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Some Physical and Mechanical Properties of Some High-Modulus Fibers Prepared from All-Para Aromatic Polyamide-Hydrazides*

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ABSTRACT

The tensile and physical properties of some high-modulus X-500 class fibers prepared from certain polyamide-hydrazides are described and the tensile properties, in particular, are compared with those of glass, steel, graphite, and several of the organic fibers. As a consequence of the wide range of densities of these fibers (glass, 2.6 g/cm^3; steel, 7.8 g/cm^3; and X-500 class fibers, ~1.45 g/cm^3), the tensile property comparisons are made in both textile and engineering units, grams/denier and pounds/inch^2, respectively. The amide-hydrazide polymers from which fibers of the X-500 class are obtained are typical fiber-forming organic polymers in the sense that fibers with a wide range of stress-strain

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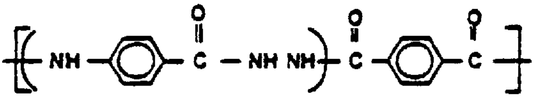
properties can be spun from them. Fibers were made with elongations-to-break as high as 60% and as low as 2-3%. For any given elongation-to-break, the modulus is much higher than that of conventional fibers. The initial moduli characteristically are greater than described by the expression, initial modulus = $1000E_b^{-0.38}$, where E_b is the elongation-to-break. Typical values for initial moduli are 600-750 g/den at 3-4% elongation, 210-230 g/den at 15-20%, and 100 g/den at 40%. The thermal properties such as melting point and glass transition temperature and the thermooxidative stability of these polyamide-hydrazide fibers place them in the heat resistant class. They are hydrolytically stable. Their electrical properties make them superior to glass for use in composites for certain electrical applications.

INTRODUCTION

In several other papers in this Symposium the properties of the recently discovered high-modulus polyamide-hydrazide fibers have been discussed briefly [1-3]. One of those fibers was studied through early pilot plant development. It is spun from a polymer derived from p-aminobenzhydrazide (PABH) and terephthaloyl chloride (TCl), and referred to as PABH-T. The structural formula (I) is shown below. Preston et al. [2, 3] have described the preparation of wholly para-oriented polyamide-hydrazides as well as the significance of this achievement in the light of the difficulty experienced in the past by research workers trying to prepare soluble high-molecular-weight wholly para-oriented aromatic polymers.

The fiber of PABH-T is but one member of a fairly broad class of high-modulus organic fibers discovered by Monsanto Co. scientists, and termed generically X-500 fibers. The one made from PABH-T is referred to in full as PABH-T X-500.



I

This paper will describe the properties of PABH-T X-500 fibers in detail. Additionally, key properties of PABH-T X-500 fibers will be compared with those of conventional organic fibers such as nylon 66 and polyethylene terephthalate, and also with some inorganic reinforcement fibers, specifically E-glass, S-glass, steel, and graphite. The greatest potential utility of the high-modulus organic fibers is for reinforcement of flexible and rigid composites where retention of tensile properties at elevated temperatures under either dry or high humidity conditions is critical. The behavior of these fibers under such conditions will be extensively reported. Because the utility of composites is frequently related to their overall weight and the reinforcement often makes up more than 50 vol % of the composite, the tensile properties of PABH-T X-500 are compared on a weight-property basis (specific property basis) as well as on a cross-sectional or volume basis.

The high-modulus organic fibers can be made with extensibilities (elongations-to-break) varying over a quite wide range in great contrast to glass, graphite, or steel fibers. For convenience, those polyamide-hydrazide fibers that have glasslike extensibility and modulus are referred to as PABH-T(G) X-500; those that have extensibilities in the range of those of high-tenacity textile fibers useful for tire cord are called PABH-T(T) X-500; and a high-elongation variant is designated PABH-T(E) X-500.

Independently, the discovery that very high-modulus fibers can be made from synthetic organic polymers has also been made in at least one (but apparently only one) other research laboratory, that of DuPont [4].

DISCUSSION

General Physical Properties

In Table 1 are listed the general physical properties of polyamide-hydrazide fibers.

Color and Appearance

Irrespective of whether the fibers are glasslike or textilelike, they are light colored, precluding their use application for products requiring colorless fibers. Generally, this is not expected to be a

TABLE 1. General Physical Properties of PABH-T(T) and PABH-T(G) X-500

	PABH-T(T)	PABH-T(G)
Color	Pale straw	Pale straw
Denier, single filament	5-10 (1)	4-8
Density, g/cm^3	1.44	1.47
Birefringence, Δn	0.3	0.57
Crystallinity index number[a]	30%	85-93%
Glass transition temp., T_g	None observed below T_d	
DTA decomposition temp., T_d	390°C	525°C
Moisture regain, 65% RH, 70°F	3.3%	2.0%

[a] The degree of crystallinity is given as the crystallinity index number. The method of J. H. Dumbleton et al. was used [5].

significant deficiency because the fibers are believed to have their greatest potential for reinforcement in rigid plastics, tires, V-belts, or military or industrial end uses for which a slightly colored fiber is acceptable.

The examination of cross sections of typical PABH-T(T) filaments, which had been drum-dried during spinning but not hot-drawn, showed no major void problems. Fine structure studies of these filaments by electron microscopy at magnifications as high as 28,000× showed a semicollapsed structure with very small micropores of 300 to 500 Å in size. Under certain spinning conditions, fibers with a well-defined skin-core relationship could be produced. Typically, the outside structure or "skin" was dense with a fine structure and the inside structure or "core" was granular in appearance.

Denier Range

A range of bundle- and single-filament deniers was spun. Bundle denier varied from about 300 to 1050 and single filaments from 4 to

10; the most common bundle denier used in these tests was a nominal 600, composed of filaments of 6.7 denier per filament (dpf). Filaments of approximately 1 denier were also studied, but not nearly so extensively. The very low denier filament was of interest because of 1) its much lower bending stiffness (a property dependent on the fourth power of the diameter and of interest in applications where weavability or fabric drape are important), and 2) its potential for greatly improved bending (flex) fatigue performance. The fatigue is a property dependent on many variables, a critical one being the tensile and compressive strains experienced on the outside of a fiber under flexure. These strains depend on the ratio of fiber radius to bending radius, and for a given flex deformation small diameter (low denier) fibers reach much lower strain levels and higher flex life (Fig. 1).

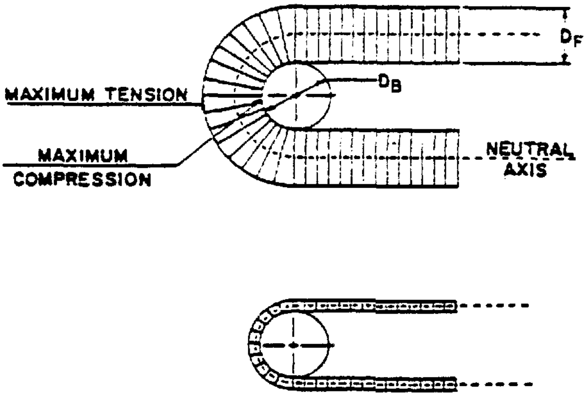


FIG. 1. Relative effect of a given bending radius on the extension and compression of a large-diameter and a small-diameter fiber. The maximum fiber strain (tension and compression) = D_F/D_B.

Density Measurements

Several determinations of density on samples with different spinning histories were carried out. The method used was to suspend samples in carbon tetrachloride-toluene mixtures. The

PABH-T(T) variant gave values of 1.435-1.443 g/cm^3 with an average of 1.44. The hot-drawn samples, PABH-T(G), showed a range of 1.465 to 1.473 g/cm^3 (average 1.47). Miller [6] and Holland [7] each report a crystallographic density of 1.51 g/cm^3. Miller obtained his value from x-ray diffraction studies on fibers, while Holland's value was determined from electron diffraction studies of thin films. The value of 1.473 observed for PABH-T(G) X-500 is within 2.5% of that of the crystallographic density, i.e., of 100% crystalline material. This finding is consistent with the ~90% crystallinity found for very high modulus PABH-T(G) fibers.

Degree of Orientation

PABH-T X-500 fibers, whether hot-drawn or not, showed a high degree of orientation. X-ray diffraction diagrams showed an increase in order as a function of the degree of stretch imposed during the spinning and drawing operations. As would be expected, PABH-T(G) samples with ultimate elongations of 2.5 to 4.0% were found to have the highest degree of orientation and crystallinity as the values for birefringence, x-ray crystallinity index, and density indicate (Table 1). Based on the considerations reviewed in the introductory paper of this Symposium [1], one could reasonably expect that a fiber of the chemical composition of PABH-T and showing a combination of high orientation and high crystallinity would have a very high modulus.

A high degree of crystalline order also renders materials more resistant to solvents and chemical attack than low crystalline order, and in the case of PABH-T X-500 the high crystalline order is considered to be partly responsible for its high resistance to solvents and its stability to wet and dry heat.

Birefringence

PABH-T X-500 shows very high birefringence values, and the individual refractive indices are also high although exact values could not be obtained because suitable immersion liquids were not available. An Ehringhaus compensator was used. PABH-T(T) samples had an estimated birefringence of 0.3, while PABH-T(G) samples showed values up to 0.6—among the highest values so far observed in any organic fiber. While no commercial use of this property is at the moment in sight, this property should be borne in mind wherever an application requires very great optical anisotropy.

Transitions in PABH-T

Neither thermal or internal friction (tan δ) measurements gave any hint that PABH-T fibers undergo a second-order transition over the temperature range from room temperature to their decomposition temperatures of 390 and 525°C for PABH-T(T) and PABH-T(G), respectively. That PABH-T(G) would have a significantly higher decomposition temperature than PABH-T(T) was not unexpected, but the amount of the increase was. Aromatic polymers with —CONH— linking groups characteristically show a higher decomposition temperature after being well-drawn [8]. One would expect this behavior also with aromatic fibers containing —CONHNH— linkages in addition to —CONH— linkages. Undoubtedly, the very large increase in thermal stability in the case of PABH-T(G) over that of PABH-T(T) is attributable to the very high degree of molecular order present (as shown by the very high per cent crystallinity and very high birefringence, Table 1).

Mechanical Properties at Room Temperature (Dry or at 65% Relative Humidity)

Single Filament Test Data (Instron Tensile Tester)*

As indicated earlier, like many other man-made polymeric fibers, PABH-T X-500 can be made with a wide range of properties depending on the spinning and drawing conditions. The basic characteristics of the several variants are:

PABH-T(E): A high energy-to-break, high extensibility material with a comparatively low modulus and tenacity (extensibility is in the range 20 to 40% but can be made up to 60+%).

PABH-T(T): A more typical high tenacity textile fiber but with modulus higher than other textile fibers of similar extensibility (ranging from 10 to 20%).

PABH-T(G): A very high modulus, low extensibility variant, very glasslike in behavior (extensibility typically 3-4% but can be made as low as 2%).

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*Unless otherwise stated, all single filament tensile properties reported in this paper were obtained at 100% extension/min using a 1-in. gauge length.

All the variants, E, T, and G, can be made from the same polymer; the differences in tensile properties result from variations in the spinning process.

One of the primary disadvantages of inorganic fibers is the very low range of extensibility of all such fibers: glass, steel, boron, etc. This limitation is especially critical with respect to those applications for which relatively high modulus plus a moderate energy-to-break is more desirable than very high modulus coupled with a low energy-to-break.

The tensile properties of the PABH-T X-500 variants (E, T, and G) and corresponding properties of some well-known fiber materials are shown in Table 2 in textile units for comparison on an equal weight or specific property basis, and in Table 3 in engineering units for equal volume or cross-sectional comparisons. Figures 2 and 3 show graphically some typical stress-strain curves in textile and engineering units, respectively. (Conversion factors and densities are given in the Appendix.) It should be pointed out here that this collection is comprised of data on very different materials which inevitably had to be tested under different test conditions of clamping, gauge length, and rate of straining. Even if standardization could have been feasible, it would still be arbitrary and tend to favor some materials at the expense of others.

PABH-T(E) could be useful for applications where a high initial modulus in the elastic region needs to be combined with a capacity to absorb large amounts of energy over an irreversible, large elongation prior to break. Such properties are important in certain impact absorbing devices, such as for single-use aircraft arresters, safety harnesses, and ballistic protection [9]. This variant of PABH-T X-500 has not been tested to the same extent as the other two and will not be discussed further.

PABH-T(T) fibers resemble certain high tenacity polyester fibers, but for equal tenacity have a considerably greater stiffness. In comparison with high tenacity nylon 66, the initial modulus of PABH-T(T) is about six times higher; PABH-T(T) also has a lower extensibility and somewhat higher energy-to-break.

PABH-T(G) behaves like a typical glass, and because of its considerably lower density compares particularly favorably on an equal weight basis (Table 2). The tensile stress-strain curve shows no clear yield point as found with steel, but is less linear than that for either graphite or glass. PABH-T(G) has good recovery (low hysteresis) properties and shows great promise where high stiffness and strength for low weight are of primary consideration.

TABLE 2. Typical Single Filament Data: PABH-T X-500 Variants and Other Fibers

[Textile units (specific quantities, per unit weight)]

Fiber	Tenacity[a] (g/den)	Extensibility[b] (%)	Initial Modulus (g/den)	Work-to-break (g/den)
PABH-T(E) X-500	5-6	20-40	90-150	1.2-1.6
Polyester (textile)	4.5-5.5	~40	40-50	1.0-1.6
Nylon (textile)	4.5-6.0	18-28	35-40	0.8-1.3
PABH-T(T) X-500	8-9	15-20	250-300	1.0-1.5
Rayon	5-8	6-15	100-140	0.2-0.4
Polyester	6-9	10-16	50-110	0.4-0.9
Nylon (high tenacity)	9.5	14-15	40-50	0.7-0.9
PABH-T(G) X-500	15-17	3-4	650-800	0.3-0.4
S-Glass	14.5	3-4	390	0.2-0.3
E-Glass	11.4	3-4	320	0.2
Steel wire	3.2-4.5	2-3	280-300	0.05-0.1
Graphite	8-20	0.6-0.7	1700-3200	0.05

[a] Tenacity is the specific stress at break—referred to the denier at start of test.

[b] Extensibility is the extension at break in per cent.

TABLE 3. Typical Single Filament Data: PABH-T X-500 Variants and Other Fibers

[Engineering units (per unit volume)]

Fiber	Breaking strength[a] (10^3 psi)	Breaking extension (%)	Initial modulus (10^6 psi)	Work-to-break (10^3 psi)
PABH-T(E) X-500	90-110	22-40	1.6-2.8	22-29
Polyester (textile)	80-100	40	0.7-0.9	
Nylon (textile)	90-150	18-28	0.3-0.7	12-19
PABH-T(T) X-500	150-170	15-20	4.6-5.5	18-28
Rayon	100-150	6-15	1.9-2.7	4-8
Polyester (high tenacity)	100-160	10-16	0.9-2.0	7-16
Nylon (high tenacity)	139	14-15	0.6-0.7	10-13
PABH-T(G) X-500	280-310	3-4	12.0-15.0	6-8
S-Glass	470	3-4	12.5	7-9
E-Glass	370	3-4	10.5	6-8
Steel wire	320-450	2-3	28	5-9
Graphite fiber	200-450	0.6-0.7	35-65	0.7-1

[a] Load per unit area of cross section at start of test.

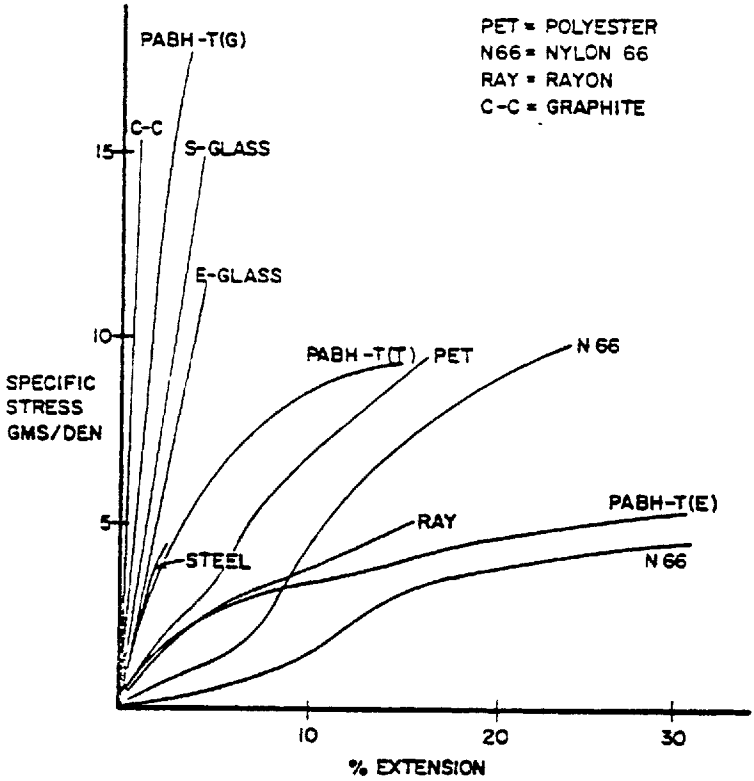

FIG. 2. Typical single filament stress-strain curves for PABH-T X-500 variants and other fibers. In textile units (specific or weight basis measurement); Instron Tensile Tester.

It is stronger and about twice as stiff as S-glass on a weight basis. Also on a weight basis, PABH-T(G) is 4-5 times stronger than steel, again has at least twice the modulus, and shows higher work-to-break. With respect to specific modulus, PABH-T(G) cannot compete effectively with such materials as graphite; its energy-to-break is, however, much greater than that of graphite—by a factor of 6 to 8.

Although PABH-T(E) fibers have higher moduli than any conventional fibers, which gives them somewhat of an advantage in energy-to-break, it is not likely that they will displace conventional fibers in many applications; one possibility, however, is for ballistic protection [9]. On the other hand, it is very likely that variants

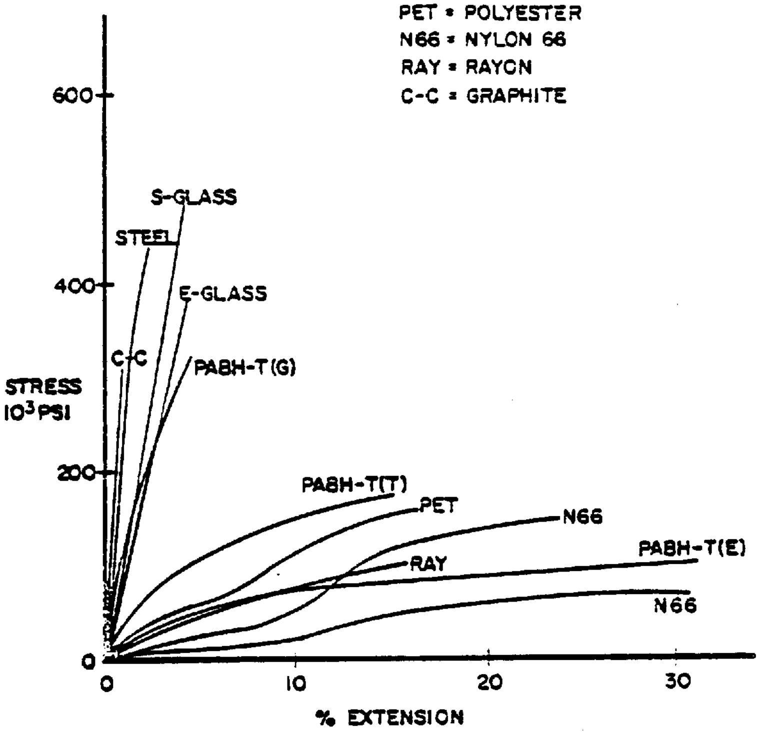

FIG. 3. Typical single filament stress-strain curves for PABH-T X-500 variants and other fibers. In engineering units (cross-sectional or volume basis); Instron Tensile Tester.

with elongations in the 5-15% range will find substantial usefulness, especially for tire cord [10]. The PABH-T(G) is certainly very satisfactory for rigid reinforced plastics [11].

There is a very strong inverse correlation between the initial tensile modulus and the elongation-to-break: the lower the elongation, the higher the modulus. Using tensile data from a large number of PABH-T fibers, the lowest observed modulus values M_i for any given elongation-at-break E_b were plotted against this elongation, E_b. Using curve fitting methods, a good fit was found of the form: $M_i = 1000E_b^{-0.58}$ for the range of E_b from 2 to 15% [1]. This relation is shown graphically in Fig. 4. The term

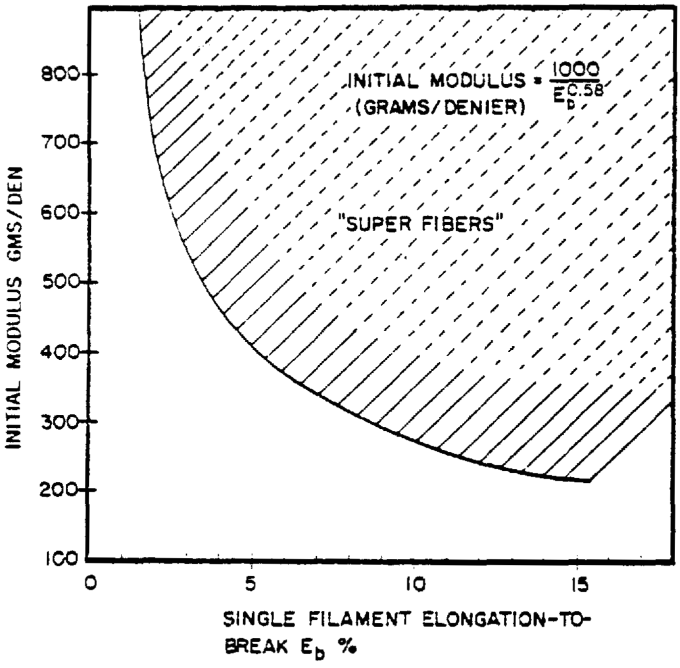

FIG. 4. Modulus vs elongation-to-break for "super-fibers" (textile units). Single filament data; Instron Tensile Tester.

"super-fibers" has been coined to denote organic fibers with the modulus-elongation combination at least equal to that given by the above expression. Such fibers would fall in the shaded area in Fig. 4. Most of the data obtained on PABH-T X-500 fell in the area indicated by the unbroken slanted lines. From this relation, fibers with 1.5 and 1.0% elongation must have moduli of 790 and 1000 g/den, respectively, to qualify as "super-fibers."

Bundle Test Data

Single filament data show the potential of a new material, but the translation of these properties into yarn, cord, and fabric properties depends partly on the uniformity of the fibers, fiber cross section, and surface characteristics and partly on the very important technical know-how. It is the result of many small improvements and optimization of details in finishing, twisting, handling, tensioning, winding, and weaving in order to reduce friction, abrasion, excessive straining, stress concentrations, and related dangers. In the case of PABH-T X-500, such optimization studies have not been carried out.

In evaluations of yarn performance the amount of twist is of great importance. For yarns of different fiber deniers, twist angles or twist multiplier rather than absolute turns per inch should be compared. Some twist studies on PABH-T yarns were carried out in connection with finish evaluation and preliminary studies for tire cord optimization and are reported separately by Raumann and Brownlee [10] in another paper in the Symposium.

Viscoelastic Effects (Room Temperature)

Viscoelasticity can be manifested and measured in many ways: creep and creep recovery, stress relaxation, hysteresis, loss factors, and temperature and time dependence of moduli.

Creep data were obtained on PABH-T(G) at fairly high stress levels. These are shown in Table 4 expressed as creep and recovery moduli and the respective rates. (Data for E-glass and S-glass are included but illustrate merely very low creep and recovery rates. Because of insufficient accuracy of the experimental technique, no meaningful values can be assigned to creep and recovery rates of the glasses.) Creep rates include secondary, nonrecoverable creep and it is preferable to use recovery rates for comparison with dynamic tan δ values.

The primary creep (or recovery) rate (d log ϵ)/(d log t) can be related to the dynamic mechanical loss factor tan δ—provided the Nutting relationship (small, constant damping) holds:

$$\tan \delta = \frac{\pi}{2} \left(\frac{d \log \epsilon}{d \log t} \right)$$

Table 5 shows a collection of modulus determinations by different experimental techniques. The expected trend is for the modulus to decrease with increasing strain and time of experiment (i.e., from left to right on the table). This trend is not consistently noted for any one of the fibers and illustrates the limitations of comparing data of related parameters but generated by very different experimental methods. The conclusion to be drawn in this case is essentially that the modulus of PABH-T is not greatly affected by strain and rate of straining. This conclusion will be shown to be supported by data on the temperature dependence.

TABLE 4. Creep Moduli, Creep and Recovery Rates for PABH-T(G) X-500 and Glasses. Room Temperature

Material	Stress (10^3 psi)	Modulus, 10^6 psi 1 min	64 min	Recovery	Creep rate	Recovery rate
PABH-T(G)	55	10.8	9.3	10.0	0.035	0.017
	85.5	10.3	9.1	10.0	0.030	0.024
	110	9.2	8.3	8.8	0.025	0.013
	137.5	8.5	7.6	8.5	0.027	0.027
Averages					0.029	0.020
S-Glass	55	14.8	14.8	15.3	0.000 (?)	0.007
	85.5	15.3	14.7	15.5	0.008	0.013
	110	13.9	14.2	14.4	-	0.003
	137.5	13.9	13.8	14.0	0.002	0.005
Averages					0.003	0.007[a]
E-Glass	55	11.7	11.7	12.0	0.000 (?)	0.005
	85.5	11.7	11.5	11.9	0.006	0.010
	110	11.2	11.2	11.3	0.000 (?)	0.002
Averages					0.002	0.006[a]

[a] See p. 150, paragraph 3, line 3.

TABLE 5. Moduli Loss Factors of PABH-T(G) X-500 and Glasses. Bundles at Room Temperature

	Sonic	Vibron	Instron	Creep	Recovery
Strain, %:	0.0025	0.05	0.5	0.4 →	1.8
Time, sec:	10^{-3}	10^{-1}	1	10^{2}	10^{4}
Moduli in 10^{6} psi					
PABH-T(G)	10.0	9.2	11.6	10.0	9.3
E-Glass	9.8	9.4	10.0	12.0	11.7
S-Glass	-	-	11.7	15.3	14.8
in g/den					
PABH-T(G)	540	490	630	540	505
E-Glass	300	290	310	370	360
S-Glass	-	-	360	470	455
Loss factors, tan δ					
PABH-T(G)		0.020		0.031	± 0.011
E-Glass		0.015		0.009[a]	± 0.006
S-Glass		(0.015)		0.011[a]	± 0.006

[a] See page 150, paragraph 3, line 3.

Table 5 also shows a comparison of tan δ values derived from Vibron and creep recovery measurements. Bearing in mind the errors of the creep recovery measurement, the agreement between the two methods is satisfactory.

Diverse Mechanical Properties

Knot and Loop Strength. The reduction in strength due to the presence of a loop or knot is considered a measure of the brittleness of the material. However, the geometry, finish, etc., can also affect the loop and knot strength. Values for bundles of PABH-T(T) and PABH-T(G) showed the knot and loop tenacities to be very similar, about 85% of straight tenacity for PABH-T(T) and 9.5% for PABH-T(G).

Flex Endurance Test. The flex life of several samples of films and fiber bundles were measured on the MIT Folding Endurance Tester. (Made by Tinius Olsen Testing Machine Co., 0.3 in. jaw width, circular roller oscillates through ±135°C at about 100 cycles/min.) The results are shown in Fig. 5 correlated to the ultimate elongation of the fiber. Other parameters, e.g., crystallinity, which also show marked dependence on spinning and drawing variables, could be selected for such a correlation, but extensibility can be more conveniently measured.

The effect of fiber geometry on flex life is strikingly shown by reducing the fiber denier from 5.6 to 1.0. The flex life increased by a factor of 18, i.e., from 90 to 1600 cycles.

For both fiber and film there was a strong inverse correlation between the flex life and the degree of crystallinity; however, since crystallinity correlated well inversely with the elongation, the correlation of crystallinity with flex life was as would be expected. Crystallinity is not believed to be the controlling property regarding flex life.

The flex life results presented here were obtained while investigating the effects of various spinning and drawing operations. These data are useful for comparisons, but they should not be used to describe a material parameter of PABH-T X-500. The MIT tester is very severe for nontextile (i.e., glasslike) fibers. Fatigue and flex tests can be useful for predicting fiber or yarn behavior in special end uses, but the tests must be carefully designed to simulate actual conditions of stress and strain levels and time and temperature factors.

Crimpability. Yarn samples of PABH-T(G) and PABH-T(T) were co-crimped with a 60,000 denier polyester tow in the Turbo

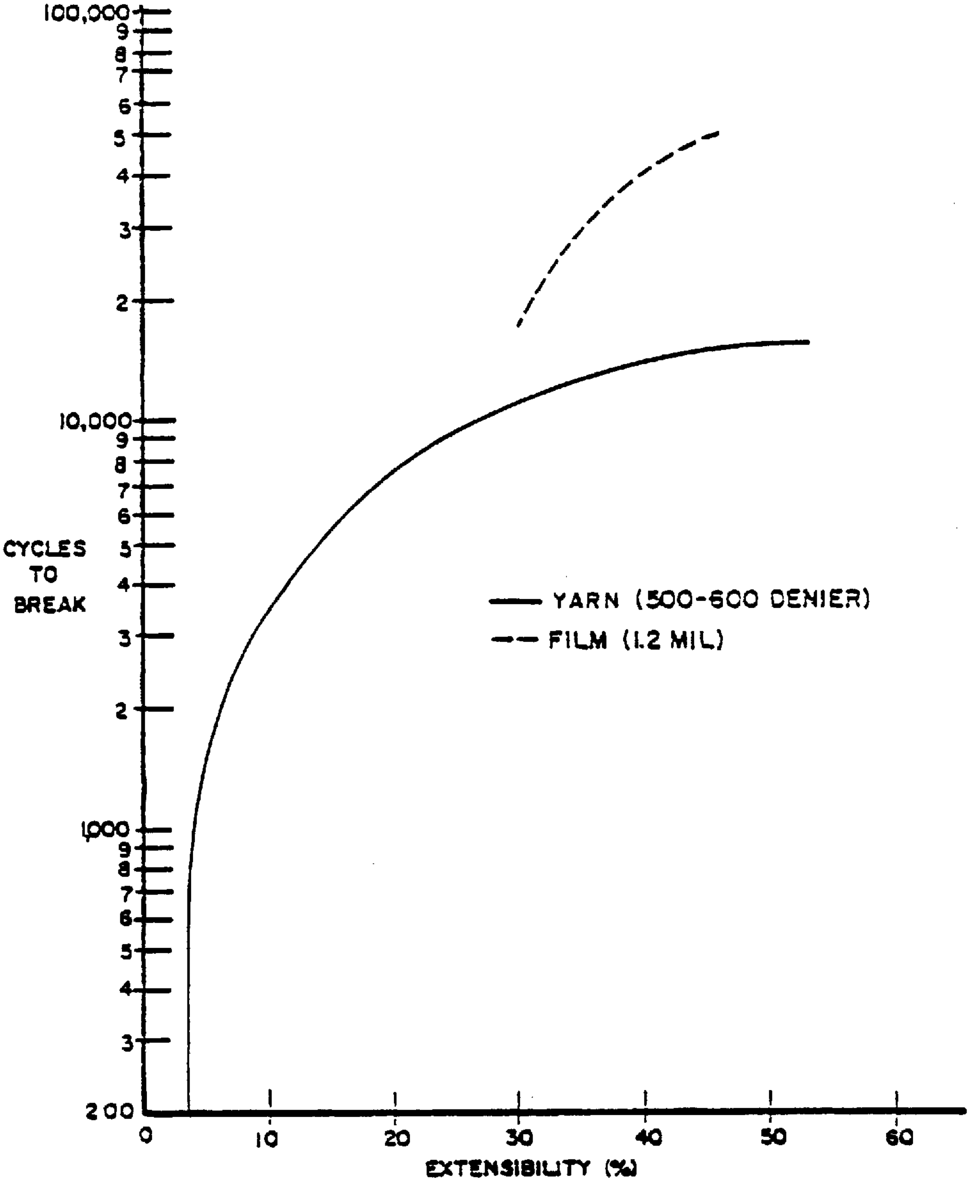

FIG. 5. Folding endurance of PABH-T X-500 yarns and film as a function of extensibility. MIT Folding Endurance Tester.

Crimper which uses the stuffer box principle and steam (10 psi, ~126°C) as a plasticizer. The PABH-T(G) sample was badly damaged as the plasticizing action of the team was insufficient for all fibers to bend without breaking under these severe conditions. The more textilelike PABH-T(T) was crimped satisfactorily to 10-15 crimps/in. under the same settings. No loss of crimp was found when the crimped yarns were immersed in boiling water for 5 min. This indicates that crimped PABH-T X-500 yarns would not need an additional heat-setting step to preserve the crimp patterns.

Effect of "Dry" Heat on Mechanical Properties

The effect of heat on PABH-T X-500 fibers was studied in two series of experiments. In the first series, fibers were introduced into a test chamber at elevated temperature and their mechanical properties measured at the elevated temperatures. This test yields information of interest to all applications; e.g., tire cord and composites in hyperthermal environments where PABH-T may be exposed to use at temperatures above (or below) ambient.

The second series was designed to show the long-term effect of heat, i.e., its chemical degradative effects, on the room temperature performance of PABH-T.

Both measures of the resistance to the effect of heat are very important. In some end uses, such as tire cord, the tensile properties measured at room temperature may not apply to actual use conditions of the tire, since running temperatures of tires are known to be well above ambient. The same is true, of course, for composites that would be used in hyperthermal environments. One certainly also needs to know how well the fiber resists degradation upon sustained exposure to elevated temperatures such as would be encountered by tire cord (particularly if it is to be used for truck and other heavy equipment tires), or by composites for certain aircraft or equipment end uses.

Both PABH-T(T) and PABH-T(G) have excellent dimensional stability. Upon heating on a metal surface for 5 min, neither fiber had measurable shrinkage up to 300°C, and neither shrank as much as 0.1% at 400°C. Such outstanding dimensional stability is of great value in building tires that are truly round and in making composites that can retain the desired geometry during curing as well as in use.

Mechanical Properties at Elevated Temperatures

Instron Tensile Data. Instron tensile data are shown in Fig. 6 for the retention of tenacity, elongation, and modulus for both PABH-T(T) and PABH-T(G) X-500 up to 300°C in dry nitrogen. The modulus of neither is greatly affected up to about 100°C: in the order of 50% of the Instron initial modulus is retained at 200°C. Extensibility is little affected for either variant up to 200°C, showing that the fibers can be heated to this temperature with neither embrittlement nor rubberiness becoming evident. The tenacity

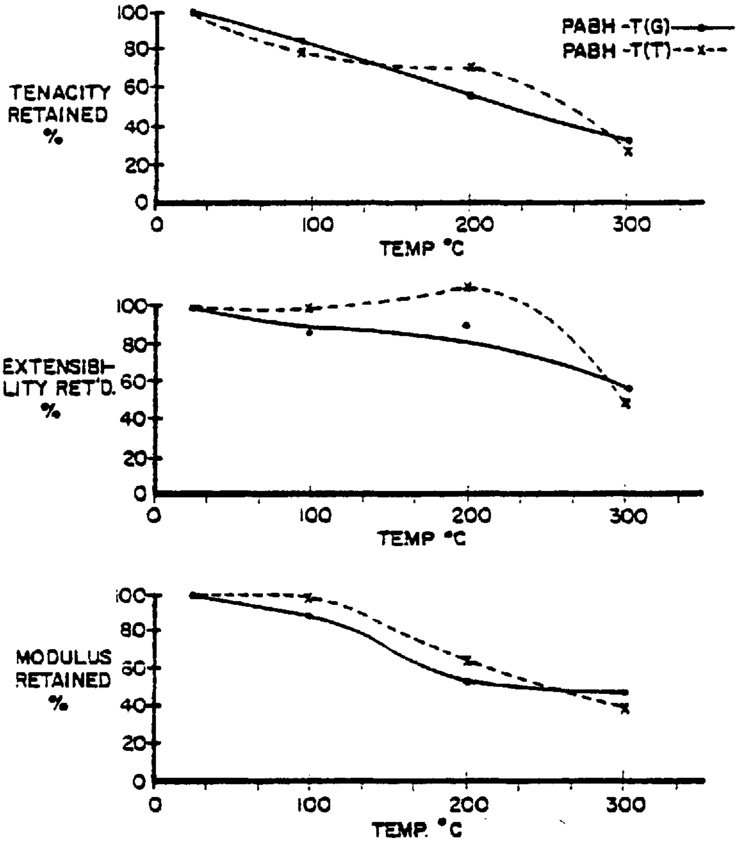

FIG. 6. Retention of tensile properties of PABH-T(T) and PABH-T(G) at elevated temperatures in dry nitrogen. Single filament data; Instron Tensile Tester.

is more sensitive to elevated temperatures than the modulus; nevertheless, over half of the strength is retained at 200°C for both the textile and glasslike variants. It is somewhat surprising that there are not considerably greater differences in the retention of tensile properties of PABH-T(G) and PABH-T(T) fibers at elevated temperatures, especially above 150°C.

Vibron Data at Elevated Temperatures. Figure 7 shows the modulus and tan δ values obtained for samples of PABH-T(G), PABH-T(T), and an undrawn film of PABH-T. The trends of the moduli are expected and the behavior of tan δ does not eliminate a possible transition region for the film at higher temperatures, but is more likely an indication of a lower decomposition or approaching melting temperature. True transition regions (T_g) are normally accompanied by tan δ values in the 0.3 to 0.5 region—a factor of ten higher than those observed here.

Change of Modulus with Temperature. The details of the strain and time ranges of the different modulus determinations have already been given in Table 5. Figure 8 shows, on semilogarithmic plot, the variation of the moduli with temperature. Some of the discrepancies of the absolute values of the moduli at room temperature have already been pointed out. The temperature dependence shows the Instron and creep moduli to be greater than the dynamic moduli (sonic and Vibron) which is the expected trend. However, the Vibron data are less affected than the sonic, and this is somewhat unsatisfactory. Further clarifying experiments are needed to reconcile these inconsistencies.

The data on PABH-T(T) from only two test methods do not show any unexpected trends and thus suggest that the difficulties met with PABH-T(G) are due to applying normal textile tests to an abnormally stiff material.

Mechanical Properties after Heat-Aging in Air

PABH-T(T) was found to retain three-fourths of its tenacity after 20 days in air at 200°C, and PABH-T(G) had half of its strength after 1 day at 300°C (Table 6). Two days at 185°C had no observable effect on the strength of either PABH-T(T) or PABH-T(G).

Figure 9 shows the changes in tenacity, elongation, and initial modulus for a PABH-T(T) fiber over a period of 20 days at the relatively high temperature of 200°C. The fiber samples were heat-aged both in an unrestrained condition and at constant length. (The tensile tests were made at room temperature and 65% RH.) The modulus was little affected in either case. There was a quite substantial loss of extensibility during the first 5 days at

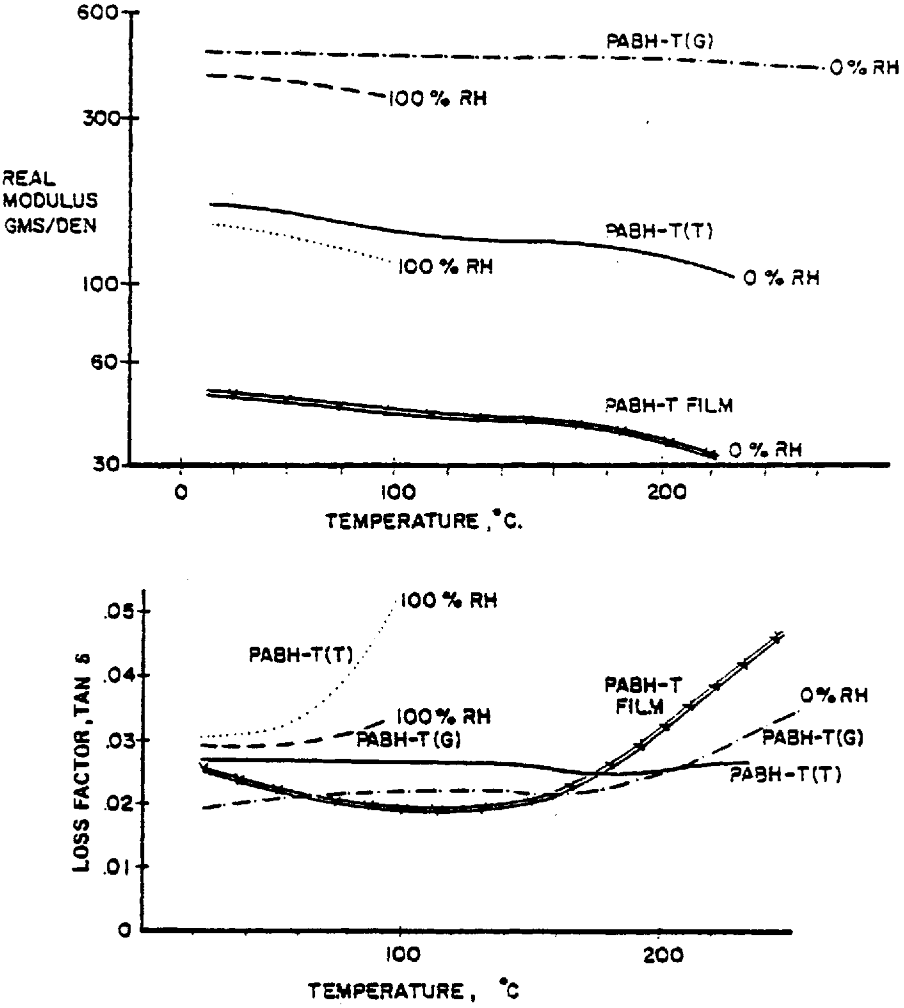

FIG. 7. Dynamic mechanical properties of PABH-T(T) and PABH-T(G) X-500 at 20 to 250°C, 0 and 100% RH. Vibron elastoviscometer, 11 Hz.

200°C, accompanied by a moderate increase in tenacity. Almost certainly the loss of elongation was primarily a consequence of crystallization, and not a consequence of chemical degradation.

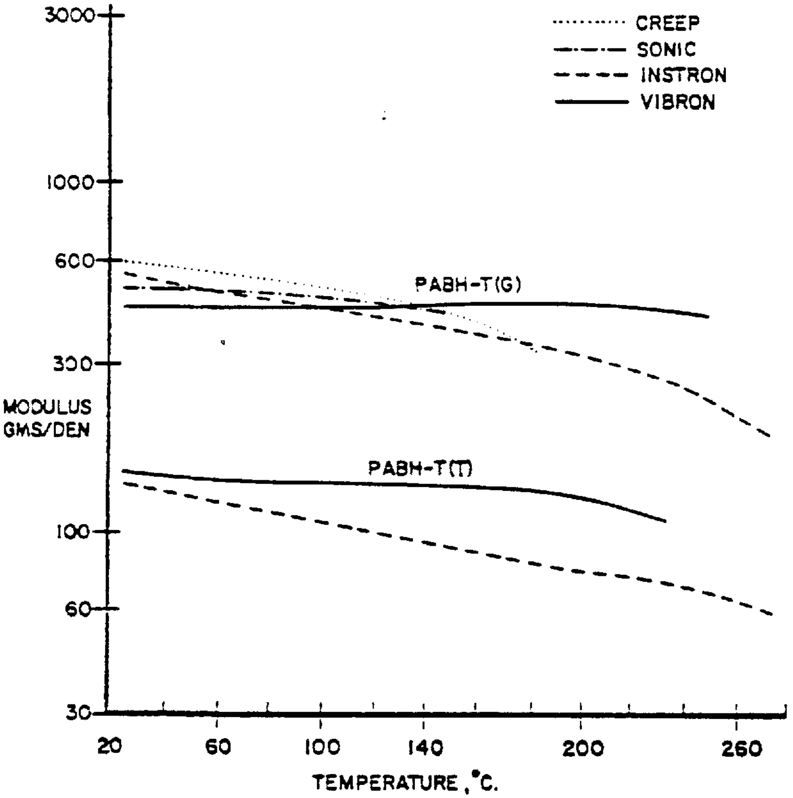

FIG. 8. Collection of modulus changes with temperature—different methods of measurement.

This interpretation is strongly supported by an increase in the sharpness of the reflections in the x-ray diffraction patterns and the increase in tenacity of about 2 g/den over the same time span. The gradual loss of tenacity after 5 days at 200°C can be interpreted as evidence of chemical degradation, but there is not an equivalent loss of elongation, the tensile property generally most sensitive to chemical degradation, indicating that the loss of tenacity may not be totally due to chemical degradation.

Clearly the unrestrained condition is preferred for retention of tenacity and elongation. The greater decreases in tenacity and elongation by the sample held at constant length are attributed

TABLE 6. Effect of Heat-Aging PABH-T(T) and PABH-T(G) X-500 in Air at Elevated Temperatures

Strength retention[a] after:	PABH-T(T)	PABH-T(G)
1 day in air at 185°C	100%	100%
2 days in air at 185°C	100%	100%
5 days in air at 200°C	111%	-
10 days in air at 200°C	100%	-
20 days in air at 200°C	84%	-
1 day in air at 300°C	-	53%
3 days in air at 300°C	26%	-

[a] Instron test at standard conditions after the heat-aging.

to physical phenomena since one would expect that the restraint imposed on the fiber by holding it at constant length would result in essentially the same or less chemical degradation than experienced by the unrestrained fiber.

It is obvious that PABH-T X-500 is truly a thermally stable fiber, although admittedly it is not quite as thermally stable as most of those reviewed recently by two of us [12, 13]. For additional information on the heat-resistant properties of polyamide-hydrazides, the reader is referred to the two papers in this Symposium by Preston, Black, and Hofferbert [2, 3].

Properties of PABH-T X-500 in the Presence of Moisture or Water

Although neither PABH-T(T) nor PABH-T(G) is completely insensitive to the effects of moisture or water, both are remarkably resistant to the effects of water. The effect of water on these fibers was looked at with regard to both the hydrolytic resistance under a variety of conditions and the physical effects of absorbed or imbibed water.

Moisture Regain (Table 1)

PABH-T(G) has a moisture regain of 2.0% under the standard conditions of 70°F and 65% RH; the regain of the textilelike variant

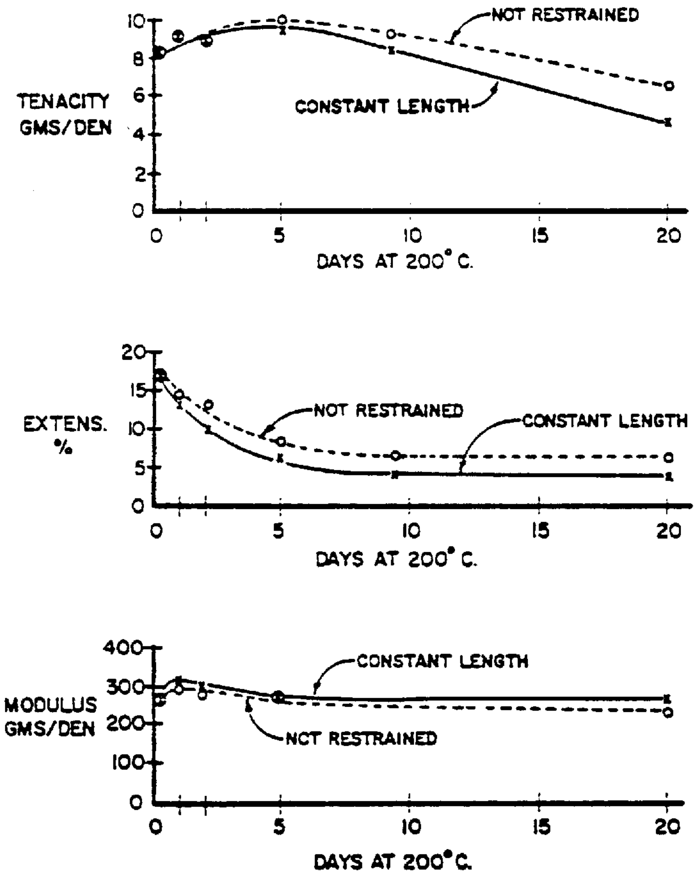

FIG. 9. Change in tensile properties of the textilelike variant of PABH-T X-500 with time upon heating at 200°C in air. Fibers tested both at constant length and unrestrained.

was appreciably higher, 3.3%. In this respect PABH-T(G) behaves more like polyamides and polyhydrazides than the glass it resembles in mechanical behavior. Estimates of expected regain of PABH-T based on the proportion of —CONH— and —CONHNH— groups to phenylene ring content are in the region of 4.5 to 5.5%. The lower actual value is attributed to the high degree of crystallinity, a trend shown by the difference of regain between PABH-T(T) and PABH-T(G). By way of comparison, polyethylene terephthalate fiber has a moisture regain of less than 1%.

Instron Tensile Properties in Water at Elevated Temperatures

The glasslike PABH-T retains only about two-thirds of its tenacity and three-fourths of its modulus in water at 90°C (Table 7). The reduction of strength and modulus was greater than for similar tests carried out in dry air.

TABLE 7. Effect of Exposure to Moist Heat on PABH-T X-500 Tensile Properties

	PABH-T(T)	PABH-T(G)
Instron tensile properties in water		
Retention in 90°C water compared to standard:		
Tenacity	-	66%
Extensibility	-	86%
Modulus	-	76%
Energy	-	58%
Boiling water shrinkage	0%	0%
Tensile property retention[a] after:		
150 Days in 50°C water		
Tenacity	63%	92%
2 Days in boiling water		
Tenacity	-	100%
Extensibility	-	83%
Modulus	-	100%
15 Min at 150°C, 50 psi steam		
Tenacity	-	84%
Extensibility	-	77%
Modulus	-	100%
15 Min at 170°C, 215 psi steam		
Tenacity	-	72%
Extensibility	-	50%
Modulus	-	100%

[a] Instron tensile properties at standard conditions.

Instron Tensile Properties after Various Treatments in Water at Elevated Temperatures

One of the most striking properties of PABH-T(G) is its retention of properties after exposure to water at elevated temperatures under a variety of conditions of time and pressure (Table 7). At one extreme, after 6 months in water at 50°C, PABH-T(G) retained 92% of its tenacity, while at another extreme it retained 100% of its modulus and three-fourths of its tenacity after exposure for 15 min to 215 psi steam. The latter treatment severely degraded both nylon 66 and polyethylene terephthalate fibers. Boiling in water for 2 days did not change the modulus or tenacity of PABH-T(G). The boiling water and steam-under-pressure treatments, however, do tend to reduce the extensibility somewhat, presumably because of further crystallization. Both S- and E-glass suffered very significant losses in tenacity upon boiling in water for 2 days (Fig. 10). Neither PABH-T X-500 variant shows any boiling water shrinkage.

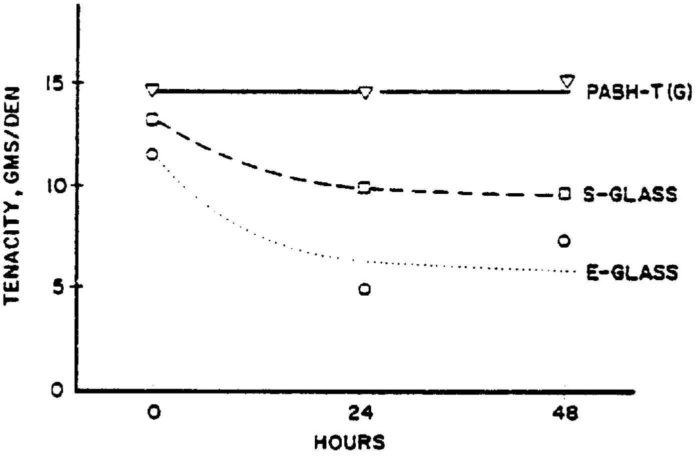

FIG. 10. Tenacity and extensibility changes for PABH-T(G) and glass fibers after boiling water exposure. Single filament data; Instron Tensile Tester.

The rather remarkable resistance of PABH-T X-500 to deleterious effects by hot water in comparison with S- and E-glass should certainly give PABH-T X-500 type fibers a distinct advantage over the glass fibers for those reinforcement applications where glass composite products require overdesigning because of the relatively poor resistance of glass to damage by water. Also, the resistance of the PABH-T type fibers to damage by water coupled with their high specific strength should make them ideal for underwater cables.

Dynamic Mechanical Properties at 100% RH in Air

Dynamic mechanical properties of PABH-T X-500 film and both the glasslike and textilelike PABH-T fibers at 100% RH are plotted in Fig. 7 along with the data at 0% RH. The 100% RH modulus was about 20% lower than for the dry surroundings. The tan δ values showed some increase—especially for PABH-T(T) X-500 at higher temperatures. The tan δ at 100% RH and 95°C for the PABH-T(T) was the highest recorded for any PABH-T sample, drawn or undrawn.

Effect of Light on PABH-T X-500

Both PABH-T(T) and PABH-T(G) to which light stabilizers have not been added are rather strongly degraded by light (Fig. 11). The extensibility of the high-elongation textile variant is rapidly lost, an almost certain indication of substantial chemical degradation. This level of light degradation would preclude the use of these fibers for products exposed to direct sunlight for long periods of time. Most likely, the degree of light stability can be greatly improved by the addition of suitable light stabilizers as in the case with polyamides.

Chemical and Solvent Resistance of PABH-T X-500 Fibers

PABH-T X-500 is degraded to a moderate extent by strong acids, to a fairly severe extent by strong base, but is moderately resistant to degradation by concentrated ammonium hydroxide by comparison. For a more detailed discussion of the effect of acids and bases on the fiber properties of polyamide-hydrazides, see the second paper in this Symposium by Preston, Black, and Hofferbert [3].

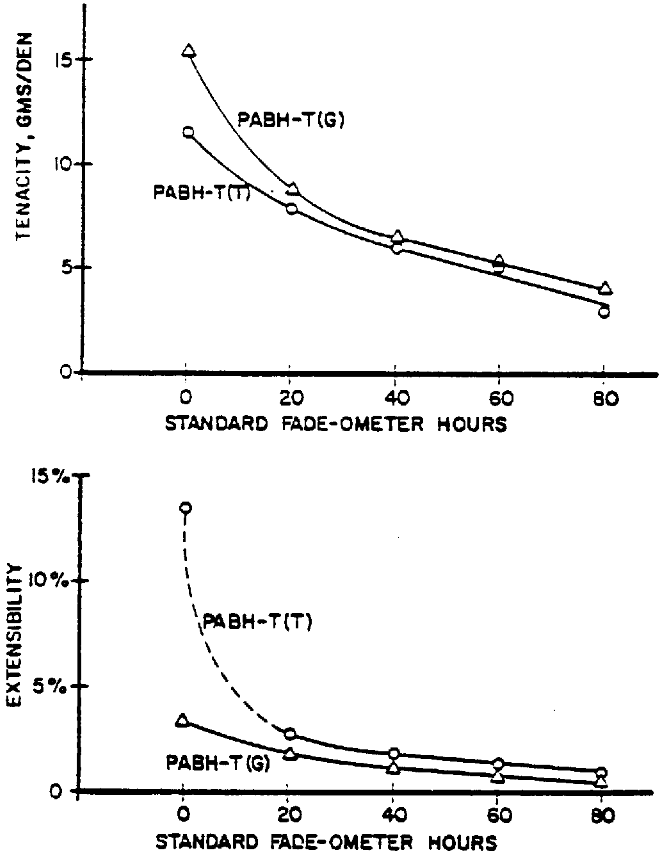

FIG. 11. Effect of light on the tenacity and extensibility of PABH-T(T) and PABH-T(G) X-500. Single filament data; Instron Tensile Tester.

PABH-T is dissolved by dimethyl sulfoxide. Although not soluble in dimethyl acetamide, the fibers are greatly weakened by this solvent. In general, however, PABH-T X-500 fibers are remarkably resistant to solvents other than those recognized as solvents for aromatic polymers containing amide and hydrazide linkages (N-methylpyrrolidone, hexamethylphosphoric triamide, and the like).

Electrical Properties of PABH-T(G) X-500

In many end uses of rigid reinforced composites (e.g., in radomes, "breadboards" for electronic circuits, and the like) electrical properties are of major importance. The electrical properties of a PABH-T(G)/epoxy and a similar E-glass/epoxy panel—both loaded to about 60 vol %—are shown in Tables 8 and 9. Tests were carried out dry and after water immersion. For most conditions the PABH-T composite showed properties similar to the glass composite.

Of particular significance was the observation that the E-glass composite absorbed more water than the PABH-T composite, and this gave rise to a greater range of measured properties for the glass panel. While at low frequencies both the dissipation factor and the loss index are greater for the PABH-T composite, both measurements are the same for each the E-glass and PABH-T composites at radar frequencies. Only in arc resistance did the PABH-T composite prove to be distinctly inferior to the E-glass composite.

Dielectric Constant (K)—Alternating Current (Table 8)

The E-glass composite has a higher dielectric constant at all frequencies than the PABH-T composite.

The E-glass composite absorbed more water during water immersion conditioning. This is shown by a greater increase in dielectric constant at 100 Hz. The dielectric constant of H_2O at 100 Hz is about 80.0 and decreases rapidly as the frequency increases; hence, a small amount of water has a large effect at 100 Hz.

Dissipation Factor (Tan δ)—Alternating Current (Table 8)

The dipolar loss for the PABH-T(G) X-500 composite was greater than for the E-glass composite. This is related to the size of the dipole and the shape of the molecule. Again the E-glass composite absorbed more water. This was shown by the greater per cent increase in dissipation factor at 100 Hz after water conditioning. Water has extremely high losses at frequencies below 10^4 Hz because of low energy ionization and conduction due to these ions.

As the frequency is increased, the dissipation factor of the PABH-T and of E-glass composites approach each other. The phenomenon is probably due to the influence of the matrix polymer.

TABLE 8. Electrical Properties E-Glass/Epoxy vs PABH-T(G)/Epoxy. Fiber Volume about 60%[a]

	PABH-T fabric, condition			E-Glass fabric (A-1100), condition		
Property	A[b]	D-24/23[c]	D-48/50[d]	A[b]	D-24/23	D-48/40
Dielectric constant						
at 1 × 10^2 Hz	5.20	5.23	5.29	5.66	5.79	6.13
at 1 × 10^6 Hz	4.38	4.40	4.50	5.18	5.20	5.32
at 32 × 10^6 Hz	4.12	4.12	4.22	4.93	4.93	5.03
at 8.2 × 10^9 Hz	3.40	-	-	4.46	-	-
Dissipation factor						
at 1 × 10^2 Hz	0.028	0.028	0.030	0.012	0.018	0.034
at 1 × 10^6 Hz	0.029	0.029	0.030	0.021	0.022	0.023
at 32 × 10^6 Hz	0.032	0.033	0.034	0.027	0.029	0.029
at 8.2 × 10^9 Hz	0.0105	-	-	0.0088	-	-
	Condition			Condition		
	23°C/40% RH	D-24/23	D-48/50	23°C/40% RH	D-24/23	D-48/50
Loss index[e]						
at 1 × 10^2 Hz	0.147	0.146	0.162	0.068	0.104	0.208
at 1 × 10^6 Hz	0.128	0.128	0.135	0.108	0.114	0.122
at 32 × 10^6 Hz	0.138	0.136	0.144	0.133	0.143	0.146
at 8.2 × 10^9 Hz	0.036			0.039		

[a] Work of J. R. Taylor, Monsanto Co.

[b] Sample conditioned at least 88 hr at 23°C and 50% RH (ASTM-D-618-61).

[c] Sample immersed for 24 hr in distilled water at 23°C prior to test (ASTM-D-709-67 and D-618-61).

[d] Sample immersed for 48 hr in distilled water at 50°C prior to test (ASTM-D-709-67 and D-618-61).

[e] Loss index = dielectric constant × dissipation factor.

TABLE 9. Electrical Resistance Properties of PABH-T(G)/Epoxy and E-Glass/Epoxy Composites Compared[a]

	PABH-T(G) composite	E-glass composite
Dielectric breakdown		
at rate of 1000 V/sec	490 V/mil	488 V/mil
step/step[b]	452 V/mil	430 V/mil
Volume resistivity, ohm cm		
as received	1.13×10^{16}	2.48×10^{15}
after 96 hr at 35°C and 90% RH (3-min electrification)	8.47×10^{15}	1.09×10^{15}
Insulation resistance, ohm cm		
as received	1.95×10^{15}	6.18×10^{13}
after 96 hr at 35°C and 90% RH (3-min electrification)	3.48×10^{14}	1.39×10^{13}
Arc resistance, sec	125	182

[a] Work of J. R. Taylor, Monsanto Co.

[b] Initial voltage is 50% of short time breakdown and is applied for 1 min. The voltage is then increased 5,000 V and held for 1 min. This procedure is followed until breakdown occurs.

Loss Index (K × Tan δ, Table 8)

The PABH-T composite has the higher loss index at 100 Hz. As the frequency increases, however, the loss index of the PABH-T composite decreases while that of the glass composite increases. At and above 32×10^6 Hz both composites have the same loss index. (Loss index is directly related to the energy lost to the composite by the electric field. It is converted to heat energy in the composite and causes a temperature rise. Since the energy lost is also directly proportional to the electric field frequency, the temperature rise below 10^6 Hz is negligible.)

Resistance (Volume Resistivity, Surface Resistivity, and Direct Current, Insulation Resistance, Table 9)

At all conditions the PABH-T composite has a higher resistance than the E-glass composite. This is primarily due to a greater ion concentration in the E-glass composite.

Arc Resistance (Alternating Current, 60 Hz, Table 9)

This is a test of the ability of a material to withstand the temperature created by a low current intermittent arc struck directly over its surface. It is intended to simulate service conditions in alternating current circuits where high voltage, low current arcs may exist intermittently. The PABH-T composite was found to be at the low end of the scale, whereas the E-glass composite was at the upper end.

Dielectric Strength (Alternating Current, 60 Hz)

This parameter is the ratio of the breakdown voltage and the average test sample thickness. It is inversely related to sample thickness; i.e., the smaller the depth the higher the dielectric strength. Both PABH-T and E-glass have good dielectric strength.

APPENDIX I

Conversion Factors

1 g/den = $8.826\ \rho \times 10^8$ dyne cm^{-2} (ρ in g/cm^3)
= $1.28\ \rho \times 10^4$ psi (ρ in g/cm^3)
= $2.05\ \rho \times 10^2$ psi (ρ in lb/ft^3)

$1\ \text{dyne/cm}^2$
$= 1.4504 \times 10^{-5}$ psi
$= 1.0197 \times 10^{-3}\ \text{g/cm}^2$
$= 1.0197 \times 10^{-2}\ \text{kg/m}^2$

Densities Used in Conversions

$\rho = 1.14\ \text{g/cm}^{-3}$	Nylon 66
1.38	Polyester
1.44	PABH-T(T) X-500
1.47	PABH-T(G) X-500
1.5	Rayon
1.6	Graphite
2.54	Glass
7.8	Steel

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We are indebted to Mr. J. Knudsen for making available his wide knowledge and understanding of fibers as an internal consultant.

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