

## Properties and Structure of Nylon Fibers in Relation to Drawing and Aqueous Phenol Treatments\*

YASUHIKO SAKUMA† and LUDWIG REBENFELD, *Textile Research  
Institute, Princeton, New Jersey*

### Synopsis

The changes in nylon 66 fiber structure and properties which take place during drawing and aqueous phenol treatments were studied by means of measurements of length, birefringence, density, moisture regain, x-ray diffraction, stress-strain behavior, and sound velocity. Drawing was found to establish molecular orientation along the fiber axis predominantly in the early stages, whereas the development of lateral order occurred primarily after a certain level of orientation had been achieved. Treatments in aqueous phenol solutions caused longitudinal contractions which depended on phenol concentration (1-5%), draw ratio (1-6), and the tension on the fiber during the treatment. The treatments resulted in an increase in the lateral order, decrease in orientation and corresponding changes in mechanical properties. Moisture regain was inversely related with density for the untreated fibers of various draw ratios, but the relationship became complex after treatments in phenol. The data are interpreted in terms of changes in the lateral order distribution, which permits an increase in the fibers' sorptive capacity despite an increase in the mean lateral order.

### INTRODUCTION

A variety of intermolecular forces are operative in polymeric systems which, in combination with the chemical structure of the monomer, confer upon the particular polymer its unique chemical, physical, and mechanical properties. There is a great deal of similarity in the molecular organization or the supermolecular structure of textile fibers. The salient feature of this molecular organization is the association of the long-chain polymer molecules into cohesive aggregates by the interplay of secondary forces which may be weak van der Waals forces, comparatively strong hydrogen bonds, or various dipolar interactions. The formation of such cohesive aggregates results ultimately in the establishment of ordered regions or crystallites which vary in their size and degree of perfection with the method of fiber development and preparation. Another important aspect of fiber structure is the preferential orientation of the fiber's structural elements with respect to the fiber axis. Thus, fibers may be defined struc-

\* Paper presented at the Spring 1965 meeting of The Fiber Society in Atlanta, Georgia, May 21, 1965.

† Present address: Mitsubishi Rayon Company, Ltd., Tokyo, Japan.

turally as semicrystalline, oriented polymers whose properties are, to a great extent, defined by intermolecular forces which are operative between the long-chain polymer molecules.

When a polymer is melt-spun, the fiber usually has poor physical properties as a textile material, and it must be drawn to acquire greater strength and appropriate extensibility. From a structural point of view, drawing allows intermolecular forces to be maximized in the formation of ordered cohesive aggregates or crystallites and causes these structural aggregates to become oriented with respect to the fiber axis. It would seem evident that the degree of structural ordering and orientation would be dependent upon the extent of drawing. It has been shown that the fiber is subjected to complex structural changes during the drawing process and that the resulting fiber has physicochemical properties differing from those of the original.<sup>1-8</sup>

When a nylon fiber is subjected to certain combinations of mechanical, chemical, and thermal actions, the internal fiber structure can be disrupted, and certain changes in fiber properties take place which are reflections of deep-seated alterations in the molecular organization. The disruption of a fiber's aggregated structure by a chemical attack on the intermolecular forces provides a means of studying the structure of the fiber in terms of the changes which take place in its physicochemical and mechanical properties. Nylon absorbs phenol from solution resulting in a considerable degree of fiber swelling. The mechanism is believed to be hydrogen-bond formation between the reagent and the amide group of the polymer,<sup>9</sup> thereby disrupting the forces between the polyamide chains. During immersion and subsequent washing and drying, severe dimensional changes occur that are accompanied by changes in the submicroscopic polymer structure and in mechanical properties.<sup>10-13</sup>

This paper presents the results of an investigation of the effect of drawing on the physical properties of nylon 66 fibers and on the effect of treatments in aqueous phenol solutions under a variety of experimental conditions in relation to the drawing history. The purpose of the investigation was to make clearer the changes in nylon fiber structure which take place as a result of drawing and as a result of certain chemical treatments. Phenol treatments at room temperature were chosen for experimental convenience, and other treatments involving different chemical and thermal stresses are contemplated.

## EXPERIMENTAL AND RESULTS

### Samples

Pigment-free nylon 66 fibers were supplied by E. I. du Pont de Nemours & Company from the same batch of polymer with draw ratios ranging from 1 (undrawn) to 6. The linear densities of the single filaments range from 3 to 0.5 tex, respectively. These fibers were previously studied in connection with infrared dichroic ratios,<sup>2</sup> elastic, bending, and torsional moduli,<sup>14</sup> and dye diffusion.<sup>15</sup>

### Phenol Treatments

Bundles of the fibers were immersed for 1 hr. in infinite aqueous phenol solutions with concentrations ranging from 0 to 5% (by weight) at a temperature of 21–23°C. The samples were washed with water at room temperature until free from phenol as determined by the formalin–sulfuric acid test,<sup>16</sup> and then air-dried. Two groups of samples were prepared: (A) fibers were slack and free to contract during the treatments, and (B) fibers were wound around a rigid frame to maintain their original length throughout the treatment. The samples are referred to as group A and group B, respectively.

### Longitudinal Contraction

The length of the group A fibers was determined before and after the phenol treatments with a traveling microscope at 21°C. and 65% R.H., under a tension of 0.5 g./tex. No significant creep was observed under these conditions. In Figure 1 is shown the longitudinal contraction of the

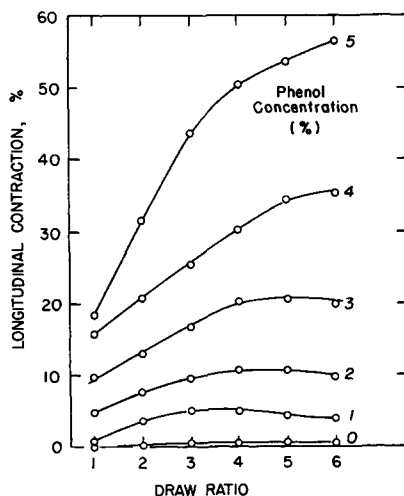


Fig. 1. Longitudinal contraction of nylon fibers treated in phenol at 23°C. as function of draw ratio.

fibers as a function of draw ratio. The shrinkage increased with increasing phenol concentration, as did the dependence on draw ratio. At the lower phenol concentrations the effect of draw ratio was less pronounced, but as the phenol concentration was increased significant differences in shrinkage were observed for each draw ratio.

### Birefringence

Birefringence was measured by means of a polarizing microscope equipped with a Berek compensator. As shown in Figure 2, birefringence in-

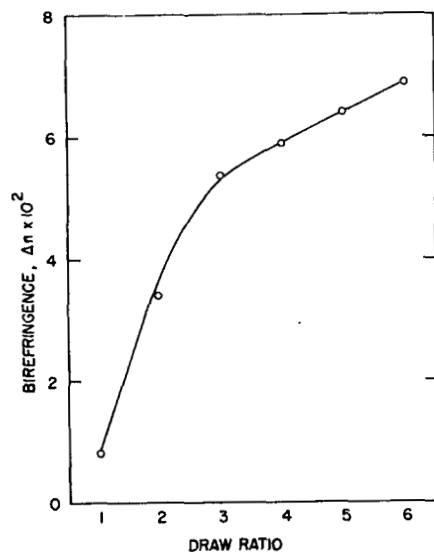


Fig. 2. Birefringence of untreated nylon fibers as function of draw ratio.

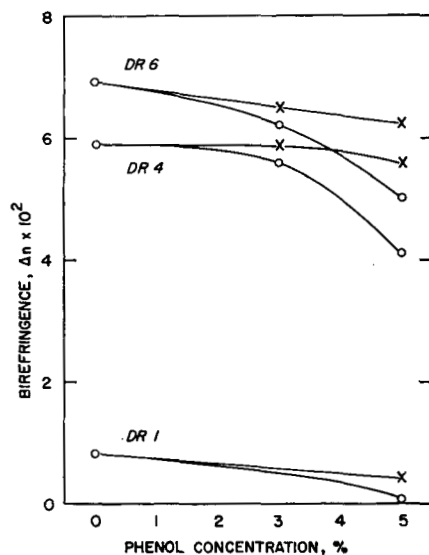


Fig. 3. Birefringence of phenol-treated nylon fibers as function of phenol concentration: (O) group A treated slack; (X) group B treated at constant length.

creased with drawing, but the dependence on draw ratio was greater at the lower draw ratio values. Figure 3 shows the birefringence of draw ratio 1, 4, and 6 fibers after the phenol treatment. Birefringence decreased with increasing phenol concentration and a consistent difference was observed between groups A and B. There is a greater decrease in birefringence of group A fibers than of the group B fibers, suggesting that a greater degree

of deorientation had taken place when the fibers were free to contract during the treatment.

### Density

A density-gradient column was prepared with appropriate mixtures of *n*-heptane and carbon tetrachloride in the manner described in ASTM Standards.<sup>17</sup> Good linearity was obtained in reference to calibrated floats ranging in density from 1.1000 to 1.1900 g./cm.<sup>3</sup>. Small bundles of the filaments, previously conditioned (21°C., 65% R.H.) and deaerated in the same liquid, were put into the column and their positions were read after 24 hr., at which time they had reached their equilibrium position. The column was kept at a temperature of 21 ± 0.5°C. In Figure 4 are shown

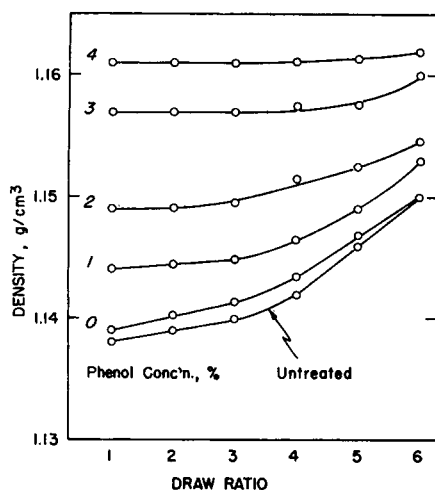


Fig. 4. Density at 21°C. of untreated and phenol-treated fibers as function of draw ratio.

the density values as a function of draw ratio. The density of the untreated fibers, which ranged from 1.138 to 1.150 g./cm.<sup>3</sup>, was essentially constant at the lower draw ratios but increased significantly with drawing. A similar dependence on draw ratio was also observed with the samples treated at low phenol concentrations although at each draw ratio the density was increased by the treatment. When the treatment became more drastic (higher phenol concentration), the dependence on draw ratio was reduced and no appreciable difference was observed among the different draw ratios when the fibers were treated with 4% phenol. It was also noted that groups A and B showed identical density values for each draw ratio and treatment condition. In general, treatments increased the density of the fibers at each draw ratio almost linearly with increasing concentration, and the lower the draw ratio, the greater was the relative increase.

### Moisture Regain

Samples were first partially dried in a desiccator over Drierite and subsequently exposed to an atmosphere of 21°C. and 65% R.H. in a conditioned room until constant weights were obtained, usually over a period of about 2 days. This procedure was followed in order to make certain that all the fibers attained their equilibrium moisture regain on the absorption rather than the desorption cycle. The bone dry weight was then obtained by heating the fiber in a weighing bottle at  $110 \pm 1^\circ\text{C}$ . to a constant weight.

As can be seen in Figure 5, the moisture regain of the untreated fiber decreased with increasing draw ratio. The particularly large decrease in moisture regain at the higher draw ratios is consistent with the previously

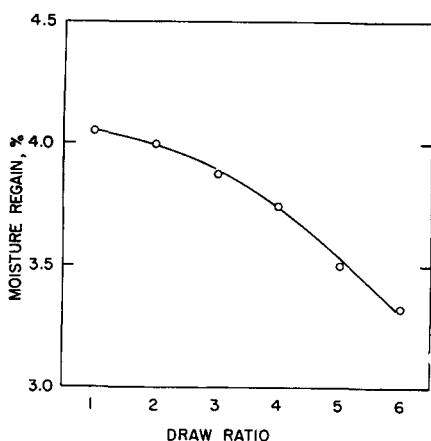


Fig. 5. Equilibrium moisture regain at 21°C. and 65% R.H. of untreated nylon fibers as function of draw ratio.

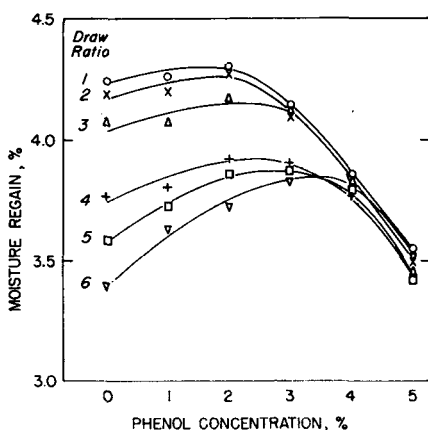


Fig. 6. Equilibrium moisture regain at 21°C. and 65% R.H. of phenol-treated nylon fibers as function of phenol concentration.

discussed large increase in density at those draw ratios. Treatments in phenol solution (group A) affected the moisture regain in a complex way as is evident from Figure 6 where moisture regain is plotted as a function of phenol concentration for each of the six draw ratios. Each curve passes through a maximum at a phenol concentration which is shifted toward higher values as the draw ratio increases. The sharpness of the maximum becomes greater with increasing draw ratio. After passing through the maxima, the curves tend to converge to a common moisture regain value where the effect of draw ratio is largely eliminated. The moisture regain of group B fibers, on the other hand, was found to change little with respect to phenol concentration.

### Mechanical Properties

**Stress-Strain Characteristics.** Stress-strain curves were recorded by means of an Instron tensile tester at 21°C. and 65% R.H. A special mounting method was employed to prevent fiber slippage during the test.\* The test specimen was 2 in. long and the extension rate was 50%/min.

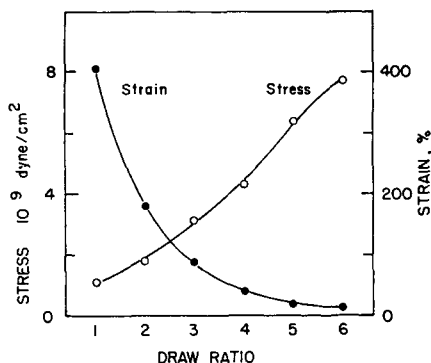


Fig. 7. Stress and strain at break at 21°C. and 65% R.H. of untreated nylon fibers as function of draw ratio: (O) stress; (●) strain.

No neck formation was observed under these conditions. The linear density of each specimen was measured with a vibroscope prior to the tensile test. In the figures each value is the average of six individual tests. Figure 7 shows the breaking stress and strain of the untreated fibers as a function of draw ratio. The stress at break increases while the strain at break decreases with the drawing process. The breaking stress dependence on draw ratio is essentially linear over the entire draw ratio range, but the decrease in the breaking strain is particularly pronounced in the initial stages of drawing. As is evident from a comparison of Figures 2 and 7, an excellent negative correlation is to be expected between the breaking strain and birefringence.

\* The fiber was wound around the end of a small paper clip 3 to 4 times and glued down with Duco cement on the side of the wire away from the test portion. Satisfactory stress-strain curves were obtained, and those samples broken at the clip were rejected.

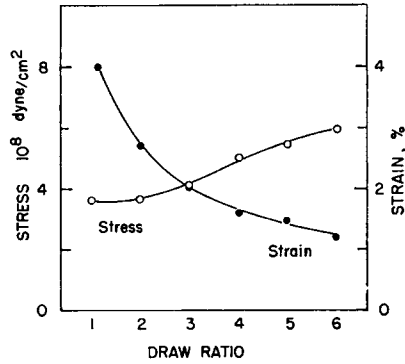


Fig. 8. Stress and strain at the yield point at 21°C. and 65% R.H. of untreated nylon fibers as function of draw ratio: (O) stress; (●) strain.

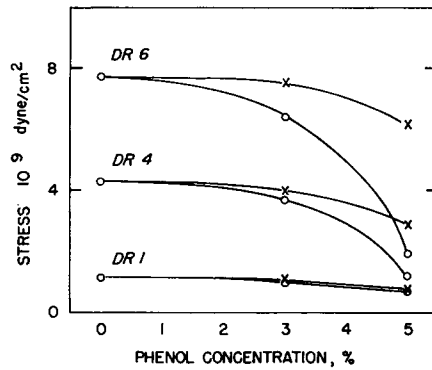


Fig. 9. Stress at break at 21°C. and 65% R.H. of phenol-treated nylon fibers as function of phenol concentration: (O) group A treated slack; (X) group B treated at constant length.

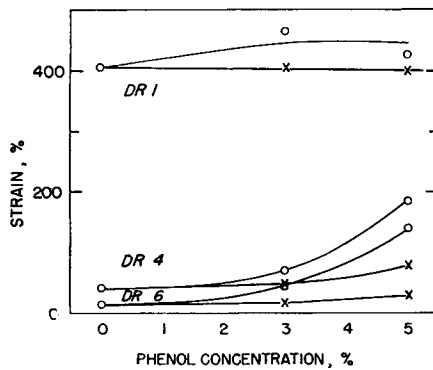


Fig. 10. Strain at break at 21°C. and 65% R.H. of phenol-treated nylon fibers as function of phenol concentration: (O) group A treated slack; (X) group B treated at constant length.



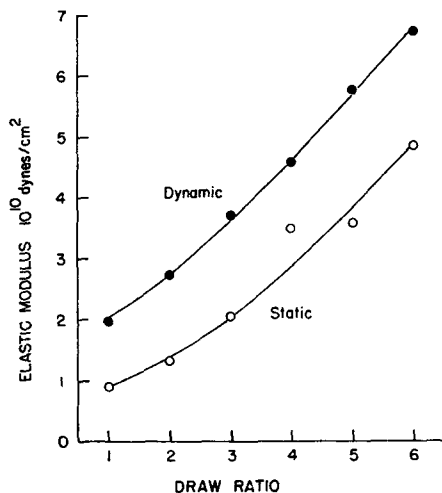


Fig. 11. Dynamic and static elastic moduli at 21°C. and 65% R.H. of untreated nylon fibers as function of draw ratio.

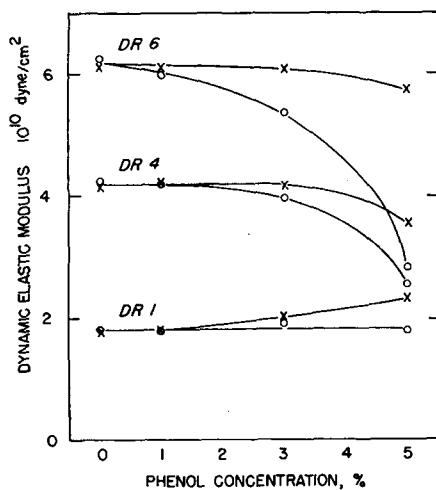


Fig. 12. Dynamic elastic modulus at 21°C. and 65% R.H. of phenol-treated nylon fibers as function of phenol concentration: (O) group A treated slack; (X) group B treated at constant length.

The stress and strain at the limit of the initial Hookean region are shown in Figure 8. The yield stress increased while the yield strain decreased with draw ratio, the dependencies on drawing bearing a resemblance to the stress and strain at break (Fig. 7).

When the fibers were treated with phenol, the breaking stress invariably decreased as the concentration increased. As is evident from Figure 9, the decrease was more pronounced for the group A fibers than for the group B fibers. The curves for the fibers in group A seem to converge to a

common point on the concentration axis. Figure 10 shows the breaking strain of the treated fibers as a function of phenol concentration. The breaking strain increased with concentration, and once again a greater effect was observed for the group A fibers.

The elastic modulus was obtained from the slope of the initial Hookean region of the stress-strain curve and is referred to as the static modulus. As would be expected, it is highly dependent on drawing, and the nearly linear dependence of the static modulus on draw ratio is shown in Figure 11.

**Dynamic Modulus.** The dynamic elastic modulus was obtained by means of a pulse propagation meter<sup>4</sup> made by KLH Research and Development Company, with two Rochelle salt transducers mounted on an optical bench. The fiber length was varied from 5 to 20 cm. under a tension of 0.5 g./tex, and the slope of the transit time versus the path length curve was calculated by the method of least squares. Each value is again the average of six individual measurements carried out at 21°C. and 65% R.H. The dynamic modulus of the untreated fibers is shown in Figure 11 as a function of draw ratio. The dynamic modulus was larger than the static one, with both moduli increasing linearly with draw ratio. Figure 12 shows the dynamic modulus of the treated fibers as a function of the phenol concentration. A marked difference can be seen in the drawn fibers between the two groups. The moduli of group A fibers decreased at the higher phenol concentration, whereas those of group B fibers retained more than 80% of their original values. This bears a striking resemblance to the previously discussed graph of the breaking stress of the treated fibers (Fig. 9). For the undrawn fibers the modulus of group A was not affected by the phenol treatments, whereas the modulus of group B treated fibers increased slightly with concentration.

### X-Ray Diffraction

Normal flat film x-ray diffraction patterns were obtained on a Norelco x-ray unit producing  $\text{CuK}\alpha$  radiation filtered through a Ni plate. The film-specimen distance was 7.5 cm. In Figure 13 are shown the patterns of the untreated fibers of draw ratio 1 and 5. The Debye-Scherrer rings for the undrawn and equatorial arcs for the drawn fibers show the development of molecular orientation along the fiber axis by drawing. The patterns of the phenol-treated draw ratio 5 fibers are also shown in Figure 13 for both group A and group B (phenol concentration 5%). In both groups the resolution of the patterns is markedly improved by the treatment as is evidenced by the resolution of the (100) arc and the (110)(010) doublet. The improvement in the lateral order is due to a rearrangement of polymer segments which was made possible by the incorporation of phenol molecules within the fiber structure. It may also be seen that the equatorial arcs became more extended azimuthally when the fibers are free to contract during the treatment (group A), indicating that deorientation occurred. Such deorientation was suggested previously from birefringence measurements (Fig. 3).

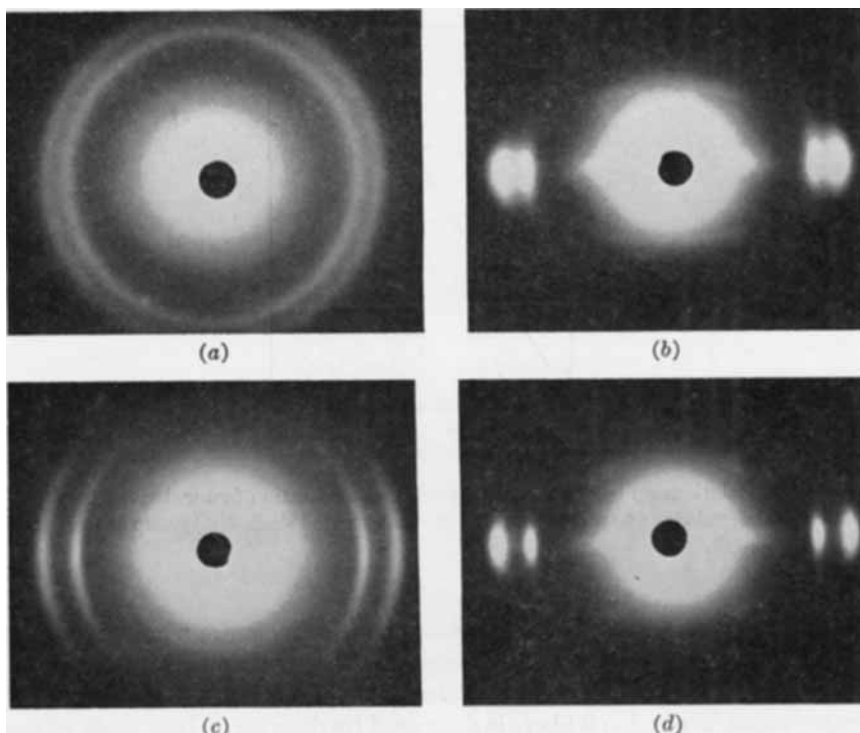


Fig. 13. X-ray diffraction patterns of nylon fibers: (a) untreated, draw ratio 1; (b) untreated, draw ratio 5; (c) draw ratio 5, treated with 5% phenol, group A treated slack; (d) draw ratio 5, treated with 5% phenol, group B treated at constant length.

## DISCUSSION

### Effect of Drawing

The development of molecular orientation during drawing, as has been previously reported<sup>1,2,7,8</sup> is clearly shown by the birefringence data (Fig. 2) and in the x-ray diagrams (Fig. 14). The greater increment of birefringence in the low draw ratio range suggests that more orientation is established in the early stages of drawing. On the other hand, the increase in density (Fig. 4) occurs mainly at the higher draw ratio range. Hookway<sup>1</sup> also found that the isotropic refractive index which is correlated with density increased rapidly after the fiber was extended three or four times its length. This suggests that the mechanical stress applied to the fiber during drawing acts at first to align polymer segments along the direction of the force until a certain degree of orientation is established and then it gradually increases the lateral order. The decrease in moisture regain at the higher draw ratio values confirms the density data. Abbott and Goodings<sup>3</sup> and Bull<sup>18</sup> also observed that drawn nylon 66 fibers absorbed less water than undrawn. Dole and Faller,<sup>19</sup> using *N*-isobutylated nylon 610, found that the moisture regain is largely affected by the extent of

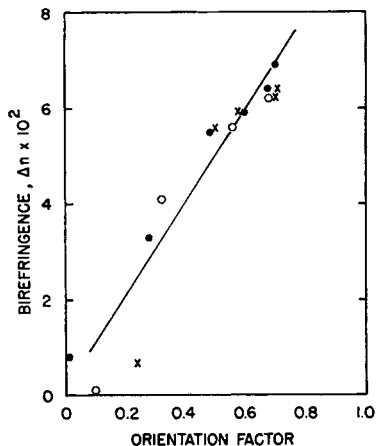


Fig. 14. Relationship between birefringence and orientation factor derived from dynamic moduli values: (●) untreated; (○) group A treated slack, (×) group B treated at constant length.

disorder. In the present case it seems that the moisture regain decreases with an increase in the degree of lateral order rather than with orientation.

According to Petukhov and Pakshver,<sup>10</sup> the diffusion coefficient of water vapor into nylon 6 fibers is decreased by drawing. In a study of the diffusion of an acid dyestuff into nylon 66 fibers, Davis and Taylor<sup>15</sup> found that the diffusion coefficient decreased markedly as draw ratio was increased, whereas the equilibrium dye uptake remained essentially unchanged. It was also found that the activation energy of diffusion increased with draw ratio. Davis and Taylor<sup>15</sup> attributed these phenomena to the increased order of the amorphous regions through which the diffusion was postulated to occur. It is apparent from these two diffusion phenomena that the rate of diffusion is reduced by drawing. The equilibrium uptake indicates that the total number of available dye sites is unchanged upon drawing, whereas the equilibrium moisture regain indicates that the amorphous regions to which water molecules are accessible are decreased. This suggests that the transition to a higher ordered state, which is caused by drawing, does not take place equally in regions of different lateral order. Thus, if one considers a given distribution of lateral order, a process which increases the mean lateral order may also affect the shape of the lateral order distribution curve. Such a change in the shape of the curve may result in the situation where certain levels of lateral order are increased while others remain unchanged. The concept of a lateral order distribution was introduced by Marchessault and Howsmon,<sup>20</sup> and more recently discussed by Rebenfeld,<sup>21</sup> Koshimo,<sup>22</sup> and Dismore and Statton.<sup>23</sup>

The stress both at the break and at the yield point increases with drawing at the expense of the corresponding strain, indicating a strong dependence on orientation. Both the static and dynamic moduli increase markedly

with drawing. Charch and Moseley<sup>4,5</sup> defined an orientation factor from dynamic modulus values as

$$F = 1 - (E_u/E)$$

where  $E_u$  denotes the dynamic modulus of the undrawn fiber. They reported that the dynamic modulus could be related to orientation and that the lateral order had little effect on the modulus when measured at temperatures below the glass transition. Morgan<sup>6</sup> found a linear relationship between birefringence and the orientation factor of various fibers. In Figure 14 (solid circles) the birefringence values of the untreated fibers of various draw ratios are plotted against the orientation factors and a good linear relation is obtained.

### Effect of Phenol Treatment

Bergman and co-workers<sup>11</sup> and Hermans and Weidinger<sup>24</sup> investigated the effects of phenol treatment of nylon 66 and 610, respectively, by means of x-ray diffraction. They observed that the treatment improved lateral order while the degree of orientation was considerably decreased. This is reminiscent of annealing in which the highly ordered parts acquire more lattice perfection and then increase in size.<sup>25</sup> Starkweather and co-workers<sup>26,27</sup> correlated the x-ray diffraction patterns with the density in terms of the degree of crystallinity. In the present case the improved resolution of the patterns (Fig. 13) was accompanied by an increase in density upon phenol treatments (Fig. 4). It is interesting to note that the differences in the density values among the draw ratios were gradually eliminated as the phenol concentration increased. This implies that sufficiently drastic treatments tend to cancel the effects of previous treatments. It should also be noted that the mechanical stress on the fiber during the treatment had no effect on the density values, while it affected the orientation to a considerable extent. A similar result was reported by Cannon and co-workers<sup>28</sup> in regard to the birefringence of nylon 66 fibers heated at 220°C. When the fibers were slack, the birefringence was decreased by as much as 6%, yet when the fibers were maintained under constant length during the heat treatment, the birefringence was not affected.

The dynamic moduli of the treated fibers were again used to calculate orientation factors which are plotted against the birefringence (Fig. 14). Good linearity is observed with no appreciable difference between groups A and B, indicating the importance of molecular orientation on the elastic modulus. It is noteworthy that the breaking stress and the modulus (Figs. 9 and 12) change in a similar manner with respect to the phenol concentration and that in both cases the curves for group A fibers converge to a point at a concentration of about 5.5% where the fibers start to disintegrate. These results indicate that the mechanical properties such as modulus and breaking stress are strongly dependent on molecular orientation.

Abott<sup>19</sup> reported a decrease in moisture regain of nylon 66 fibers when treated with 1% aqueous *m*-cresol solution. He also observed an increase in moisture regain when nylon was treated in a saturated benzoic acid solution. Petukhov and Pakshver<sup>10</sup> found that the regain of nylon 6 fibers decreased at low and increased at high relative humidities when treated slack in aqueous phenol solution, whereas treatments under tension did not affect the regain. On the other hand, heat treatments invariably decreased the regain. In the present work, the interesting observation was made that the equilibrium moisture regain passes through a maximum as a function of the phenol concentration for each of the six levels of draw ratio, as shown in Figure 6. This suggests that two opposing factors are operative on the fiber structure during the phenol treatments, one tending to decrease the lateral order resulting in an increase in moisture regain, and the other tending to increase the lateral order and thereby decreasing the moisture regain. These two opposing factors may be better visualized in terms of a lateral order distribution, and the concept that the shape of the distribution curve is altered in different ways during the treatment depending upon the phenol concentration. It is significant, however, that the density does not pass through a corresponding minimum as a function of phenol concentration, as may be seen in Figure 4. These results are consistent with those of Kanetsuna,<sup>12</sup> who observed that phenol treatments tended to increase the amount of both highly ordered and amorphous portions at the expense of an intermediate part, the net effect being accompanied by an increase in density. On this basis then, the lower phenol concentrations disrupt a certain level of lateral order, thereby allowing greater moisture sorption which is not offset by their ability to increase the overall order as indicated by the increased density. The higher levels of phenol concentration, on the other hand, are able to induce sufficient chain mobility to increase the mean lateral order to such an extent that a decrease in the equilibrium moisture regain is observed.

The sharpness of the maxima in Figure 6 are related to the draw ratio, and the maxima are shifted along the phenol concentration axis with increasing draw ratio. As was discussed in the previous section, drawing appears to convert a portion of the amorphous region to a higher ordered state which is not capable of participating in moisture sorption. This region of intermediate order, or some portion of it, may again participate in the moisture sorption process after a phenol treatment which is capable of disrupting it. With increasing draw ratio, this region of intermediate order is shifted to levels of higher order which, in due course, will respond only to higher phenol concentrations. On this basis, then, it would be expected that the maxima be shifted to higher phenol concentrations with increasing draw ratio.

It is also interesting to note that the 5% phenol treatment is drastic enough to cancel the effects of drawing as far as lateral order in an intermediate region is concerned since the equilibrium moisture regain of these samples is independent of draw ratio. This was also seen in the density data after the 4% phenol treatment.

Grateful acknowledgment is made to the Mitsubishi Rayon Company, Ltd. for financial support to Yasuhiko Sakuma during his tenure as a TRI Visiting Fellow. The authors are also pleased to acknowledge the assistance of Mr. Arthur B. Coe, who performed the birefringence measurements.

### References

1. Hookway, D. C., *J. Textile Inst.*, **49**, 292 (1958).
2. Caroti, G., and J. H. Dusenbury, *J. Polymer Sci.*, **22**, 399 (1956).
3. Abott, N. J., and A. C. Goodings, *J. Textile Inst.*, **40**, T232 (1949).
4. Charch, W. H., and W. W. Moseley, Jr., *Textile Res. J.*, **29**, 525 (1959).
5. Moseley, W. N., Jr., *J. Appl. Polymer Sci.*, **3**, 266 (1960).
6. Morgan, H. M., *Textile Res. J.*, **32**, 866 (1962).
7. Cumberbirch, R. J. E., and J. D. Owen, *J. Textile Inst.*, **56**, T389 (1965).
8. Adams, N., *J. Textile Inst.*, **47**, T530 (1956).
9. Pakshver, A. B., and E. K. Mankash, *Zh. Priklad. Khim.*, **27**, 182 (1954).
10. Petukhov, B. V., and A. B. Pakshver, *Zh. Priklad. Khim.*, **29**, 1236 (1956).
11. Bergman, M. E., I. Faulkuchen, and H. Mark, *Textile Res. J.*, **18**, 1 (1948).
12. Kanetsuna, H., *J. Soc. Textile Cell. Ind. Japan*, **14**, 434 (1958); *ibid.*, **18**, 784 (1962); *ibid.*, **18**, 794 (1962).
13. Forward, M. V., and H. J. Palmer, *J. Textile Inst.*, **45**, T510 (1954).
14. Wakelin, J. H., E. T. L. Voong, D. J. Montgomery, and J. H. Dusenbury, *J. Appl. Phys.*, **26**, 786 (1955).
15. Davis, G. T., and H. S. Taylor, *Textile Res. J.*, **35**, 405 (1965).
16. Feigl, F., *Spot Test*, 4th English Ed., Vol. II, Elsevier Press, New York, 1954, p. 106, Procedure I.
17. *1961 Book of ASTM Standards*, Part 9, American Society for Testing and Materials, Philadelphia, Pa., 1962, D 1505-60T, p. 701.
18. Bull, H. B., *J. Am. Chem. Soc.*, **66**, 1499 (1944).
19. Dole, M., and I. L. Faller, *J. Am. Chem. Soc.*, **72**, 414 (1956).
20. Marchessault, R. H., and J. A. Howsmon, *Textile Res. J.*, **27**, 30 (1957).
21. Rebenfeld, L., *J. Polymer Sci.*, **C9**, 91 (1965).
22. Koshimo, A., and Tagawa, T., *J. Appl. Polymer Sci.*, **9**, 117 (1965).
23. Dismore, P. F., and W. O. Statton, *J. Polymer Sci.*, **B2**, 1113 (1964).
24. Hermans, P. H., and A. Weidinger, *J. Polymer Sci.*, **4**, 709 (1949).
25. Fuller, C. S., W. O. Baker, and N. R. Pape, *J. Am. Chem. Soc.*, **62**, 3275 (1940).
26. Starkweather, H. W., and R. E. Moynihan, *J. Polymer Sci.*, **22**, 363 (1956).
27. Starkweather, H. W., J. H. Whitney, and D. R. Johnson, *J. Polymer Sci.*, **A1**, 715 (1963).
28. Cannon, C. G., F. P. Chappel, and J. I. Tidmarsk, *J. Textile Inst.*, **54**, T210 (1963).

### Résumé

Les changements dans la structure fibreuse et les propriétés du nylon 66 qui se passent en cours d'étirement et des traitements par le phénol aqueux ont été étudiés au moyen de mesures de longueurs, de mesures de réfringence, de densité, regain d'humidité, diffraction aux rayons-X, comportement étirement-tension et vitesse de propagation du son. L'étirement provoque une orientation moléculaire le long de l'axe de la fibre, principalement au début de l'opération tandis que le développement de l'ordre latéral se passe principalement après un certain degré d'orientation. Les traitements par des solutions de phénols aqueux provoquent une contraction dans l'ordre longitudinal qui dépend de la concentration en phénol, du rapport d'étirement (1 à 6) et de la tension de la fibre au cours du traitement. Le traitement entraîne un accroissement d'ordre latéral, une diminution dans l'orientation et des changements correspondants dans les propriétés mécaniques. Le regain d'humidité est lié inversement à la densité pour les fibres, non-

traitées et à différents rapports d'étirement, mais cette relation devient plus compliquée après traitement avec le phénol. Les résultats sont interprétés sur la base de changements de distribution d'ordre latéral qui permet un accroissement de la capacité de sorption des fibres malgré un accroissement d'ordre latéral moyen.

### Zusammenfassung

Die während der Reckung und Behandlung mit wässrigem Phenol auftretenden Änderungen der Struktur und Eigenschaften von Nylon 66-Fasern wurden mittels Längenmessungen, Doppelbrechung, Dichte, Feuchtigkeitsaufnahme, Röntgenbeugung, Spannungs-Dehnungsverhalten und Schallgeschwindigkeitsmessungen untersucht. Die Reckung führte vornehmlich in den frühen Stadien zu einer Molekülorientierung längs der Faserachse, während die Entwicklung einer seitlichen Ordnung hauptsächlich nach Erreichung eines gewissen Orientierungsgrades auftritt. Die Behandlung mit wässriger Phenollösung verursachte eine longitudinale, von der Phenolkonzentration (1-5%), dem Reckungsverhältnis (1-6) und der Spannung der Faser während der Behandlung abhängige Kontraktion. Die Behandlung führte zu einer Zunahme der seitlichen Ordnung, einer Abnahme der Orientierung und zu entsprechenden Änderungen der mechanischen Eigenschaften. Die Feuchtigkeitsaufnahme stand bei unbehandelten Fasern mit verschiedenem Reckungsverhältnis in umgekehrter Beziehung zur Dichte, nach Behandlung in Phenol wurde die Beziehung jedoch sehr komplex. Die Daten werden auf Grundlage einer Änderung der seitlichen Ordnungsverteilung interpretiert, was eine Zunahme der Sorptionskapazität der Fasern bei einer Zunahme der mittleren seitlichen Ordnung als möglich erscheinen lässt.

Received November 15, 1965

Revised December 17, 1965

Prod. No. 1331