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Steam and Heat Setting of Nylon 6 Fiber. V. Investigation of Wide- and Small-Angle X-Ray Diffraction*

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Synopsis

Crystalline content, crystalline orientation, and long period of heat-set nylon 6 fibers were investigated. Fibers subjected to dry heat setting or steam setting, have x-ray diffraction patterns which suggest that an increase of crystallinity occurs on treatment, especially in the case of steam setting. The degree of crystalline orientation does not decrease greatly in either dry heat setting or steam setting. Therefore, the increased dyeability of nylon 6 fiber on heat setting is not attributable to a decrease of orientation of crystallites. The large increase of long period produced by steam setting corresponds to the increase in density noted.

1. INTRODUCTION

X-ray studies on nylon 6 have been reported by Brill,[1] Holmes, Bunn, and Smith,[2] Fuchino and Okada,[3] and other workers. In small-angle scattering Hess and Kiessig,[4] Zahn and Winter,[5] Fankuchen and Mark,[6] and others have showed the increase of long period for heat-set polyamide. However, no comparison between steam-set and dry-heat-set nylon has been previously published.

In a previous report[7] we indicated that there is a distinctive phenomenon of steam-set nylon 6 fiber, namely, increased dyeability in spite of higher density than dry-heat-set fiber.

Results of measurements of relative viscosity and amino and carboxyl endgroup contents,[8] do not support hydrolysis, and data from the same measurements for undrawn fiber, do not indicate the occurrence of a change in orientation.

In this report we attempted to confirm the above facts by measuring crystallinity, orientation, long period, and the like by means of x-ray wide- and small-angle scattering.

2. EXPERIMENTAL

Samples of heat-set nylon 6 filament (100 den./24 fil.) were prepared under the conditions shown in Table I.

X-ray diffraction patterns of the specimens were obtained with a flat-

* This material appeared in part in *Kobunshi Kagaku*, **16**, 391 (1959).

plate camera (Shimazu x-ray diffraction photometer type GX-I) using nickel-filtered CuKα radiation.

Estimation of the intensity along the equator or Debye-Scherrer ring of the plane (200) and (002) was made for the comparison of crystallinity

TABLE I
Heat-Setting of Nylon Filament

Sample	Treatment	Temp., °C.	Time, min.	Tension, g/den.
1	Unset	—	—	—
2	Dry-heat-set	138	20	0
3	"	140	30	0
4	"	190	20	0
5	"	140	30	1
6	"	150	20	1
7	"	180	30	1
8	"	190	20	1
9	Steam-set	110	20	0
10	"	110	60	0
11	"	120	20	0
12	"	130	20	0
13	"	135	20	0
14	"	140	20	0
15	"	110	20	1
16	"	110	60	1
17	"	120	20	1
18	"	135	60	1
19	"	140	20	1

TABLE II
Change of the Orientation of Nylon Filament
Subjected to Various Heat-Setting Treatments

Treatment	Temp., °C.	Tension, g/den.	Degree of orientation, %	
			(200)	(002)
Unset		0	88.3	89.5
Steam-set	110	0	89.4	89.4
"	140	0	89.6	87.8
Steam-set	110	1	91.0	91.0
"	140	1	91.7	91.2
Dry-heat-set	138	0	88.9	89.5
"	180	0	84.8	86.7
Dry-heat-set	150	1	86.8	88.3
"	160	1	90.4	90.0
"	180	1	84.8	89.3

and orientation among these specimens. Further, the small-angle scattering of these samples was determined to get some information about long period.

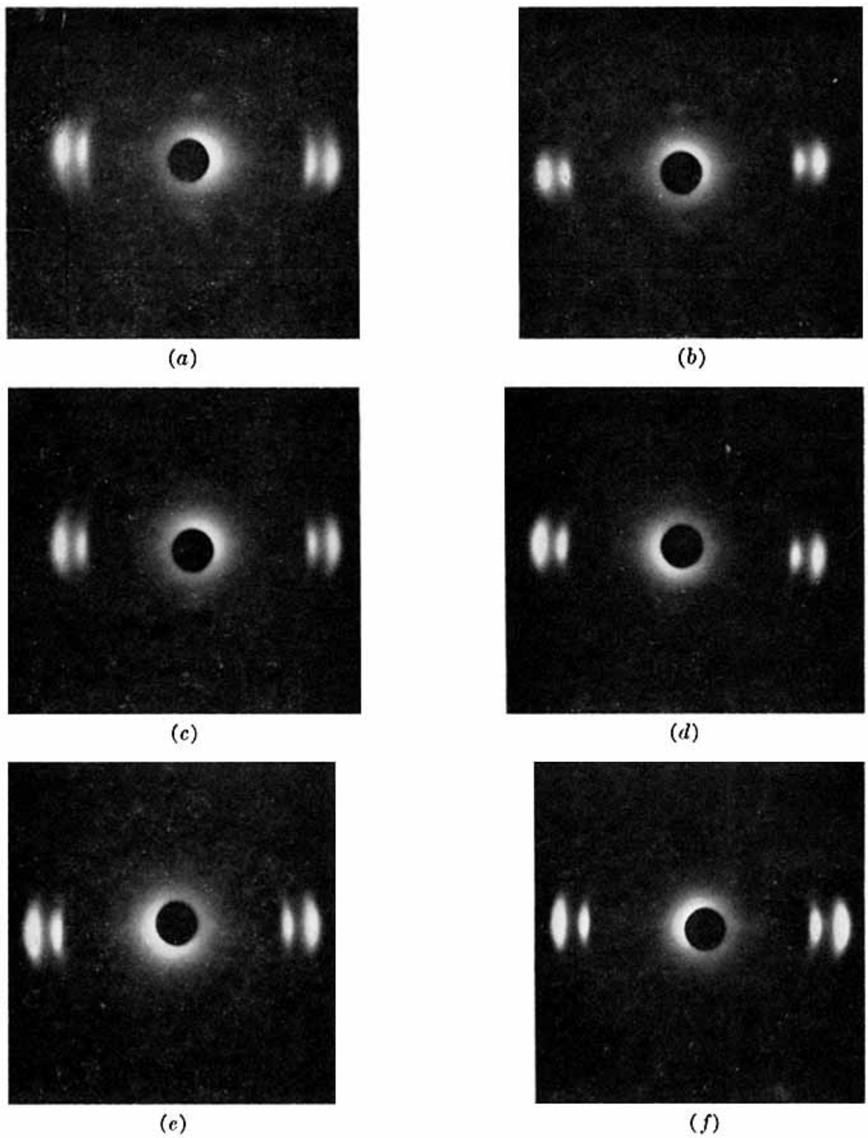

Fig. 1. X-ray diffraction patterns of nylon filaments subjected to various heat-setting treatments: (*a*) sample 1; (*b*) sample 2; (*c*) sample 4; (*d*) sample 9; (*e*) sample 11; (*f*) sample 14. See Table I for conditions of heat treatment.

3. RESULTS AND DISCUSSION

Investigation with Wide-Angle Scattering

Results for samples 1, 2, 4, 9, 11, 14 are shown in Figure 1, and the intensity distribution on the equator and the degree of orientation calculated from the half-width value by the intensity distribution curve on the

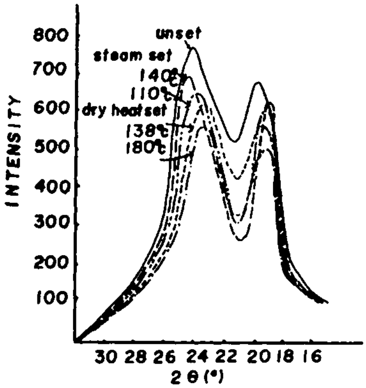

Fig. 2. Equatorial scan of the nylon filaments subjected to various heat-setting treatments without tension.

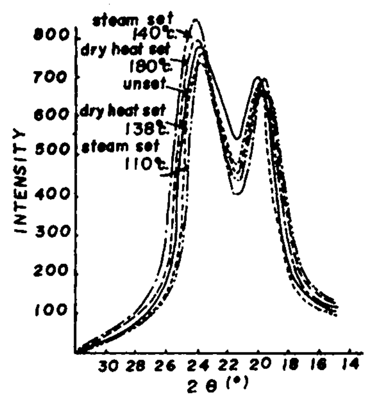

Fig. 3. Equatorial scan of nylon filaments subjected to various heat-setting treatments under 1 g./den. tension.

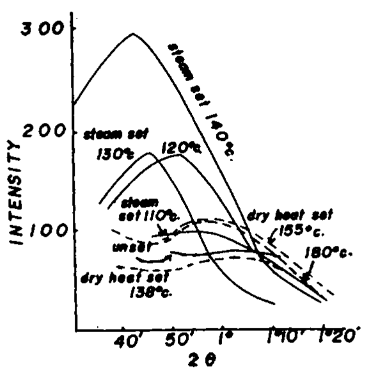

Fig. 4. Small-angle meridional scattering of the nylon filaments subjected to various heat-setting treatments without tension.

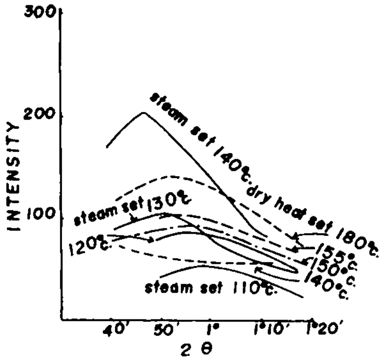

Fig. 5. Small-angle meridional scattering of nylon filaments subjected to various heat-setting treatments under 1 g./den. tension.

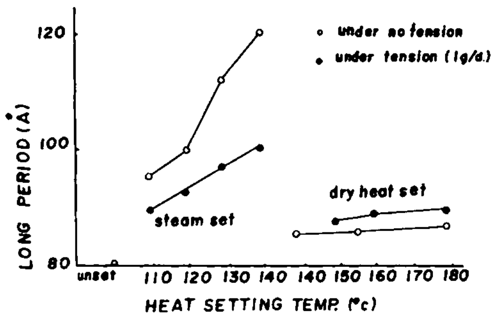

Fig. 6. Change of the long period of nylon filaments subjected to various heat-setting treatments.

(200), (002) planes are shown in Figures 2 and 3 and Table II, respectively.

The spots on the (200) and (002) planes become sharper with increasing heat-setting temperature. This is remarkable and due to the development of the crystalline plane or of orientation in steam setting.

The intensity of the (020) plane along the meridian decreases more with steam setting than with dry heat setting, and the seventh layer line separates into two lines on steam setting.

The separation of the peaks of the (200) and (002) planes on the diffraction curve is more distinct with steam setting than in the other treatments. This tendency becomes more marked with increasing heat-setting temperature, and is indicative of the development of crystallinity.

No decrease of orientation on steam setting is found (Table II) except for fibers dry-heat-set under no tension at 180°C.

Investigation with Small-Angle Scattering

The results of intensity measurement in the range $2\theta = 0 - 1°\,20'$ on the meridian for each fiber heat-set without or with tension are shown in Figures 3, 4, and 5, respectively. Generally, the higher the heat setting temperature is, the higher the peak of the curve and the more the peak shifts in position toward lower angle. The small-angle scattering of steam-set and dry-heat-set fibers show very large differences in intensity.

Untreated fiber gives very broad curve, so it is difficult to assign a position for the peak.

Long periods were calculated by the substitution of $2\theta_{max}$ into Bragg's equation; results are shown in Figure 6. The results are very similar to those reported by Zahn et al.[5] for polyurethane. The marked increase of the long period of steam-set fiber in comparison with dry-heat-set fiber corresponds to the increase of the density,[7] and also agrees with the results reported by Sakurada and Nukushina[9] that there is a linear relation between the increase of long period and crystallinity for dry-heat-set nylon 6.

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Résumé

On a étudié le contenu cristallin, l'orientation crystalline et la longue période de fibres de nylon-6 chauffées. Les fibres chauffées à sec ou chauffées à la vapeur donnent par diffraction de rayons-X un modèle qui suggère un accroissement de la cristallinité spécialement marqué dans le cas d'un chauffage à la vapeur. Le degré d'orientation cristalline ne décroît pas aussi fortement, que ce soit dans le cas d'un chauffage à sec ou dans celui d'un chauffage à la vapeur. C'est pourquoi il ne faut pas attribuer les propriétés colorantes des fibres de nylon 6 à la décroissance de l'orientation des cristallites. Une grande augmentation de la longue période, par chauffage à la vapeur, correspond à un effet de densité.

Zusammenfassung

Der Kristallinitätsgehalt, die kristalline Orientierung und die Langperioden von hitzebehandelter Nylon-6-Faser wurden untersucht. Die trockenhitze- oder dampfbehandelte Faser gibt ein Röntgenbeugungsdiagramm, das deinen Zuwachs der Kristallinität, besonders auffallend bei Dampfbehandlung, nehelegt. Der Grad der kristallinen Orientierung nimmt sowohl bei Trockenhitze- als auch Dampfbehandlung weniger ab. Daher kann die Verbesserung der Färbeeigenschaften der Nylon-6-Faser nicht der Abnahme der Kristallitorientierung zugeschrieben werden. Der grosse Zuwachs der Langenperiode bei Dampfbehandlung entspricht dem der Dichte.

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