

Future Organic Tire Fibers

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Synopsis

In the history of the automobile, organic fibers have dominated the tire reinforcement field, starting with cotton and progressing through a series of man-made fibers, each finding its place on the basis of its special attributes and overall performance. In general, these fibers were engineered for textile applications, but were subsequently adapted by special processing to make them as suitable for tires as possible. However, each has had limitations which have kept it from certain segments of the market. Moreover, the performance demands on tires have become progressively more stringent, and new tire designs have evolved, so that new tire reinforcement materials are needed. While glass and steel wire are contributing some of the desired properties, they also have their limitations. On the other hand, the potential for creating new, more favorable property balances from organic fibers is far from exhausted. This paper will discuss the main tire yarn property criteria and the polymer and fiber structural factors which control them. Then, the properties and performance of an entirely new fiber, specifically engineered chemically and physically for tire reinforcement, will be described. Fiber properties discussed will include tensile strength, modulus, dimensional stability, fatigue resistance, adhesion, and thermal stability.

INTRODUCTION

From the advent of the pneumatic tire for automobiles, organic fibers have played the dominant role in rubber reinforcement, starting with cotton and progressing through a series of man-made fibers. These fibers were all originally developed for textile applications but were subsequently adapted for tire reinforcement by special processing, and each found its place on the basis of its special attributes and overall performance characteristics. However, each one has had limitations which have kept it from certain segments of the market. Moreover, the performance demands on tires have become progressively more stringent, and new tire designs have evolved, so that new tire reinforcement materials are needed. While glass and steel are contributing certain desired properties, they also have their limitations.

This paper will discuss the main tire yarn property criteria, i.e., tensile strength, dimensional stability, durability, and cost, along with the polymer and fiber structural factors which control them, and will demonstrate that the potential for creating new, more favorable property balances from organic fibers is far from exhausted.

TIRE YARN PROPERTY CRITERIA

Tensile Strength

The tensile strength of a tire yarn has always been one of the foremost factors in its acceptance. In some cases, lower tensile strengths have been acceptable where low fiber prices permitted construction of a tire with adequate carcass strength at acceptable cost. However, this has sometimes been at the expense of tire weight and operating temperature and of ride aesthetics.

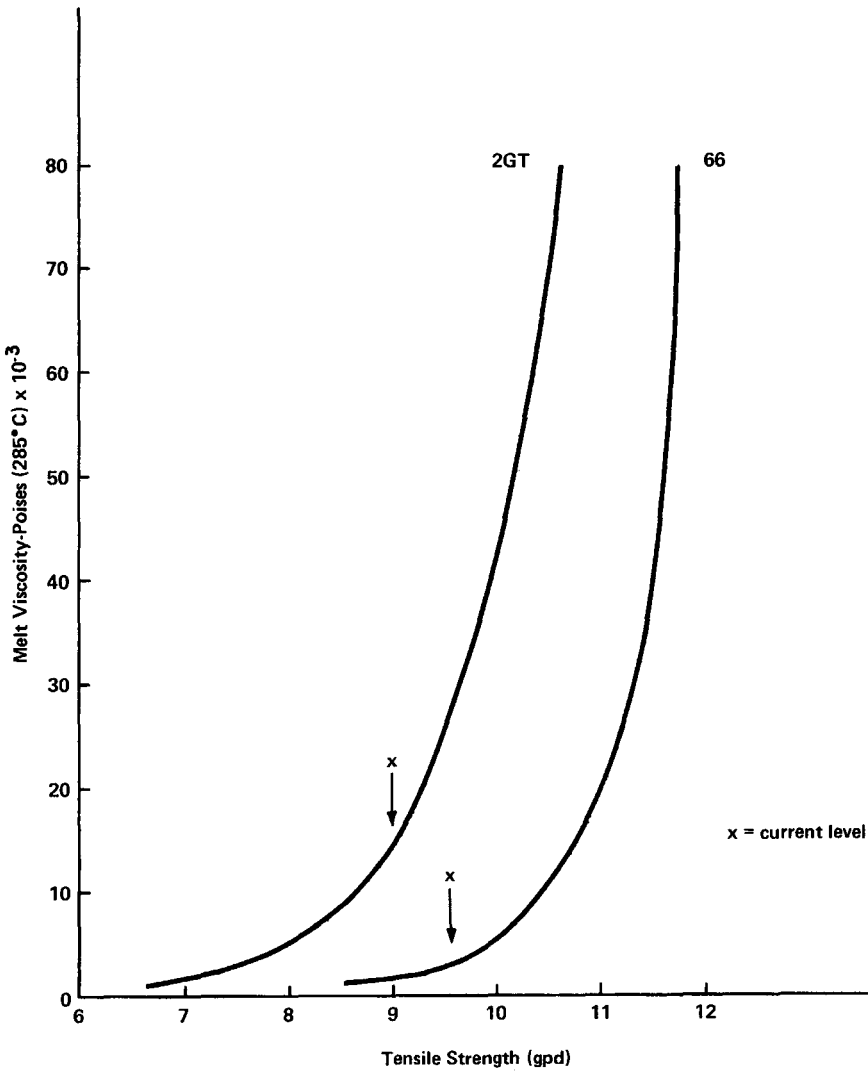


Fig. 1. Melt viscosity requirements vs. tensile strength of nylon 66 and 2GT.

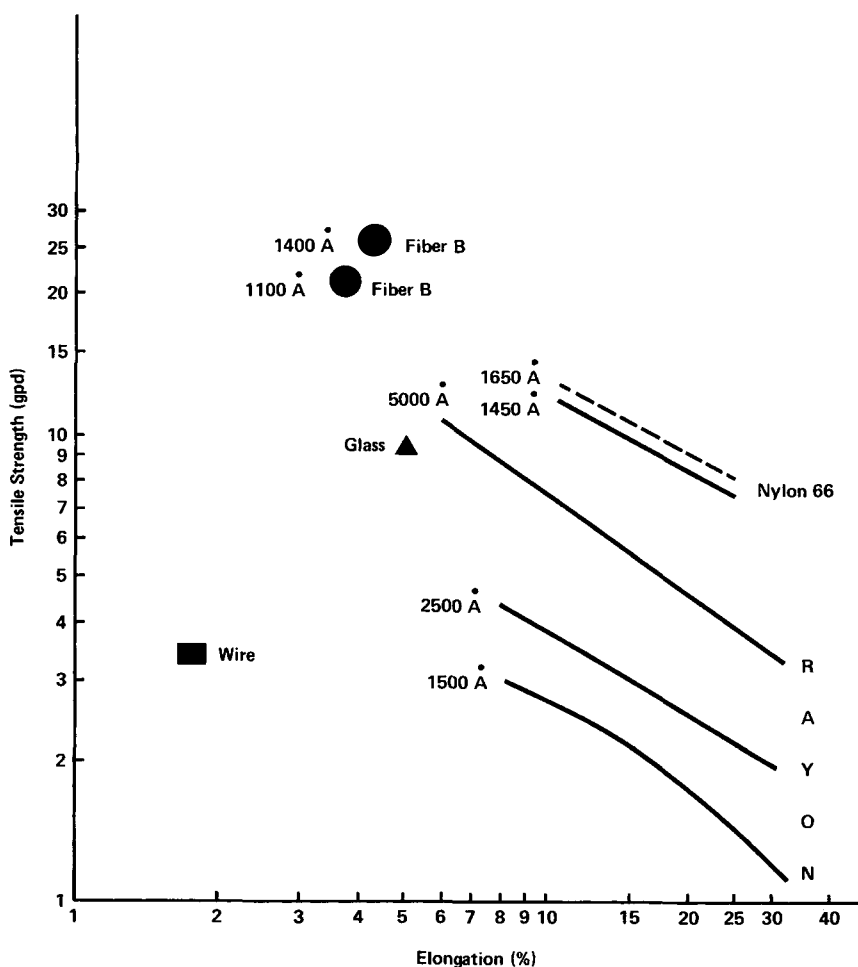


Fig. 2. Tensile strength vs. elongation (effect of chain length).

In developing fiber technology for high strength, one selects polymers with high intermolecular forces (e.g., H bonding) and maximum symmetry and chain regularity to provide the highest possible resistance to creep within the crystalline regions. These factors also contribute to a high melting point which in turn results in improved strength retention at elevated temperatures.

To achieve the highest possible strengths with any given polymer base, molecular weights must be maximized. With the incumbent melt-spun fibers [nylon and poly(ethylene terephthalate)], this involves an exponential increase in melt viscosity for each increment of tensile strength so that the processing problems become progressively more formidable. From Figure 1, it can be seen that an increase in tensile strength by 1 gpd from present levels through molecular weight increases will require a three- to fourfold increase in melt viscosity.

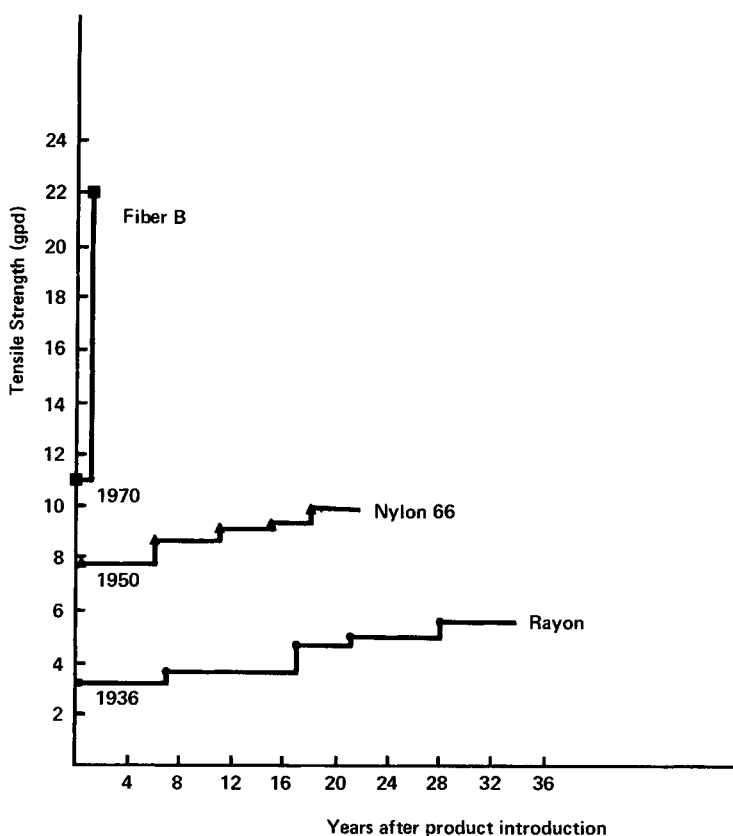


Fig. 3. Tire yarn tensile strength trends.

In addition to these polymer structure and molecular weight factors, tensile strength is strongly influenced by the spinning and drawing processes as well as by denier and orientation uniformity and freedom from defects (voids, particles, etc.). All of these influence the fraction of load-bearing chains in the fiber. In adjusting orientation, there is a trade-off between tensile strength (T) and elongation to break (E), which is shown in Figure 2 for rayon and nylon. The position of the T/E profile is a function of number-average molecular weight or chain length. For reference, data points are indicated for wire, glass and DuPont's new aromatic polyamide tire yarn, Fiber B. Although Fiber B has a tensile strength above 20 gpd, at less than 5% elongation, it still has the general flexibility and toughness characteristics of a conventional textile fiber, as will be shown later.

The problems described in increasing tensile strength through continuing increases in molecular weight can be illustrated by the historical trend in strength versus time for rayon and nylon.¹⁻⁵ As one can see clearly from the trends in Figure 3, while steady progress was made over the years, a

major jump in strength (by a factor of almost 2) was made only by going to a new fiber. Fiber B continues this pattern, initially introduced to the tire companies in 1970 at about 11 gpd and then greatly improved to 20–22 gpd in 1971.

Dimensional Stability

Modulus, growth and creep, and the glass transition temperature (T_g) are crucial properties of a tire yarn since they influence such important tire performance characteristics as stability, flat spotting, treadwear, and operating temperature. The main molecular factors which influence these properties include, most importantly, chain stiffness, the intermolecular forces, orientation, and crystallinity. The combined effects of these parameters on retention of modulus and tensile strength at elevated temperatures are shown in Figure 4. Strength retention depends on melting point, while modulus retention depends on T_g . Fiber B, whose melting point is over 570°C , with a T_g over 300°C , still has a modulus of about 300 gpd and a tensile strength of about 15 gpd at 200°C (well over maximum tire operating temperatures). Measurements at -45°C show virtually identical strength and toughness values to those at room temperature.

Flat spotting, which is a function of the modulus at tire operating temperatures and the modulus ratio (tire temperature versus ambient temperatures),⁶ is insignificant for all of the ring-containing polymers and has been a limiting factor in acceptance for original equipment passenger tires only for nylons 66 and 6.

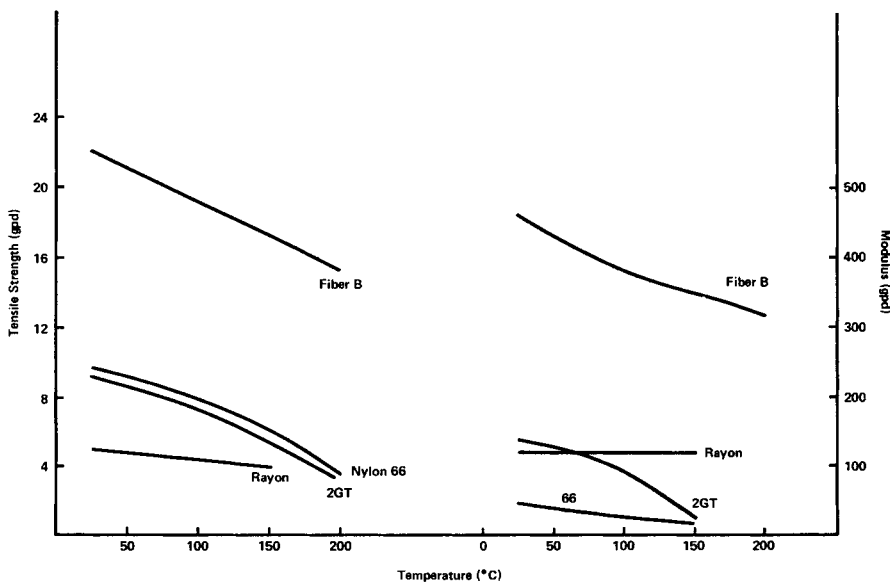


Fig. 4. Effect of temperature on tensile properties.

TABLE I
Dimensional Stability of Dipped Tire Cords

Fiber	160°C Shrinkage, %	Growth, ^a %	Creep, ^b %	Dry T_g , °C
T-728 Nylon	6.8	4.8	0.4	50
T-68 Dacron polyester	6.0	2.1	0.3	75
Rayon	0	4.9	1.4	—
Fiber B	0-0.2	0.5	<0.03	300+
Wire	0	0.7	<0.03	—
Glass	0	0.5	<0.03	—

^a Test conditions: 1 gpd, 30 min, 24°C.

^b Growth between 30 sec and 30 min.

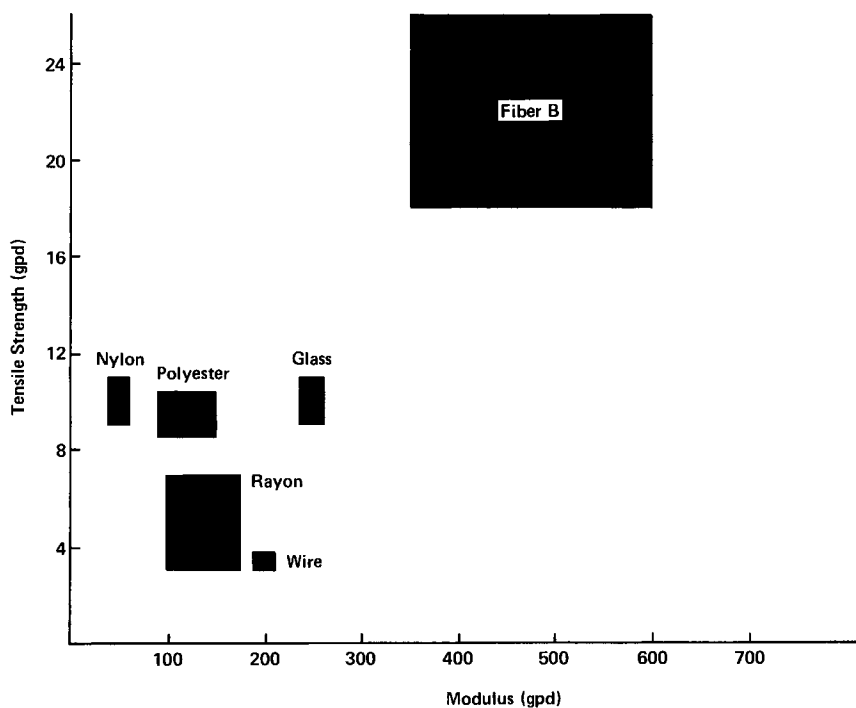


Fig. 5. Tensile strength-modulus relations for tire fibers.

Shrinkage at tire curing temperature (160–170°C) is another dimensional stability parameter which affects tire size and uniformity and should be kept as low as possible. It depends on T_g , degree of crystallinity, and the degree of amorphous region orientation (i.e., on yarn and cord processing temperatures and tensions). A comparison of dipped cord shrinkage, growth, creep, and T_g for the various fibers discussed is given in Table I. It should be noted that the dimensional stability of Fiber B is in the range

of the inorganic fibers, with essentially no shrinkage and creep and very low growth.

At this point, it might be well to examine the regions in a tensile strength/modulus map occupied by the various tire yarns, inorganic as well as organic (Fig. 5). It is evident that Fiber B is uniquely situated in a highly desirable region and thus provides an opportunity for engineering tires with a new balance of strength, weight, and dimensional stability.

Durability

Fatigue Resistance

A relatively large number of fiber characteristics affect tire durability. Of course, fiber modulus, rubber composition, and tire construction have an important bearing on treadwear. Once these factors are established, it is important to have the degree of abrasion and flex resistance needed to minimize fiber damage from compressional deformations. The capacity to absorb such deformations can be increased by an increase in the twist multiplier or helix angle of the fibers in the cord, but intrinsic fiber factors must still be controlled. Fatigue resistance is especially important in carcass cords and is a direct function of polymer molecular weight or chain length. With respect to abrasion, fiber fractional properties, including finish variables, are important. An increase in filament diameter improves abrasion resistance, but this variable must be handled with caution since flex resistance tends to be reduced with increased denier per filament, at least up to a point (properly designed monofilaments as exemplified by Du Pont's P-20 nylon industrial monofil⁵ have good flex resistance since buckling and kinking do not occur under compression). Since flex and abrasion resistance are related to fiber transverse properties, they can be adversely affected by excessive fiber orientation. Thus, it is generally best to avoid drawing the melt-spun fibers to very low breaking elongations, even if permitted by considerations of process continuity and yarn quality.

On the other hand, the morphology of Fiber B is such that fatigue resistance is surprisingly high in spite of the low elongation of the fiber. For example, data in Table II for bias tires show that the fatigue strength loss

TABLE II
Fatigue Resistance of Carcass Cords. 4-Ply 7.75-14 Bias Tires

Fiber	Twist multiplier	Tenacity, gpd	Elongation, %	Tire Fatigue strength loss, ^a %
T-728 Nylon	6.6	8.7	21	1-10
T-68 Dacron	6.6	7.2	15	10-20
Fiber B	8	15	—	8-16

^a Wheel test, 3000 miles at 21% dynamic deflection, 18 psi inflation pressure at tire running temperature, 35 mph.

TABLE III
Transverse Properties of Belt Fibers and Cords

Fiber	Fiber Flex Life, ^b KC	Denier	Cords ^a			
			Tenacity, gpd		Elong., % (Straight)	"Tough- ness" ($T \times$ $E/2$)
			Straight	Knot		
Fiber B	60	4500	18.0	8.3	4.0	36.0
Wire	(0.055) ^c	7800	3.4	2.2	1.7	2.9
Glass	0.003	3650	9.8	1.5	4.8	24.0
Rayon	22	3650	3.9	2.0	15.0	29.0

^a TM = 6.5 for Fiber B, 9.5 for rayon; wire and glass ready for tires [TM = (turns per inch) (denier)^{1/2}/73].

^b 0.6 gpd load, flexed over 3-mil wire.

^c Load reduced tenfold, i.e., 0.06 gpd, to permit running test.

TABLE IV
Durability of Bias-Belted Tires. Polyester Carcass

	Belt fiber	
	Glass	Fiber B
Weight of belt fiber, lb	ca. 0.6	0.13
Belt cords broken, ^a %	100 ^b	0.25
Relative treadlife, ^c %	210	210
Wheel test failures		
high speed, mph	100	110
step-load endurance, %	120	130
plunger energy, in.-lb	4100	4300

^a ARA F-3GC rough road test route—14,400 miles.

^b Cords broken or too weak to be removed from tire (no difficulty in removing cords after only 2000 miles).

^c Fleet test vs. 4-ply bias rayon control.

for Fiber B in an overloaded, underinflated tire can be brought to the same level as nylon and polyester with only a moderate increase in twist multiplier, in part necessary to correct for the higher density. In comparison with other high-modulus fibers used in tire belts, Fiber B has remarkably high transverse properties and toughness permitting an increase in twist, if required to control fatigue, while still retaining very high strength. This aspect of Fiber B is shown in Table III by such criteria as single-fiber flex life and cord toughness and knot strength. As indicated by the footnote of Table III, the single-fiber flex results for the 8-mil wire were obtained at one tenth the normal load in order to obtain meaningful data.

As shown in Table IV, the value of these properties can be demonstrated by fleet and wheel test results with bias-belted tires (polyester carcass) in which belts containing 0.13 lb of Fiber B were compared with belts containing ca. 0.6 lb of glass fiber. In the Automotive Research Associates F-3GC rough road test, after 14,400 miles over the Texas route, all of the

TABLE V
Durability of Radial Tires. Polyester Carcass

	Belt fiber	
	Steel wire	Fiber B
Weight of belt fiber, lb	2.5	0.5
Relative treadlife, ^a %	350	350
Wheel test failures		
Step-load endurance, %		
(Sidewall failures at ply turnups)	130	130
High speed, mph	100	100-105
		(105-110) ^b
Cleated Wheel, ^c miles	900	1500
		(3500) ^b

^a Relative to 4-ply bias rayon controls. ARA Severe XHA-1 test route, 28,000 miles.

^b Edges of Fiber B belts were folded to remove cut edges from high-stress shoulder zone, a difficult operation for wire because of its stiffness.

^c Twelve rounded cleats, $\frac{3}{4}$ in. high by $2\frac{1}{2}$ in. wide, bolted at various orientations to surface of the 5.6-ft-diameter test wheel. Tires are inflated to 24 psig and run 40 mph at 125% of rated load until failure.

glass belt cords were either broken or were too weak to be removed from the tires for testing (no difficulty was encountered in doing this after only 2000 miles). Less than 1% of the Fiber B belt cords were broken. Tread-life of the tires containing Fiber B belts was equivalent to glass in spite of the fourfold lower belt weight, while laboratory wheel test durability was somewhat better, as indicated by the high speed, step-load endurance, and plunger energy tests. In the high speed test, tires are run on a 5.6-ft-diameter steel test wheel at rated loads (after preliminary break-in at 60 mph) at progressively higher speeds (5-mph increments) for 1 hour at each speed until failure occurs. In the step-load endurance test, tires are broken in at 60 and then 75 mph at 110% of rated load; and then, while at 75 mph, the load is increased in 5% increments for 500 mile periods, i.e., to 115% for 500 miles, 120% for the next 500 miles, etc., until the tire fails.

In typical comparisons in wheel tests just described, Fiber B-belted radial tires have equaled wire-belted controls at a 1 to 5 replacement ratio (Table V). Both tires gave 3.5 times the treadlife of the 4-ply bias rayon control tires in track tests. In the high-speed and cleated-wheel tests, in which radial tires usually fail by belt-edge separation, the durability of Fiber B was increased to a level substantially higher than wire, by folding the belt edges. This operation is easily carried out with a flexible textile material but is difficult with wire because of its stiffness. Folding the edge of the belt removes the adhesive-free cut cord ends from the high shear zone at the tire shoulder.

As judged by tire and automotive experts, Fiber B belted radial tires generally give a smoother, quieter ride than wire-belted counterparts, apparently because of less weight near the tire periphery, lower bending stiffness of the belts, and greater vibration damping by Fiber B.

Thermal Stability

The susceptibility of fibers to strength loss in hostile environments can be an important factor in their utility as tire yarns. Oxidation can be a problem, particularly in high-temperature cord processing, with aliphatic polyamides since these are particularly vulnerable to free-radical attack at the carbon atom adjacent to the amide nitrogen.^{7,8} However, stability can be increased by a factor of 40 or more through the use of regenerative Cu^{++} /halide-based antioxidants. Such materials are used in commercial nylon tire yarns so that oxidation is not an important factor in nylon tire durability. Aromatic polyamides are inherently more stable to oxidation,⁹ and even without antioxidant protection they are considerably more stable

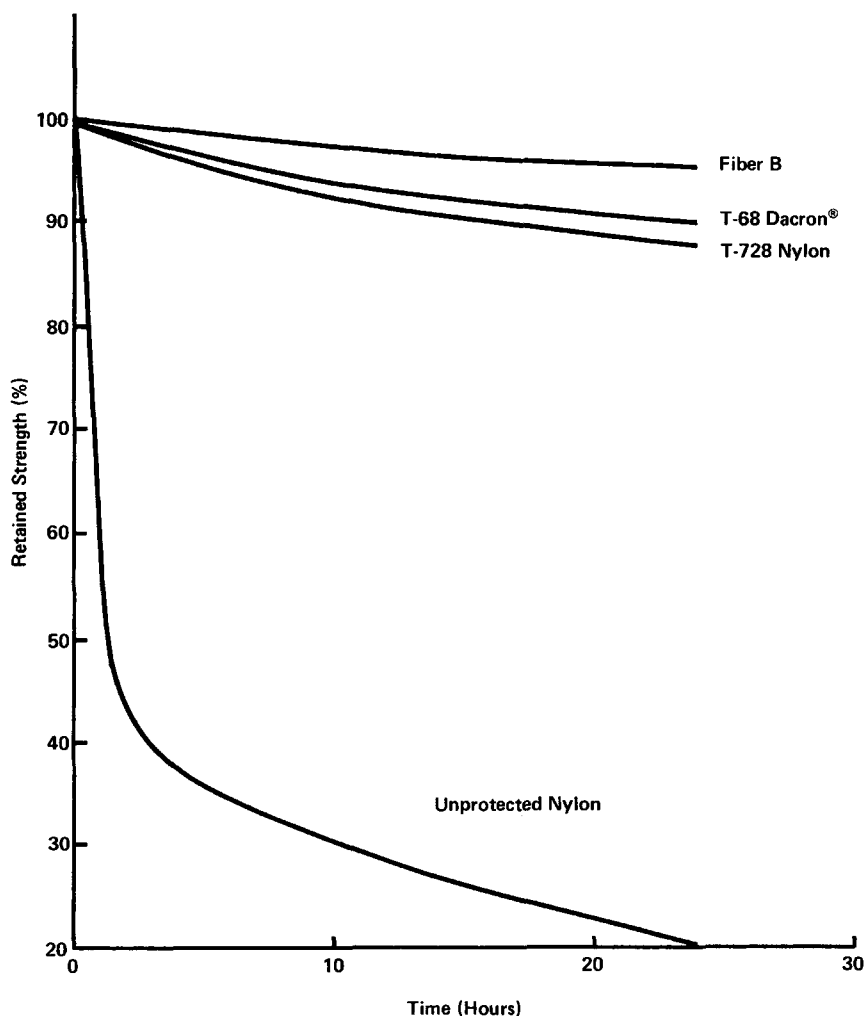


Fig. 6. Oxidative stability of tire yarns. Retained strength vs. time at 180°C in air.

than nylon or polyester, as shown in Figure 6 where strength retention versus time in air at 180°C is plotted.

With polyester tire yarn, the major stability concerns are with respect to hydrolysis and aminolysis. Both reactions are catalyzed by carboxyl endgroups in the polymer, but the amine content of the rubber stock plays a major role in aminolysis. Since both reactions have a relatively strong temperature dependence, they can be controlled through use of cooler-running rubber stocks and minimal weights of rubber and fiber consistent with other tire needs. Polyamides, including the all-aromatics, are essentially free from these reactions and are thus more suitable for heavier, hotter-running tires (e.g., for trucks).

Hysteresis

While the major portion of heat generated in a tire results from rubber hysteresis, a significant increment is contributed by the reinforcing fiber. In general, T_g has a significant effect on this property and for minimum

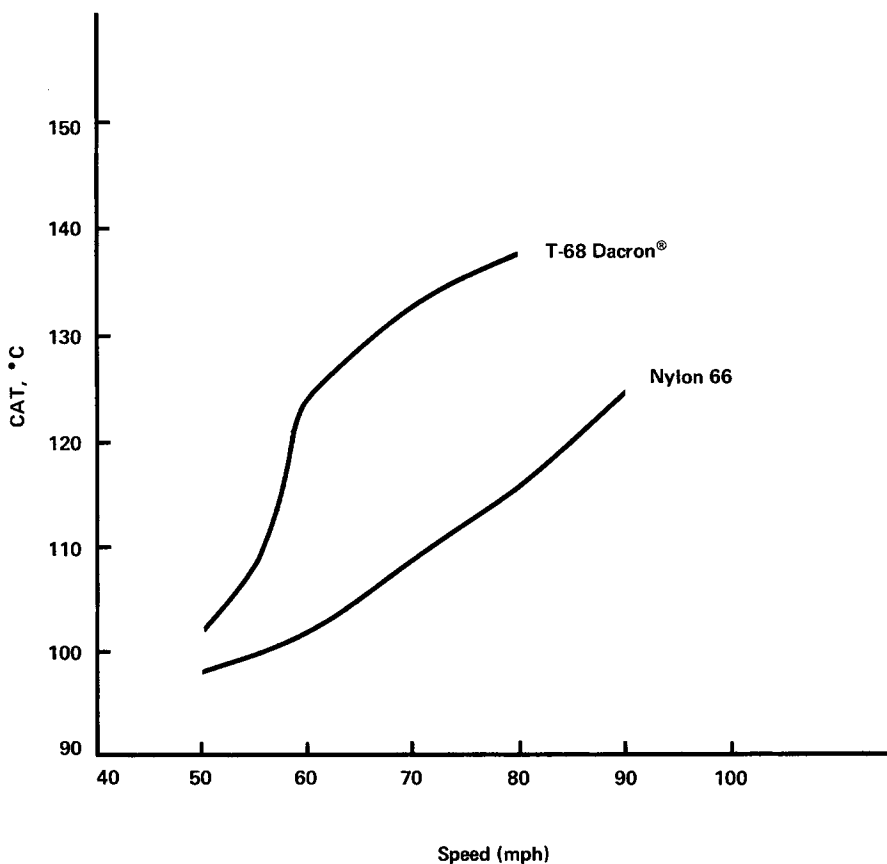


Fig. 7. Contained air temperature vs. speed. 7.75-14, 2-ply bias tires, 18 psi, 1480-lb load (117%).

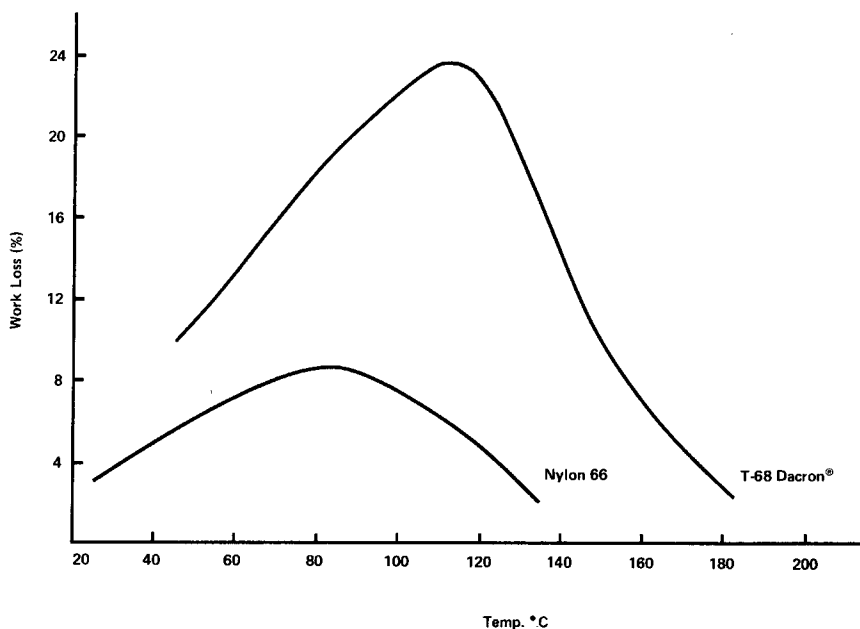


Fig. 8. Dynamic work loss vs. temperature (0.1 cycles per sec).

fiber hysteresis one should operate well below or well above T_g . One potential problem of polyester tire yarn is the increase in hysteresis as one approaches the temperature of maximum work loss (105–120°C), while nylon 66 reaches a maximum at about 60–90°C (depending on cord moisture content and rate of cycling). This factor is demonstrated in Figure 7, where contained air temperature is shown as a function of speed (7.75–14 two-ply bias tires). Note the rapid rise in temperature in the range of 105–125°C for polyester. In Figure 8, the dynamic work loss-versus-temperature relationship is given for polyester and nylon yarn at the somewhat low frequency of 0.1 cycle/sec and deformations of 1% from a zero stress point. Although the yarns may not be strictly comparable to dip-stretched cords in an operating tire, they do show the important differences in both temperature of maximum work loss and amount of hysteresis between nylon and polyester. It should also be noted that the operating temperatures in a normally inflated and properly loaded tire would be considerably less than those shown and that polyester passenger tires are not normally operated in the critical temperature range. The temperature problems do get greater in truck tires, however. For a given polymer type, hysteresis also depends in an inverse manner on the degree of crystallinity. Data available thus far for Fiber B indicate that the per cent work loss is essentially independent of temperature over the range of 25–250°C but is at a somewhat higher level than that of nylon. In spite of this, the reduced work input arising from the higher modulus of Fiber B results in high-speed tire operating temperatures essentially the same as those of nylon

tires. Moreover, Fiber B is not subject to the thermal degradation problems of polyester.

Adhesion

Strong adhesion between the tire rubber and the fiber is attained by the use of appropriate adhesive coatings. These are ideally selected on the basis of (1) the closest possible match in fiber and adhesive surface energies,¹⁰ (2) chemical stability of the adhesive, and (3) mechanical properties of the adhesive. The most popular adhesives are based on resorcinol-formaldehyde resin/latex (RFL) combinations. To achieve fully satisfactory results with polyester, subcoats have generally been used, applied either by the fiber producer or in cord processing. With the high-modulus Fiber B, fully satisfactory adhesion has been obtained with an epoxy subcoat and a modified RFL formulation.

Cost/Performance

The ultimate test of commercial success for a new tire yarn is its ability to deliver a desirable balance of properties at a cost commensurate with its performance. In today's highly competitive tire market, this imposes a need to select low-cost ingredients and efficient fiber-processing methods and to develop the versatility of end-use application needed to achieve large-scale market penetration. We believe that this can still be done with a new organic fiber of the type exemplified by Fiber B.

In summary, the more important tire yarn property criteria and the fiber and polymer factors which control them have been briefly described. We have shown, using Fiber B as an example, that the potential for creating new, more favorable property balances from organic fibers is far from exhausted. Fiber B is currently undergoing thorough evaluation by the tire industry.

This paper is based on the research of a large number of people in Du Pont's Textile Fibers Department, particularly at the Pioneering Research and Industrial Products Research Laboratories in Wilmington, Delaware.

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End of Symposium