The Unique Story of a High-Tech Polymer

Panchanan Pramanik and Ruby Chakraborty

Man has always dreamt of making a strong, diamond-like fiber. The hardness of diamond is due to its unique structure with only C-C single bonds. It is presumed that long straight chain of C-C bonds may produce the fiber which could have super-strength. Most polymers, due to random orientation of the back-bone chain, produce fibers of weak strength. It is realized from molecular modeling that rigidity of the chain may introduce the directional orientation. The invention of textile fibers such as nylon was aimed at producing super-fibers having outstanding mechanical properties. The initial thrust was to develop fibers with the heat-resistance of asbestos and the stiffness of glass. Molecular modeling indicated that stiff aromatic polyamides could be the suitable materials. But their extreme insolubility and intractability baffled the researchers.

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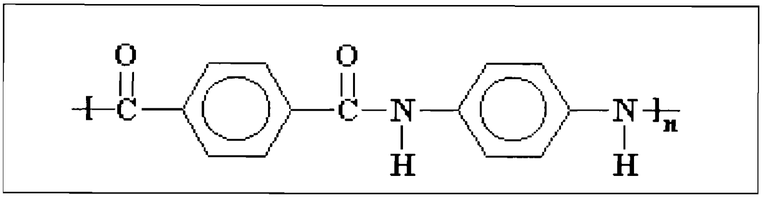
The story of Kevlar provides an excellent example of innovation through molecular engineering needed by modern technologies. Fibers of Kevlar, an aromatic polyamide, consist of long molecular chains produced from poly-paraphenylene terephthalamide. The amide groups in Kevlar are separated by para-phenylene groups, that is, they are attached to the phenyl rings at carbons 1 and 4. The chains are highly oriented with strong inter-chain bonding which results in a unique combination of properties. Kevlar para-aramid fiber possesses a remarkable combination of properties that has led to its adoption in a variety of end-uses since its commercial introduction in the early 1970's.

Keywords
Kevlar, polyamide, terephthalic acid, para-phenylenediamine.

The whole process started in 1960s and by 1982 full commercialization was reached. Several reality gaps and tough hurdles were encountered during the period from discovery to full commercialization. In 1965 a breakthrough was achieved by Stephanic Kwolek of Du-Pont [1] who found that para-amino benzoic

In Kevlar the aromatic groups are all linked into the backbone chain through the 1 and 4 positions called para-linkage.



acid could be polymerized and solubilized under special conditions to yield a rigid rod spinnable polymer. When the polymer solution was first made, it was believed that solution would not spin into fibers after observing the opacity of the solution and its inability of clarification by heating or filtration. It was expected that some inert matter would be in dispersed phase in spin dope that could plug spinneret holes. But when it was extruded through spinneret, it spun well. It was found that opacity was due to the formation of polymer liquid crystals, which had never been prepared before.

The liquid crystal is a material, which has properties in between liquid and solid state with respect to crystal structure. Liquid state has short-range order and long-range disorder, whereas solid has short and long-range orders. When the molecular arrangement is in between the two states then it is called liquid crystal. Heat or solvent may bring about liquid crystal formation. When solvent produces liquid crystal it is called lyotropic.

It is well understood that the behavior of rigid and flexible molecules is different. Flexible molecules such as nylon in dilute solution have low levels of entanglement. But in concentrated solution the random coils become highly entangled so that spinning and drawing leads to only partially extended chains. Hence properties such as tenacity and modulus attain only a small fraction of the theoretical value.

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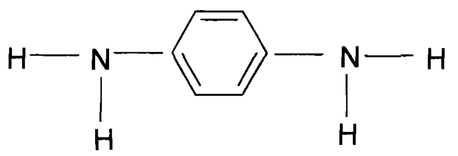
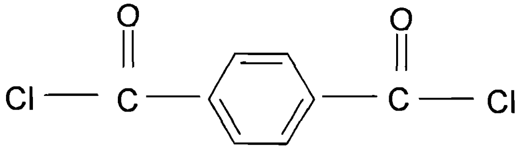
Rigid molecules like para-aramids cannot form random coils when their solutions are concentrated, because their movement is restricted. They have rod-like structure with poor flexibility. So at a critical concentration, they cannot populate the solution randomly. Under such a condition, for packing more molecules within the solvent, they are forced to align parallel to each other



1, 4-Phenylenediamine



Terephthaloyl chloride (para substituted)

[2,3]. Due to the shear force in spinneret capillary, the liquid crystalline phase orients in the direction of deformation leading to fully extended chains of fibers with high strength.

The first reality gap was encountered in scaling up, because of the high cost of para-amino benzoic acid. Efforts were made to understand better the liquid crystalline polymer solutions, and to identify a rigid-rod polymer system having lower cost. As a result, varieties of rigid polymers with potential of liquid crystalline spinning solutions were developed to produce super strong stiff fibers. The best materials were based on the liquid crystalline polymer produced from p-phenylene diamine and terephthalic acid (PPD-T). The advantages were low cost, high symmetry in molecular structure and high stiffness compared to other similar systems.

The best solvent for optimum spinning was found to be 100% sulfuric acid and the resulting spin dopes were very viscous. This gave rise to low spinning speeds which were needed for good mechanical properties of fiber [4,5].The process was not practical even though the ingredients were of low cost and the product properties were good. Some of the problems were:

- Spinning solvent (H_2SO_4) was unconventional and highly corrosive.
- The yield and throughput were very low.
- Investment was very high.

To overcome these hurdles, a major improvement was introduced by the discovery by Herbert Blades [6,7] of the crystalline complex of PPD-T and sulfuric acid at a polymer concentration

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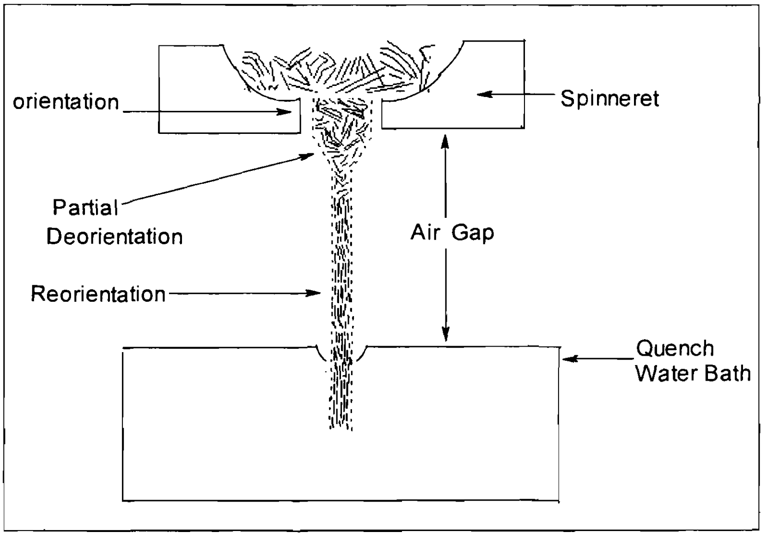

of 20% as compared to the previous concentration of 10-12%. It was developed by heating the polymer solution containing 100% sulfuric acid. This complex melts at around 70° C and is composed of 1 mole of PPD-T and 10 moles of sulfuric acid. Melting and freezing are reversible and reproducible. This enabled spinning at much higher polymer concentrations than was previously possible.

Simultaneously, Herbert Blades developed a spinning process that used an air-gap between the spinneret face and the quench bath. The process of spinning the melt of PPD-T/ sulfuric acid through the air gap into cold water introduced a very high spinning speed, improving the yield per unit time. Although deorientation occurred as the polymer solution emerged from the spinneret, the very high extensional shear in the air gap resulted in extraordinary re-orientation and the tensile properties of the final spun fibers were excellent. This process was economical and worthy of scale-up.

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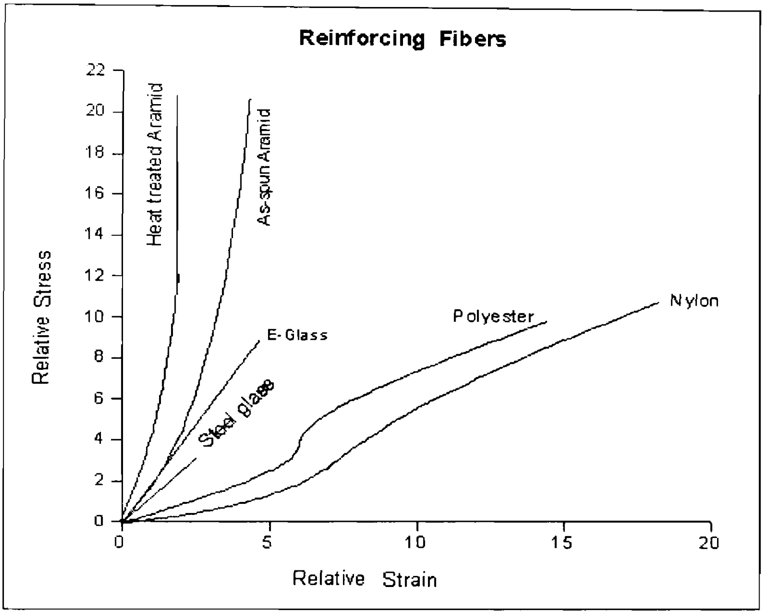
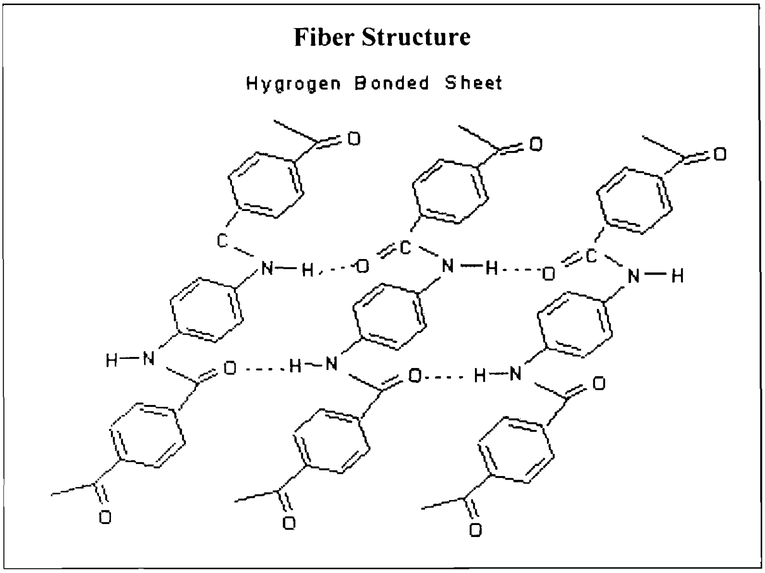
It is well understood that the microstructure of Kevlar is the main reason for its outstanding properties. Kevlar is a highly crystalline material and forms hydrogen bonded sheet-like structure. The sheets stack together radially [8], as determined by wide-angle X-ray diffraction studies. This type of radial crystal-



line order is characteristic of para-aramids spun using air gap process.

The next reality gap was met in an effort to move the process from a laboratory scale to large-scale production. The ingredients were corrosive, polymerization solvent was extremely toxic, and there were environmental concerns of waste disposal.



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The spinning solution was based on the complex containing 5 moles of sulfuric acid per mole of PPD-T amide bond. The problem was to dispose the spent acid after spinning.

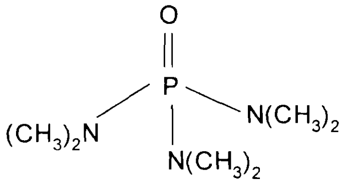
The best method found was to convert sulfuric acid into calcium sulfate (gypsum). Every pound of fiber generated 7 pounds of gypsum. Pure crystalline gypsum is useful in the manufacture of cement and wallboards.

The spinning solvent was sulfuric acid and the polymerization solvent was hexamethylphosphoramide (HMPA). The toxicity of HMPA posed a serious hurdle in the process of scale-up. Experimental results proved it to be carcinogenic for animals [9]. For ensuring the protection of workers, community and customers, efforts were made to find a replacement for HMPA. The combination of N-methylpyrrolidone (NMP) and calcium chloride was selected as the solvent for polymerization This approach provided a less toxic alternative and at the same time was capable of producing polymers with high inherent viscosity.

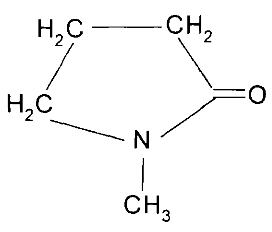
However, one drawback was that the polymer from the NMP approach did not yield the same high tenacity fibers that the polymer from HMPA did, despite their similar inherent viscosities. The problem turned out to be related to the molecular distribution. The number average molecular weight of polymer in NMP/$CaCl_2$ system was lower than in HMPA system. It was due to the presence of a large number of low molecular weight

Polymerization Solvents

Hexametylphosphoramide(HMPA)



N-Methylpyrrolidone(NMP)/$CaCl_2$



Performance apparel	Hunting chaps, gaiters and pants; high performance outerwear; motorcycle apparel; sailing outerwear
Adhesives and sealants	Thixotropes
Ballistics and defense	Anti-mine boots; gloves–cut resistant (police and military); composite helmets; vests–bullet and fragmentation
Belts and hoses	Automotive heating/cooling systems; automotive and industrial hoses; automotive and industrial synchronous and power transmission belts
Composites	Aircraft structural body parts and cabin panels; boats; sporting goods
Fiber-optic and electro-mechanical cables	Communication and data transmission cables; ignition wires; submarine, aerostat and robotic tethers
Friction products and gaskets	Asbestos replacement; automotive and industrial gaskets for high-pressure and high-temperature environments; brake pads; clutch linings
Protective apparel	Boots; chainsaw chaps; cut resistant industrial gloves; helmets–firefighter and consumer (bicycle); thermal and cut-protective aprons, sleeves, etc.
Tires	Aircraft; automobiles; off-road; race; trucks
Ropes and cables	Antennae guide wires; fish line; industrial and marine utility ropes; lifting slings; emergency tow lines; netting and webbing; pull tabs

Table 1.

fraction in NMP/$CaCl_2$ system. This resulted from the precipitation of oligomers from polymerization mixtures. This did not happen in HMPA due to its superior solvent power. This problem was solved by developing a reactor system to prevent earlier nucleation and precipitation of low molecular weight polymers.

Kevlar has a great commercial success for its wide application in various high-tech applications. A broad range of applications are listed in *Table* 1.

Some of the interesting specialized applications are as follows:

- Ropes that secure the airbags in the crucial landing apparatus of the Pathfinder.
- Small-diameter, lightweight ropes that hold 22,000 pounds and help moor the largest US Navy vessels.

- Shrapnel-resistant shielding in jet aircraft engines that will protect passengers in case of an explosion.
- Run-flat tires that allow for greater safety because they will not ruin the rim when driving to the nearest assistance.
- Gloves that protect hands and fingers against cuts, slashes and other injuries that often occur in glass and sheet metal factories.
- Kayaks that provide better impact resistance with no extra weight.
- Strong, lightweight skis, helmets and racquets that help lessen fatigue and boost exhilaration.

The importance of Kevlar in making ropes and cables is its high strength per unit weight, inherent low elongation and low creep. In air, its specific strength is 7 times that of steel and in seawater, the specific strength is more than 20 times that of steel. So one can use thinner and lighter ropes making it easier to handle.

Riser-tensioner line is an excellent example of its application. These lines are used in floating offshore oil drilling platforms. The purpose of riser-tensioner line is to keep the riser pipe or outer drill casing at a constant elevation and under uniform tension while the vessel surges with the waves. System technology designed a specially engineered rope to reduce internal stresses to increase wear life. These were made of 44mm diameter steel ropes which experienced considerable cycling over pulleys as the platform moved.

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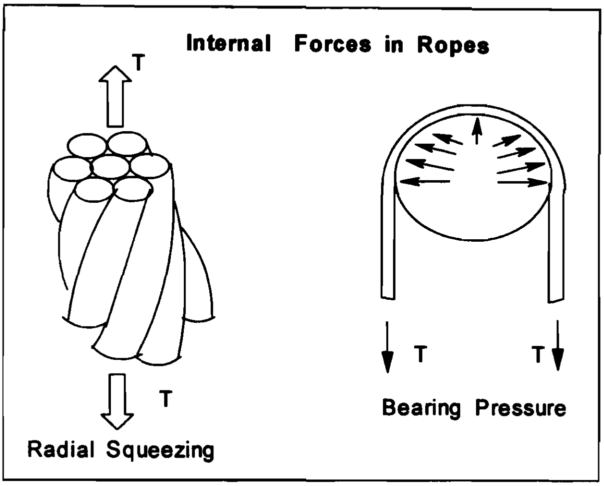
Laboratory experiments showed that small diameter ropes of Kevlar made in low twist stranded wire rope constructions could far surpass steel in cycling performance over pulleys. The experiment with a rope of 44 mm diameter surprisingly showed that the life-time of Kevlar surpassed that of steel only by 5-10%. Analysis showed that internal forces in the twisted rope rise rapidly with increasing diameter. But radial squeezing forces


Internal Forces in Ropes

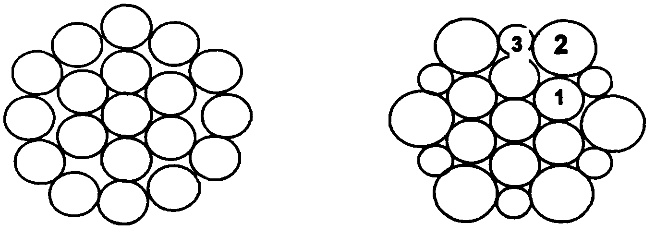
Radial Squeezing

Bearing Pressure

which increase rapidly with increasing twist levels give rise to internal load. These bring pressure against pulleys and lead to frictional heating, high internal abrasion and shear fatigue failure of yarn as rope elements move.

Over 50-fold improvement in lifetime of Kevlar ropes was attained by improved design obtained through theoretical and experimental analysis.

One change was to increase the number of strand sizes from one to three. The purpose was to minimize the crossovers of inner and outer strand layers by nesting the outer strand in the valleys of inner layers. This compacted the structure and spread the



Earlier construction:
Strands same size,
Unlubricated,
Layers at same helix angle,
High helix angle.

Redesigned rope:
Three strand sizes,
Strands nested (5x),
Lubricated (6x),
Lower helix angle (2x).

load uniformly over a greater area giving a five-fold improvement in lifetime. A second change was to lubricate the strands with a braid impregnated with fluorocarbons. This reduced the friction, heat buildup, abrasion and internal shear stresses which resulted in a 6-fold improvement. The third approach was to optimize the twist helix angle to minimize the radial squeezing forces without affecting other rope properties. This resulted in an additional 2-fold improvement. These improvements produced a rope having more than 3-times the life of steel.

In future another major development of Kevlar ropes can be in its use as deep water mooring lines for fiber optic cable.

In future another major development of Kevlar ropes can be in its use as deep water mooring lines for fiber optic cable. Here the light weight of Kevlar gives less sag than a heavy steel chain or steel wire rope thus allowing the operation at depths several times those when steel is used.

Another important example of the use of Kevlar is the formation of composites with superior strength for application in aircraft. The material base is Kevlar/carbon fibers and epoxy resin. The driving force is the high tensile strength and modulus per unit of weight and higher toughness. The system technology involves hybrid of Kevlar and carbon fibers reinforced epoxy resin to gain best balance of mechanical properties and damage tolerance, which are most required for aircraft structural parts. Carbon fibers confer high stiffness and compressive strength. However because of its rigid coplanar ring structure, carbon fibers alone are unyielding and fail by brittle fracture. Hence they are unable to survive catastrophic impact. Thus Kevlar introduces a good solution as a hybrid.

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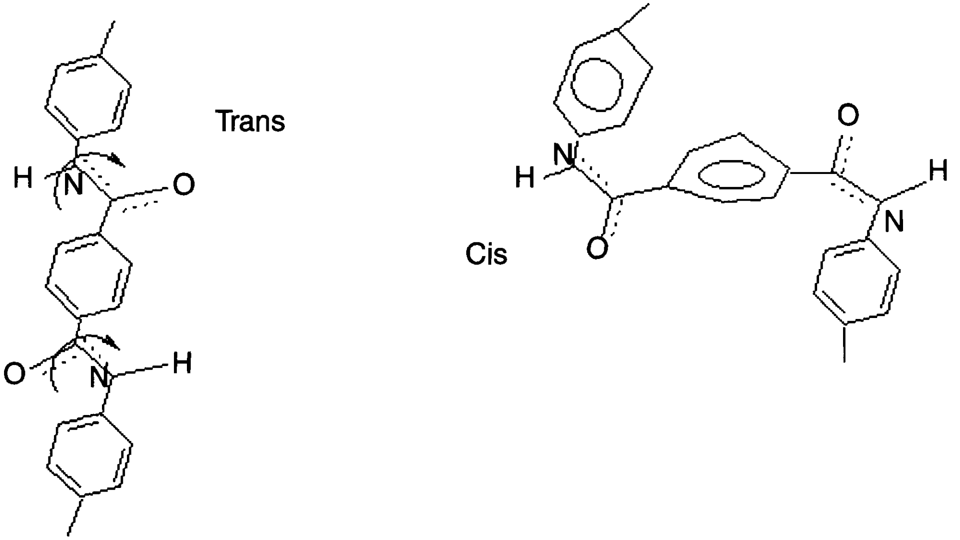
Kevlar has other structural features. It leads to good damage tolerance because of a ductile compressive failure mode. This occurs by compressive buckling of PPD-T chains. At a compressive strain of about 0.5%, buckling of para-aramid molecules follows a molecular rotation around the amide carbon-to-nitrogen bonds to accommodate configurational changes. This changes the configuration from *trans* to *cis*. This results in a yielding to the imposed stress without any bond cleavage.



Compressive Buckling of PPD-T

The metal-like ductility of Kevlar due to this molecular mechanism is illustrated by flexural stress-strain behavior of epoxy matrix composites containing carbon, glass, Kevlar and aluminum. The response to the compressive strain for Kevlar is similar to that of aluminum. This is because in bending, one side of the composite is in compression.

There is a marked difference in the failure mode of Kevlar aramid and carbon fiber-wound tubes. The tube reinforced by Kevlar fails by a progressive buckling mode, similar to an aluminium tube. The structure is damaged but still remains intact and is able to sustain load. The carbon fiber-wound tube shatters. However it sustains higher load just prior to failure and absorbs more total energy in crushing process than does the tube wound with only Kevlar.

Hybrid technology that combines Kevlar and carbon fiber as a wound structure offers a better balance of properties. High-energy absorption within 7% of that of all carbon tubes, and good structural integrity after crushing is achieved; approach-

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ing that of aramid wound tubes. Hybrid composites of Kevlar and carbon fibers are used in commercial aircrafts such as Boeing 767,757 and 737, as well as in helicopters and commuter aircraft. Other applications may involve filament wound structures to be used in missile cases and in pressure vessels. The Kevlar provides external damage protection, particularly during transport.

The story of innovation of Kevlar exemplifies the nature of the hurdles that had to be overcome and the need of the interdisciplinary skills and systems approach to bring a laboratory discovery to a commercial reality.

Suggested Reading

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Science is facts; just as houses are made of stones, so is science made of facts; but a pile of stones is not a house and a collection of facts is not necessarily science.

Henri Poincare
(1854 - 1912)