurational changes without resulting in bond cleavage.[8,9] Consequently, although damaged, the structure will continue to sustain a load and the material collapses accordion-like upon stress. This material ductility compared to carbon fibre materials can be illustrated by the flexural stress–strain behaviour of unidirectional epoxy material composites and of aluminium; this is illustrated in Fig. 2.12.

These considerations have brought about the development of hybrid composites of para-aramid and carbon fibre that are used in commercial airliners and helicopters today. The more favourable strength-to-weight

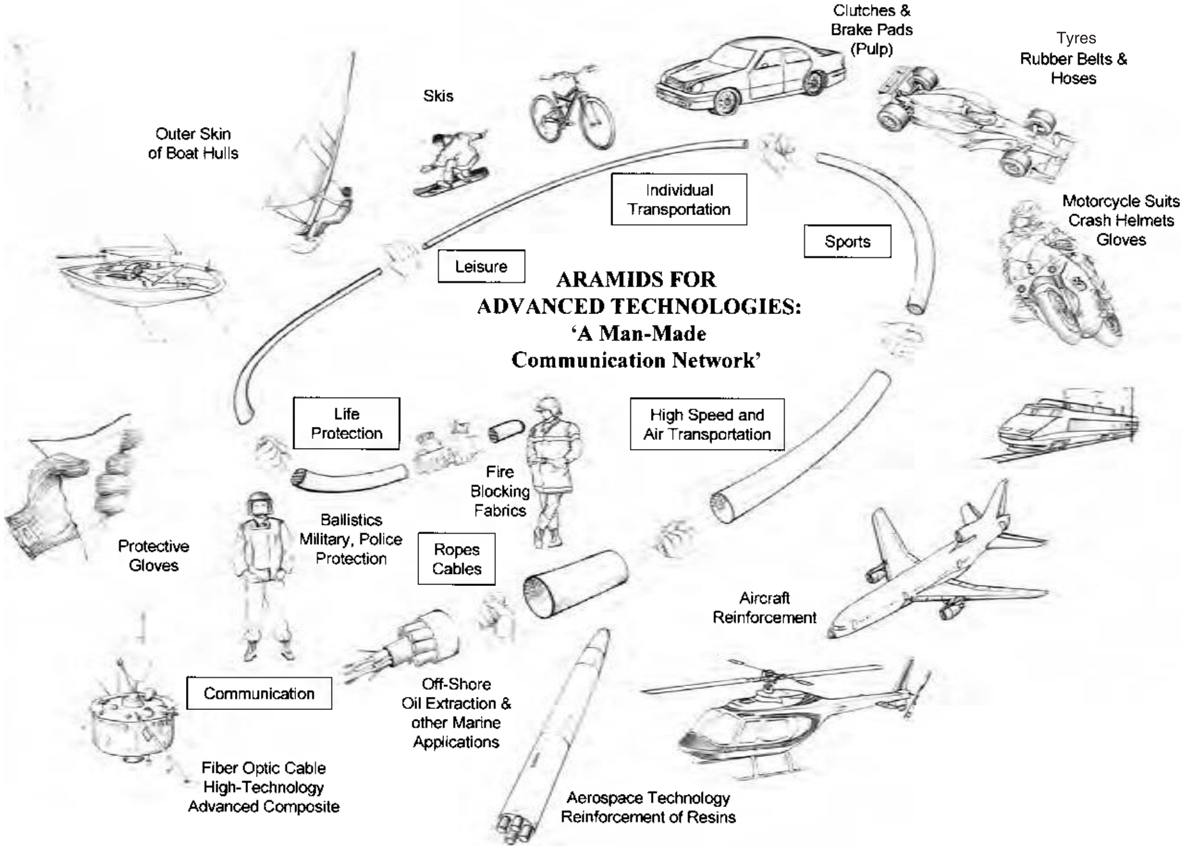


2.12 **Stress–strain behaviour for unidirectional reinforced epoxy matrix composites.**

ratio of *Kevlar® 49*/epoxy composite is the key reason for their use in floorings, doors fairings and radomes for airliners. Filament-wound pressure vessels developed using *Kevlar® 49* have been used to successfully contain high-pressure gases in space ships and aircraft. The flammability resistance is also of great obvious advantage for these applications.

2.5.5 Other important applications and future directions

There are several other end-use technologies where aramids have provided significant benefits. These are listed in Table 2.4,[87] which categorises most applications in seven classes outlining the key benefits for each. For the sake of uniformity we have adopted, after minor modifications, the well accepted classification described in the recent literature.[87] Notice that each specific advantageous property can be almost seamlessly related to the polymer or the fibre attributes that have been described before in other sections of this chapter. The system engineering approach, which we have attempted to illustrate with the selected end-use segments described earlier in this section, has been adopted in most cases given in Table 2.4 and can be revisited in the literature.[7,10,95] *Technora®* copolyamide fibre, to a lesser extent, is used in several applications listed in this table. The associated Fig. 2.13 provides a concrete illustration of the 'man-made' dynamic network established since the inception of the aramids. This network outlines the dynamic integration of aramids in advanced and modern technologies, with constant adaptation to the new challenges associated with various



2.13 Applications of para-aramid fibres.

generations of product. There are end-use market segments that have been rethought because of the aramids, such as the replacement of asbestos by para-aramid pulps. There are other areas that will continue to evolve because of the ever-growing stringent requirements for energy saving in transportation for example. The aramid contribution in this sector is outstanding. Clearly, communications, including transportation as well as transmission, leisure and sports, life protection, and health and safety in general, have been tremendously improved and adapted to modern technologies in part because of the aramids. The present chapter has brought, hopefully, a refreshing scientific description of state-of-the-art knowledge, with an effort to stimulate the desire to go beyond the knowledge and applications of today. There are properties of the aramids that can still be optimised via the system approach. These materials have the potential to participate in the solutions of tomorrow.

2.6 Acknowledgements

Special thanks are due to:

- S. R. Allen and V. Gabara for their useful suggestions.
- Nicolas Pont for the literature compilation.
- Benoît Steffenino for the data compilation, the chapter illustrations and for his contribution to the artistic interpretation of Fig. 2.13.

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