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Relation Between Physical Structure and Dyeability of Nylon 6 Fibers. I. Effect of Tension and Heat Setting on Dyeability of Nylon 6 Fibers*

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Synopsis

Orientation by x-ray diffraction, dichroic orientation, and orientation by birefringence were measured on nylon 6 fibers subjected to stress relaxation or dry heat setting after stress relaxation. Orientation in the crystalline and noncrystalline regions increases with tension to an especially great extent in heat setting. Dyeability of the fibers subjected to stress-relaxation treatment is only slightly affected by tension, and dyeability of fibers subjected to dry heat setting or steam setting decreases with tension. The larger the molecular weight of dye used, the more marked the behavior becomes. Thus, depending on the dyes used, tension variations in weaving or knitting of nylon 6 fibers may be a cause of stripiness of dyed fabrics.

1. INTRODUCTION

Melt-spun nylon 6 fibers in commercial use are usually subjected to various processes, such as drawing, twisting, sizing, warping, weaving, heat setting, scouring, dyeing, and so on. When knit or woven goods thus produced are dyed, dyeing irregularities and stripes are often found. The differences in physical structure should be dealt with first among the causes of dyeing irregularities and stripes. Many studies have reported the change of dyeability due to drawing,[1,2] the relationship between residual strain and dyeability,[2] and effects of dry heat setting on dyeability,[3-7] but very few detailed investigations of effects of tension variations in heat setting on dyeability of nylon 6 fibers have been made. Shimizu[2] reported on the effects of variations in tension during winding upon dyeing properties of nylon fibers and concluded that residual strains due to extension at normal temperature and humidity in weaving and knitting of Amilan fibers would not affect dyeing properties when the fibers were dyed with a leveling acid dye. In this experiment, only stress-relaxation treatment was dealt with and heat-setting was not considered. Various stresses caused by unevenness of fibers in the weaving process will be relaxed to some extent, but the strain remaining in the fibers composing a textile may result in different effects of heat-setting under tension when the textile is heat-set on a tenter

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* This material appeared in part in *Sen-i Gakkaishi,* **16,** 215 (1960).

or scoured with a jigger. Crystallinity, orientation, and closeness of packing in the noncrystalline region of a fiber may vary depending upon the degree of remaining stress and heat-setting temperature. It is easy to infer that the rate of diffusion and the exhaustion of dye at a finite dyeing time will be so altered in the above situation that stripes and differences in color shades will occur.

In the present consideration of practical conditions in finishing processes, investigations were carried out on orientation, crystallinity, and dyeing properties of nylon 6 fiber heat-treated under various conditions of tension and setting temperature.

2. EXPERIMENTAL

Materials

The sample used was in the form of drawn nylon 6 filaments (100 den/24 filaments semi-dull, Grilon).

Stress-Relaxation and Dry Heat Setting Treatments

By using the apparatus shown in Figure 1, nylon 6 fibers (100 den/24 fil.) were wound around an aluminum bobbin at 20°C. and 60% R.H. under a tension of 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.70, or 1.00 g./den.

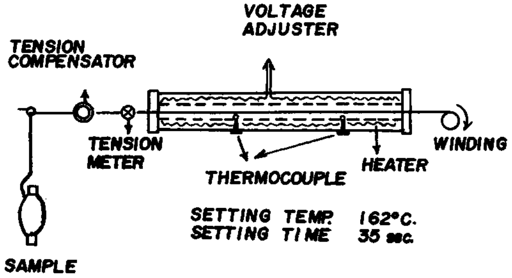

Fig. 1. Apparatus for dry heat setting of nylon 6 filaments.

The fibers were subjected to stress-relaxation treatments in the tensioned state for 100 hr. in a conditioned desiccator. The thus stress-relaxed fibers were dry-heat-set at 162 ± 1°C. for 35 sec. in hot air under the same tension as was used in the stress-relaxation treatment.

Measurement of Molecular Orientation by X-Ray Diffraction and of Birefringence by Polarized Microscopy

Ring scanning of intensities diffracted from the (200) and (002) planes was made by using a Geiger counter, and the orientation of crystallites was determined according to the rule of half-width. Measurement of the birefringence was carried out with a polarizing microscope with a Berek compensator.

Measurement of Molecular Orientation by Dye Dichroism

C.I. Disperse Orange 3 which had been twice recrystallized from ethanol solution was used. The nylon fibers were dyed at 60°C. for 60 min. at a bath ratio of 1:300 in a dyebath of various concentrations of dye in 1:1 ethanol water solution. By using a microphotometer, consisting of a polarized microscope and a photoelectric tube, the optical density along or across the fiber axis was determined. Dichroic orientation was calculated according to eq. (1).[8]

$$f_D = 100(D_{\parallel} - D_{\perp})/(D_{\parallel} + 2D_{\perp}) \tag{1}$$

where f_D is orientation, $D_{\parallel}$ is optical density along the fiber axis and $D_{\perp}$ is that across the fiber axis.

Figure 2 shows the relationship between dichroic orientation and concentration of dye on the fiber. Test specimens were dyed over the range of dyebath concentration determined by the curve where a constant degree of orientation was obtained, at which point orientation was independent of dye concentration on the fiber. Thus experimental errors due to the difference of dye concentration were removed.

Measurement of Specific Gravity

A density gradient column was made of CCl_4 and ligroin, and specific gravities of the specimens were measured. Apparent values of specific gravity were read from positions of specimens in the column after immersion in the solution, and plotted against time (0–80 min.). The specific gravity of a specimen was determined by extrapolating the relation of specific gravity and time to zero time. In that case of steam-set specimens, specific gravities were determined from a near equilibrium position at 49 min.

Dyeing Properties of Specimens Subjected to Stress-Relaxation and Dry Heat Setting

The specimens were knitted side by side into a tube with a circular knitting machine and scoured and dyed in a bath. Scouring was carried

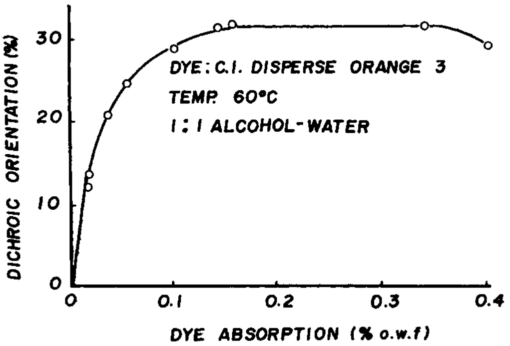

Fig. 2. Relationship between dye absorption and dichroic orientation.

TABLE I

Dyeing Conditions

Dyestuffs	Molecular weight	Treatment	Bath ratio	Dyebath concentration, % o.w.f.	Dyeing time at 60°C., min.	pH
Amacel Heliotrope I	238.236	Stress relaxation	1:50	0.3	60	
(C.I. Disperse Violet 1)		Stress relaxation and dry heat setting	1:50	0.3	60	
Naphthalene Red EAS	502.438	Stress relaxation	1:50	0.35	60	pH = 4
(C.I. Acid Red 13)		Stress relaxation and dry heat setting	1:50	0.35	60	pH = 4
Congo Red	854.670	Stress relaxation	1:100	0.5	15	Neutral
(C.I. Direct Red 28)		Stress relaxation and dry heat setting	1:100	0.5	15	"
Supranol Cyanine G	854.007	Stress relaxation	1:50	0.3	15	pH = 5
(C.I. Acid Blue 90)		Stress relaxation and dry heat setting	1:50	0.3	15	pH = 5
Cibalan Violet RL		Stress relaxation	1:50	0.3	10	Neutral
		Stress relaxation and dry heat setting	1:50	0.3	10	"
Solar Cyanine 5R (C.I. Acid Blue 120)	600.94	Stress relaxation and steam setting	1:100	0.3	[a]	pH = 4

[a] Dyeing at 80°C. for 1 hr.

out in a bath containing 2 g./l. of Scourol (polyoxyethylene alkyl ether) 400 at 50°C., for 30 min. at a bath ratio of 1:100. The temperature was raised from 30°C. to 60°C. for 30 min. and dyeing was continued until a suitable dyeing depth was obtained. Table I shows the dyeing conditions and commercial dyes used. A proper weight of each dyed specimen was taken from the tube and dried under vacuum (5 mm. Hg.) over P_2O_5 in a desiccator at 65°C. for 2 hr. A dried and weighed sample was dissolved in suitable solvent and the optical density of the solution was measured photometrically. By the use of a calibration curve, the dye concentration (as per cent on weight of fiber) was determined from optical density measured at a constant wavelength. Formic acid (80%) was used for a solvent for Naphthalene Red EAS, and *m*-cresol was used for the other dyes.

Effects of Steam Setting on Dyeing Properties

Drawn nylon 6 filaments were wound around an aluminum bobbin under various tensions and steam-set at 120°C. for 5 min. Dyeing was carried out in the relaxed state according to the condition shown in Table I. The dyebath temperature was raised from 30°C. to 80°C. for 1 hr. and dyeing was continued for 1 hr. The per cent dye absorption (per cent on weight of fiber) was measured spectrophotometrically on a dyed sample dissolved in solvent.

3. RESULTS AND DISCUSSION

Orientation

Figure 3 shows various degrees of orientation measured by x-ray diffraction which were obtained on the basis of the half-width rule by ring-scanning of the intensities diffracted from the (200) and (002) planes. Orientation increased a little for the fibers subjected to stress-relaxation only, but orientation of both planes, especially of the (200) plane associated with hydrogen bonds, was increased markedly for the fibers dry-heat-set after stress

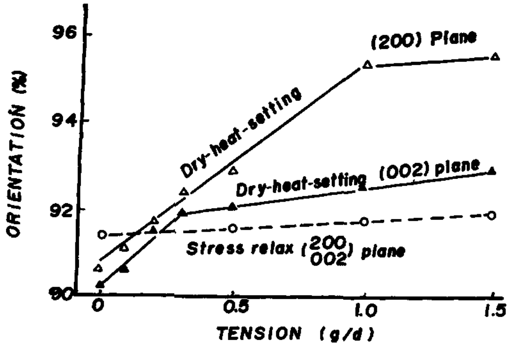

Fig. 3. Orientation obtained by x-ray for the fiber subjected to stress relaxation and dry heat setting.

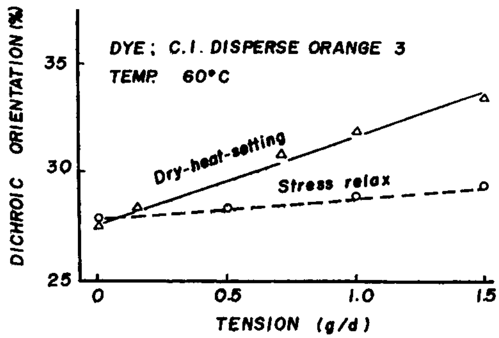

Fig. 4. Dichroic orientation of fibers subjected to stress relaxation and dry heat setting.

relaxation. These facts show that orientation of crystallites is improved by heat setting under tension. Figure 4 shows dichroic orientation as measured by the dichroic property of dye as a function of tension for these fibers. The dichroism is considered to be related to the degree of molecular orientation in the noncrystalline regions.[9] Thus, considering the low molecular weight of C.I. Disperse Orange 3, the above results suggest that orientation in more the highly ordered part of the noncrystalline regions is improved by stress relaxation and dry heat setting. The results obtained by birefringence measurement (Fig. 5) also supported the above conclusion of increased orientation of fiber with rise of tension in the treatments.[10]

Specific Gravity

Figure 6 shows specific gravities of treated specimens. Specific gravity was changed by both dry heat setting or steam-setting and was independent of tension in these treatments. If the crystallinity of fiber is increased with tension during such treatments as stress relaxation, dry heat setting,

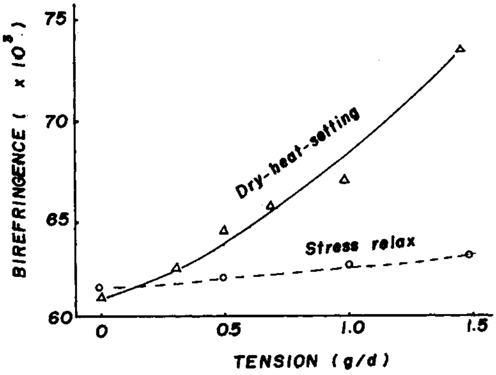

Fig. 5. Birefringence of fibers subjected to stress relaxation and dry heat setting.

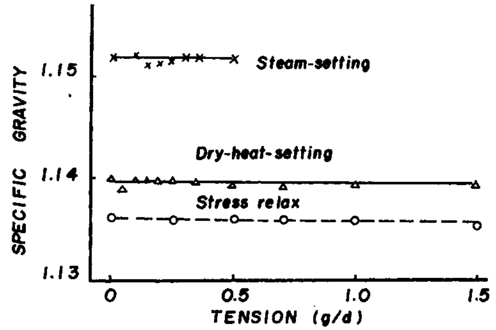

Fig. 6. Specific gravity of fibers subjected to stress relaxation and steam setting or dry heat setting.

and steam setting, specific gravity may increase. However, the experimental results show that crystallinity is not changed, only the orientation of crystallites and molecular chains in noncrystalline regions being increased.

Dyeability

For the examination of dyeability, the test specimens were knitted into a tube and dyed in one bath in relaxed state. Figures 7 and 8 show the relationship between dye uptake and tension for the fibers subjected to stress relaxation and for the fibers subjected to dry heat setting, respectively. A dependence of dye uptake on tension in the treatment is observed. The stress-relaxation treatment results in a very slight decrease of dye uptake, depending on tension. This indicates that molecular orientation is increased a little by stress-relaxation treatment, but dyeability is not changed. On the other hand, the viscosity of the fiber is decreased at high temperatures in dry heat setting. The mobility of molecular chains and crystallites is thus increased. Therefore, increased tension under these conditions may give rise to increased orientation of molecular

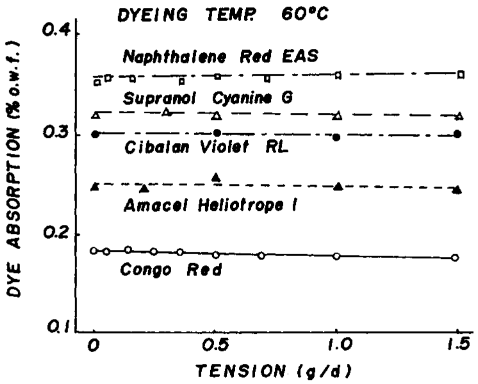

Fig. 7. Dyeability of fibers subjected to stress relaxation.

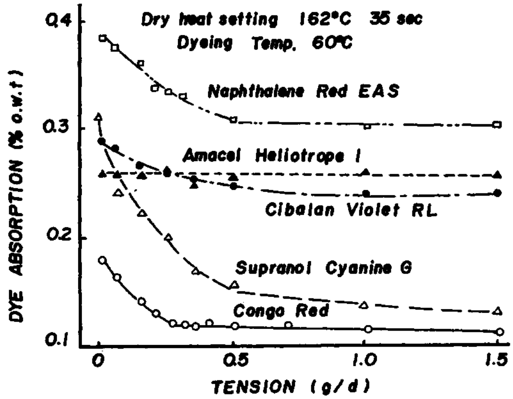

Fig. 8. Dyeability of fibers subjected to dry heat setting.

chains in noncrystalline regions and of crystallites. As a consequence there will be an increase in closeness of packing of noncrystalline regions, as indicated previously.[3,4] Figure 8 clearly shows that the dyeability of heat-set fibers drastically decreased with an increase of tension when a dye having greater molecular weight was used. This behavior is quite marked in the range of tension of 0–0.5 g./den. When a dye of smaller molecular weight, such as Amacel Heliotrope I, was used in dyeing, the dyeability of fibers was little affected. This may be explained by assuming that the size of pores changed in the network structure of the fiber may be just the same or larger than the molecular size of Amacel Heliotrope I. Figure 9 shows the relationship between dye uptake and tension in steam setting of nylon fibers. In this case, the greater the tension during heat setting, the more the dyeability decreased, just as was the case in dry heat setting.

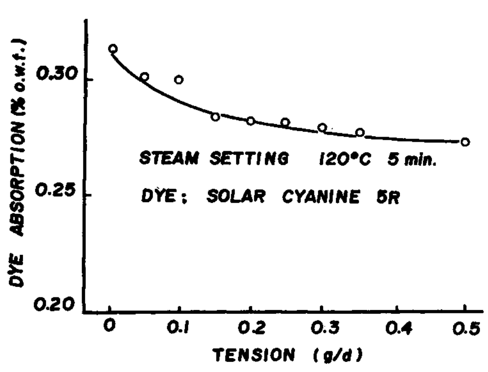

Fig. 9. Dyeability of fibers subjected to steam setting.

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Résumé

On a étudié l'orientation par diffraction aux rayons-X, l'orientation dichroïque et l'orientation par biréfringence des fibres de nylon-6 soumises à des tests de tension-relaxation ou bien traitées à chaud après le traitement de tension-relaxation. L'orientation dans les régions cristallines et non-cristallines augmente avec la tension et d'une façon spécialement importante dans le cas du traitement à chaud. La possibilité de coloration des fibres soumises au traitement de tension-relaxation est peu affectée par la tension, et la possibilité de coloration des fibres soumises à la chaleur séche ou à la vapeur diminue avec la tension. Plus le poids moléculaire du colorant employé est élevé, plus le comportement devient remarquable dans le dernier cas. Des variations de tension pendant le tissage ou le tricotage des fibres de nylon 6 peuvent être la cause de la formation de raies sur les tissus colorés.

Zusammenfassung

An Nylon-6-Fasern, die einer Spannungsrelaxation oder Trockenhitzebehandlung nach Spannungsrelaxation unterworfen wurden, wird die Orientierung durch Röntgenbeugung, dichroitische Orientierung und Orientierung durch Doppelbrechung gemessen. Die Orientierung im kristallinen und nichtkristallinen Bereich nimmt mit der Spannung besonders in einem grossen Ausmass bei der Hitzebehandlung zu. Die Anfärbbarkeit der einer Spannungsrelaxationsbehandlung unterzogenen Fasern wird durch die Spannung wenig beeinflusst, und die Anfärbbarkeit von trockenhitze- oder dampfbehandelten Fasern nimmt mit der Spannung ab. Je grösser dans Molekulargewicht des verwendeten Farbstoffes ist, desto auffälliger wird das Verhalten im letzteren Falle. Spannungsänderungen beim Weben oder Wirken von Nylon-6-Fasern können eine Ursache für die Streifenbildung in Abhängigkeit von den Farbstoffen bei gefärbten Geweben sein.

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