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Studies of the ζ-Potential of Natural and Synthetic Fibers in Dye Solutions. XVIII. ζ-Potential and Surface Dyeability of Heat-Set Nylon 6 Fiber in an Acid Dye Solution

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In order to ascertain the relation between the change in the fibrous fine structure and the dyeability of nylon 6 fiber caused by its heat-setting, the ζ-potential, the surface dye adsorption, and the total dye adsorption of the heat-set nylon 6 fiber in an acidic solution (pH 3.0) of acid dye—Orange II were determined. The crystallinity and the birefringence of the fiber increase in the order of the untreated, the wet-heat-treated, and the dry-heat-treated fiber. The isoelectric points of the untreated, the wet-heat-treated, and the dry-heat-treated fiber are pH 5.4, pH 4.6, and pH 2.8 respectively. With the increase in the dye concentration, the sign of the ζ-potential of the untreated and the wet-heat-treated fiber in a dye solution change from positive to negative because of the electrostatic bonds between the NH_3^+ of the fiber and the dye anion, RSO_3^-, while the ζ-potential of the dry-heat-treated fiber increases its negative value because of the van der Waals' forces between the fiber and the dye. The surface dye adsorption, as calculated from the difference between the surface charge density, $\Delta\sigma$, of the system with dye and that without dye, increases in any case as the dye concentration increases. The total dye adsorption increases as the dye concentration increases and attained the plateau regions at higher dye concentrations. The surface dye adsorptions become smaller in the order of the untreated, the dry-heat-treated, and the wet-heat-treated fiber. The total dye adsorptions become smaller in the order of the wet-heat-treated, the untreated, and the dry-heat-treated fiber. The differences in behavior among the fibers may be attributed to the adsorption of the dye to the loosely-packed portions in the amorphous region of the wet-heat-treated fiber, in addition to the differences in crystallinity and birefringence among the fibers. Moreover, the surface areas covered by adsorbed dye molecules, which were calculated from the reciprocal of the slope of the surface dye adsorption *vs.* the total dye adsorption curve of each fiber, were 1.8, 4.0, and 0.6×10^6 cm²/g fiber in the order of the untreated, the wet-heat-treated, and the dry-heat-treated fiber.

In manufacturing synthetic fibers such as polyamide nylon fibers, heat-setting is the usual processing practice. It is known that this treatment causes changes in the fibrous fine structure.

Hitherto, several articles on the relation between the changes in the fibrous fine structure and the dyeability of nylon 6 fiber caused by the heat-setting treatment have been published,[1] but few reports on the relation between the changes in the fine structure and the dyeability of the surface of the nylon 6 fiber caused by the heat-setting treatment are to be found. In this report the dyeability of the heat-treated nylon 6 fiber surface in an acid dye solution will be studied in relation to the ζ-potential, the surface dye adsorption, and the total dye adsorption in order to ascertain the influence of the changes in the fine structure upon the dyeability of the fiber surface.

1) *E.g.*, A. Koshimo and T. Kakishita, *Chem. High Polymers Japan*, **19**, 506 (1962).

Experimental

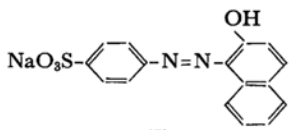
Fiber. Nylon 6 filaments (manufactured by the Toyo Rayon Co., Ltd.) were extracted with ethanol for about 24 hr at room temperature, and then dried in air. Three kinds of fiber were used. Some of the filaments were heat-treated as follows, while the rest were untreated specimens.

TABLE 1. NYLON 6 FIBERS USED

Fiber	Method of heat-treatment
Untreated fiber	(Draw ratio 4, 200 denier)
Wet-heat-treated fiber	Untreated fiber was treated 30 min in hot water (100°C) without tension
Dry-heat-treated fiber	Untreated fiber was treated 30 min in air at 170°C without tension

(All specimens were composed of 30 filaments)

Dye. The acid dye Orange II (I), which had been purified by recrystallization from an aqueous solution, was used.



(I)

ζ-Potential. The ζ-potential was measured by the method of the streaming potential, described in previous papers.[2] The dye solution was kept at pH 3.0 at 25°C with hydrochloric acid. Sodium chloride was added to the solution in order to prevent any influence of the ionic strength on the ζ-potential; its concentration was 10^{-4} mol/*l*.

Surface Charge Density and Surface Dye Adsorption. The surface charge density, σ, and the surface dye adsorption were calculated by method described in previous papers.[3]

Total Dye Adsorption, Crystallinity, Birefringence, Intrinsic Viscosity and End Groups. These values were measured and determined by the methods described in a previous paper.[3b]

Results and Discussion

End Groups, Crystallinity, Birefringence, and Intrinsic Viscosity of Nylon 6 Fiber. The values determined are shown in Table 2.

The end amino group decreased and the end carboxylic group increased in the order of the untreated, the wet-heat-treated, and the dry-heat-treated fiber. The intrinsic viscosity of the untreated fiber and that of the wet-heat-treated fiber were almost the same. However, the intrinsic viscosity of the dry-heat-treated fiber was about half of that of two former fibers; this result suggests that the decrease in the degree of polymerization is caused by the dry-heat-treatment. The crystallinity and the birefringence increase in the order of the untreated, the wet-heat-treated, and the dry-heat-treated fiber. These results suggest some change in the fine structure of these fibers, especially an increase in the crystalline region and in the degree of orientation.

The Isoelectric Point of Fiber. The ζ-potential of the fiber in solutions of hydrochloric acid or sodium hydroxide of various concentrations was measured in order to ascertain the influence of the pH on ζ. The results are shown in Fig. 1.

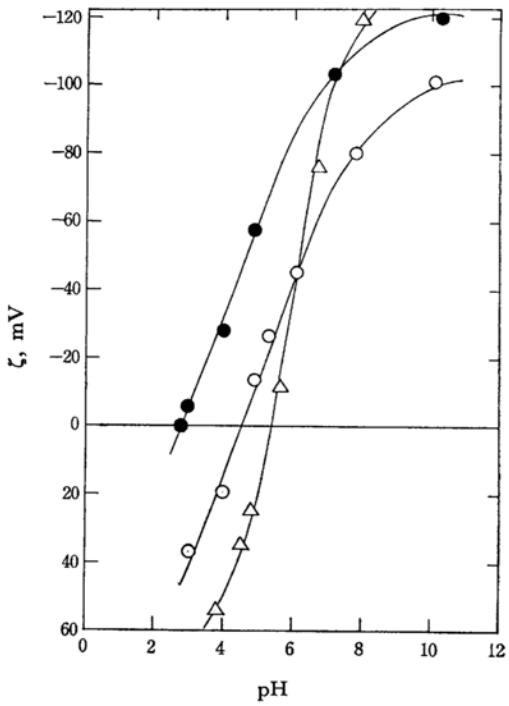


Fig. 1. Influence of pH on ζ-potential of heat-set nylon 6 fibers.
△: Untreated fiber
○: Wet-heat-treated fiber
●: Dry-heat-treated fiber

The ζ-potential of any fiber is positive in an acidic solution and negative in an alkaline one. From these results, it was found that the isoelectric points of the untreated, the wet-heat-treated, and the dry-heat-treated fiber are pH 5.4, pH 4.6, and pH 2.8 respectively. These differences in the isoelectric point among the fibers correspond to the differences in the end amino group and the end carboxylic group with the fibers, differences which are caused by the heat-treatment.

ζ-Potential with Dye Concentrations. The ζ-potential of the fiber *vs.* dye concentration curves

TABLE 2. END GROUPS, CRYSTALLINITY, BIREFRINGENCE AND INTRINSIC VISCOSITY OF THE NYLON 6 FIBERS USED

Fiber	End amino group (mol/g fiber) $\times 10^5$	End carboxylic group (mol/g fiber) $\times 10^5$	Crystallinity %	Birefringence $\times 10^3$	$[\eta]$
Untreated fiber	5.02	6.65	39.5	51.4	1.12
Wet-heat-treated fiber	4.28	7.92	42.5	53.2	1.10
Dry-heat-treated fiber	1.39	12.27	53.7	57.6	0.54

2) T. Suzawa, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **62**, 232 (1959); **63** 1069 (1960).

3) a) T. Suzawa, *ibid.*, **63**, 148 (1960); b) T. Suzawa, T. Saito and H. Shinohara, This Bulletin, **40**, 1596 (1967).

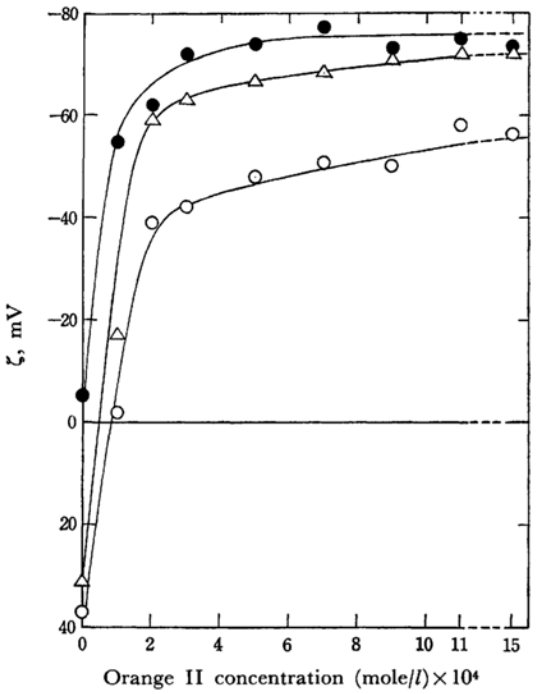


Fig. 2. ζ-Potential of the fibers with Orange II concentration.
△: Untreated fiber
○: Wet-heat-treated fiber
●: Dry-heat-treated fiber

are shown in Fig. 2. The ζ-potential was measured every hour on the hour; the values recorded in Fig. 2 are the equilibrium values, to which the potentials were approximated after four hours of immersion.

As the ζ *vs.* dye concentration curves in Fig. 2 show, the ζ-potentials of the untreated and the wet-heat-treated fiber are positive in a solution without dye, while the ζ-potential of the dry-heat-treated fiber is negative in the same solution. Such behavior may be expected from the dissociation of the NH_3^+ groups of the fiber in the former and that of the COO^- groups in the latter, because the pH of the solution used is smaller in the former, and larger in the latter, than the pH corresponding to the isoelectric point of the fiber.

Upon the addition of dye to this system, the ζ-potentials of the untreated and the wet-heat-treated fiber changed from positive to negative, while the ζ-potential of the dry-heat-treated fiber increased in its negative value. These facts may possibly be attributed to the formation of the electrostatic bond between the NH_3^+ of the fiber and the dye anion RSO_3^- in the former, and to the van der Waals' force between the fiber and the dye in the latter, because the pH of the dye solution used is smaller in the former, and larger in the latter, than the pH corresponding to the isoelectric point of the fiber. The ζ *vs.* dye concentration curves change rapidly in the range of concentrations smaller than 3×10^{-4} mol/*l*, and then the ζ-potentials (negative) approximate the saturated value.

Surface Dye Adsorption with Dye Concentration. The surface dye adsorptions increase with the dye concentration, as Fig. 3 shows.

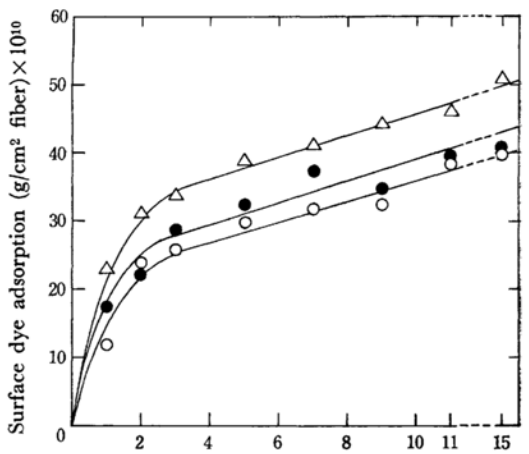


Fig. 3. Surface dye adsorption with Orange II concentration.
△: Untreated fiber
○: Wet-heat-treated fiber
●: Dry-heat-treated fiber

Throughout the range of dye concentrations, these values become smaller in the order of the untreated, the dry-heat-treated, and the wet-heat-treated fiber. This means that the surface of the untreated fiber, with a smaller crystallinity, a lower degree of orientation, and more end amino groups, adsorbs more dye than that of the dry-heat-treated fiber, with a larger crystallinity, a higher degree of orientation, and fewer end amino groups. Of course, this fact may also be related to the fact that the pH of the solution used is larger than the pH of the isoelectric point of the dry-heat-treated fiber.

In the case of the wet-heat-treatment, the intermolecular hydrogen bonds between the polymer-chain molecules of a fiber are broken by water molecules and the swollen, loosely-packed portions are formed in the amorphous region of the fiber.[1] The dyes adsorbed on these loosely-packed portions in the amorphous region cause the decrease in the dye concentration of the dye solution. This decrease in the dye concentration of the solution in the case of the wet-heat-treated fiber then gives rise to the decrease in the surface dye adsorption.

Therefore, it may be attributed to the adsorption of the dye to these loosely-packed portions in the amorphous region in the case of the wet-heat-treated fiber that the surface dye adsorption of the

wet-heat-treated fiber becomes smaller than that of the dry-heat-treated fiber, in spite of the smaller crystallinity and the lower degree of orientation of the former.

Total Dye Adsorption with Dye Concentration. The total dye adsorptions increase with the dye concentration, as Fig. 4 shows. Moreover, the plateau regions are attained at higher dye concentrations. The total dye adsorptions decrease in the order of the wet-heat-treated, the untreated, and the dry-heat-treated fiber. This means that the untreated fiber, with a smaller crystallinity, a lower degree of orientation, and more end amino groups, adsorbs more dye than does the dry-heat-treated fiber, with a larger crystallinity, a higher degree of orientation, and fewer end amino groups. Of course, this fact may also be related to the fact that the pH of the solution used is larger than the pH of the isoelectric point of the dry-heat-treated fiber. Moreover, the adsorption of the dye to the loosely-packed portions in the amorphous region of the wet-heat-treated fiber may be supposed to be the reason why the total dye adsorption of the wet-heat-treated fiber becomes larger than that of the untreated fiber, in spite of the larger crystallinity and the higher degree of orientation of the former.

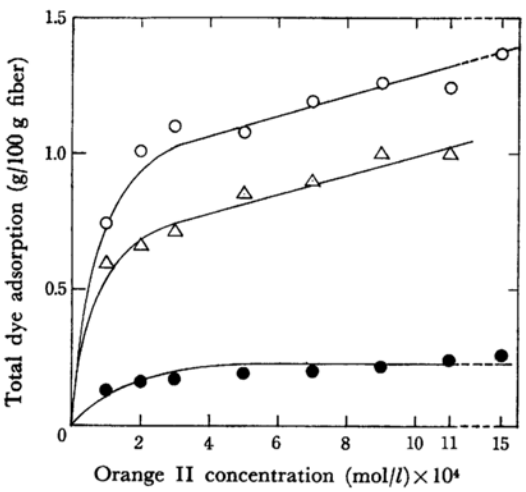


Fig. 4. Total dye adsorption with Orange II concentration.
△: Untreated fiber
○: Wet-heat-treated fiber
●: Dry-heat-treated fiber

Surface Area Covered by Adsorbed Dye Molecules on Fiber. The surface dye adsorption *vs.* the total dye adsorption curves were found to be linear, as Fig. 5 shows. These slopes are considered to be reciprocals of the surface area covered by adsorbed dye molecules on the fiber. These surface areas, as calculated from Fig. 5, are shown in Table 3.

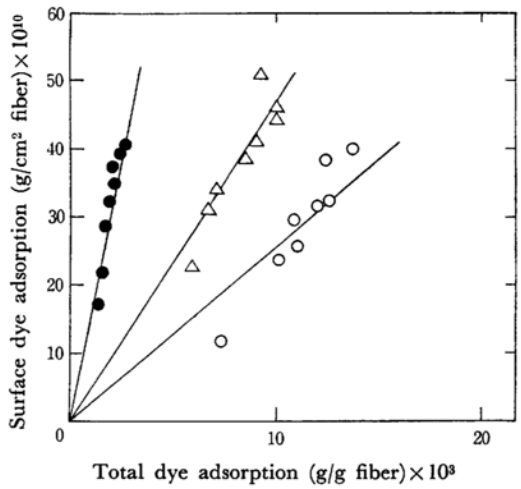


Fig. 5. Relation between surface dye adsorption and total dye adsorption.
△: Untreated fiber
○: Wet-heat-treated fiber
●: Dry-heat-treated fiber

TABLE 3. SURFACE AREA COVERED BY DYE MOLECULES ON FIBER

Fiber	Surface area (cm^2/g fiber)
Untreated fiber	1.8×10^6
Wet-heat-treated fiber	4.0×10^6
Dry-heat-treated fiber	0.6×10^6

The surface area of the wet-heat-treated fiber is twice of that of the untreated fiber, while that of the dry-heat-treated fiber is 1/3 that of the untreated fiber. The large surface area of the wet-heat-treated fiber is supposed to be caused by the loosely-packed portions in its amorphous region. Moreover, the small surface area of the dry-heat-treated fiber may possibly be attributed to its larger crystallinity and higher degree of orientation, and also to be related to the fact that the pH of the solution used is larger than the pH of its isoelectric point.

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