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TECHNICAL REPORT

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**SCANNING ELECTRON MICROSCOPY AS RELATED
TO THE STUDY OF HIGH-SPEED FIBER IMPACT**

by

Roy C. Laible

Frank Figucia

Barbara Kirkwood

October 1973

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UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760



Clothing & Personal Life Support Equipment Laboratory
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Scanning			8		10	
Impact Strength	8		4			
Ballistic Resistance	8		4			
High Speed Tests					10	
Low Speed Tests					10	
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Aromatic Polymers	9		9		7	
Aliphatic Polyamides	9		9		7	
Impact					6	
Ballistic Impact					6	

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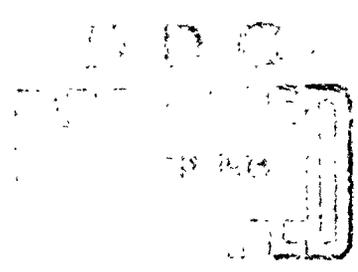
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FOREWORD

Aliphatic polyamide fibers of the nylon 6 and nylon 6,6 type have been important materials for many industrial and military applications. Their properties of high strength, high work-to-rupture, relatively high melting points, and high durability (i.e. abrasion resistance) have led to this importance. Nylon does exhibit melting as a result of some mechanical deformations and this melting may be a limiting factor in the use of nylon in tires or ballistic clothing.

New aromatic polyamides have become available which have advantages over the aliphatic polyamides such as higher melting points, higher moduli and higher strengths. These aromatic polyamide fibers fracture quite differently than aliphatic nylon fibers and the investigation of the fracture process is most conveniently conducted by the use of the SEM.

The strength of the best of these aromatic type fibers is more than double that available from the other commercially available fibers. Both sources of this strength and estimations of the theoretical strength expected for such fibers become important subjects in assessing the future importance of these fibers to the military.

ABSTRACT

Visual observation of nylon impacted at very high speeds, including ballistic speeds, shows a large amount of plastic deformation and melting of the broken fiber ends. In attempts to produce fibers for specialty applications, manufacturers have produced organic fibers with moduli equal to or greater than that of glass and heat resistance far greater than that of nylon. The initial products of this type showed a typically brittle fracture because of their low ductility but in addition showed a tendency to split longitudinally. The better products show this splitting to a more marked degree until it reaches a state best described as fibrillation.

This process is thought to be of considerable importance because: (1) it tends to minimize premature brittle failure, and (2) considerable energy is absorbed in creation of the many subsurfaces.

The potential for high strength in these new aromatic polymers* is probably due to extended polymer chains which are broken more nearly in unison during extension. However, the realization of these high strengths with such low elongation fibers depends upon the process of fibrillation to prevent premature catastrophic failure. The strength of the aromatic polyamide "Fiber B" is 23 grams/denier (400,000 psi) as contrasted with 10 g/d (150,000 psi) for the strongest nylon tire cord previously available and approximately 200 g/d (4,000,000 psi) for the theoretical value calculated on the basis of all primary bonds breaking at once.

*History

DuPont developed a series of high modulus fibers which were originally designated PRD 49-IV, PRD 49-III and Fiber B. The PRD 49-IV and the Fiber B both acquired the designation Fiber B while PRD 49-III exists as a separate entity and is used for laminates rather than as unlaminated fabric. The term PRD 49-IV is used at least parenthetically in this paper because it was the proper designation at the time this work was initiated. Actually as of September 1973 the name Kevlar 29 was assigned to these fibers by DuPont as a trade designation. No generic term has yet been assigned.

SCANNING ELECTRON MICROSCOPY AS RELATED TO THE STUDY OF HIGH-SPEED FIBER IMPACT

1. Introduction

The effect of high-speed impact upon fibrous materials has been the subject of numerous papers in the last forty years. A monograph by Lyons summarizes a good deal of this work (1). The major objectives were: 1) to investigate the fundamental viscoelastic properties of polymeric fibrous materials and 2) to predict the performance of fibrous materials under field conditions by laboratory procedures. Many devices were used in an attempt to simulate field conditions such as the action of the cords in an auto or truck tire, the opening of a military parachute, high speed stitching and ballistic impact. The devices included relatively low constant speed testers such as the Instron, falling weight devices in which the testing speed is governed by the drop height, pendulums, rotating disk machines, pneumatic testers and actual transverse impact in which a missile strikes a yarn perpendicular to the long fiber axis. The testing speeds covered the range from fractions of a millimeter per second to a thousand meters per second. The transverse impact test can be varied to include most velocities encountered in the field of ballistic protection where the fibrous materials may be destined for use in a vest to provide protection against pistol fire or fragmenting munitions.

These studies led to an understanding of the significant rate dependence exhibited by fibrous materials. The general trends of increasing breaking strength and modulus and decreasing elongation-to-break with increasing rate of testing have been documented by Lyons, Meredith, Hall, Laible, Figucia and others (1, 2, 3, 4, 5, 6). Most of these same articles relate this behavior to the concept of relaxation times and/or the ability of molecular groupings to move in a given time frame (3, 4, 5).

A dramatic example of the inability of an important process to take place in a short testing time is furnished by undrawn nylon. This material possesses a huge capacity for work absorption when tested in tension at slow speeds (i.e. Instron). Attempts to capitalize upon this property by using undrawn nylon for a ballistic vest have failed (1). Obviously the process of drawing is incapable of occurring in the time-frame of interest in ballistic impact. Wilde, Ricca and Robers of the Army Materials and Mechanics Research Center have shown this behavior of undrawn nylon more clearly with transverse impact experiments on yarns (7). They took a series of nylon 6,6 yarns differing systematically

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in mechanical properties and subjected these yarns to static rates of straining as well as to ballistic rates of straining. The undrawn nylon specimen absorbed 260 joules/gram in a slow tensile test (1.67%/second) because of its large elongation at that rate of testing, but only 10 joules/gram under transverse impact at highspeed (5000%/second). The other more highly drawn yarns exhibited a much more modest loss in breaking energy with the increase in rate of straining. This work showed that an undrawn nylon would not be an effective energy absorber at the high rates of loading characteristic of those encountered in aerial delivery. Wilde conducted some additional tests with undrawn nylon at even higher rates of loading and the energy absorbed just rose slightly, confirming experimentally the poor performance demonstrated practically in a ballistic vest.

In any failure process, it is useful to investigate the morphology of the material after fracture. In previous years, the investigation of the fracture surfaces was necessarily limited to that possible with light microscopy and, later, the transmission electron microscope. Susich, Dogliotti and Wrigley at the US Army Natick Laboratories conducted an extensive microscopic study of a Multi-layer Nylon armor panel after transverse impact with the .22 caliber missile but, as this was in 1958, they were restricted to the use of light microscopy (8). In this study, some valuable information was obtained concerning the fusion of nylon fibers and the extreme localization of the effect of the impact. This information was very painstakingly obtained due to the small depth of focus characteristic of light microscopy.

Now, with the advent of the SEM, it is possible to investigate more efficiently the morphology of fibrous materials degraded by high speed impact.

Such a study has been conducted and is the subject of the present paper. The materials considered have included not only nylon but also the new high modulus aromatic polyamides.

2. Experiments

a. Tensile Test

Tensile data was generated at two rates of straining, one a conventional textile testing rate (1.67%/sec) and the other the fastest rate available with a pneumatic tester

(5000%/sec). The latter rate of testing is still slower than that characteristic of ballistic impacts but is the highest rate of tensile testing for which transducers can give an accurate measure of load and deflection. This limitation is due mainly to wave effects.

The conventional tests were performed with a standard Instron Tensile Tester operating at a constant extension rate of .0021 m/sec.

The high speed tests were performed on the FRITS* Piston Tester which is pneumatically driven by compressed nitrogen gas at approximately 6.42 m/sec.

All tests at both strain rates were performed on specimen lengths of .128 meters (5 inches) with a pre-tension of approximately 12 grams applied immediately before clamping. The specimens were individually weighed after test to establish the denier (linear density) in each case.

b. Scanning Electron Micrographs

The broken ends of the fractured yarns were mounted on specimen studs using silver paint and single-faced adhesive aluminum tape. The samples were coated in a vacuum evaporator at 3×10^{-5} Torr with a thin layer of carbon followed by a thin layer of gold. (The carbon deposition allows better distribution of the subsequent gold coating.) During the coating process the samples were rotated 360° and tilted 180° to obtain a uniform and complete coating. The fracture patterns of the coated samples were observed in an AMR Model 900 Scanning Electron Microscope using the secondary electron mode.

3. Results and Discussion

The availability of the Scanning Electron Microscope has allowed us to investigate the morphology of fibers after high-speed impact. In Figure 1 fractured ends of nylon fibers resulting from impact with a small cylinder (10 caliber weighing .087 grams) are shown. The depth of focus available with the SEM allows many fibers to be observed at once. Fusion is clearly indicated and it results in a mushroom-like appearance at the end of almost every broken fiber. Although ballistic impact has been emphasized, it should

*Fabric Research Impact Test System

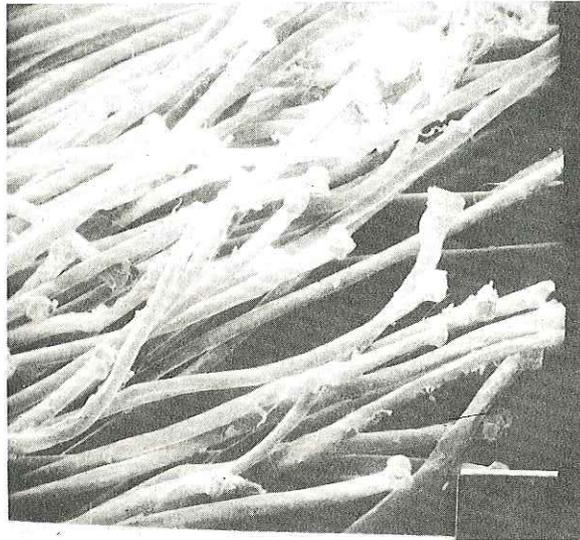


Figure 1. Nylon Fibers Broken and Fused From Missile Impact (130X)

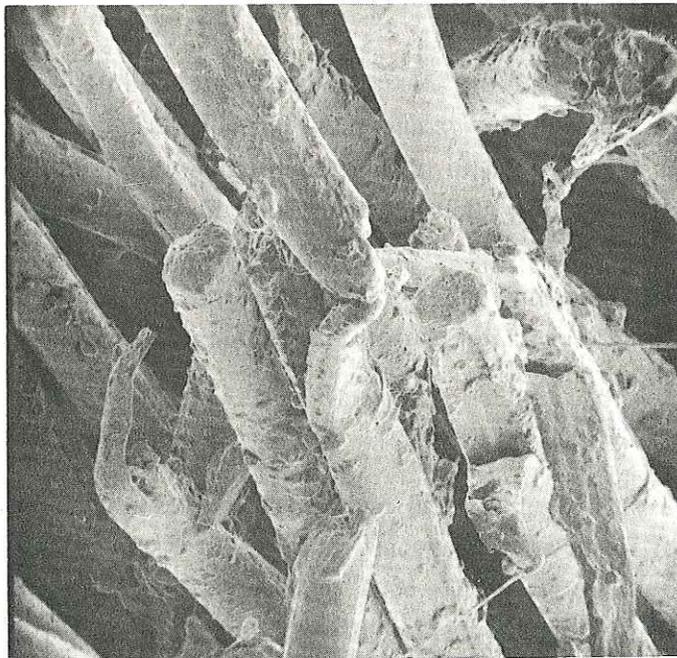


Figure 2. X-500 Fibers Broken From Ballistic Impact (400X)

be pointed out that this fusion and mushroom shape have also been observed in fibers after longitudinal impact at only 30 m/sec (100 ft/sec), as well as in ballistic impact (8, 9).

In order to develop fibrous materials with a greater potential for high performance industrial and military applications (tire cords, parachute suspension lines and ballistic protective items) it is necessary to address one or more of the following factors:

(1) Improved mechanical properties of yarns (especially strength) generally yield better candidates in fabric form for defeating fragments. Decreased creep can eliminate flat-spotting in tires.

(2) Raising the melting point and strength retention at high temperatures of a fiber may yield better candidates for resistance to high speed impact.

(3) A higher modulus to density ratio (specific modulus) would increase the ability of the fiber to respond quickly to high speed impact. This would mitigate the extreme localization of the deformation previously noted by Susich (8).

The first of these factors, improvement in the mechanical properties of nylon 6 or nylon 6,6, has been studied by tire cord manufacturers. The results have been fairly negative as the changes in molecular weight necessary to produce stronger fibers produce polymers which are impossible to spin on a production basis. This is due to the fact that the intrinsic viscosity rises very fast with molecular weight and the polymers, although having super-strength potential, are intractable (10, 11).

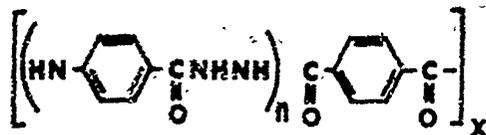
The second and third objectives, higher heat resistance and faster response to impact (higher modulus favors higher wave velocity), could be addressed by the introduction of aromatic groups in the polymer backbone. Tippetts discussed this problem in 1964, showing that both modulus and melting point could be significantly raised by the introduction of benzene rings in the main chain (12). Black and Preston have listed the properties of many aromatic and aromatic-aliphatic polyamides which tend to verify this contention (13). Poly (p-phenylene adipamide), the product of adipoyl chloride and paraphenylene diamine, has a melting point of 340°C as contrasted with the 255°C characteristic of nylon 6,6 which is the product of essentially the same acid unit (adipic

acid) but with an aliphatic amine component (hexamethylene diamine) (13, 14). The aromatic ring can also be introduced by using an aromatic acid such as terephthalic acid (or its diacid chloride). Shashoua and Eareckson prepared polyterephthalamides by interfacial polymerization and found generally high melting points. For example, the product of tetramethylene diamine and terephthaloyl chloride, namely poly tetramethylene terephthalamide, had a melting point of 436°C (15).

This rise in melting point when compared to nylon is of course partially due to the reduction in the number of methylene groups in the diamine, but the major influence of the phenyl groups is apparent. This major influence can be demonstrated with atomic models by contrasting the flexibility of polyethylene with that of either the model for poly p-phenylene or the model for the aliphatic-aromatic polymers described here. The stiffness of the aromatic polymers results in a lower change in entropy from the solid to the liquid because of the restrictions in the number of configurations possible compared to an aliphatic polymer. The melting point of a material is inversely proportional to the entropy change upon melting and would necessarily rise with its stiffness.

Modulus is also related to stiffness. We can refer back to Shashoua's work on interfacial polymerization to show this effect. Poly-tetra methylene terephthalamide exhibited a modulus of over 90 g/denier (approximately 1.5 million psi) as contrasted with 40 g/denier (580,000 psi) for the all aliphatic nylon 6,6 (15). A fairer comparison with nylon 6,6 would be the polymer prepared from hexamethylene diamine and terephthaloyl chloride, polyhexamethylene terephthalamide, which has a modulus just 50% greater than that of the aliphatic nylon. In any event the potential for the preparation of fibers with increased heat resistance and moduli by the introduction of aromatic groups had been clearly demonstrated some years ago. Problems arise when one wishes to prepare large quantities of these polymers and to convert them into fibers. Only two processes were available for preparation, namely interfacial polymerization and low temperature solution polycondensation. The former method yields a product from the diacid chloride and diamine which is never really in solution. One is forced then to find a method of spinning the fiber. Even the aliphatic-aromatic polyamides such as polyhexamethylene terephthalamide cannot be melted without decomposition. An all aromatic polymer would be even more likely to decompose upon melting. Even solution spinning, a less desirable process, is impossible because of the insolubility of these aromatic polymers. Solvents such as concentrated sulfuric acid, which are not convenient for large scale production, are generally required. These difficulties have in the past restricted the fiber preparation to laboratory quantities.

The first appearance of aromatic polyamide fibers in more substantial quantities was the family of fibers produced by Monsanto and designated as X-500. These fibers are reported to have an aromatic polyamidehydrazide structure as shown below:

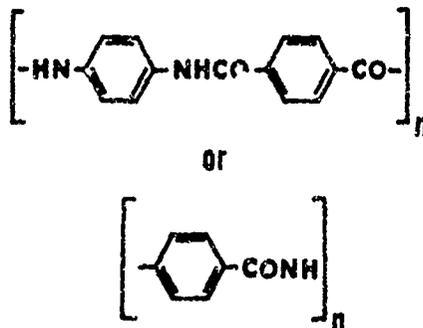


Black and his co-authors have discussed these fibers in some detail (16, 17).

The X-500 yarns are quite temperature resistant showing little weight loss up to 400°C (17). The temperature resistance is also shown in the absence of fused fibers resulting from ballistic impact (Figures 2 and 3). Also evidence from these micrographs is the brittle type of fracture which predominates. This brittle fracture might have been predicted from the stress-strain properties of the X-500 type yarns given in Figure 4 in comparison to nylon 6,6. The yarns were tested both at a static (1.67%/sec) and at a dynamic rate of straining (5000%/sec). The increased modulus is quite apparent from the curves but we can see that the strength and work-to-rupture are rather modest.

One of the reasons for these modest strength values may be the intentional breakup of the order by introduction of co-monomers.

A more successful product has been marketed by DuPont under the designation PRD 49-IV or more recently Fiber B. This material is reported (17, 18) to have a structure such as:



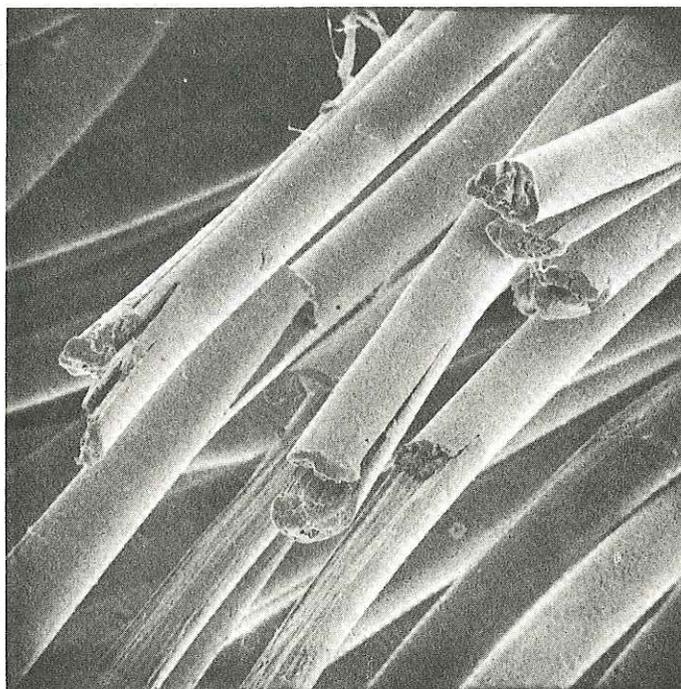


Figure 3. X-500 Fibers Exhibiting the Tendency to Split Longitudinally From Impact (410X)

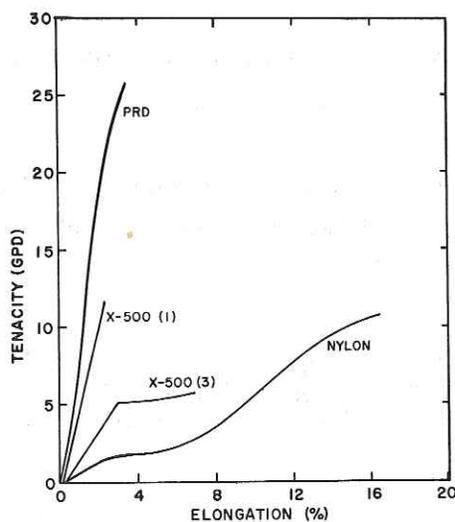


Figure 4. Tensile Stress-Strain Properties of New High Modulus Fibers at a Strain Rate of 5,000%/Sec

The first structure is analogous to nylon 6,6, the second to nylon 6 (polycaprolactam) in its repeat structure. This all-para aromatic polyamide possesses a strength of 23 g/d at slow rates of straining. The properties of Fiber B at this slow strain rate (1.67%/sec) are given in Table I in various forms familiar to either physical scientists, engineers or textile technologists.

TABLE 1

Mechanical Properties of Fiber B (PRD 49-IV) at Strain Rate of 1.67%/Sec

	Eng Units	Textile Units	Metric Units
Strength	430,000 psi	23 g/d	2.9×10^{10} dynes/cm ²
Modulus	11,000,000 psi	600 g/d	4.1×10^{11} dynes/cm ²
Elongation	3.7%	3.7%	3.7%
Sound Velocity	31,300 ft/sec	1000 g/d	9.5×10^5 cm/sec

It is interesting to compare these values with those for nylon or other conventional fibers. The sound velocity value of 9500 m/sec is higher than the value of 2400-3400 m/sec for nylon or even the 4800-6000 m/sec for steel. The high value is due to the high modulus value which is approximately equal to glass on a psi basis but vastly superior on a specific modulus or textile basis (g/d). Fielding-Russell has shown that moduli in the range of 10^{12} dynes/cm² can be estimated for poly (1,4 benzamide) and poly (1,4 phenylene terephthalamide) (18). The calculations are based upon values of the force constants of the chemical bonds of the polymer chain derived from vibration frequencies.

The strength values exhibited by Fiber B are the highest exhibited by any fibrous material. They can be compared with the 10 g/d exhibited by nylon tire cord (the strongest fiber used commercially) and with theoretical estimates which can be advanced.

A simple calculation can be made to estimate the theoretical strength possible in an organic polymer such as Fiber B. For this purpose the following assumptions are made:

*This 1000 g/d is a sonic modulus in textile terms and not a velocity. It is listed in the table because it is derived from the sonic velocity.

- (1) Bond breaking predominates — a primary bond is broken in every chain.
- (2) The lowest bond energy involved is that of a C-C single bond which is 80 Kcal per molecule or 5.5×10^{12} ergs per bond.
- (3) The effective distance for force application is .2Å.
- (4) The cross-section occupied by each polymer molecule is a square 10Å by 10Å.

Based upon the above assumptions, the force involved in breaking each molecular chain would be 2.8×10^3 dynes from the formula:

$$E = \int Fds$$

The theoretical strength would be obtained from the product of the individual chain strength and the 10^{14} chains which could fit in a one square centimeter cross section. This product, 2.8×10^{11} dynes/cm², is equivalent to 4.1×10^6 psi in English units. For conversion to the units characteristic of the textile industry it is necessary to use the density of 1.45 g/cm³. The figure obtained, 220 g/d, is almost 10 times that found for Fiber B, 23 g/d. One conclusion from this comparison is that the 23 g/d achieved may only be the beginning with further improvements to 30 or 40 g/d possible just by breaking a larger fraction of molecules simultaneously. On the other hand, a review of the assumptions made shows that Assumption 1 is the most unlikely because it leads to a calculation based upon all of the polymer chains (10^{14} of them) breaking simultaneously to achieve the calculated strength. Even the observed strength of 23 g/d requires that over 10% of the chains break simultaneously. Because chain folding appears to be the rule in crystalline morphology, simultaneous breaking of many molecular chains at once does not occur.

It is proposed that the structure of the new aromatic polyamide polymers favors extended chains in which simultaneous rupture is much more likely than for folded chains. Lindenmeyer has discussed chain folding in some detail and has indicated some of the factors favoring them. These factors include (1) a single molecular weight species, (2) low molecular weight and (3) high temperatures and pressures (19).

Actually, Lindenmeyer points out that folded chains are not favored energetically by themselves because energy is needed to insert a crystalline fold. However, the energy needed is more than compensated by the decrease in energy resulting from the molecular portions brought into crystalline register. This is probably the real key to the new polymers — the ability for the extended chains to be brought into crystalline register.

The previous discussion of properties is somewhat speculative and it is useful to go back to the use of the SEM in an attempt to determine the morphological characteristics of the fractured B fibers. Figure 5 shows a single fiber from a yarn after tensile impact failure at 5000%/sec. The fibers of Fiber B are much smaller than usual for most industrial fibers (i.e. diameter of Fiber B is less than 11.7 microns as contrasted with over 27 microns for nylon tire cord fibers). Measurement of the microfibrils produced by the tensile test in Figure 5 shows that they are approximately 10,000 Å (1 micron) in diameter. This fiber breakup can possibly be related to the high strengths observed. The splitting of the fibers longitudinally nullifies the more conventional process in which failure is propagated perpendicular to the fiber axis. This tendency to split rather than melt has been seen previously (Figure 3) with X-500 aromatic type fibers but the amount and degree of splitting was less pronounced (20). The fibrillation of Fiber B is not limited to impact speeds. In Figure 6, Fiber B yarn fractured at a relatively slow tensile rate of straining of 1.67%/sec shows the same fibrillation, and fibrils are again produced of less than 1 micron in diameter.

The new high modulus fibers [X-500, PRD 49-III, Fiber B (PRD 49-IV)] were actually developed for applications such as tire cord and laminates where superior strength and modulus properties could produce longer wearing tires without flat spotting and composite structures with high strength and stiffness-to-weight ratios (21). A laminate was prepared from Fiber B fabric and phenolic modified polyvinyl butyral resin. The resulting laminate was impacted transversely with .22 caliber fragments of the type used by Susich (8). A great deal of fibrillation was noted in the vicinity of the missile hole. This is shown in Figure 7. Although changes were made in the structure (laminate vs. yarn), type of straining (transverse impact vs. tensile extension), and rate of impact (440 m/sec vs. .2 m/sec for the slowest tensile test), a similar type of fibrillation is observed in Figure 7 as had been shown in Figures 5 and 6.

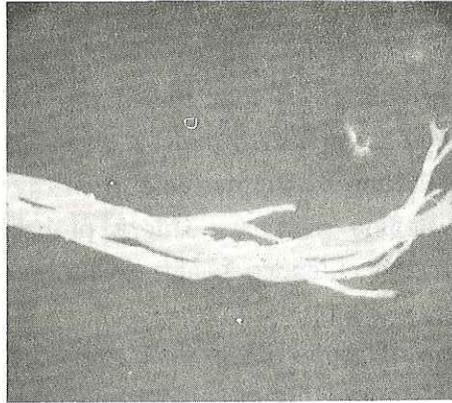


Figure 5. Fibrillated Appearance of Fiber B (PRD 49-IV) After Tensile Impact (5,000%/Sec) (650X)

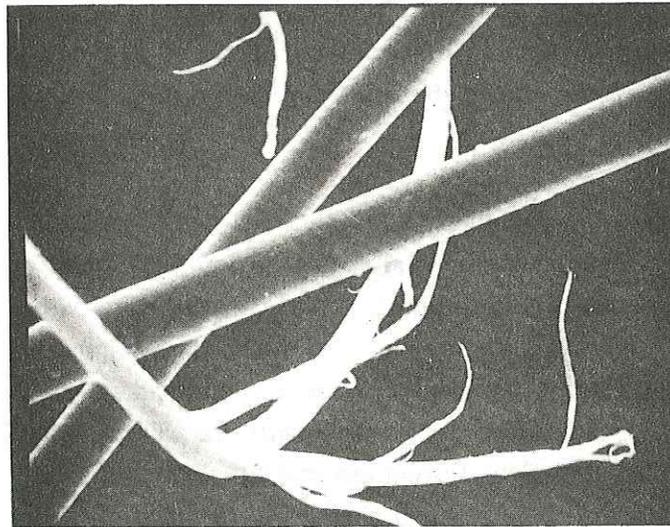


Figure 6. Fibrillated Fiber of Fiber B (PRD 49-IV) From Slow Speed Test (800X)



Figure 7. Fiber B (PRD 49-IV) in Composite Form After Impact with .22 Caliber Missile (360X)

4. Conclusions

In summary it has been shown that new fibers are now available with moduli as high as glass. The most successful of these, the Fiber B developed by DuPont, is probably based upon an all para condensation product of p-phenylene diamine and terephthalic acid. The strengths exhibited, 20-25 g/d, are double those previously available commercially. The SEM photographs of the fractured fiber ends show that fibrillation appears to be characteristic regardless of testing speed, type of impact or even lamination. The superior properties exhibited by Fiber B are probably due to:

- (1) extended chain tie molecules,
- (2) a more nearly perfect crystalline register, and
- (3) the crack blunting due to fibrillation.

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