

Polymers as Fibers*

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Synopsis

The relation between polymer and fiber structure and fiber properties is discussed. The specific effects of intermolecular forces, chain stiffness, monomer unit regularity, crystallinity, crosslinking, orientation, molecular weight, and chemical composition on the important fiber properties of melting point, modulus, elasticity, or recovery from strain, tensile strength, moisture adsorption, and dyeability are discussed in some detail. An example is given to illustrate the role of today's sophisticated engineering in further controlling and modifying fiber properties.

Three-quarters of a century ago the first successful man-made fiber, Chardonnet's "artificial silk," created a sensation at the 1889 Paris Exposition. However, the basic discovery of nitrocellulose by Swiss Professor Dr. Schönbein preceded the Paris Exposition by forty-five years. In contrast, Carothers' basic discoveries leading to nylon were made only seven years before commercialization. This latter-day rapid "reduction to practice" is a tribute to today's highly sophisticated and ingenious engineering supporting the man-made fiber industry.

Fully matching the advances in man-made fiber process engineering has been an understanding of the interrelations between polymer structure and fiber properties. We are not only able to "engineer" highly complicated and efficient fiber-making processes and equipment, but since Chardonnet's time we have developed a comprehensive, well-ordered background of basic science from which the fiber technologist can draw as he goes about his job of improving synthetic fibers or tailoring new ones for new applications. It is the objective of this paper to present a sketchy outline of the current state of our basic understanding of the interrelations between polymer and fiber structure and fiber properties.

Our present uses of fibers require an extremely wide variety of raw materials. From materials found in nature we use as fibers such diverse natural products as rubber and metals, animal fur, and glass. The range of just one fiber property, fiber stiffness, or modulus, to cover present day textile uses is shown in Figure 1, which depicts the initial stress-strain properties of fibrous materials derived from natural sources. This figure shows the wide variety in initial stress-strain properties as we traverse

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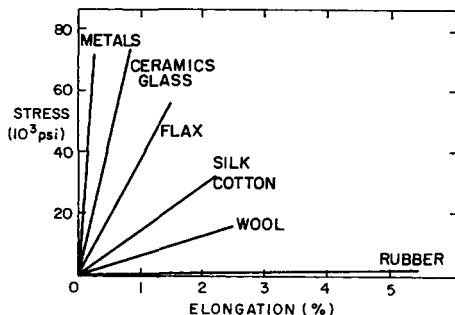


Fig. 1. Modulus range for fibers from naturally occurring substances.

the range from rubber, with a modulus of only about 100 psi, to steel, with a modulus of 30×10^6 psi.

Today, our synthetic polymer technology provides commercial fibers covering the range of modulus from rubber to flax. Fibers having the extremes of this range are infants of the synthetic fiber industry (e.g., the new spandex fibers having rubberlike properties and HT-1, the new high-modulus polyamide which has a modulus equivalent to flax). Our older synthetic fibers, conventional nylon, the polyesters, and the acrylics, fall between these newcomers. Another newcomer, polypropylene, also falls in the mid-range.

Of course modulus is only one of many properties important in the wide range of end-uses for fibers. Requirements with respect to other properties are equally diverse. Although much can be done in adjusting properties in the fiber manufacturing process through mechanical and thermal treatment, these treatments merely realize the potential in the polymer. For really fundamental changes in fiber properties, we have to go back to the polymer.

We will consider in some detail the important fiber properties of melting point, modulus, elasticity, or recovery from strain, tensile strength, and moisture absorption and dyeability and those important polymer structure factors which determine or importantly contribute in turn to these key fiber properties.

Let us first consider the factors which govern the melting point. With polymers, as with ordinary low molecular weight materials, the melting point depends on the ratio of heat of fusion to entropy of fusion and on the purity of the substance. Specifically, the melting point of a polymer is related to the strength of the intermolecular forces (which affects the heat of fusion), the stiffness of the polymer chains (which affects the entropy of fusion), and the regularity of placement of the monomeric units. This latter effect is analogous to the effect of impurities in low molecular weight materials. Impurities are introduced into the polymer by random copolymerization of two or more different monomers.

The effect of intermolecular forces provided by hydrogen bonds in polyamides is shown in Figure 2. Here, melting point is plotted against concentration of amide groups per 100 A. of extended chain length.¹

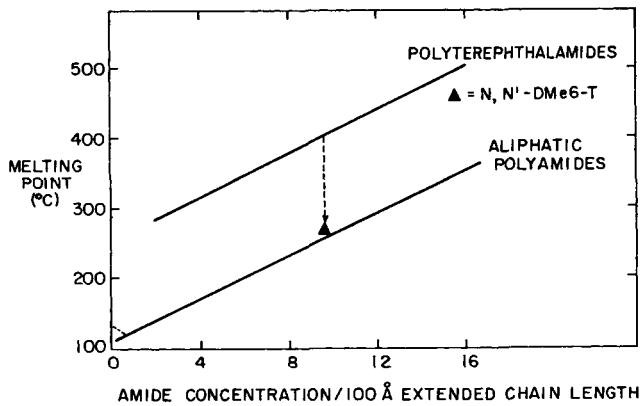


Fig. 2. Polyamide melting points vs. amide concentration and chain stiffness.

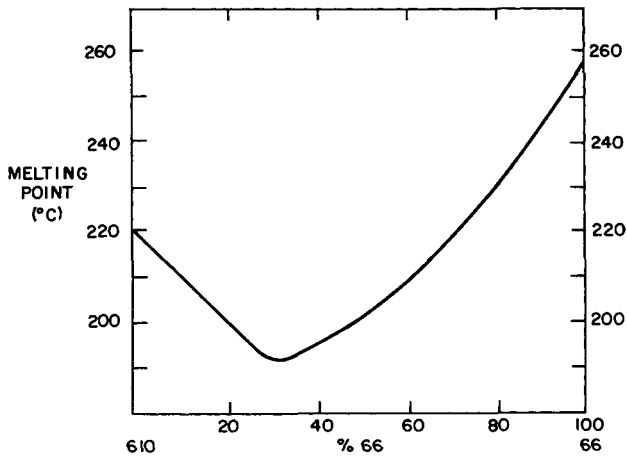


Fig. 3. Effect of random copolymerization on melting point (610/66 system).

Note first that the melting point is essentially a linear function of the amide concentration. The heat of fusion increases directly with the increase in hydrogen bonding stemming from the increase in amide concentration. One might expect the melting point to extrapolate to that of linear polyethylene (or polymethylene) at zero amide concentration where only Van der Waals forces determine the heat of fusion. However, the extrapolated melting point is actually somewhat lower. One possible explanation for this is an initial melting point depression resulting from the introduction of just a few foreign amide groups in a polymethylene chain.

The effect of chain stiffness is illustrated in the highest curve on this slide, which describes the melting behavior of the terephthalamides.² These polymers, which contain benzene rings along the main chain, do not coil as flexibly in their amorphous state and thus have a lower entropy of fusion. This effect of aromatic rings on chain stiffness can be seen by

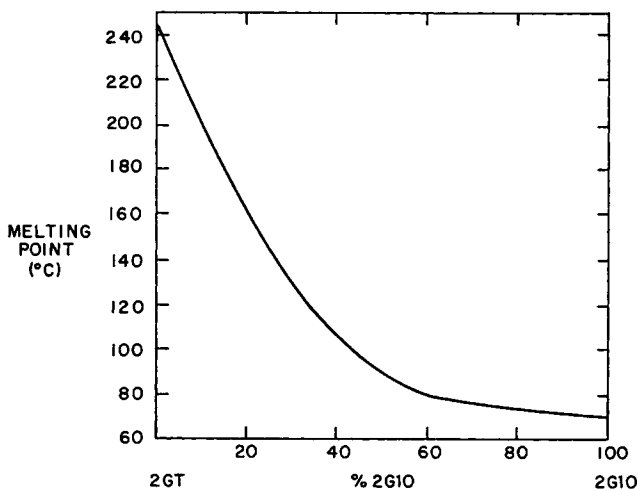


Fig. 4. Effect of random copolymerization and reduction in stiffness on melting point of polyester (2GT/2G10 system).

making atomic models of a polymethylene chain and a chain containing *p*-xylylene groups. From these one can note the flexibility of the all-aliphatic polymethylene chain. In contrast, in the poly-*p*-xylylene chain the entire benzene ring acts as a unit and the rotational degrees of freedom are markedly reduced. At an amide group concentration of 10 per 100 A., the melting point of the aromatic polyamide is increased by almost 150°C. as compared with the aliphatic polyamide. If hydrogen bonding in the terephthalamides is removed by replacing the hydrogens on the amide nitrogen by methyl groups, the melting point is decreased ca. 140°C. An analogous effect is observed (although not shown on the figure) for the corresponding aliphatic polyamide.

Melting point is also markedly affected by modifications in the regularity with which the monomer groups are spaced; that is, by random copolymerization. This is shown in Figure 3 in the phase diagram for the random copolymer system 610/66, where a eutectic of about 190°C. is reached at about the 70/30 composition. Disturbing regularity of amide groups reduces hydrogen bonding and thereby reduces ΔH of our basic melting point equation.

Monomer unit regularity is also of pronounced effect on melting point of polyesters even though in polyesters hydrogen bonding is not an important factor. In Figure 4 we see that the polyester based on ethylene glycol and sebacic acid (2G10) is amorphous and softens at about 70°C.³ The polyester based on ethylene glycol and terephthalic acid (2GT) is crystalline and melts at about 240°C. Thus, a 170°C. increase in melting point is contributed by the stiff benzene ring in the main chain. The melting point-composition diagram for the random copolymer system based on these two polymers is shown on this figure, and one can see the progressive effect of reduction in stiff segment content and regularity.

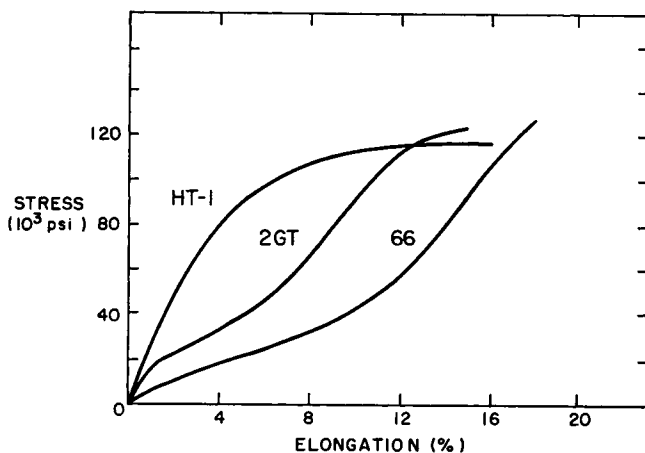


Fig. 5. Stress-strain curves for hard fibers.

(Some of the melting point data in the last few figures are more analogous to sticking temperatures and not true crystalline melting points, which are a few degrees higher.)

We turn now from melting point to fiber modulus. All the factors which affect melting point also affect modulus, and for much the same reasons they affect melting point. In addition to the melting point factors which are related to basic polymer stiffness, we have superimposed all those factors of fiber organization which determine the degree to which the basic chemical structure of the polymer can contribute to fiber stiffness. We are referring, of course, to orientation, crystallinity, and crosslinking.

Crystallinity and its attendant crosslinking by chains running through crystallites in a well-oriented fiber is extremely important in determining fiber modulus. The modulus of a perfect nylon 66 or 2GT crystal has been calculated to be in the range of 20×10^6 psi.⁴ However, the density of commercial nylons and polyesters shows them to be only about 50–60% crystalline. This, then, accounts for the fact that observed moduli are only about one-hundredth of the calculated value since at small deformations it is the amorphous parts of the fiber which deform under the influence of the applied load. Even so, for high fiber modulus, we prefer regularly spaced crystallizable groups in the chain and also we want them highly oriented parallel to the fiber axis.

However, at best, we do not get much above 60% crystallinity, and some fibers are almost wholly amorphous. Failing to attain high modulus by increasing crystallinity, we fall back on chain stiffness. Chain stiffness is as important a factor in determining fiber modulus as it is in determining melting point. Figure 5 shows the changes in stress-strain fiber properties by substituting two aromatic ring structures for the two aliphatic monomers of nylon 66. The new all-aromatic polyamide, HT-1, has an initial modulus over four times that of its all-aliphatic relative. In addition, the stiffness of HT-1 polymer yields a melting point in excess of 400°C.⁶

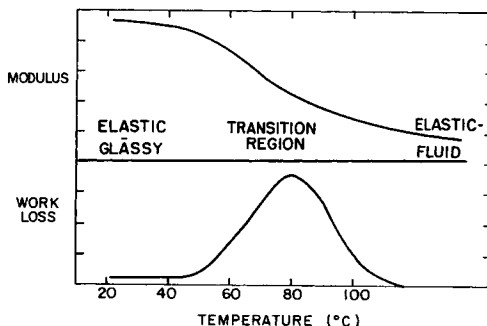


Fig. 6. Dynamic modulus and work loss vs. temperature.

Decomposition sets in before melting. The 2GT (polyethylene terephthalate) polyester with one monomer containing a ring yields an intermediate fiber modulus.

In the discussion of fiber modulus, the data presented have been limited to measurements made at room temperature. Let us now consider briefly the characteristic way in which the modulus of a fiber changes with temperature. This is illustrated in Figure 6 without reference to any particular polymer. It should be noted that for a given degree of crystallinity, initial modulus is chiefly a property of the amorphous regions in the fiber. At the low temperature end of this curve, the modulus is relatively high and varies little with temperature. This region finds the amorphous regions of the polymer in a glassy state; and at relatively small deformations, the restoring force results from an increase in the energy of the bonds being deformed. At the high temperature end of the curve, although the modulus is considerably reduced, it is again relatively temperature-independent. In this low modulus region, the amorphous portions of the fiber are fluid, are quite readily deformed, and the restoring force produced by extension results from the decrease in entropy of the polymer chains. At this end of the curve, the magnitude of the restoring force and of the modulus is proportional to the concentration of crosslinks between polymer chains, as well as to the amount of essentially non-deformable crystalline regions. The crosslinks may be either individual hydrogen bonds or covalent bonds or small crystallites. There is little hysteresis on cyclic loading of the fiber in either of these two regions, and recovery from deformation is good in both. However, in the intermediate or so-called glass or second-order transition region, the onset of sluggish responses in the partially melted amorphous regions results in a high hysteresis and relatively poor recovery. The temperature of maximum work loss may be viewed as the glass transition temperature T_g .

As we reduce the crystallinity of a polymer drastically, the curve tends to move to the left, as well as to decrease in modulus level. Eventually the T_g is well below room temperature, the modulus becomes quite low, and, if the crosslink concentration between crystallites is adequate, we have an elastomer with rapid response to deformation and good recovery.

For maximum recovery, we prefer not to have stress-sensitive crosslinks such as H-bonds because these rupture and reform in new configurations and contribute to poor recoveries. Without the crosslinks of any kind, we would have a liquid with no recovery.

Thus, polymer factors which influence fiber modulus also affect the glass transition temperature. It is obvious that ideally the glass transition temperature should not be in the range of normal end-use temperature. Table I illustrates the dramatic effects of juggling polymer structure factors

TABLE I
Stress-Strain Properties and T_g of Copolyamides and Copolyesters

Polymer	Properties at 25°C.			
	Modulus \times 10 ³ , psi	Tenacity \times 10 ³ , psi	Break elongation, %	T_g (approx.), °C.
610	280	63	25	50
610/ <i>N</i> -alkylated 610 (50/50)	6	18	400	0
2GT/2G10 (40/60)	7	12	300	-20

by reducing polymer crystallizability through disrupting chain regularity and reducing hydrogen bonding.³ A 50% substitution of *N*-alkylated 610 polymer for regular 610 and a 60% substitution of 2G10 for 2GT in random copolymers has given us a marked reduction in fiber modulus, has reduced the glass transition temperature to below 25°C., and has for both the polyamide and the polyester given us an elastomeric fiber. We should note, however, that neither is a very good elastomer.

We can improve the elastic polyester if, instead of preparing the random copolymer, we blend in the melt the two homopolymers (2GT and 2G10) in the 40/60 ratio, allowing a limited extent of ester interchange to occur. This way we obtain a block copolymer (Table II) which is also an elastomer but whose melting point is ca. 50°C. higher than that of the random copolymer (170°C. versus 120°C.). The difference in monomer unit regularity between the two types of copolymers is shown schematically.

Still further improvements in properties can be achieved in the block polymer framework by copolymerizing a long chain (4000 molecular weight) polyethylene glycol with 2GT.³ Here, because of the chemical inertness of the ether links with respect to interchange reactions, one may obtain substantial weight per cent modification at a relatively small mole per cent modification and melting point depression. Thus, with a 60 wt.-% polyethylene glycol modification, the melting point-elasticity relationship is even better than for the partially interchanged block copolymer. This effect is shown in Table III and compared with the two other polyester polymers previously discussed. Note the improvement in stress decay for the block copolymers as compared to the random copolymer. Long discrete blocks of 2GT polymer are required in the chain to provide crystallite crosslinks to minimize creep under sustained stress.

TABLE
Random versus

Copolymer	Structure
Random copolymer 2GT/2G10 (40/60)	-X-X-X-X-X-X-X-X-X-X-X-X-X-X-
Block copolymer, 2GT/2G10 (40/60)	-----XXXXXXXXXXXX-----

This is the type of crosslinking in Lycra spandex fiber. However its basis structure is that of a polyurethane rather than a polyester.⁵ Among the advantages of the polyurethane structure is greatly improved hydrolytic stability as compared with the polyester.

While discussing polymer factors which influence modulus or fiber stiffness, it is apparent that we have been forced into discussing factors which govern elasticity and recovery from deformation. Thus the list of polymer factors influencing elasticity and recovery are essentially those which also influence modulus. For a highly extensible fiber having high elongation and high recovery from strain, as is Lycra spandex fiber, we have the polymer with low modulus and a T_g below the use temperature. On the other hand, all our important natural and synthetic apparel fibers (except spandex) have a balance of polymer structure factors yielding much higher modulus and a T_g above normal end-use temperature.

Let us now turn to factors which govern fiber tensile strength. Most linear polymers with T_g above room temperature are capable of yielding high tensile strength if molecular weight is above about 10,000 and the chains are well oriented by drawing in the fiber manufacturing process. Thus, nylon 66 of molecular weight 18,000 can yield a fiber having well above 100,000 psi tensile strength (Fig. 7). This behavior is not unique. Many linear polymers can be drawn to develop high strength at normal temperatures. However, if tensile testing is done at a variety of tempera-

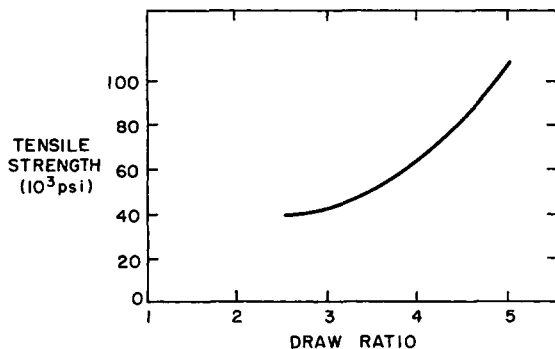


Fig. 7. Effect of orientation on tensile strength (nylon 66).

II
 Block Copolymers

Melting point, °C.	Elongation to break, %	Modulus, psi
120	300	7000
170	200	9000

tures or at varying rates of loading, then the polymer structure factors clearly show their influence.

A kinetic theory of the creep failure bringing in the important variables of rate and temperature of tensile testing has been worked out by Coleman and Knox⁷ starting from the Eyring absolute rate theory for viscous flow. This theory treats the failure process as the flow of non-Newtonian viscous elements in the fiber and predicts that the log of the breaking time t_B increases linearly as the load is reduced but remains finite as summarized in eq. (1).

$$\ln t_B = A + \frac{\Delta F^\ddagger}{RT} - \frac{fv}{2kT} \quad (1)$$

Here, f is stress (in dynes/cm.²), v is displacement volume divided by the fraction of chains bearing the load, e.g., 300 A.³, k is Boltzmann's constant, R is the gas constant in cal/mole-deg, ΔF^\ddagger is the free energy of activation, e.g., 40 kcal./mole, and A is relatively constant at ca. 32 for most fibers. From a given load yielding a break in normal testing times (e.g., 1 sec.), decreasing load will increase breaking time most rapidly with fibers having

TABLE III
Elastic Properties-Melting Point Relationship for Various Copolyesters

Polymer	Melting point, °C.	Elongation to break, %	Short-term stress decay, %
2GT/2G10 (40/60)	120	300	20
2GT/2G10(BL) (40/60)	170	200	13
2GT/PEG(BL) (40/60)	200	350	8

TABLE IV
Effect of Testing Time on Tensile Strength (25°C.)

	Time to break at a load of		
	130,000 psi	65,000 psi	52,000 psi
Nylon 66	1 sec.	3 yr. ^a	130 yr. ^a
66/6 80/20)	1 sec.	29 days ^a	580 days ^a
Linear polyethylene	1 sec.	10 min.	30 min.

^a By linear extrapolation of experimental log time versus stress relation.

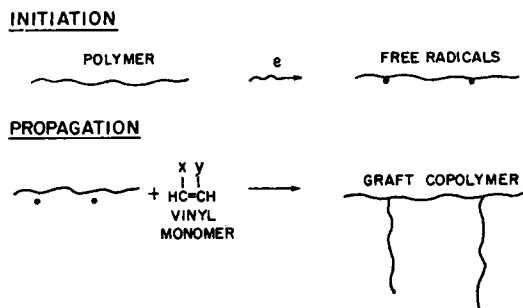


Fig. 8. Radiation-induced graft copolymerization.

the highest ΔF^\ddagger . Thus, it is important to characterize tensile properties over a wide range of testing times to assess them adequately. Wide variations which can exist are shown in Table IV. From conventional tests, linear polyethylene appears to be a material with good strength potential, yet it is not capable of bearing large loads for a long period of time. The lower free energy of activation of the creep failure process for this polymer is related to its relatively weak intermolecular forces. The random copolymer of polyamides 66 and 6 shows the intermediate effects of less drastic reductions in intermolecular forces.

Up to now in this discussion we have used homopolymers, random copolymers, and block copolymers to show polymer structure-fiber property relationships. In block and random copolymers, the copolymer can also be made by creating free radical sites along the parent polymer chain and initiating a vinyl polymerization in the presence of a desired monomer as outlined in Figure 8. The product is a graft copolymer in which the polymer backbone is unchanged and the chemical modification is a branch. Either high energy radiation or chemical free radical initiators can be utilized to promote the grafting process. Grafts on preformed fibers may be uniformly distributed throughout the cross section of a fiber or confined to surface regions by utilizing knowledge of the diffusion and solubility characteristics of various monomers in the substrate.

TABLE V
Property Comparison of Graft versus Random Copolymers (Nylon 66 Base)

Fiber	Moisture regain at 50% R.H., %	Static propensity (log <i>R</i>)	Fibers stick temp., °C.	Wet crease recovery, %	Dye rate
Nylon 66	2.5	13.3	240	70	Normal
20% Acrylic acid graft (Na salt)	7.5	8	380	94	Rapid
20% Acrylic acid graft (Ca salt)	5	13	420	70	Normal
66/6 (80/20)	3.5	13	200	65	Rapid

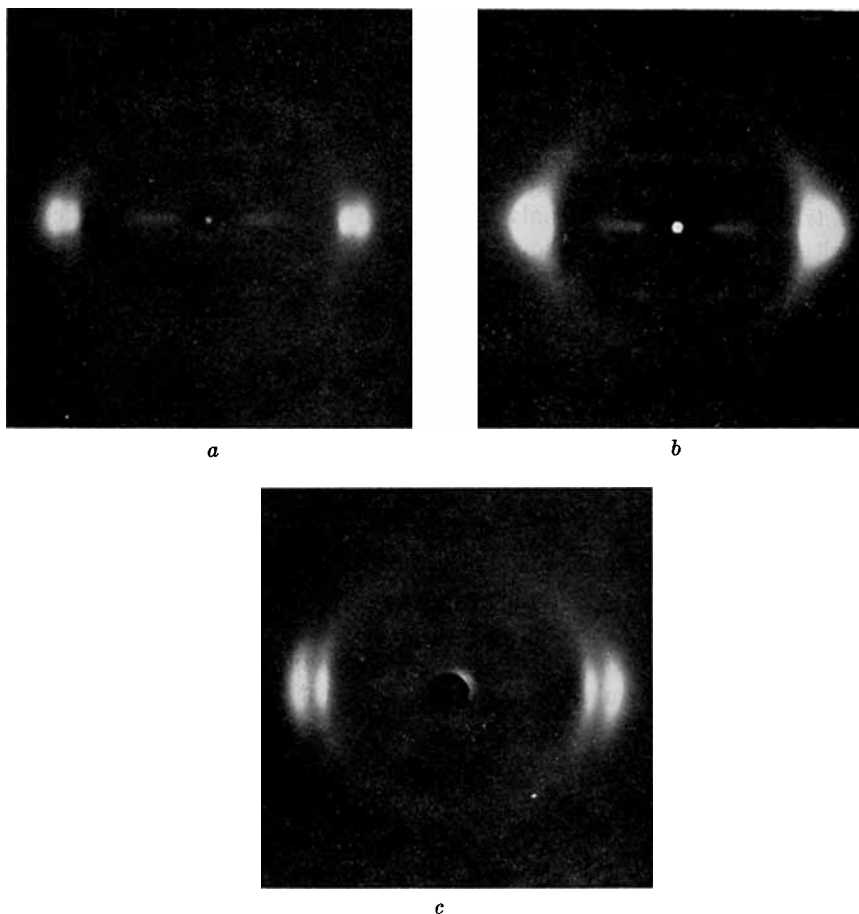


Fig. 9. X-ray patterns for (a) nylon 66; (b) 66/6 random copolymer; (c) acrylic acid graft on nylon 66.

By proper selection of the modifying monomer in light of its properties as monomer and polymer, it is possible to increase or decrease fiber modulus and recovery properties or to impart such other properties as hydrophily, increased dye receptivity, and resistance to melting (through crosslinking). In grafting to a preformed fiber, the crystal structure of the backbone polymer is essentially unimpaired. One example, the acrylic acid graft on preformed nylon 66 fibers will illustrate these effects.

In Table V we see how the balance of some key fiber properties is altered by grafting 20% acrylic acid to nylon 66 fiber and converting the graft to the sodium or calcium salt of polyacrylic acid.⁸ These properties are compared with those of a random copolymer of nylons 66 and 6. These data show (1) that a significant increase in moisture regain is obtained with the hydrophilic graft, (2) the static propensity as indicated by the log of the electrical resistance of a fabric is markedly reduced with the sodium salt of the graft (for comparison, the log R of cotton is 11), (3)

the sodium salt of the graft also shows improved wet crease recovery because of the highly swollen nature of the graft in water, (4) the rate at which dyes are sorbed is also considerably higher with the graft as it is also for the random copolymer, and (5) that the divalent calcium ion produces ionic crosslinks in the fiber yielding a marked increase in fiber stick temperature or melting point. In contrast, the random copolymer contributes improvement only in dye rate but at a marked sacrifice in melting point. Figure 9 shows x-ray diffraction patterns of the graft and random copolymer fibers and, in comparison, of an unmodified fiber. Note the retention of crystallinity in the grafted fiber as opposed to the relatively amorphous character of the random copolymer.

Thus, with moisture absorption and dyeability, we come to the end of the list of key fiber properties chosen for discussion. The data presented and examples illustrating principles have been drawn mainly from condensation polymers and their fibers. This has been done for clarity and brevity of presentation. The principles discussed and the conclusions drawn hold for fibers made from both natural and man-made linear polymers. In vinyl and acrylics, steric isomerism is important in governing intermolecular forces. Random, block, or graft copolymerization has effects with vinyl or acrylic polymers analogous to those observed in condensation polymers. With vinyls or acrylics one relies on the nature of the side group to regulate chain stiffness, since it is not possible to insert a ring in the chain.

In Table VI we have drawn together in summary form the list of fiber properties discussed along with the pertinent polymer structural factors which govern these properties.

TABLE VI
Fiber Properties versus Polymer Structure Factors

Fiber property	Polymer structure factor
Melting point	(a) Intermolecular forces (b) Chain stiffness (c) Monomer unit regularity
Modulus	(a), (b), (c) (d) Crystallinity (e) Crosslinking (f) Orientation
Elasticity and recovery	(a), (b), (c), (d), (e), (f)
Tensile strength	(a), (c), (d), (f) (g) Molecular weight
Moisture absorption and dyeability	(a), (b), (c), (d), (e), (f) (h) Chemical sites (for H-bonding or salt formation)

At the beginning of this paper we commented on the role of increasingly sophisticated engineering to harvest the fruits of a rapidly expanding basic science in polymers and fibers. We conclude with an example which

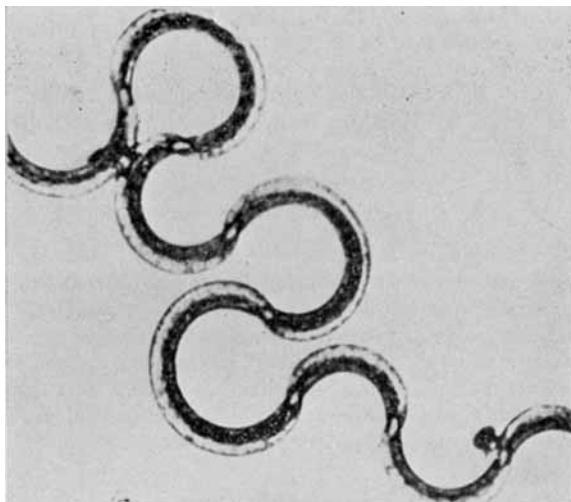


Fig. 10. Two-component Orlon acrylic fiber.

dramatically illustrates this point (Fig. 10). The Orlon acrylic bicomponent fiber shown here is now in commercial production and is made, not from one, but from two polymers.⁹ It is $15\ \mu$ in diameter. The polymer composition of each component of this bicomponent fiber has been so chosen that a differential in hydrophily is obtained. The fiber has a spiral, corkscrewlike crimp when dry and tends to uncrimp when wet. Fine apparel wools also have this spiral structure and crimp properties which are important among wool's characteristic properties in fabrics. The spiral fiber structure contributes bulk, and the reversible crimp operates to restore bulk and life to a fabric upon cleaning. One may ask why the sheep goes to the trouble of making a fiber of this kind. A speculative answer to this question is that, in the process of natural selection, the sheep evolved this structure to provide himself with a fiber which in the rain loses its crimp, giving him a thatched-roof type of covering to reduce body heat loss by irrigation, but which in weather that is cold and dry recrimps forming a bulky, fluffy blanket of insulation.

We shall not try to estimate the millions of years required for evolution of the ingenious hair follicle that "spins" the bicomponent wool fiber from the back of a Merino sheep; however, we do know that present-day engineering solved the "hair follicle" problem for Orlon in a matter of months.

References

1. Champetier, G., *Bull. Soc. Chim. France*, **1956**, 853; unpublished work by S. T. Polyak at Carothers Research Laboratory.
2. Shashoua, V. E., and W. M. Eareckson, III, *J. Polymer Sci.*, **40**, 343 (1959).
3. Charch, W. H., and J. C. Shivers, *Textile Res. J.*, **29**, 536 (1959).
4. Lyons, W. J., *J. Appl. Phys.*, **29**, 1429 (1958).

5. Hicks, E. M., *Textile Res. J.*, **32**, 791 (1962).
6. McCune, L. K., *Textile Res. J.*, **32**, 262 (1962).
7. Coleman, B. D., and A. G. Knox, *Textile Res. J.*, **27**, 393 (1957).
8. Tanner, D. (to du Pont), U. S. Pat. 2,999,056 (September 5, 1961).
9. Hicks, E. M., Jr., J. F. Ryan, Jr., R. B. Taylor, Jr., and R. L. Techenov, *Textile Res. J.*, **30**, 675 (1960).

Résumé

On discute la relation entre la structure de polymères et leurs propriétés comme fibres. On discute aussi les effets spécifiques des forces intermoléculaires, la rigidité d'une chaîne, la régularité de l'unité monomérique, de la cristallinité, du pontage, de l'orientation, du poids moléculaire, et de la composition chimique sur les propriétés importantes de fibres telles que: point de fusion, module, élasticité ou le recouvrement après tension, la force d'allongement, absorption de l'humidité et la tinctoriabilité. Un exemple est donné pour illustrer le rôle de l'art de l'ingénieur d'aujourd'hui dans le contrôle ultérieur et la modification des propriétés des fibres.

Zusammenfassung

Die Beziehung zwischen Polymer- und Faserstruktur und den Fasereigenschaften wird diskutiert. Die spezifischen Einflüsse von zwischenmolekularen Kräften, Kettensteifheit, Regularität der Monomereinheit, Kristallinität, Vernetzung, Orientierung, Molekulargewicht und chemischer Zusammensetzung auf die wichtigen Fasereigenschaften wie Schmelzpunkt, Modul, Elastizität oder Verformungsrückbildung, Zugfestigkeit, Feuchtigkeitsabsorption und Anfärbbarkeit werden im Detail diskutiert. Ein Beispiel zur Illustrierung der Rolle der heutigen verfeinerten Verfahrenstechnik bei der weiteren Kontrolle und Modifizierung der Fasereigenschaften wird gegeben.

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