

# Physical Properties of Polyester Fibers Degraded by Aminolysis and by Alkaline Hydrolysis

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## Synopsis

Permeant degradation affects the brittleness, flexural fatigue, and ultimate tensile properties of polyester fibers more drastically than topochemical degradation. Topochemical degradation was obtained by hydrolysis with aqueous NaOH and permeant degradation by aminolysis with aqueous ethylamine. Treatment with aqueous sodium hydroxide appears to leave the polyester fiber surfaces more resistant to abrasion damage.

## INTRODUCTION

This work examines the effects on the physical properties of polyester fibers of topochemical degradation vis-à-vis permeant degradation. Topochemical degradation is defined as a reaction which primarily causes scission of polymer chains and is confined to the fiber surface. It was obtained by hydrolysis with aqueous sodium hydroxide. Permeant degradation is defined as a reaction causing chain scission throughout the fiber and was obtained by aminolysis with aqueous ethylamine. Aqueous ethylamine penetrates polyester and reacts initially in the less ordered regions of the fiber. The physical properties of fibers were studied by measuring breaking twist angle (BTA), cyclic 180° flexural fatigue resistance, and tensile ultimate properties. Fibers were characterized by density, intrinsic viscosity, and scanning electron microscopy (SEM).

There appears to be unanimous agreement among authors that reaction between an aqueous solution of NaOH and polyester takes place at the fiber surface and that reaction does not occur in the interior.<sup>1-7</sup> It appears that short-chain molecules located at fiber surfaces are removed in hydrolysis leaving the undissolved part of the fiber unaffected. There has been some work on the effect of the treatment on the morphology of the fiber surface.<sup>8,9</sup>

In contrast, amines diffuse into and react throughout polyester fibers resulting in a weakening of the fibers, the extent of which is in proportion to the severity of the treatment.<sup>2</sup> Farrow et al.<sup>10</sup> observed three stages in the aminolysis of polyester with 20% aqueous methylamine. In the first stage, there is an attack in the amorphous regions with little change in the sample weight and crystallinity. In the second stage, chain scission leads to a rapid fall in sample weight and a rise in degree of crystallinity. During the third stage, a gradual decrease in reaction rate occurs and is attributed to a slower attack on both amorphous and crystalline regions. Alternatively, Kurita<sup>11</sup> reported two stages of decomposition during aminolysis of polyester with 70% aqueous monoethylamine. The first

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stage is rapid degradation of amorphous regions indicated by a rapid weight loss, increases in crystallinity and amide group content, and a sharp drop in molecular weight. The second stage is a slower degradation of crystalline regions indicated by a slow weight loss and constant values of molecular weight and crystallinity. Tucker and Murray<sup>12</sup> using SEM reported the morphologic changes in polyester fibers treated with *n*-propylamine.

The mechanical tests used in the present investigation represent tests of brittleness, fatigue resistance, and strength. They provide a measure of the ultimate properties in the shear, tension-compression, and simple tension modes of mechanical deformation. Thus, a fairly complete description of the mechanical behavior of the fibers is obtained.

Previous work in our laboratories<sup>13,14</sup> has shown the sensitivity of BTA tests to changes in the fiber morphology, chemical composition, and supramolecular structure.

Most of the published results on fatigue resistance are for tensile fatigue.<sup>15-17</sup> Flexural fatigue, incorporating torsional and abrasion effects, of polyester fibers has been studied by Hearle and co-workers.<sup>18,19</sup> The flex test alternately compresses and extends the material, with the position of the neutral axis of deformation depending on the relationship between the compression and extension moduli.<sup>20,21</sup> The effective strain in the fiber depends on the relative values of fiber diameter and bending radius.

Although important in any test of ultimate properties, the presence of existing defects to serve as crack nucleation centers is of increased significance in fatigue tests because the magnitude of the strain is small and, therefore, generation of nucleation centers via the actual mechanical deformation is minimal.

The ability of the material to absorb mechanical energy without permanent damage is also an important factor in determining fatigue life. Pliable, amorphous materials will generally have a higher resistance to fatigue failure than stiff, crystalline materials.

The tensile test is, of course, the most extensively studied of the mechanical tests. In the present work, in addition to the information about the material it supplies in its own right, tensile testing was used to determine the linear, or Hookian, region of the stress-strain behavior of the material for use in determining load values in the other tests.

## EXPERIMENTAL

### Materials

The starting material was heat-set 100% Dacron polyester type 54 fabric obtained from Test Fabrics Inc., Middlesex, NJ. All chemicals used, with the exception of ethylamine, were reagent grade; 70% aqueous ethylamine was practical grade. The treatments were performed on the fabric, and the fibers were then removed for mechanical testing.

### Methods of Treatment

**Sodium Hydroxide Treatment.** Three test samples were individually treated at each of three different treatment times: 15, 60, and 120 min. A 20-cm<sup>2</sup> sample of the polyester fabric was conditioned at 65% RH and 21°C and

weighed before immersion in a resin reaction kettle containing 1 L 10% aqueous NaOH preheated to 60°C. Agitation during the prescribed treatment times was effected by bubbling nitrogen gas through the solution. At the end of the designated time, the fabric was removed from the kettle and rinsed thoroughly in distilled water at room temperature. This was followed by immersion in 1% HCl for 2 min and then thorough rinsing again with distilled water until the rinse water showed neutral on litmus. The sample was air dried, conditioned for 24 h at 65% Rh, 21°C, and reweighed. The moisture contents of the conditioned samples were determined on portions of the fabrics and used to calculate the dry weights of the fabrics before and after hydrolysis. These data were then used to determine the loss in weight of the samples due to hydrolysis. Samples used for determination of moisture contents were discarded and not used for further characterization of the fabrics.

**Ethylamine Treatment.** Similar to the NaOH treatment, three test samples were treated individually at each treatment time. A 20-cm<sup>2</sup> sample was conditioned, weighed, washed at 60°C for 2 h, and air dried. This sample was immersed in 900 ml 70% aqueous ethylamine at 21°C. The bottles were placed on a laboratory shaker for the designated times: 4 or 8 h. The samples were then rinsed with distilled water until the water tested neutral with litmus, air dried, conditioned at 65% RH, 21°C, for 24 h, and reweighed. Weight losses were determined as above.

**Topical Finish.** This treatment was done by the Technical Laboratory of the Speciality Chemicals and Products division of E. I. duPont de Nemours & Co. A pad heat-set process was used. The pad bath was composed of Zelcon, a nonionic polymeric hydrophile (to give 4% on weight of fabric based on pickup), and 2.5 g/L monosodium phosphate. After padding and drying, the fabric was heat set for 30 s at 195°C.

## CHARACTERIZATION OF PRODUCTS

**Breaking Twist Angle.** The BTA apparatus has been described in detail elsewhere.<sup>13</sup> The present tests were done in air at 65% RH and 21°C. The fiber was pretensioned with a load of 1 g into the linear region of its load-extension curve to prevent snarling. After relaxing for 60 s under this tension, the sample was twisted until rupture. The number of turns and the length were read off their respective indicators. The values quoted for the BTA are averages of a minimum of six values as calculated from the following formula:

$$\text{BTA} = \tan^{-1} \left( \frac{l}{\pi d \Upsilon} \right)$$

where  $l$  is length of fiber,  $\Upsilon$  is number of turns to break, and  $d$  is diameter of the fiber, as determined optically.

**Flexural Fatigue Tests.** Figure 1 shows the salient features of the flexing apparatus. The machine itself consists of 36 such stations situated in a controlled environment chamber. For these tests, the chamber was maintained at 65% RH and 21°C. A detailed description of the instrument and experimental procedures will be given elsewhere.<sup>22</sup>

A tensioning weight of 0.5 g was selected. This weight loads the samples into the Hookian region, but not close to the yield point, as the degraded samples

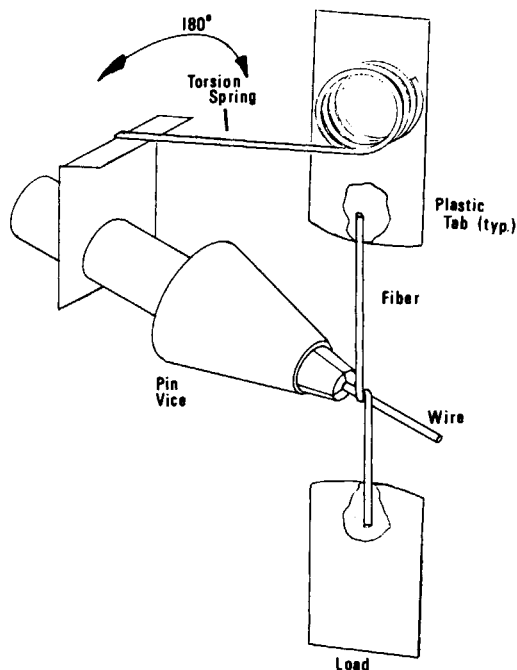


Fig. 1. Salient features of the flexing apparatus.

failed at or near their yield point in tension. The weight was low for the controls and the less severely degraded samples in that the number of flexes to break was quite large, but a heavier weight caused premature failure of the more severely degraded samples. The same tensioning weight was used for all experiments to facilitate cross comparisons. The wire gripped by the pin vice for the bulk of these tests was a 51- $\mu\text{m}$ -diameter tungsten wire. Some additional tests were done with a 41- $\mu\text{m}$  diameter stainless steel music wire.

Flexural fatigue, being an extremal process,<sup>23</sup> admits of data reduction procedures other than averaging. If a large standard error is acceptable, a simple averaging process may be used. However, for a more detailed evaluation the individual data points can be plotted as fraction broken vs log (number of flexes to failure).

**Tensile Tests.** The tensile tests were performed on a standard table model Instron fitted with the A cell. A gauge length of 3.0 cm and a rate of extension of 200% of the initial length per minute was used. A minimum of 10 tensile tests were done and averaged. Data reduction was effected by using a digitizing plotter to read the significant points from the chart into a microcomputer.

**Viscosity.** Intrinsic viscosities were determined using Ghosh's method.<sup>24</sup>

**Density.** The density of polyester samples was measured using a standard density gradient column (Techne Incorporated, Princeton, New Jersey) thermostated at 21°C. A suitable combination of xylene and carbon tetrachloride was mixed together to produce a uniform gradient of 1.3 to 1.5 g/ml. The column was calibrated using glass floats of known density.

**Scanning Electron Microscopy.** The procedure was essentially that reported earlier.<sup>25</sup>

## RESULTS AND DISCUSSION

## Fiber Characterization

As the time of NaOH hydrolysis was progressively increased from 15 min to 2 h, the loss in weight of the polyester fabric increased from 1.08 to 10.1% (Table I). The ethylamine treatment times were selected so that the weight losses of the treated polyester fabrics extended only from 0.039 to 2.11% and thus ranged from lower to slightly higher than the weight loss of the polyester fabric treated for 15 min with NaOH. The weight loss results, at first sight, might be taken as an indication that the NaOH treatments have degraded the physical properties of the fiber more severely than the ethylamine treatments. However, when the mechanical properties (Table II and III) and intrinsic viscosities (Table I) of the samples were determined, it was found that, in fact, the opposite was true, i.e., the ethylamine treatment had affected the physical properties more severely than the NaOH treatment. For example, the 4-h ethylamine-treated polyester with a fabric weight loss of 0.039% had an intrinsic viscosity, fiber tensile strength, and number of flexes to break for fibers of 0.414 dl/g, 26.7 g/tex, and 21,306, respectively. The values for 120-min NaOH-treated polyester with a fabric weight loss of 10.15 were 0.534 dl/g, 37.0 g/tex, and 78,012, respectively. These results are in line with the hypothesis that the reaction of polyester fiber with sodium hydroxide is topochemical and that aminolysis of polyester is a permeant reaction with preferential attack initially in the low-ordered regions of the fibers. If chain scission is confined to the fiber surface, the effect on physical properties would

TABLE I  
Characterization of Polyester Samples

Treatment	Weight loss, %	Intrinsic viscosity, dl/g	Density, g/cm <sup>3</sup>
H <sub>2</sub> O, 60°C, 2 h	-0.19	0.576	1.403
Ethylamine, 4 h	0.039	0.414	1.405
Ethylamine, 8 h	2.11	0.324	1.412
None	—	0.576	1.403
NaOH, 15 min	1.08	0.570	1.402
NaOH, 60 min	5.18	0.563	1.403
NaOH, 120 min	10.1	0.534	1.403

TABLE II  
Tensile Properties of Polyester Fibers after Various Treatments

Treatment	Ultimate properties				Yield properties			
	Specific stress		Extension		Specific stress		Extension	
	g/tex	S.E. <sup>a</sup>	%	S.E. <sup>a</sup>	g/tex	S.E. <sup>a</sup>	%	S.E. <sup>a</sup>
H <sub>2</sub> O, 60°C, 2 h	46.5	0.44	31.6	0.53	8.7	0.15	1.9	0.05
Ethylamine, 4 h	26.7	0.23	18.1	0.28	9.4	0.04	2.2	0.02
Ethylamine, 8 h	11.2	0.18	3.8	0.21	9.8	0.17	2.9	0.04
None	48.9	0.31	30.5	0.33	8.9	0.11	1.8	0.03
NaOH, 15 min	48.6	0.31	31.9	0.42	9.1	0.15	2.5	0.05
NaOH, 60 min	42.5	0.36	26.4	0.35	8.4	0.10	1.8	0.03
NaOH, 120 min	37.0	0.57	24.0	0.41	8.5	0.27	2.0	0.04

<sup>a</sup> Standard error of the mean.

TABLE III  
Breaking Twist Angle (BTA) and Flex Life of Polyester Fibers After Various Treatments

Treatment	BTA Deg.	S.E. <sup>a</sup>	Flex life <sup>b</sup>	S.E. <sup>a</sup>
H <sub>2</sub> O, 60°C, 2 h	46.22	1.39	44,510	11,850
Ethylamine, 4 h	58.74	1.06	21,306	5,036
Ethylamine, 8 h	71.61	0.54	5,126	989
None	45.16	0.65	56,626	16,189
NaOH, 15 min	46.28	0.47	137,139	55,837
NaOH, 60 min	48.87	0.98	62,777	19,703
NaOH, 120 min	50.62	0.80	78,012	40,852

<sup>a</sup> Standard error of the mean.

<sup>b</sup> Mean number of 180° flexes to failure; tungsten wire used in flexing instrument

be expected to be less than when chain scission is occurring in amorphous regions throughout the fiber and thus destroying the structural integrity of the fiber. The constancy of fiber density as the polyester progressively loses weight with increasing time of reaction with sodium hydroxide (Table I) indicates also that this reaction is topochemical. The higher density of the 8-h ethylamine-treated sample indicates that ethylamine is preferentially eliminating the amorphous regions. The marked increase in brittleness, as indicated by BTA (Table III), of the polyester fibers after treatment with ethylamine in contrast to the much smaller increase in brittleness after NaOH treatment should also be noted.

The difference in the mode of attack of NaOH and ethylamine can be seen quite clearly from SEM micrographs. The untreated polyester fiber has a relatively smooth surface (Fig. 2), while NaOH treatment causes pitting of the fiber surface (Fig. 3) and ethylamine treatment causes cracking (Fig. 4).

The data obtained on the NaOH-treated samples had some unusual features and will therefore be discussed in more detail.

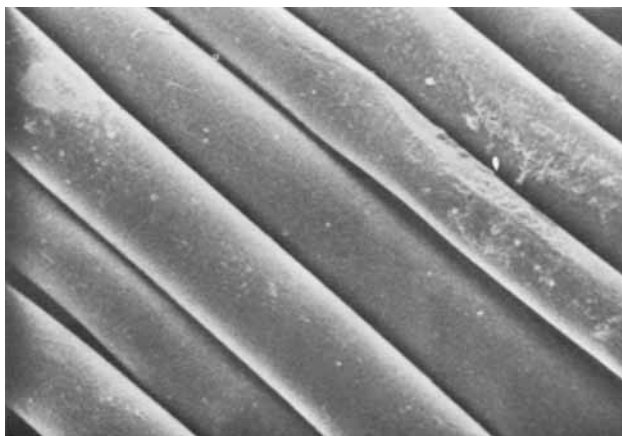


Fig. 2. Scanning electron micrograph of starting polyester fiber (820×).

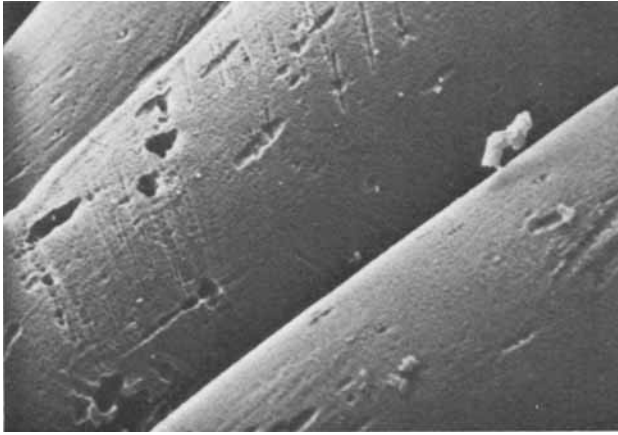


Fig. 3. Scanning electron micrograph of polyester fibers treated for 2 h with aqueous NaOH (2430 $\times$ ).

### Sodium Hydroxide Treatment

The maximum reaction time in aqueous sodium hydroxide was 2 h. The small increase in BTA of the polyester fiber found after heating in water alone at 60°C for 2 h is not significant (Table III). Again, the increase in fiber BTA after 15 min of reaction with aqueous sodium hydroxide is not significant. However, the increase in BTA of the fiber is significant when the reaction time is 60 or 120 min, indicating the fibers are more brittle than the non-NaOH-treated control. The increase is due to the reaction with sodium hydroxide. The ultimate stress and extension at break of the NaOH-treated samples is significantly lower than the non-NaOH-treated controls when the reaction time is 60 or 120 min also (Table II).

The pits, caused by treatment with aqueous NaOH, probably serve as nucleation centers for crack formation. SEM micrographs of polyester fibers treated for 15 min with aqueous sodium hydroxide (Fig. 5) indicate that treatment has caused little pitting on fiber surfaces. The pits increase in number and depth

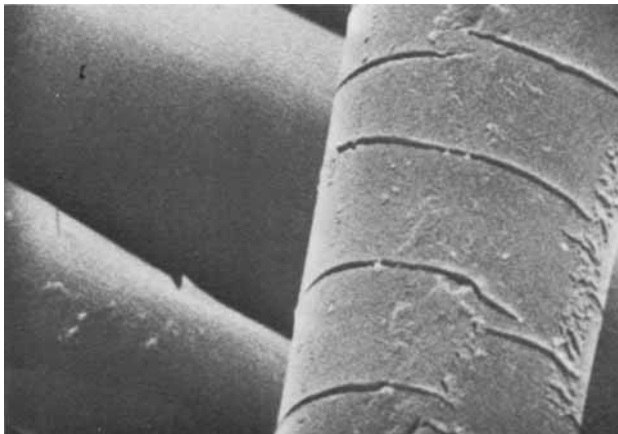


Fig. 4. Scanning electron micrograph of polyester fiber treated for 8 h with aqueous ethylamine (2200 $\times$ ).

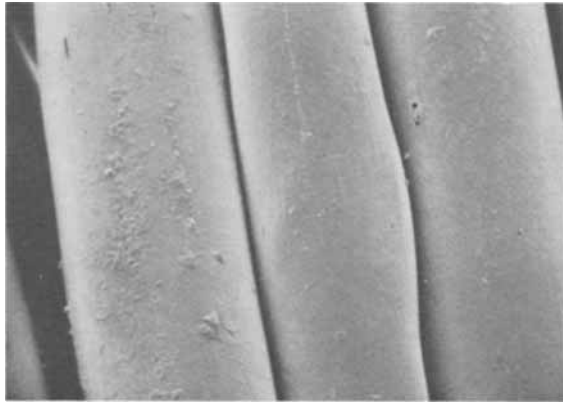


Fig. 5. Scanning electron micrograph of polyester fiber treated for 15 min with aqueous NaOH (1560 $\times$ ).

as the time of hydrolysis is lengthened (Figs. 6 and 3), and a concomitant rise in the BTA is obtained.

The changes in flex life with these same treatments offer some interesting comparisons. Reaction with NaOH for 15 min causes an apparent marked increase in flex life of the fibers (Table III), whereas neither the fiber brittleness as measured by BTA (Table III) nor the tensile properties (Table II) are markedly affected. The reason for calling the increase in flex life "apparent" will become clear in the next section. At longer treatment times, a marked reduction in flex life of the fiber is found to approximately the level of the non-NaOH-treated control. With these longer treatment times, increased brittleness and decreased tensile properties are also obtained.

We speculate that the NaOH treatment causes gelatination of the fiber surface during the treatment. Upon rinsing and drying, the surface hardens, but it is now more amorphous than before the treatment. Thus, the fiber surface is tougher and more resistant to flex fatigue and abrasive damage after a short period of NaOH treatment (i.e., 15 min). Increasing the treatment time causes

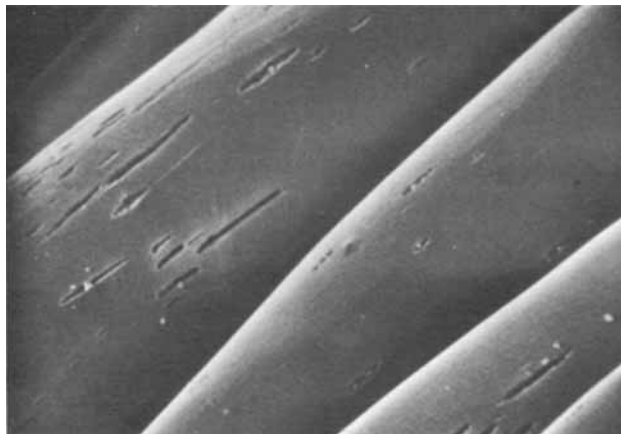


Fig. 6. Scanning electron micrograph of polyester fiber treated for 1 h. with aqueous NaOH (2200 $\times$ ).



increased pitting of the fiber surface; and since the pits may function as crack nucleation centers, the flex life drops off again. The toughening of the skin maintains the level of flex resistance at about that of the untreated material, irrespective of pitting.

The decrease in ultimate properties with increased NaOH treatment time may also be ascribed to formation of crack nucleation centers on the surface of the fiber (Table II).

### Abrasive Effects of Wire During Flexing

The wire gripped by the pin vice of the flexing equipment used in the tests described above was tungsten. Examination of the wire by SEM revealed a fairly rough surface. Therefore, the possibility for some abrasion of the fibers exists, the necessary rubbing action deriving from the elastic nature of the fibers. To test this possibility, a stainless steel music wire, which displayed a substantially smoother surface, was used in place of the tungsten wire for some ancillary studies.

Substituting the steel wire for the tungsten wire resulted in a significant increase in flex life for the 8-h ethylamine-treated sample (Fig. 7) and for the starting polyester control fiber (Fig. 8). Thus, we conclude that the roughness of the tungsten wire does cause some surface abrasion of the fiber. However, the 15-min NaOH-treated sample showed only a slight increase of flex life (Fig. 9). It appears, therefore, that the modification of the fiber surface by the NaOH treatment reduces the abrasion effect to a large extent, lending support to the speculation on the toughening effect of NaOH on the fiber surfaces. It will be noted that the flex life of the control increased and was similar to that of the 15-min NaOH-treated sample when the tests were done on the stainless steel wire (cf. Figs. 8 and 9), but the 8-h ethylamine-treated sample still had a lower flex life than the 15-min NaOH-treated fiber (cf. Figs. 7 and 9). Thus, the conclusion drawn in the last section from comparisons made between the flex life of NaOH-treated fibers and the ethylamine-treated samples using the tungsten wire remain valid.

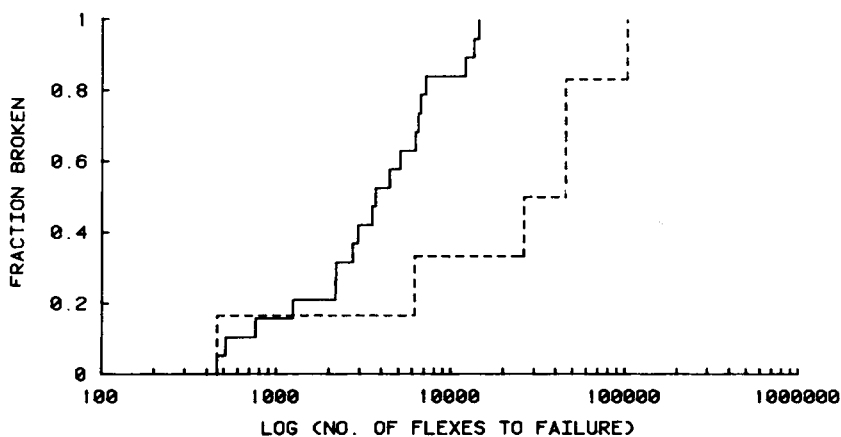


Fig. 7. Failure diagram for polyester fiber treated for 8 h with aqueous ethylamine: (—) tungsten wire; (---) stainless steel wire used in flexing instrument.

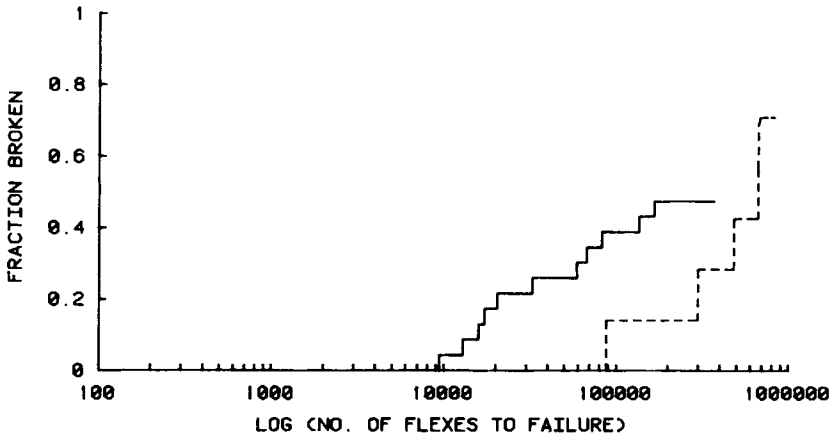


Fig. 8. Failure diagram for starting polyester fiber: (—) tungsten wire; (---) stainless steel wire used in flexing instrument.

As further support that surface modification can reduce the abrasive effect of the wire, an additional experiment was performed with the polyester fiber treated with a topical nonionic polymeric hydrophile finish. Polyester fiber treated with this finish had a markedly higher flex life than the control polyester when tests were carried out using the tungsten wire. Similar to the 15-min NaOH-treated sample, the flex life of the polyester treated with the topical finish was not markedly increased when the steel wire was substituted for the tungsten wire (Fig. 10). Using the stainless steel wire, the flex life of the topically finished polyester fiber was similar to that of the control fiber; whereas with the tungsten wire, the flex life of the former sample appeared to be greater (cf. Figs. 8 and 10). Thus, it appears that the finish has acted as a lubricant and has reduced fiber abrasion.

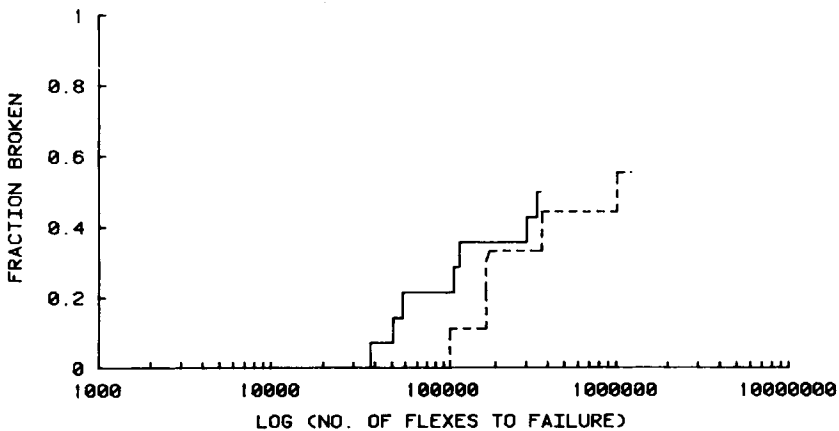


Fig. 9. Failure diagram for polyester fiber treated for 15 min with aqueous NaOH: (—) tungsten wire; (---) stainless steel wire used in flexing instrument.

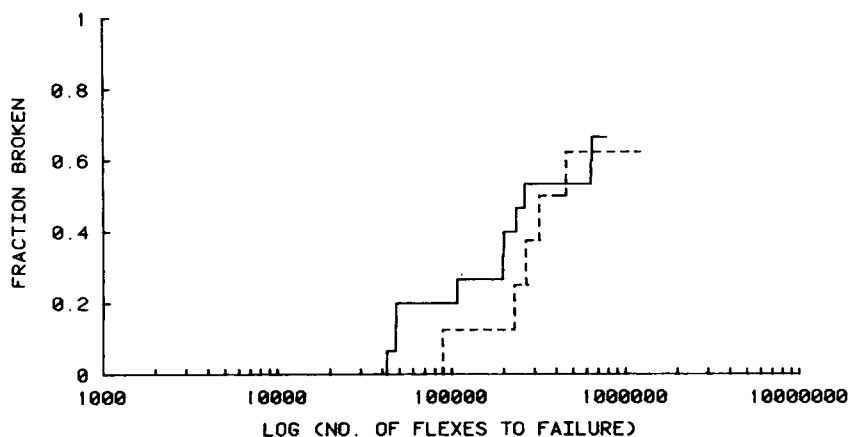


Fig. 10. Failure diagram for polyester fiber treated with a nonionic polymeric hydrophile: (—) tungsten wire; (---) stainless steel wire used in flexing instrument.

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Received March 6, 1981

Accepted May 14, 1981