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The Kevlar Story—an Advanced Materials Case Study

Process Development
High Performance Fibers
High Impact Composites
Rigid-Rod Polymers

By David Tanner, James A. Fitzgerald, and Brian R. Phillips[*]

1. Introduction

The Kevlar story is an excellent example of the innovation process where a laboratory discovery is placed into commercial production. It started in the early 1960's with an identified need. In 1965, this led to an important scientific discovery. At this time the research and development phase was entered and in 1972 a 1 000 000 lb per year market development plant was built. By 1982 full commercialization was reached with a 45 000 000 lb/yr. plant. During this period several tough hurdles were encountered. To overcome these obstacles a multi-disciplinary approach was almost always required.

2. The Need for a Heat Resistant Stiff Fiber

The invention of Nylon and subsequent textile fibers provided powerful vision and direction for the research effort aimed at 'super' fibers. In the early 1960's Du Pont was driven by two goals, a fiber with the heat-resistance of asbestos and the stiffness of glass. A fiber of this type could be visualized to fill many market needs. Experimental work indicated that the route to such a material lay with stiff chain aromatic polyamides. These materials, however, had evaded the scientist by virtue of their extreme insolubility and intractability.

3. The Discovery of a Rigid Rod Spinnable Polymer

In 1965 *Stephanie Kwolek*, a research scientist at the Du Pont Experimental Station in Wilmington, made a major discovery. She found that *p*-aminobenzoic acid could be polymerized and solubilized under special conditions to yield a rigid-rod spinnable polymer. Initially, when these polymer solutions were first made, it was not believed that they would spin into fibers since the solution was opaque and could not be clarified by heating or filtration. This implied that there was inert matter dispersed in the spin dope which would plug the spinneret holes. However, the fibers spun well. We now know that this capacity was due to the formation of polymer

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liquid crystals. The stress–strain curve of the first aramid fiber tested was startling, and the test was re-run several times for confirmation. A true step change in properties was achieved vs. existing synthetic textile fibers.[1]

The behavior of rigid-rod molecules in solution is quite different from flexible molecules (Fig. 1). Flexible polymers like Nylon, in dilute solution, have a low level of entanglement. However, at higher concentrations the random coils become highly entangled. Spinning and drawing lead to only partially extended chains due to the high level of entanglements. Hence, properties such as tenacity and modulus reach only a small fraction of the theoretical values.

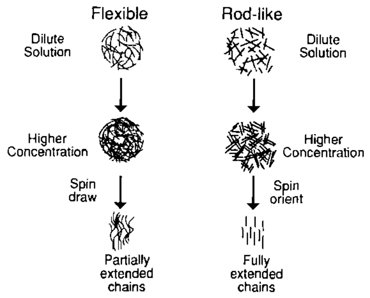


Fig. 1. Schematic illustration of the solution behavior of rigid and flexible polymers.

On the other hand, due to their rod-like conformation, more rigid polymers like the *p*-aramids, in going from dilute to higher concentration do not form random coils. At a critical concentration they can no longer populate the solution randomly. At this point, in order to pack more molecules into the solvent, they are forced to align parallel to each other in randomly oriented liquid crystalline domains.[2, 3] Under shear, as in a spinneret capillary, the liquid crystalline domains orient in the direction of the deformation. This leads to fully extended chains in fibers and the observed high strength and modulus.

4. Research and Development

Following *Kwolek*'s discovery, the first obstacle was encountered, i.e., the *p*-aminobenzoic acid raw material was too costly to justify scale-up. At this point a major research and development program was launched. The aim was to develop a deeper understanding of the formation of liquid crystalline solutions and to identify a lower cost rigid-rod polymer system. This effort led to a variety of rigid polymers with potential for formation of liquid crystalline spinning solutions and strong, stiff fibers.[4–6] The best candidate was the polymer from *p*-phenylenediamine and terephthalic acid (PPD-T). This polymer eventually became the basis for Kevlar. It had the lowest cost ingredients, the highest symmetry, and theoretically the highest stiffness. However, to produce the best properties the spinning solvent had to be 100% sulfuric acid, and the resulting spinning solutions were very viscous. Low spinning speeds were needed for good properties and therefore the process was uneconomical.

Thus, the second obstacle was encountered; the process was not practical. This became starkly apparent when the researchers first described the invention to the manufacturing and engineering groups who would have to design, build and operate the plant. They didn't want it! The sulfuric acid solvent was unconventional and highly corrosive, process yields and throughput were very low, and investment very high. These are the realities that research people do not pay much attention to when they are at the frontiers of discovery.

A major breakthrough came when another Du Pont research scientist, *Herbert Blades*, made two crucial discoveries.[7, 8] First, he found that PPD-T and sulfuric acid form a crystalline complex at a polymer concentration of 20% (vs. 10–12% by previous workers). He unexpectedly formed this complex by going against conventional wisdom and heating the polymer solution containing the 100% sulfuric acid. This complex melts around 70 °C and is composed of PPD-T:sulfuric acid in the ratio 1:10. This enabled spinning at much higher polymer concentrations than had been previously possible.

The second advance was in spinning where he used an air gap between the spinneret face and the quench bath (Fig. 2). When the PPD-T/sulfuric acid complex was melted and spun through the air gap into cold water, very high spinning speeds could be obtained through attenuation of the molten spinning solution in the air gap. Although partial deorientation occurs as the polymer solution emerges from the spinneret, the very high extensional shear in the air gap results in extraordinary orientation and tensile properties of the final as-spun fiber (Fig. 3). The air gap spinning technology gave birth to an improved product version which is today's Kevlar and ultimately led to Du Pont's heat strengthened high modulus Kevlar 49 product.

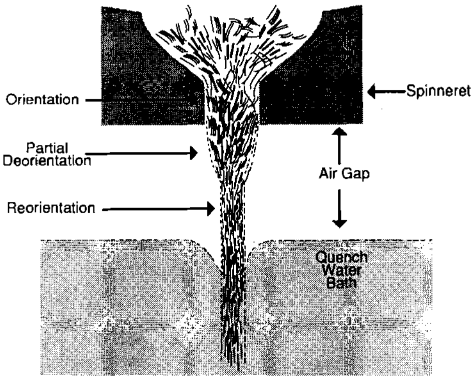


Fig. 2. Schematic of air gap spinning high concentration PPD-T solutions in sulfuric acid.

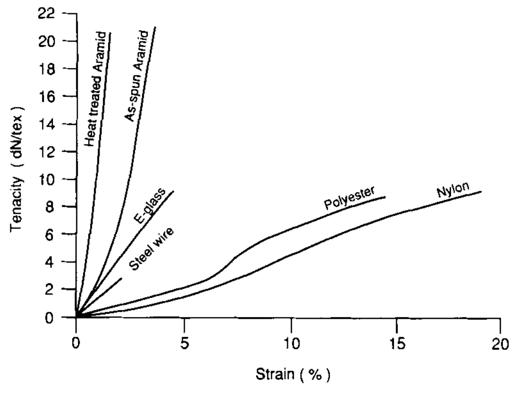


Fig. 3. Stress strain curves of reinforcing fibers.

The reason for these truly outstanding mechanical properties most likely lies in the microstructure of the fiber. Kevlar is a hydrogen bonded highly crystalline material.[9] Sheets of cells extend across the radius of the fiber resulting in almost perfect radial as well as longitudinal order. This level of three-dimensional order had never been observed in a fiber before. Kevlar has a molecular orientation parallel to the fiber axis, and a well defined radial crystalline orientation (Fig. 4).

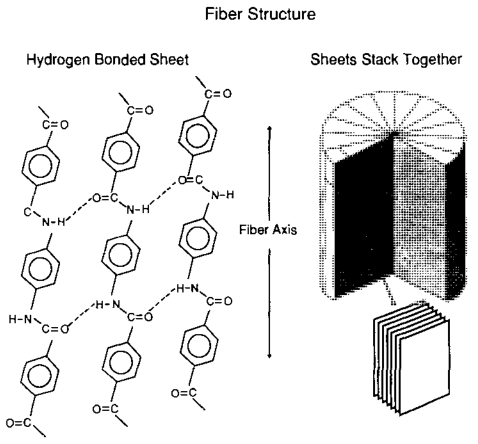


Fig. 4. The arrangement of PPD-T crystallites in a Kevlar fiber.

5. Scale-Up to a Market Development Plant

The air-gap spinning discovery was an invention worthy of scale-up. The product was certainly unique, the process scalable and the economics satisfactory. The next step in the innovation process and the next obstacle was to scale-up to a market development plant. Translation of a laboratory discovery to a practical, scalable, commercializable process is one of the hardest tasks faced by any technology-driven industry. In the case of Kevlar, a task force of dozens of scientists and engineers of many disciplines was assembled. Some of the Wilmington researchers moved to the plant site in Richmond, VA, USA. The task was to develop the manufacturing basic data and tackle scale-up. In less than two years from *Blades'* laboratory discoveries, Kevlar was being shipped from a 1 000 000 lb per year market development plant. This timetable, considering the complexity of the process, was unprecedented in the Du Pont Fibers Department. Five years later the commercial product was being produced in a 15 million pound per year plant.

During the scale-up stage several difficult hurdles were encountered, some quite unusual and unexpected. A complex laboratory process had to be translated into a workable plant operation. The ingredients were corrosive, there were environmental concerns such as waste disposal, and the polymerization solvent had an unexpectedly high level of toxicity. Two of these hurdles are described below.

An unusual environmental problem arose involving waste disposal. The spinning solution is based on a complex containing five moles of sulfuric acid per PPD-T amide bond (or four pounds of sulfuric acid per pound of polymer). Disposal of the spent acid after spinning was a problem. The best option turned out to be conversion of the sulfuric acid into calcium sulfate (gypsum). For every pound of fiber seven pounds of gypsum is generated. This year the Kevlar plant is generating a lot of gypsum—quite a storage problem! As a matter of interest, the produced gypsum is attractive to both wallboard and cement manufacturers, and eventually the gypsum will be recycled.

The second hurdle deals with toxic materials. In the Kevlar process, two solvents are used. The spinning solvent is sulfuric acid, discussed above, and the polymerization solvent was hexamethylphosphoramide (HMPA). The Kevlar business was in the scale-up stage on a fast track heading toward full commercialization. Suddenly it came to a self-imposed barrier—the toxicity of the HMPA polymerization solvent. Du Pont pays much attention to the toxicity and handling of hazardous materials. Use of HMPA on a large scale was new, but the material was well known for many years and there were no highly unusual toxic effects reported. To be completely sure about HMPA toxicity, a lifetime exposure study with rats was initiated by Du Pont to determine any possible carcinogenicity potential.[10] This study was one of the first of its kind, and carried out purely as a precautionary measure. The results of that study showed that HMPA was an experimental animal carcinogen. Immediate steps were taken in the handling of HMPA to be certain that there was no hazard to the workers, the community, or the customers.

It is, however, preferable not to use a potentially hazardous material if a safer alternative can be found. Therefore, a crash technical program was mounted to find an HMPA replacement. The task was to find an acceptable polymerization solvent of low toxicity; one that would give polymer yielding fiber properties identical to those already introduced to the trade, as well as fitting into the process and the expensive equipment layout designed for polymerization in

HMPA. The chemistry turned out to be relatively straightforward.[11] The combination of *N*-methylpyrrolidone (NMP) and calcium chloride was selected as the solvent of choice. The engineering and product development were, however, formidable challenges.

Polymerization in NMP/$CaCl_2$ proceeded smoothly and a high inherent viscosity polymer was obtained with no difficulty. The polymer, however, could not be spun to the equivalent tenacity of the same inherent viscosity polymer prepared in HMPA. The problem turned out to be molecular weight distribution. The data showed that at equal inherent viscosity, the average molecular weight of polymer made in the NMP/$CaCl_2$ system was lower than in the HMPA system. Using a gel permeation chromatography technique, this difference was traced to the presence of a large low molecular weight fraction in the NMP/$CaCl_2$ system (Fig. 5). Further analysis showed that this resulted from precipitation of oligomers from the polymerization mixture. These were not present in the HMPA system because of it's superior solvating power. The problem was solved through the design of a reactor system to eliminate early nucleation and precipitation of low molecular weight polymer. This is another example where solving a problem required multidisciplinary chemical and engineering skills. Extensive internal and trade testing demonstrated that the Kevlar fibers made in the two polymerization systems were indistinguishable.

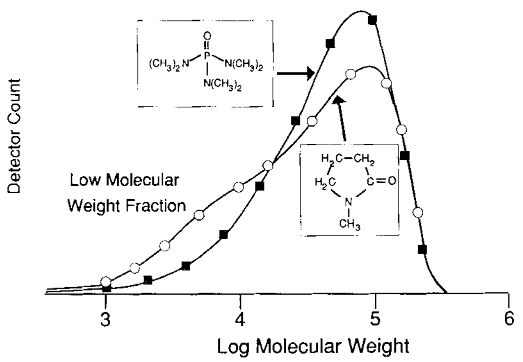


Fig. 5. Molecular weight distribution curve for PPD-T prepared in HMPA and in NMP/$CaCl_2$ by gel permeation chromatography (GPC).

The program to find an alternative solvent took an estimated 40 man-years of technical effort. Throughout the scale-up phase there was an underlying confidence in the multidisciplinary team. There was no hurdle that could not be jumped, although at times it took considerable energy and support to do so.

6. Full Commercialization of Kevlar

Thus far, the need, the discovery phase, the obstacles in moving the R & D along, and the process development hurdles in scale-up to a market development plant have been described. Perhaps an even greater challenge was to demonstrate the market potential of Kevlar. This was necessary to justify the final step in the innovation process, a full scale commercial plant requiring a huge US $ 400,000,000 investment. Hence, throughout the development there was intensive parallel effort to find practical applications for this new fiber. For Kevlar to be a commercial success a sufficient value in use had to be found versus incumbent fibers like Nylon, steel, fiberglass and carbon to warrant a pricing structure that made economic sense.

7. Systems Approach to Applications for Kevlar

Early in the development, it was recognized that Kevlar was a unique fiber that would not automatically fit into existing applications. This became apparent from initial evaluation in tires, ballistics, composites, ropes, cables, etc. Each application had to be looked at as a "system" requiring a systems approach. Early partnerships with customers were vital to success. This part of the program can be as scientifically challenging and exciting as the *p*-aramid discovery itself.

As a framework for thinking about the total system a simple tetrahedral model can be visualized (Fig. 6). At the base, each corner represents a different knowledge center in the development. At the left corner is the chemical structure, e.g., the polymer composition. At the right corner is the physical structure, e.g., the degree of orientation or crystallinity. The back corner represents the fiber properties, e.g., tensile or surface characteristics. Ongoing iteration between these three base corners, which can be referred to as molecular and process engineering, is important. However, this model adds a third dimension at the apex of the tetrahedron. It involves the creative integration of the base technologies to give an advanced, composite structure. The selection of design criteria for parts, devices, and objects, i.e., "systems" engineering, has been vital to Kevlar product development. It requires the combined talents of professionals in many disciplines. A final advanced structure usually involves much interaction between each corner of the tetrahedron and

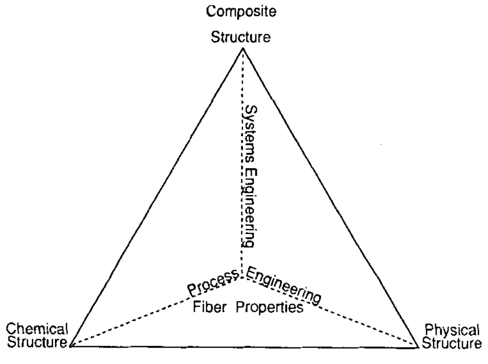


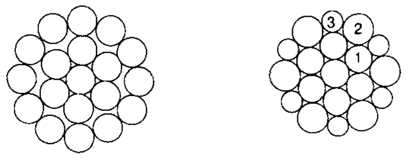
Fig. 6. Tetrahedral model of a systems approach to applications development.

sometimes multiple products organized into an integrated total system.

To illustrate the systems approach, two examples have been selected: Kevlar in ropes and cables and in composites. The main driving force for Kevlar in ropes and cables is the high strength per unit weight, inherent low elongation and low creep. In air, the specific strength is seven times, and in sea water more than twenty times that of steel. This means one can use smaller, lighter more easily handled lines. In long lengths where the self-weight of steel becomes critical, Kevlar can offer a greater payload.

The application to be described is that of a riser-tensioner line. The systems technology involved a specially engineered rope design to reduce internal stresses in order to increase wear life. Riser-tensioner lines are used on floating offshore oil drilling platforms, where their purpose is to keep the rise pipe or outer drill casing at a constant elevation and under uniform tension while the vessel surges with the waves. These are normally 44 mm diameter steel wire ropes which experience considerable cycling over pulleys as the platform moves. Laboratory studies had shown that small diameter Kevlar ropes could far surpass steel in cycling performance over pulleys. However, scale-up of the best small constructions to 44 mm diameter surprisingly gave rope lifetimes that were only 5–10% that of steel wire rope. Analysis showed that internal forces in the twisted rope rise rapidly with increasing diameter.[12, 13] These internal loads stem from radial squeezing forces which increase rapidly with increasing twist levels, bringing pressure against the pulleys and leading to high frictional heating, high internal abrasion, and shear fatigue failure of yarn as the rope elements move.

Cooperation with steel cable manufacturers lead to several design changes (i.e., Fig. 7) which improved the lifetime of Kevlar ropes over 50-fold. On the left is the former construction, and on the right the redesigned rope. One change was to increase the number of strand sizes from one to three. The purpose was to minimize cross-overs of inner and outer strand layers by nesting the outer strands in the inner layer. This compacted the structure and spread the lateral loads uniformly over a greater area giving a five-fold improvement in lifetime. A second change was to lubricate the strands by jacketing each strand with a braid impregnated with fluorocarbons. This reduced friction, heat buildup, abrasion and internal shear stresses resulting in a six-fold improvement. The third approach was to optimize the twist helix angle to minimize radial squeezing forces without seriously affecting other rope properties. This gave an additional two-fold improvement. The result was a rope having more than three times the life of steel in severe laboratory tests and more than five times in service. More than a dozen oil rigs have utilized Kevlar riser-tensioner lines, including those from major drilling contractors such as Santa Fe International, Western Oceanic, Zapata and Sedco.



Former Construction
- Strands same size
- Unlubricated
- Layers at same helix angle
- High helix angle

Redesigned Rope
- Three strand sizes
- Lubricated (5.9x)
- Strands nested (5 x)
- Lower helix angle (1.7x)

Fig. 7. Rope constructions.

A future application of Kevlar rope under development is that of deep water mooring lines for the same type of oil platforms that use riser-tensioner lines. Here the light weight of Kevlar gives less sag than heavy steel chain or steel wire rope. This allows operation at water depths several times that of steel. A one million pound break strength Kevlar rope has been deployed by Conoco in the Gulf of Mexico and by Petrobras off the coast of Brazil.

The next systems example involves the use of Kevlar in aircraft composites. The materials base is Kevlar, carbon fiber, and epoxy resin. The driving force is high tensile strength and modulus per unit of weight and toughness. The systems technology involves hybrids of Kevlar and carbon fibers reinforcing an epoxy resin to gain the best balance of mechanical properties and damage tolerance, i.e., the ability to tolerate abuse and to survive a catastrophic impact. Carbon fiber confers high stiffness and compressive strength but because of its rigid coplanar ring structure it is unyielding and fails by brittle fracture. Hence, it is unable to survive a catastrophic impact.

Kevlar has structural features that lead to good damage tolerance because of a ductile compressive failure mode. This can occur by a compressive buckling of PPD-T chains. At a compressive strain of about 0.5%, we believe that a buckling of *p*-aramid molecules occurs by molecular rotation of the amide C–N bonds to accomodate configurational changes. Figure 8 shows the shift that we believe is occurring from the *trans* configuration shown on the left to the *cis* shown on the right. This can result in a yielding to the imposed stress without bond cleavage. The result is an accordion-like collapse on impact. This continues to be a useful model for explaining the compressive properties of Kevlar composites.[14]

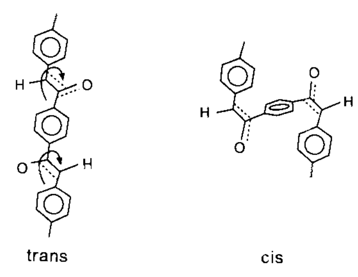


Fig. 8. PPD-T chain buckling under compression.

The response of Kevlar to compressive strain resembles that of aluminum. This metal-like ductility of Kevlar reinforced composites is illustrated by the flexural stress-strain behavior for epoxy matrix composites containing carbon, glass, Kevlar, and aluminum (Fig. 9). This is because in bending, one side of the composite is in compression and the accordion-like "yielding" contributes to the metal-like behavior. Crashworthy composite systems have been explored using a crushed tube test to compare materials. This test involves the crushing of filament wound tubes with a drop-weight impact tester. There is a marked difference between the failure modes of Kevlar aramid and carbon fiber-wound tubes. The tube reinforced with Kevlar fails by a progressive buckling mode, similar to that observed for an aluminum tube. The structure is damaged but still intact and able to sustain a load. The carbon fiber-wound tube shatters. However, it does reach and sustain a higher load just prior to failure, and absorbs more total energy in the crushing process than does the tube wound with Kevlar.

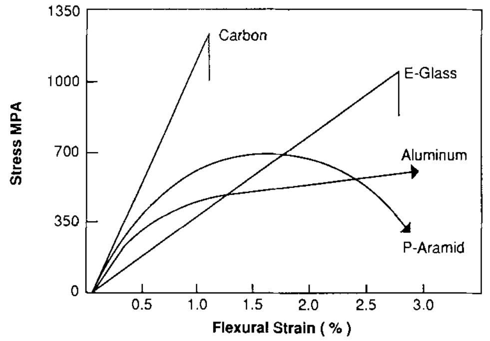


Fig. 9. Flexural stress strain curves of unidirectional epoxy matrix composites.

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 the all-carbon tubes, and good structural integrity after crushing, approaching that of the aramid-wound tube, is achieved. Hybrid composites of Kevlar and carbon fibers are used in commercial aircraft such as the Boeing 767, 757, and 737, as well as in helicopters and commuter aircraft. Other applications under development include filament wound structures, for example, those used in Trident missile cases and in pressure vessels. The Kevlar provides external damage protection, particularly during transport.

8. Summary

Limited space permits description of only two examples of Kevlar applications research. There are numerous others. In the early product development there were some indications that Kevlar would go mainly into tire reinforcement. This has turned out not to be true. In the mid-seventies Kevlar was participating in only ten market segments and less than fifty specific applications, but today, it is in more than twenty market segments, serving more than two hundred applications, and continued growth is anticipated. Kevlar is produced in a 45 million pound plant in Richmond, VA, USA. In 1988, a second plant was started up in Northern Ireland and plans for a third plant in Japan were announced. The Kevlar innovation story exemplifies the kind of obstacles, interdisciplinary skills and systems approach involved in bringing a laboratory discovery to commercial reality. The story is still unfolding and applications currently not envisioned will undoubtedly become important in the future.

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