
Fibres from Extended Chain Aromatic Polyamides

E. E. Magat

Phil. Trans. R. Soc. Lond. A 1980 **294**, 463-472

doi: 10.1098/rsta.1980.0055

Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click [here](#)

To subscribe to *Phil. Trans. R. Soc. Lond. A* go to: <http://rsta.royalsocietypublishing.org/subscriptions>

Fibres from extended chain aromatic polyamides

BY E. E. MAGAT

Pioneering Research Laboratory, Textile Fibers Department, E.I. du Pont de Nemours & Company, Wilmington, Delaware 19898, U.S.A.

This paper covers some of the basic principles which have led to (1) discovery of liquid crystalline solutions of *para*-oriented aromatic polyamides, (2) direct spinning of these solutions to fibres with highly oriented extended chain configurations, and (3) realization of very high fibre tensile properties. Unusual characteristics of liquid crystalline solutions of aromatic polyamides are reviewed.

Kevlar aramid fibres are based on this type of technology. Fibres have tensile strengths of 2.8 GPa and moduli ranging from 65 to 126 GPa with elongations at rupture of from 4 to 2.5 % respectively. Some of the unique properties of Kevlar fibres are described.

What is the ultimate strength and stiffness of organic fibres? This is a question of long standing which has generated, and continues to generate, a great deal of discussion among polymer chemists and physicists. Many attempts have been made to predict limits of strength and stiffness of organic fibres. These attempts are based on applying bond strength concepts to organic polymers.

According to Mark & Tobolsky (1971), the maximum cohesive force in a polymer such as polyethylene would correspond to rupture of carbon–carbon bonds when all polyethylene chains are packed parallel to each other. Knowing the carbon–carbon bond dissociation energy and the crystal packing of polyethylene, one calculates a maximum strength of 250 grams force per denier (gf/denier)†. This maximum value would be realized only if packing of the molecules were completely uniform and regularly arranged without flaws or discontinuities. There are a number of reasons why these values have not been reached: (1) chains are not perfectly parallel to each other and do not break simultaneously over the same cross section; (2) imperfections in the structure and chain ends lead to stress concentration on a statistically favoured few chemical bonds which are then ruptured; this initial crack propagates catastrophically leading to fibre breakage; and (3) there is a high loss in strength from slippage of molecular chains or fibrils. Similarly, theoretical moduli have been calculated on the basis of force constants of bonds in the polymer chain and crystal lattice extensions observed by X-ray on stressed fibres (Treloar 1960; Fielding-Russell 1971).

According to these principles, the more tightly packed the polymer chains, the higher the theoretical strength and modulus. Calculated maximum strengths and moduli of typical fibres are shown in table 1.

One of the highest strength polyethylene fibres made was flash spun from a high molecular mass polymer in solution in a halogenated hydrocarbon to yield fibrillated yarns of 23 gf/denier

† 1 gf/denier = 0.088 Newton/tex = lbf in⁻²/12 800 × density (denier is the mass in grams of a 9000 metre length of one fibre; tex is the mass in grams per 1000 metres).

strength after drawing. While their tensile moduli were as high as 1000, these high tenacity-high modulus polyethylene fibres were not generally useful because of their low melting point and propensity to creep. Polyethylene fibres with tenacities as high as 44 gf/denier have been reported recently by A. J. Pennings (private communication), by a special growth technique from solution. Highest moduli reported for nylon 66 and polyethylene terephthalate fibre do not exceed 80 and 175, respectively.

TABLE 1. CALCULATED MAXIMUM STRENGTH AND MODULUS OF FIBRES†

	strength (gf/denier)	modulus (gf/denier)
polyethylene	250	2060
polyester (2G-T)	200	950
polyamide (66)	215	1780
<i>p</i> -oriented aromatic polyamide	165	1500

† Black, W. B. & Preston, J. 1973. *High modulus wholly aromatic fibers*. New York: Marcel Dekker.

Para-oriented aromatic polyamides provide the closest approach to theoretical property limits. Fibres have been prepared with tenacities exceeding 30 gf/denier and moduli as high as 1400.

From these considerations it becomes quite evident that to reach high strength and high stiffness one needs to extend polymer chains and pack them as tightly as possible. When chain extension is carried out during the fibre-forming process, relaxation of the extended chains just after extrusion, and before solidification and crystallization, must be overcome. When chain extension is effected on the spun fibre as in drawing, it is difficult to disentangle the chains and align them perfectly. For these reasons special techniques must be used, such as flash spinning, extruding below the melting point under high pressure and growing oriented fibrillar crystals from flowing solutions. All of these processes work best with a high molecular mass, linear, highly crystalline polymer such as polyethylene. These techniques cannot be used with rigid polymers such as aromatic polyamides for a number of reasons. These polymers melt at too great a temperature for melt spinning, and isotropic solutions are of such high viscosity as to make spinning difficult. Also, the high second order transition temperature of these fibres makes it difficult, if not impossible, to achieve good chain alignment by drawing.

Another approach was needed to prepare extended chain aromatic polyamide fibres. The new approach is based on the formation of liquid crystalline spinning solutions which inherently contain highly ordered domains consisting of extended polymer chains. This approach can lead to fibres which are spun directly in a highly oriented, chain extended form. These fibres are extremely strong as-spun and do not require drawing. Actually, one cannot draw them in the conventional sense of the word because polymer chains are already highly extended and oriented.

This approach originated when P. Morgan (of our Laboratory) published his book on *Condensation polymers: by interfacial and solution methods*. In 1965, he observed that no fibres had been reported from *para*-oriented aromatic polyamides. Polyamides from *p*-aminobenzoic acid and from *p*-phenylenediamine and terephthalic acid were reported to be too intractable to form fibres. At that time there was no experimental basis for predicting higher tenacity or higher modulus for *p*-oriented aromatic polyamides as compared to those oriented *meta*. There was no clear recognition in the literature of the possibility of preparing fibres with the modulus of glass from organic polymers.

Stephanie Kwolek, working with P. Morgan, was the first to find a spinning solvent for poly-*p*-benzamide (1,4B) and was able to dry-spin strong fibres from tetramethylurea–LiCl solutions (Kwolek *et al.* 1977). The as-spun fibres had a tenacity of 6 gf/denier and a modulus of 430, quite unusual properties for an undrawn fibre. Thus, for the first time the modulus of glass, which is 300 gf/denier, was clearly exceeded.

In the course of these experiments, Stephanie Kwolek made two important observations:

(1) The solutions of poly-*p*-benzamide in tetramethylurea–lithium chloride were fluid but hazy. The more they were stirred, the more opaque and pearlescent they became. Later work showed that this was the first observation of liquid crystalline solutions of synthetic linear chain extended polymers. Up to that time, only certain polypeptides existing in solutions as rigid helical structures had shown liquid crystalline behaviour.

(2) The fibres underwent a recrystallization on brief heat treatment at 500 °C, which was accompanied by a remarkable increase in tenacity and modulus. Tenacity increased from 6 to 9 gf/denier and modulus from 430 to 700 gf/denier or more than twice that of glass.

Compounds capable of forming liquid crystals have been known for some time. In the liquid crystalline state these compounds have the structure of solids and exhibit birefringence but at the same time they exhibit flow properties characteristic of liquids. For example, nematic liquid crystals are threadlike in order. They are most easily represented by a bunch of aligned pencils with random arrangement of their ends. One of the simplest examples of a material forming a liquid crystalline melt is an azobenzene with *p*-butoxy substituents. This compound is a solid up to 90 °C, where it becomes liquid crystalline, and maintains this state up to 150 °C. At higher temperatures it becomes an isotropic liquid.

Basic principles of liquid crystals have been extended to solutions of rigid molecules. In general, polymers in solution exist as random coils. On the other hand, if the polymers exist as rigid rods in solution, once the concentration reaches a certain level the molecules aggregate to form ordered domains. These domains are easily oriented by shear, magnetic fields or electric fields. Liquid crystalline polymer solutions, by virtue of the ordered domains, are optically anisotropic; they are therefore birefringent. When these liquid crystalline polymer solutions are extruded through a small spinneret hole, the extensional flow causes rotation and alignment of the domains, ultimately leading to excellent orientation of the polymer chains with very little shear. This provides a novel method of preparing oriented polymer molecules as compared to the traditional method of orienting fibres by drawing. One capitalizes on the inherent property of liquid crystalline solutions to form preordered domains which can be aligned with a minimum of energy.

These liquid crystalline solutions have a number of unusual characteristics which will be reviewed briefly: (1) theoretical basis for their existence, (2) typical phase diagram, (3) relaxation of oriented solutions, (4) solution viscosity against shear stress, (6) Mark–Houwink constant of polymers in solution.

A theoretical study dates back to 1956 when Flory (1956) predicted that phase separation in solutions of monodisperse rigid rods above a critical concentration could be expected; the concentration would, however, be highly dependent on the axis ratio of the rigid rods and solvent–solute interaction χ . Figure 1 shows his predicted phase diagram indicating phase changes as a function of concentration and the solvent–solute interaction parameter χ at an axis ratio of 100 (approximately equivalent to the molecular mass required to give good fibres from aromatic polyamides). At concentrations below *ca.* 10 % the solution is isotropic; there is a

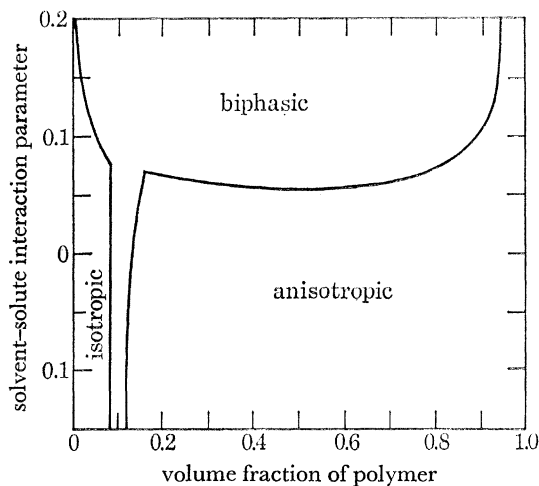


FIGURE 1. Phase diagram of monodisperse rigid rods (see Flory 1956).

narrow biphasic region spanning the 10–15% volume concentration region, and above *ca.* 15%, random arrangement of monodisperse rigid rods in solution becomes impossible and there is only an anisotropic phase.

p-Aromatic polyamides under certain specific conditions of concentration, type of solvent, molecular weight and temperature give liquid crystalline solutions. A typical phase diagram is shown in figure 2 as a function of polymer concentration and the concentration of lithium chloride in tetramethylurea. Conditions need to be quite specific to give a liquid crystalline or anisotropic state for these polydisperse systems.

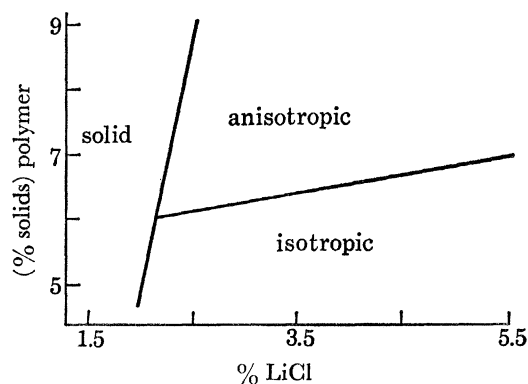


FIGURE 2. Phase diagram of poly-*p*-benzamide in tetramethylurea–LiCl solutions.

Another observation is that liquid crystalline solutions retain the high degree of orientation imparted in the spinning operation. Conventional polymers relax very rapidly and orientation imparted by spinning is lost before coagulation. Liquid crystalline solutions relax considerably more slowly. Thus, highly oriented as-spun fibres can be formed at very low spin-stretch factors.

Liquid crystalline polymer solutions exhibit an anomalous relationship between solution viscosity and polymer concentration. This is shown in figure 3. At first viscosity increases as the concentration increases as in any normal isotropic polymer solution. At the critical point an anisotropic, i.e., liquid crystalline phase, separates and as additional polymer is added, the bulk

viscosity drops. Continued addition and dissolution of polymer forces more polymer into the ordered phase. Liquid crystalline domains act almost like particulates which contribute little to solution viscosity. As the polymer solution concentration is increased, the proportion of liquid crystalline phase increases until a point is reached where the viscosity concentration curve once more assumes an upward trend.

Solution viscosity of liquid crystalline solutions shows non-Newtonian behaviour and a marked drop at two decades lower shear stress than polymer melts. This behaviour is ascribed to alignment of liquid crystal aggregates in shear fields.

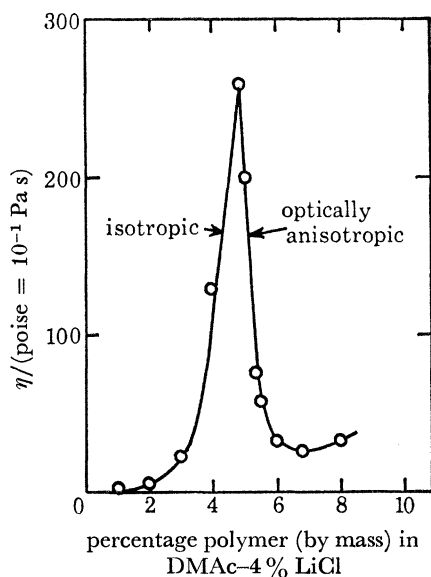


FIGURE 3

FIGURE 3. Critical concentration curve for poly(1, 4-benzamide), $\eta_{inh} = 2.41$.

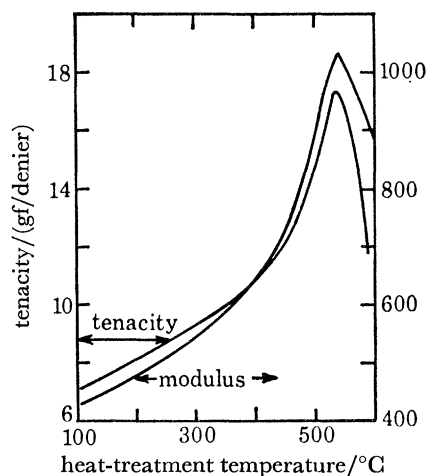


FIGURE 4

FIGURE 4. Effect of heat treatment on properties of poly(1, 4-benzamide) fibres.

Chain extension and rigidity of polymers giving anisotropic solutions is indicated by the high value ($\alpha > 1$) of the exponent in the Mark-Houwink relationship and in the high value of the persistence length in solution found by Arpin & Strazielle (1976).

As-spun fibres spun from aromatic polyamide liquid crystalline solutions undergo recrystallization on brief heat treatment at temperatures above 350 °C. This recrystallization which involves improved perfection of lateral order of polymer chains is accompanied by an increase in modulus and at times tenacity. Figure 4 shows the tenacity and modulus achieved with poly-*p*-benzamide fibres depending on the temperature of the heat treatment. Tenacities as high as 18 gf/denier can be achieved and moduli above 10^3 . With further development as-spun poly-*p*-benzamide fibres were prepared with $T/E/M = 12/7/450$ † which could be converted by heat treatment around 500 °C to $T/E/M = 20/2/1100$. These fibres were introduced to the trade as Fibre B and PRD-49 respectively. An intensive end-use programme was aimed at capitalizing on the unique properties of these fibres. Fibre B was soon found to be an excellent tyre yarn for belted tyres (Wilfong & Zimmerman 1973) (for the first time, an organic fibre could compete with glass and steel in these tyre constructions), and PRD-49 was an attractive candidate for reinforcement

† $T/E/M$ is tensile strength/elongation at fracture/Young modulus in units of gf/denier.

of resins. An initial concern was that these high modulus fibres would be stiff and brittle. Fortunately, this was not the case; the fibrillar structure of fibres spun from liquid crystalline solution imparts a high degree of flexibility.

Simultaneously with the development of Fibre B, we continued to search for other polymer structures giving liquid crystalline solutions. We found that *p*-oriented rigid diamines and dibasic acids generally lead to polyamides giving liquid crystalline solutions. Examples of such polyamide precursors are shown in figure 5.

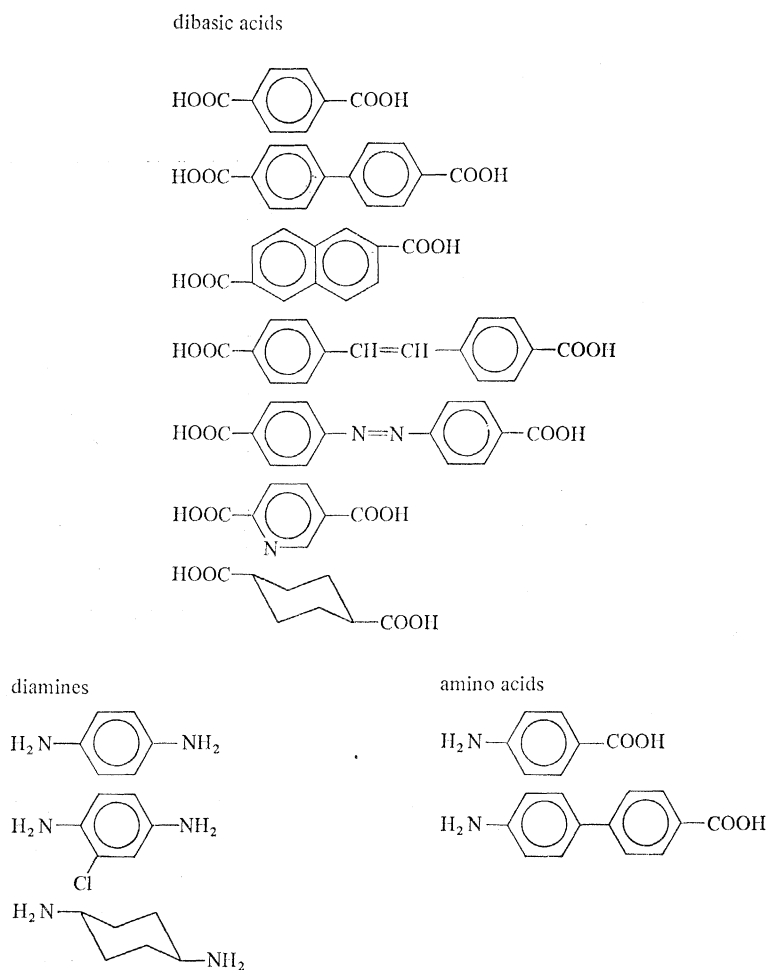


FIGURE 5. Polyamides yielding liquid crystalline solutions.

One of the most attractive polymers from this group is PPD-T, the polyamide based on *p*-phenylenediamine and terephthalic acid. None of the amide solvents was found to be useful for 1,4B dissolved PPD-T. A breakthrough came from the work of T. I. Bair (of our Laboratory) with the finding that a mixture of hexamethylphosphoramide and *N*-methylpyrrolidone with lithium chloride is an effective solvent both for the polymerization and also for spinning the polymer. A 6% solution of PPD-T in this solvent was anisotropic and upon wet spinning gave as-spun yarns approaching Fibre B in tensile properties. (Hexamethylphosphoramide has been found in laboratory experiments to be a carcinogen in rats. Proper precautions must be taken in handling this chemical.)

Continued search for solvents showed that liquid crystalline PPD-T solutions can be obtained in 100 % sulphuric acid at high enough solid concentrations and high inherent viscosities. Wet spinning again gave Fibre B-like properties.

Figure 6 shows a phase diagram of PPD-T of inherent viscosity 2.7 in sulphuric acid as a function of polymer concentration and sulphuric acid concentration. To achieve the anisotropic state a very specific sulphuric acid concentration must be used as well as a high solids concentration. Above 10 % solids, the viscosity becomes so high that it is difficult to prepare higher concentrations at room temperature.

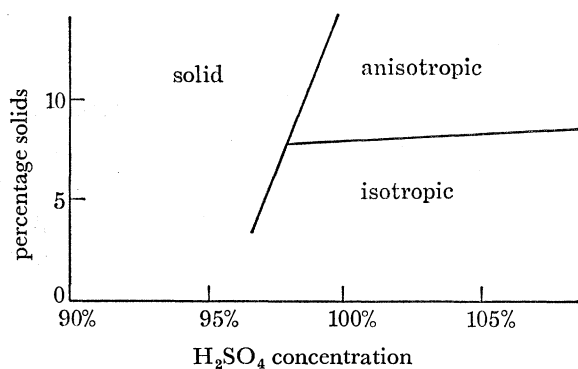


FIGURE 6

FIGURE 6. PPD-T/ H_2SO_4 phase diagram (PPD-T $\eta = 2.7$).

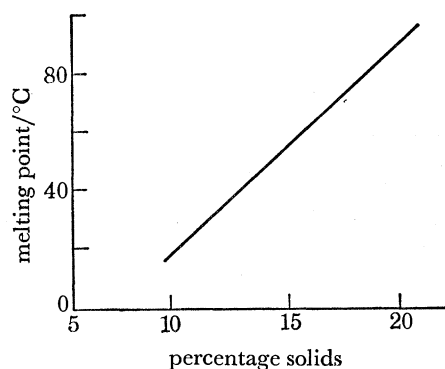


FIGURE 7

FIGURE 7. Effect of solids concentration on melting point of PPD-T/ H_2SO_4 solutions.

A further improvement in properties of PPD-T fibre came when H. Blades recognized that solutions above 10 % could not be made because higher solids solutions of PPD-T (over 12 %) melt above room temperature (figure 7). Thus, at 100 °C, 20 % PPD-T solutions in H_2SO_4 can be prepared. The viscosity against concentration is quite typical of liquid crystalline solutions. Solution viscosity starts to decrease beyond 10 % solids and reaches a minimum around 20 %.

Thus, one can spin directly by air gap spinning fibres with $T/E/M = 22/4/500$. X-ray orientation angles of these fibres can be as low as 13° as compared to 20° for Fibre B fibres spun from liquid crystalline amide solution.

Kevlar aramid fibres

With this background let us examine Kevlar aramid fibres and review their unique combinations of properties and some of their applications. Their most outstanding characteristic is high strength and modulus per unit mass. Kevlar has a resistance to creep like that of steel wire, quite unlike that of nylon or polyester fibres. It is inherently flame resistant, does not melt and has a wide range of utility from -200 to 250 °C.

We have made a thorough study of the structure of Kevlar by X-ray and electron diffraction and electron microscopy. We find that crystalline orientation in Kevlar fibres is not only parallel to the fibre axis, but that there is also a radial order. Certain crystal planes in Kevlar are oriented along the fibre radii, much like the spokes of a wheel.

Kevlar fibres have been engineered to provide an optimum balance of high tensile properties and end-use performance. They are available in three types (table 2), each designed for specific applications.

TABLE 2. KEVLAR ARAMID FIBRE TYPES

Kevlar	$T/E/M = 22/4/475$
tyres	
mechanical rubber goods	
Kevlar 29	$T/E/M = 22/4/500$
ropes and cables	
protective and ballistic fabrics	
coated fabrics	
Kevlar 49	$T/E/M = 22/2.5/970$
tensile strength = 400 000 p.s.i.	
modulus = 18 000 000 p.s.i.	
resin reinforcement	

Rubber reinforcement for tyres is the largest potential use for Kevlar. Stress-strain curves comparing Kevlar with existing tyre yarns are shown in figure 8. Kevlar, on a gf/denier basis, is twice as strong as any other tyre yarn and is five times as strong as steel at equal mass. Comparing Kevlar and steel at equal cross-sectional areas, the two fibres have equal strength but because of the fivefold difference in density, the Kevlar fibre has one-fifth the mass of steel.

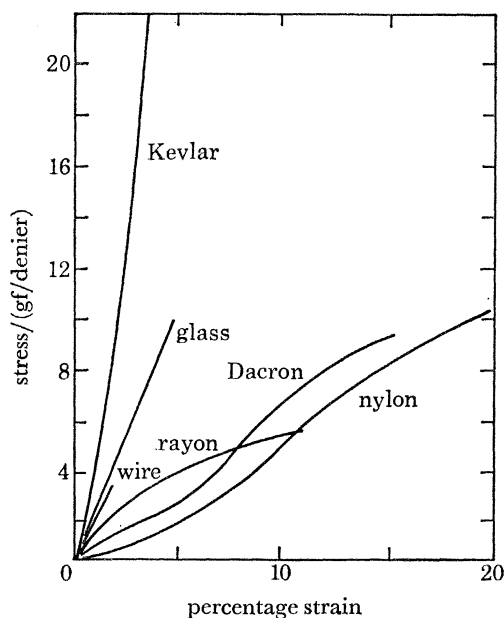


FIGURE 8. Yarn stress-strain curves.

Based on several years of testing, radial passenger tyres with belts of Kevlar at a 5/1 replacement ratio to steel have shown equal treadwear to steel tyres. They are superior to steel in road hazard resistance, higher speed capability and softer ride. Kevlar has been adopted in the United States as the premium passenger radial tyre fibre in a number of lines, including those of Goodyear and Sears.

Market opportunities for Kevlar have also emerged in an area broadly labelled 'mechanical rubber goods', which includes a wide variety of reinforced rubber or thermoplastic products, largely engineered around the properties of Kevlar. As an example, Kevlar is being used successfully in high tension conveyer belts for mining, where belts often are miles long.

Compared with steel, belts reinforced with Kevlar provide longer life because of improved flex fatigue and lighter mass which results in lower power requirements to drive the belt.

The second type of Kevlar is Kevlar 29. This is the yarn that goes into speciality uses such as ropes and cables, coated fabrics and protective ballistic fabrics. Ropes of Kevlar are available with almost 5×10^5 lb (2.27×10^5 kg) break strength. Currently, 1.7 lb/ft (2.53 kg/m) ropes of Kevlar 29 are being tested in the anchor system of an oil drill ship in the Gulf of Suez to replace a 7.4 lb/ft (11.01 kg/m) steel wire rope. Inflatable boats made of urethane-coated Kevlar have higher puncture and tear resistance, making them much more reliable for heavy duty uses such as white water running. One of the most publicized applications of Kevlar 29 recently has been for ballistic protection. Vests of Kevlar have already saved the lives of many law enforcement officers.

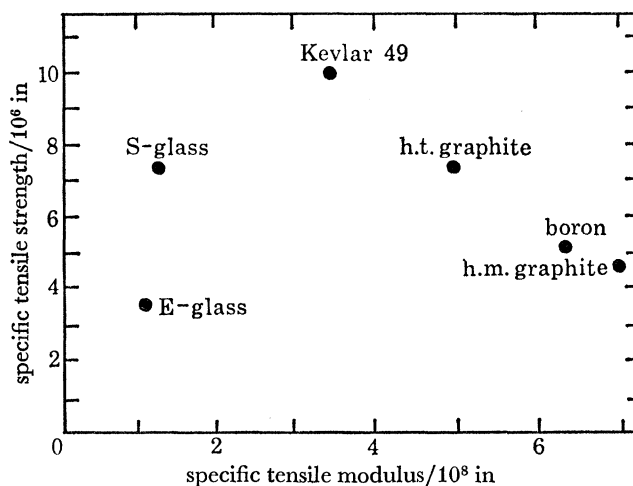


FIGURE 9. Specific tensile strength and modulus of reinforcing fibres.

Fabrics of Kevlar are also very hard to cut. This liability has been turned into an asset and is the basis of new highly successful protective garments such as work gloves. This concept has been adapted to stylish protective motorcycle apparel which gives far superior protection than leather.

Beyond Kevlar for tyres and Kevlar 29 for speciality uses, a third type is being offered as Kevlar 49. Kevlar 49 has twice the modulus of Kevlar and Kevlar 29. Specific tensile strength and modulus of Kevlar 49 are compared to other reinforcing fibres such as glass, graphite and boron in figure 9. Kevlar 49 has the highest strength/mass ratio of any existing commercial fibre and is outstanding for reinforcing resins to give strong and rigid, yet low density, composites. While Kevlar 49 fibres have high tensile properties, their compressive strength is only moderate. As a result, composites of Kevlar 49 are not used in primary load bearing structures. Compression failure is manifested by formation of kink bands at an angle of about 60° from the fibre axis, which may reflect buckling of fibrils.

In uses where compressive strength is important, hybrids with graphite and other inorganic fibres show an attractive balance of fracture toughness, stiffness and compressive strength. Kevlar competes successfully with glass in composites where mass savings provide a strong economic and performance advantage. For example, Kevlar 49 is being used in boats ranging in size from canoes to ocean racing boats. Racing kayaks and canoes built with Kevlar 49 have

won major international races in the past few years. Kevlar 49 brings a high degree of flexibility to the design of new small class sailboats as well as high powered ocean racing motor boats. In these marine applications, Kevlar provides high strength, resistance to damage and structural rigidity with the added advantage of significantly lighter weight than glass. The same principle has been applied in the use of Kevlar 49 as the structural reinforcing member for filament wound pressure vessels and as reinforced laminates in non-structural and semi-structural parts for commercial aircraft such as the Lockheed L-1011, de Havilland DHC-7, and Canadian Challenger. Weight savings which are of prime importance are of the order of 25–40 % over glass.

This paper covers some of the basic principles which have led to (1) the discovery of liquid crystalline solutions of aromatic polyamides, (2) direct spinning of these solutions to fibres with highly oriented extended chain configurations, and (3) realization of very high fibre tensile properties.

Kevlar has been established in the trade on a commercial scale as a new and superior product in tyres, mechanical rubber goods, and other special products, including composites. As supply of this product increases, we will see further penetration into these markets, and the development of additional end-uses for this new, unique fibre.

REFERENCES (Magat)

- Arpin, M. & Strazielle, C. 1976 *Makromol. Chem.* **177**, 581.
Fielding-Russell, G. S. 1971 *Text. Res. J.* **41**, 861.
Flory, P. J. 1956 *Proc. R. Soc. Lond. A* **234**, 73.
Kwolek, S. L., Morgan, P. W., Schaefergen, J. R. & Gulrich, L. W. 1977 *Macromolecules* **10**, 1390.
Mark, H. & Tobolsky, A. V. 1971 *Polymer science and materials*, ch. 11. New York: Wiley-Interscience.
Treloar, L. R. G. 1960 *Polymer* **1**, 95, 290, 270.
Wilfong, R. E. & Zimmerman, J. 1973 *J. appl. Polymer Sci.* **17**, 2039.