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Steam and Heat Setting of Nylon 6 Fiber. III. Changes in Viscosity and Amino and Carboxyl Endgroups by Heat Setting*

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Synopsis

The relative viscosity and amino and carboxyl endgroup contents for unset, dry-heat-set, and steam-set nylon 6 fiber were determined. The results for the heat-set fibers are almost the same as those for the unset fibers. Therefore, it is difficult to explain the increase of dye uptake in steam setting on the basis of hydrolysis of nylon molecules. The differences in amino endgroup contents as determined by the *p*-toluenesulfonic acid and 2,4-dinitrofluorobenzene methods indicate that 20–30% of the amino groups might be occluded in the crystalline regions after steam setting.

1. INTRODUCTION

Ueda and Kimura[1] have reported on the basis of measurement of viscosity that the oxidative degradation of nylon begins at about 130–140°C. in dry heat setting.

Weltzien[2] reported that carboxyl endgroup contents and viscosity changes slightly with dry heat setting, and amino endgroup content, which does not change with steam setting, decreases markedly with the rise of temperature above 180°C. and consequently the absorption of acid dye on the fiber decreases. From these results, it was supposed that the decrease of amino endgroups is caused by the adhesion of oiling agent on the fiber.

In the present study, in which dry heat setting of nylon 6 fiber was carried out at less than 190°C. in nitrogen atmosphere or liquid paraffin in a manner similar to that of the previous report,[3] degradation with oxidation did not occur. The amino endgroups were measured by the *p*-toluenesulfonic acid method (PTS method) and further by the 2,4-dinitrofluorobenzene method (DNFB method). The latter was described by Sanger,[4] Zahn,[5] and Yoshida,[6] and provides an accurate method of measurement of amino endgroups available for dyeing.

2. EXPERIMENTAL

Materials

Drawn nylon 6 fibers (100 den./24 fil.) were subjected to heat setting under the same conditions as described in the first report.[3]

* This material appeared in part in *Kobunshi Kagaku*, **16**, 321 (1959).

Measurement of Viscosity

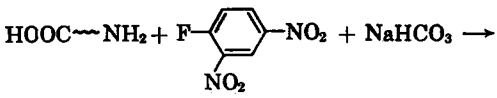
A 1-g. portion of sample was dissolved in 100 ml. of concentrated H_2SO_4 (purity 95%) and relative viscosity was measured with an Ubbelohde viscometer at 30 ± 0.2°C.

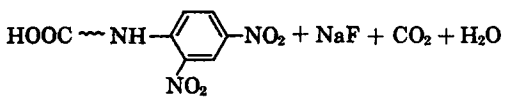
Measurement of Amino Endgroups

PTS Method. Nylon 6 fiber (0.5 g.) was dissolved in 25 ml. of *m*-cresol and titrated with 0.1*N* *p*-toluenesulfonic acid, Thymol Blue being used as indicator.

DNFB Method. To ethyl alcohol (25 ml.) containing 250 mg. 2,4-dinitrofluorobenzene, 20 ml. water containing 200 mg. sodium bicarbonate was added and stirred. Nylon 6 fiber (500 mg.) was immersed in this solution for 6 hr. at 60°C. After removal from this solution the fiber sample was allowed to stand overnight, then washed with aqueous acetic acid of pH 4–5 and successively with ethyl alcohol till all unreacted DNFB was removed completely, and dried. A 100 mg. portion of the sample was then dissolved in 100 ml. of *o*-chlorophenol, and subjected to colorimetric analysis. The amount of amino endgroups on the fiber was calculated by reference to a calibration curve of the optical density of an *o*-chlorophenol solution containing the aminocapronic acid reacted with DNFB versus the concentration.

The reaction involved is:





Measurement of Carboxyl Endgroups

In determining carboxyl endgroup contents, 20 ml. of benzyl alcohol containing 0.5 g. sample was titrated under nitrogen atmosphere with 0.1*N* KOH dissolved in a mixed solution of benzyl alcohol–methanol (9:1) The titration was carried out at the temperature of boiling point of xylene in an apparatus as shown in Figure 1.

3. RESULTS AND DISCUSSION

The results are shown in Tables I and II. The drawn fiber has a slightly lower degree of polymerization than the undrawn one. The former has high amino and carboxyl endgroup contents.

The results confirm that the viscosity, the amino endgroup contents determined by PTS method, and the carboxyl endgroup content of the undrawn and the drawn fibers subjected to heat setting under various

TABLE I
Change of Amino and Carboxy Endgroup Contents by Heat Setting

Sample	Conditions of heat setting: Type	Tension, g./den.	Temperature, °C.	η_{rel}	Amino end-groups, meq./g.	Carboxyl end-groups, meq./g.
Undrawn	None	—	—	2.561	0.0599	0.0594
Drawn	None	—	—	2.437	0.0644	0.0710
Undrawn	Steam	None	110	2.556	0.0587	0.0579
			120	2.577	0.0576	0.0571
			130	2.567	0.0582	0.0620
			135	2.563	0.0588	0.0617
Drawn	Steam	None	110	2.417	0.0632	0.0737
			120	2.457	0.0630	0.0724
			130	—	0.0611	0.0773
			140	2.433	0.0625	0.0676
Drawn	Steam	0.5	110	2.447	0.0643	0.0614
			120	2.406	0.0657	0.0640
			130	2.436	0.0636	0.0631
			140	2.464	0.0612	0.0591
Undrawn	Dry heat	None	140	2.574	0.0575	0.0599
			160	2.579	0.0577	0.0635
Drawn	Dry heat	None	140	2.420	0.0671	0.0663
			160	2.415	0.0688	0.0620
Drawn	Dry heat	0.5	140	2.429	0.0674	0.0657
			160	2.434	0.0671	0.0646

TABLE II
Change of Amino Endgroup Contents on Heat Setting (DNFB Method)

Sample	Setting temperature, °C.	Amino endgroup content, meq./g.
Undrawn, unset	—	0.0444
Drawn, unset	—	0.0500
Steam-set	110	0.0470
"	120	0.0494
"	130	0.0444
"	140	0.0484
Dry-heat-set	140	0.0454
"	160	0.0480

conditions are almost the same as those of unset fiber within the experimental error. However, the amino endgroup content determined by the DNFB method of the heat-set fiber was slightly lower than that of the unset fiber, as shown in Table II. This shows a similar trend as the equilibrium dye uptake of Azo Geranine 2G described in the previous report.[7] This appears to be due to occlusion of the amino endgroups in crystals because of the increase of the crystallinity with heat setting; consequently

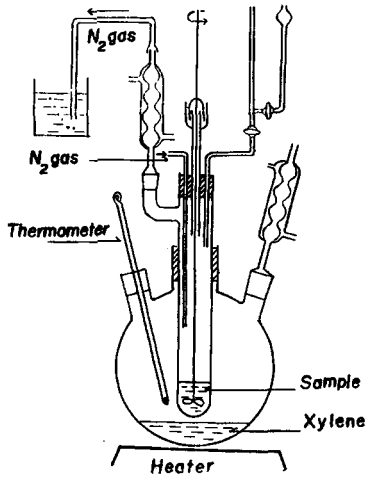


Fig. 1. Apparatus for measuring carboxyl endgroups.

the amino groups are inaccesible to the dye molecules or 2,4-dinitrofluorobenzene and the reaction proceeds with difficulty.

Thus, the DNFB method gives considerably lower values for amino endgroup contents than the PTS method. The results of neither the PTS method or the DNFB method agreed with the report by Zahn.[5]

From the above results, the decrease of amino endgroups by heat setting, and the equivalent relation of amino endgroups in nylon fiber with HCl, as reported by Wall and Beresniewicz,[8] it is obvious that the DNFB method does not give the total amino endgroup content of the fiber, so that 20–30 wt.-% might possibly be occluded in the crystalline regions.

Therefore, from the results of viscosity, and amino and carboxyl endgroup contents, it is difficult to explain the increase of dye uptake in steam setting from the view points of hydrolysis of the nylon molecules as described in the previous paper.[7]

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Résumé

La viscosité relative et la teneur en groupements terminaux aminé et carboxyle ont été mesurées pour la fibre de nylon 6, non-chauffée, chauffée en atmosphère sèche ou traitée à la vapeur. Les résultats obtenus pour les fibres soumises à la chaleur sont à

peine différents de ceux obtenus pour les fibres non chauffées. Aussi il est difficile d'expliquer l'augmentation de tinctabilité par le traitement à la vapeur du point de vue de l'hydrolyse des molécules de nylon. En considérant les différences entre la méthode à l'acide *p*- toluène sulfonique et au 2,4 dinitro-fluorobenzène la teneur en groupement aminé, terminal 20–30% de ceux-cipeuvent être occlus dans la partie crystalline.

Zusammenfassung

Die relative Viskosität und der Gehalt an Amino- und Carboxylendgruppen wird bei nicht erhitzten, trockenerhitzten und mit Dampf behandelten Nylon-6-Fasern gemessen. Die Ergebnisse bei den hitzebehandelten Fasern unterscheiden sich kaum von denen der ohne Hitze behandelten. Daher ist es schwierig, die Zunahme an Farbstoffaufnahme bei Dampfbehandlung vom Gesichtspunkt der Hydrolyse der Nylonmoleküle aus zu erklären. In Anbetracht der Unterschiede zwischen den Ergebnissen der *p*-Toluolsulfosäure- und der 2,4-Dinitrofluorobenzol-Methode kann ein Aminoendgruppenhalt von 20–30% im kristallinen Anteil eingeschlossen sein.

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