Studies on Dyeing and Mechanical Properties of Nylon 6 Filaments Subjected to Swelling Treatments

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Synopsis

Drawn nylon 6 filaments were subjected to swelling treatment with benzyl alcohol and aqueous solution of phenol and formic acid under slack condition and under tension. The pretreated samples were dyed with a disperse dye Foron Yellow SE-FL (C.I. Disperse Yellow 42). A considerable increase in the equilibrium dye uptake was observed as a result of swelling treatment. Studies on lateral order by X-ray methods showed that lateral order has increased considerably as a result of preswelling treatment. This apparent contradiction, viz., increase in lateral order and at the same time increase in dye upstake, is explained as due to increased void volume. Studies on mechanical properties showed that the percentage elongation is increased as a result of swelling treatment under slack condition in spite of increased lateral order. This is explained as due to the slippage of chain-folded crystallites.

INTRODUCTION

The structural and morphologic parameters of fiber-forming polymers have profound influence on their dyeing behavior and mechanical properties. Diffusion of dye into individual fibers and the eventual extent of dye absorption depend largely on the physics and chemistry of the fiber structure and its ability to be modified before or during dyeing. Studies on the stress–strain behavior of fibers have proved the importance of the structural parameters like molecular weight, crystallization, orientation, temperature, and moisture. Several studies have been reported correlating the above mentioned structural parameters of nylon 6 filaments with the observed dyeing behavior and mechanical properties.

The drawing history of nylon 6 filaments and its influence on the diffusion of dyestuff were studied by Takagi and Hattori.[1] Similar studies to correlate with mechanical properties were carried out by Yumoto.[2] Tsruta et al.[3] have studied the effect of steam and dry heat setting on the dyeing behavior and mechanical properties of nylon 6. It has been reported that the dye uptake and diffusion coefficient are increased by steam setting while the tensile strength decreases with steam setting temperature. These observations have been explained as due to the loosening of structure due to the water molecules. But such an explanation is not compatible with the results of X-ray studies, which reported increased packing and perfection on steam setting. The effect of dry heat treatment on dyeability of nylon 6 was studied by Warwicker,[4] and it was reported that dye uptake increased with increase in temperature of heat setting at higher temperature.

Dyeing Procedure

The control and pretreated filaments of draw ratio 5 were dyed with a disperse dye Foron Yellow SE-FL (C.I. Disperse Yellow 42). The dye bath consisted of 0.5 g dye, 2 g/L trisodium phosphate, and 2 g/L dispersing agent. Approximately 50 mg of filament samples was immersed in beakers each containing 50 ml dye solution maintained at 65°C. The dyeing was carried out for different durations, viz., 10, 20, 30, 60, and 120 min. The dyed samples were first rinsed in distilled water and then in hot water and dried. The dye uptake, in g dye/100 g filament, was estimated spectrophotometrically. Dye solutions of the same concentration were prepared also by adding different amounts of phenol, i.e., 1, 2, and 3%, in dye bath. The untreated nylon 6 filaments of different draw ratios, were dyed in these dye baths containing phenol at 30°C for 45 min, after which the dyed samples were thoroughly washed with water to remove the phenol and unfixed dye. The percentage dye fixed was estimated as before.

Experimental Method for Studying the Mechanical Properties

The nylon 6 filaments of draw ratio 5 subjected to swelling treatments were tested on an Instron tensile tester 1026 for studying the single-fiber stress–strain behavior. The gauge length used was 1 cm. The average tenacity and breaking elongation were calculated for each sample from 25 load elongation curves. The work of rupture, in gm-wt-cm/den, was also calculated from the load–elongation curves.

X-Ray Studies

Wide-angle X-ray scattering studies were carried out on the nylon 6 filaments to assess the degree of lateral order and crystalline orientation. The X-ray diffractograms of the samples were taken on a Philips 1009 unit fitted with a texture attachment and vertical goniometer. All the scans were taken by the symmetrical transmission method by placing a parallel bundle of filaments, with its fiber axis horizontal in the 2θ range from 10 to 30°. The azimuthal intensity distribution of the two intense equatorial peaks was taken by rotating a fiber bundle whose 2θ position is fixed in a plane perpendicular to the direction of the X-ray beam.

Measurement of Lateral Order

The various polymorphic forms of nylon 6 have been discussed in an earlier report.[7] It is the stable α-form (draw ratio 5) which is under consideration in the present work. The measurement of crystallinity by X-ray methods has always posed problems to the workers in this field. It involves the assumption of the two-phase model. Experimental methods to measure the degree of crystallinity by separating the contribution due to different crystalline phases have been reported by several workers.[8,9] In all these methods, the separation of intensity of crystalline scattering from that of total scattering involved many assumptions. Hence, in the present work, it was thought better to calculate the total order in the sample by a relatively simple and reproducible method rather than measuring the absolute crystallinity, a term which has lost its significance

of late. The change in lateral order was followed by measuring the change in resolution of the two equatorial peaks in the diffractogram, viz., those of (200) and (002 + 202) reflections based on the method of Manjunath et al.[10] Thus, the X-ray order factor which gives a trend in the variation of degree of crystallinity was calculated.

Measurement of Molecular Orientation

Measurement of molecular orientation involves the measurement of the parameters of the total orientation and crystalline orientation. The crystalline orientation factor f_c was calculated from the azimuthal intensity distribution of the reflections (200) and (002 + 202) in the X-ray diffractograms using Hermans orientation factor[11]:

$$f_c = \frac{3 \cos^2 \phi - 1}{2}$$

The value of $\cos^2 \phi$ was calculated by the method derived by Stepaniak et al.[12] based on Wilchinsky's formula[13] and the crystal structure of nylon 6. The total orientation factor f was calculated from the birefringence values. The birefringence was measured using a polarizing microscope equipped with a Berek compensator. It has been reported by Morgan[14] that the intrinsic birefringence of nylon 6 is the same for both crystalline and noncrystalline phases and is equal to 0.073. From this, the total orientation factors f for all the samples were calculated. From the values of crystalline orientation factor f_c and total orientation factor f, the amorphous orientation factor f_a was calculated using the formula of Stein and Norris[15] neglecting the effect of form birefringence:

$$\Delta = X f_c \Delta_c^0 + (1 - X) f_a \Delta_a^0$$

where Δ is the measured birefringence, $\Delta_c^0 = \Delta_a^0$ is the intrinsic birefringence, and X is the crystalline fraction. For this calculation, the X-ray order factor was used as the fraction of ordered region. From these values, the approximate fractions of oriented matrix in the ordered and less ordered regions were calculated. Similar methods have been used by Samuels in the case of polypropylene.[16]

RESULTS

The dye uptake of untreated and pretreated samples of nylon 6 filaments of draw ratio 5 for different durations are shown in Figure 1. It can be seen that the equilibrium dye uptake is higher for samples treated with swelling agents than that of untreated samples. In the case of samples pretreated with aqueous solutions of phenol and formic acid, the dye uptake was found to increase with increase in the concentration of the swelling agents. Table I shows the dye uptake of nylon 6 filaments of different draw ratio dyed in baths containing different amounts of phenol. It is of interest to note that dye uptake is considerably increased by the presence of phenol.

In Table II are presented the values of shrinkage in boiling water of pretreated samples as reported in our earlier article.[7] The shrinkage in boiling water gives the residual shrinkage of the filaments. Measurement of residual shrinkage has
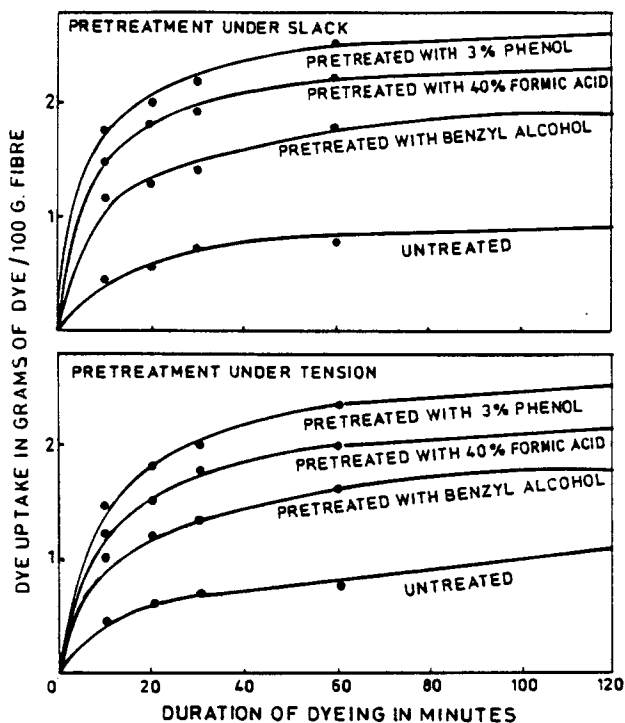
Fig. 1. Curves showing dye uptake of nylon 6 filaments of draw ratio 5 subjected to preswelling treatment.

been a method of following the stabilization of the structure. The less the residual shrinkage, the larger the degree of stabilization. A drastic reduction in the value of residual shrinkage as a result of preswelling treatment can be observed.

The X-ray order factor values of treated samples are presented in Table III. The considerable increase in the X-ray order factor of the pretreated samples is indicative of the increase in lateral order in treated samples.

The various functions of molecular orientation are presented in Table IV. It can be seen from Table IV that in the untreated filaments, the orientation is

TABLE I

Dye Uptake of Nylon 6 Filaments of Different Draw Ratios Dyed in Dye Baths Containing Different Amounts of Phenol at Room Temperature[a]

	Dye uptake, dye/100 g fiber			
Draw ratio	Control (without phenol)	With 1% phenol	With 2% phenol	With 3% phenol
1	0.479	1.28	3.12	5.33
2	0.486	1.38	3.11	5.05
3	0.318	1.11	2.87	5.10
4	0.272	0.79	2.88	4.89
5	0.231	0.78	2.75	4.56

[a] Dye: Foron Yellow SE-FL (C.I. Disperse Yellow 42).

TABLE II
Shrinkage in Boiling Water of Pretreated Nylon 6 Filaments

| | Percent shrinkage in boiling water of samples of draw ratio 5 | |
Treatment	Slack treated	Treated under tension
Untreated	13.07	—
Phenol 1%	8.5	9.5
Phenol 2%	4.2	8.5
Phenol 3%	0	5.6
Benzyl alcohol	8.2	11.4
Formic acid 10%	8.9	12.0
Formic acid 20%	7.4	10.5
Formic acid 30%	6.5	9.0
Formic acid 40%	0	8.0

predominantly in the less ordered region.   In the treated samples, the fraction of amorphous orientation is reduced.

Table V shows the values of denier, tenacity, elongation, and work of rupture of samples of draw ratio 5 subjected to preswelling treatments.   It can be seen that as a result of swelling treatment under slack condition, the breaking elongation is increased.   The tenacity is not appreciably affected except at high concentration of phenol and formic acid under slack condition.   The average load elongation curves of the samples treated with benzyl alcohol, 40% formic acid, and 3% phenol are shown in Figure 2.

DISCUSSION

Correlation of Structural Parameters with Results on Dyeing

The microphysical state of a fiber influences the reactivity and dyeability of the fiber by controlling the access of dye and water molecules in the accessible and inaccessible crystalline regions.   Figure 1 shows that there is an increase in dye uptake as a result of preswelling treatment.   The fact that the entry of the

TABLE III
X-Ray Order Factor Values of Nylon 6 Fibers of Draw Ratio 5 Treated with Various Swelling Agents Under Slack Condition and at Constant Length

| | X-ray order factor | |
Treatment	Treated under slack	Treated at constant length
Untreated	0.32	—
Benzyl alcohol	0.57	0.50
Formic acid 10%	0.50	0.45
Formic acid 20%	0.56	0.52
Formic acid 30%	0.65	0.57
Formic acid 40%	0.69	0.63
Phenol 1%	0.58	0.56
Phenol 2%	0.63	0.60
Phenol 3%	0.72	0.65

TABLE IV
Orientation Functions of Nylon 6 Filaments of Different Draw Ratios Subjected to Swelling
Treatments Under Slack Condition

Draw ratio	Lateral order or crystal-linity X_c	Birefri-ngence	Total orien-tation f	Crystalline orientation factor f_c	Amorphous orientation factor f_a	Fraction of crystal orientation f_c, X_c	Fraction of amorphous orientation $f_a, (1 - X_c)$
Untreated							
1	—	0.008	0.109	—	—	—	—
2	—	0.035	0.480	—	—	—	—
3	0.14	0.046	0.630	0.86	0.590	0.120	0.507
4	0.29	0.053	0.720	0.88	0.66	0.255	0.469
5	0.32	0.058	0.790	0.90	0.74	0.288	0.503
Treated with Benzyl Alcohol							
1	0.22	0.008	0.11	—	—	—	—
2	0.24	0.040	0.55	0.80	0.48	0.192	0.363
3	0.39	0.046	0.63	0.86	0.48	0.335	0.295
4	0.56	0.053	0.73	0.88	0.53	0.493	0.233
5	0.57	0.055	0.75	0.88	0.58	0.502	0.251
Treated with 40% Formic Acid							
1	0.53	0.008	0.11	—	—	—	—
2	0.64	0.043	0.59	0.78	0.23	0.499	0.083
3	0.69	0.053	0.73	0.86	0.45	0.590	0.140
4	0.69	0.055	0.75	0.87	0.48	0.600	0.148
5	0.69	0.053	0.72	0.87	0.40	0.600	0.124
Treated with 3% Phenol							
1	0.58	0.008	0.11	—	—	—	—
2	0.60	0.045	0.62	0.81	0.33	0.486	0.132
3	0.74	0.054	0.74	0.86	0.38	0.636	0.098
4	0.72	0.054	0.74	0.87	0.31	0.626	0.086
5	0.72	0.052	0.71	0.87	0.31	0.626	0.086

dye molecules and water into the fiber is through the less ordered regions necessitates an increase in less ordered regions. Accordingly, the increase in dye uptake observed in this work should mean that the order is poor in the samples

TABLE V
Tensile Properties of Preswollen Nylon 6 Filaments of Draw Ratio 5

| Treatment	Pretreated under slack condition				Pretreated under tension			
	Denier	Tenacity, g/den	Elonga-tion, %	Work of rupture, g-wt. cm/den	Denier	Tenacity, g/den	Elonga-tion, %	Work of rupture, g-wt cm/den
Untreated (control)	6.6	8.78	20.2	2.284	—	—	—	—
Benzyl alcohol	6.7	8.32	29.5	2.602	6.6	8.50	25.7	2.568
Phenol 1%	6.8	8.25	28.2	2.783	6.7	8.28	23.7	2.806
Phenol 2%	6.9	7.67	35.6	3.822	6.8	8.16	24.7	2.611
Phenol 3%	7.1	6.36	72.6	5.882	6.8	7.71	28.9	2.949
Formic acid 10%	6.7	8.47	25.7	2.786	6.7	8.60	22.4	2.787
Formic acid 20%	6.7	8.18	28.5	2.347	6.7	8.39	21.5	2.326
Formic acid 30%	6.7	7.91	35.3	3.883	6.7	7.91	23.5	2.403
Formic acid 40%	7.0	7.23	50.8	4.532	7.0	7.23	26.3	2.690
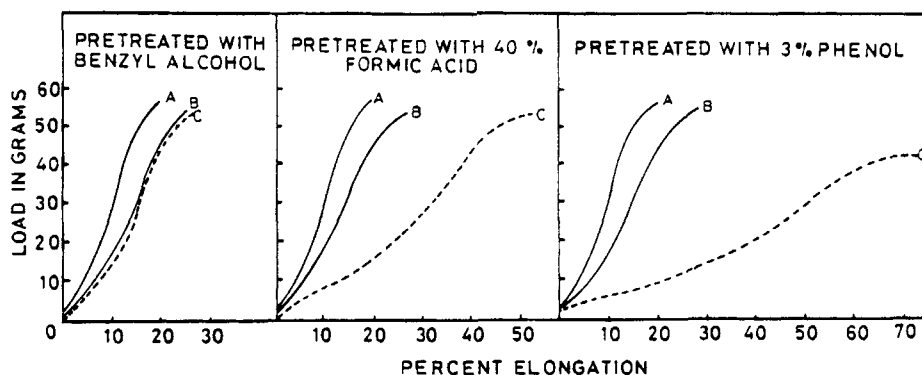
Fig. 2. Load–elongation curves of nylon 6 filaments of draw ratio 5 pretreated with swelling agents:
A, untreated; B, pretreated under tension; C, pretreated under slack.

treated with swelling agents. This is contrary to the results shown in Table III, where an increase in lateral order is observed as a result of swelling treatment. Thus, the existing theories on the general relationship between lateral order and dye uptake fail to explain the present observations.

The two-phase concept of crystalline and amorphous regions is being replaced by one in which all intermediate states between the two extremes are present with no clear boundary between the two phases. The concept does not necessarily describe the ideal model, as the recent studies have resulted in the development of the folded-chain model of crystalline structure. This model has been used to explain the variation in the shrinkage and tensile properties of nylon 6 fibers with temperature. Its significance in terms of dyeability of fiber is not yet fully understood.

The influence of deformation on the structure development during drawing of nylon 6 filament is considerable. During the drawing process, the original crystalline units in the undrawn filament are deformed by chain slip, and those which are unfavorably oriented become better aligned. This results in partial chain unfolding into small blocks of folded chains with many tie molecules.[17] At higher draw ratios, some of the tie molecules crystallize in the form of extended chains. Thus, the drawn material contains folded-chain crystals (lamellar crystals), extended-chain crystals (fibrillar crystals) and the less ordered regions consisting of crystal defects, voids, irregular chain folds, free chain ends, etc. From the above discussion, it can be inferred that during drawing, changes in lateral order are not considerable. This is mainly due to the two competing processes, viz., breaking of the initial crystal structure and subsequent crystallization, which is appreciably lower. Table V shows that the aligned molecules in the as-drawn filaments are predominantly in the less-ordered region.

Now let us examine what happens on swelling treatment. The increase in lateral order as a result of swelling treatment is reminiscent of thermal treatment. In the case of thermal treatment, increase in lateral order has been explained as mainly occurring due to regular chain folding.[18] The same sort of mechanism can be responsible for the formation of new crystalline units and the growth in thickness of the original crystalline units, on swelling treatment. It has been postulated that the polymer matrix contains highly crystalline sheetlike units[19] possibly held together by tie molecules. The changes caused by heat treatment increase the lateral order of these units.

It has been reported from studies on small-angle X-ray scattering that the long period is irreversibly increased as a result of annealing as well as swelling treatments. The discrete meridional reflection with high intensity has been attributed to alternating of crystalline and amorphous regions. But the electron density contrast is too small to give such a dramatic increase in intensity. On the other hand, if drawing of fibers destroys most of the folded-chain lamellae and if annealing or swelling treatment results in redevelopment of folded-chain lamellae interspersed with fissures or very sparsely occupied interstices, the large contrast in electron density between lamellae and interstices caused by large increases in the number of folded chains can easily explain the pronounced rise in intensity. This gives rise to void theory.

It has been inferred from SAXS that microvoids are a logical consequence of the fact that long chain polymers cannot efficiently fill all space. Thus, voids may be unfilled spaces around polymer chains, around fibrils, or between lamellae. According to Geil,[20] the growth in thickness of crystals during annealing would involve a self-diffusion of each molecule along its own backbone. The extension of the fold period by means of migration of point defects along a molecular chain under annealing condition has been suggested by Renekar.[21] The overall effect of self-diffusion of the folded molecules during annealing is to make individual regions of the platelike crystalline units taller but thinner, thus producing a distribution of void spaces.

Within the ribbon-like morphologic units, the chain-folded crystallites and tie molecules are such that the void spaces are large in number but smaller in size and distributed throughout the unit. On swelling treatment, the tie-molecular segments in the intervening, less ordered regions either get folded along with the existing folded crystalline nuclei which are comparatively smaller in size or form new chain-folded crystallites. Thus, the size of the void space is increased. The drastic reduction in the fraction of amorphous orientation is indicative of this. Actually, the void space is not created. As a result of swelling treatment and subsequent increase in chain folding, the voids are redistributed in such a way as to increase the size of the voids. The dye molecules are held in these void spaces by hydrophobic bonds with the surface of the chain-folded crystallites. A study of the SAXS coupled with diffusion phenomena might throw more light on this concept.

The data presented in Table I show that the dye uptake at room temperature is increased considerably with increase in the concentratin of phenol in the dye bath. This shows that dyeing in the presence of a swelling agent is identical to dyeing at elevated temperatures. It is pertinent to note, therefore, that whereas thermal treatment involves the consumption of a large amount of heat energy, the use of a swelling agent does not.

Studies on Mechanical Properties

It is the general belief that an increase in crystallinity brings about increase in modulus and yield strength but decreases the elongation to yield and break. The present observation shows that the tensile strength is not considerably affected but elongation is increased as a result of swelling treatment, except at high concentrations of phenol and formic acid under slack condition. According to general belief, the increase in elongation should reveal a fluidlike behavior or

decreased lateral order after swelling treatment.   However, X-ray data show increased perfection.

The data in Table V show that the total orientation is not affected considerably.   Hence, the increase in elongation cannot be attributed to reduction in orientation.   Although the crystallites in drawn fibers are perfectly oriented, the load-bearing chains are the tie molecules which are predominantly in the noncrystalline region.   The increased elongation can be attributed to either of two factors: low orientation of chains in the noncrystalline region or unfolding of folded-chain crystallites.   The latter is only observable at high temperature.   Hence, the increased elongation could be attributed to the flexibility of chains in the noncrystalline region.   It has already been stated that swelling treatment induces chain folding.   These chain-folded crystalline regions are embedded in void spaces.   The increased elongation before break can be attributed to the slippage of the folded-chain crystalline units due to the action of deforming force.   The work of rupture is increased due to the additional work done during slippage.   As the chain folding is in the crystalline region, the increased elongation cannot be attributed to the unfolding of chains.   As such, there is no disorientation taking place in the noncrystalline region.   But the fraction of oriented chains in the noncrystalline regions which rigidifies the structure is considerably reduced.

CONCLUSIONS

Studies on disperse dyeing and tensile properties have shown that the existing theory on the relationship between crystallization phenomena and these properties cannot explain the observed behavior.   The increased dye uptake inspite of an increase in crystallinity has been explained on the basis of a possible increase in void volume.   Similarly, an increase in elongation with increase in crystallinity has been explained on the basis of slippage of folded-chain crystallites.

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