Effect of Nonionic Surfactant and Heat on Selected Properties of Nylon 6,6

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Synopsis

Heat treatment of nylon 6,6 in the temperature range of 100–175°C in the presence and absence of a nonionic surfactant (Triton X-100) had little effect on the physical properties of the nylon, although the density of the nylon increased with increasing heat treatment temperature. The moisture regain value for the treated nylons did not change substantially, whereas the overall wettability of the heat-treated nylon in the presence of nonionic surfactant showed a marked improvement. Both heat treatment of the nylon alone or in the presence of surfactant had a substantial effect on the uptake of three 1,4-substituted anthraquinone dyes on the nylon and on the resultant color of the dyed nylon.

INTRODUCTION

In a recent study,[1] the effect of heat and surfactants plus heat on the dyeing and physical properties of selected fabrics including nylon-6,6 was determined. At the heating temperature selected (150°C), heat alone had little effect on the physical properties of the nylon compared to untreated fabric. Surfactant treatments plus heat (150°C) caused the nylon to shrink somewhat more and improved the wicking and moisture absorbency and dyeing properties of the nylon compared to nylon that had been heat treated in the absence of surfactants. Anionic and nonionic surfactant-treated nylons dyed to lighter shades with the acid dyes used, whereas cationic surfactant-treated nylon dyes deeper with these same acid dyes. Residual surfactant present on the nylon was thought to be responsible for the observed variation in depth of dyeing and color of the nylon.

The effect of heat treatment alone on the dyeing and physical properties of nylon 6,6 in the temperature range 100–200°C has been studied previously.[2–4] The tensile properties of nylon 6,6 were found to be only slightly affected, and the x-ray properties of the nylon were essentially unchanged[3,4] on heating in the range 100–175°C. However, the relative rate of dyeing and relative dyeability of nylon 6,6 decreased as the heat setting temperature was increased[2,4] with the effect being observed for disperse, acid, and premetallized acid dyes.

In this study, we have examined the effect of application of a common nonionic surfactant Triton X-100 followed by heat treatment at 100–175°C on the dyeing and selected physical properties of nylon 6,6. We have compared the properties of these surfactant heat-treated nylons with the corresponding nylons subjected

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to heat treatment only in order to establish the effect of surfactant on selected properties of nylon 6,6.

EXPERIMENTAL

Fabric Treatment

Nylon 6,6 woven fabric, style 361 (0.1315 kg/m^2), made from du Pont type 200 nylon was obtained from Test Fabrics, Inc. Fabric samples (15 × 15 cm) were washed in 60°C water, distilled water, and dried at 100°C prior to treatment. The fabric samples subjected to heat treatment only were heated at 100 ± 5, 125 ± 5, 150 ± 5, and 175 ± 5°C for 5 min in a flatbed press (U.S. Testing, model 6584) and then thoroughly washed in 60°C water, followed by distilled water, and dried at 100°C. Surfactant-treated fabrics were immersed for 5 min in neat nonionic surfactant (Triton X-100) and passed through a pad (280 kPa) to remove excess surfactant. Then the treated fabrics were heated, rinsed, and dried as described above.

Dyeing and Color Measurement Procedure

Fabric samples were dyed for 1 hr at 100°C using 2% on weight of fabric (owf) anthraquinone disperse dye (Eastman reagent grade) at a liquor ratio of 115:1. After dyeing, the fabric samples were thoroughly rinsed in 60°C water and dried at 100°C. The uptake of dye on the fabrics (mg dye/g fabric) was determined by the technique of Weigmann et al.[5] The color of the undyed and dyed fabrics was measured on a MacBeth MS-2000 color spectrophotometer and expressed as x, y, and Y color coordinates (Tables III and IV). The color differences (ΔE) were measured in CIELAB units.

Test Procedures

The test procedures used were described in our earlier article[1] and they were based on standard AATCC and ASTM test methods (Tables I and II). Density measurements were conducted using a Techne TC-1 density gradient column using xylene and carbon tetrachloride at 21°C. Scanning electron micrographs were taken on a Cambridge Stereoscan II instrument operating in the secondary mode at 5 kV on small samples cut from the center of fabrics and coated with silver. Differential scanning calorimetry was performed on 4-mg samples using a Mettler TA 2000 analyzer at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The effect of heat in the presence and absence of the nonionic surfactant Triton X-100 on nylon 6,6 in the temperature range 100–175°C was determined through examination on various physical and chemical properties, as well as the dyeing properties of the nylon (Tables I–III). Heat alone and heat in the presence of surfactant were found to slightly affect selected physical properties (Table I), moisture-related properties (Table II), the color (Table III), and the disperse dyeing characteristics of the nylon (Table IV). These findings are outlined below.

The overall physical properties of the nylon 6,6 fabric changed only slightly on heating at various temperatures within the 100–175°C temperature range both in the presence and absence of nonionic surfactant (Table I). Under the semirestrained heating condition used, little shrinkage in the overall fabric dimensions was found, although surfactant-treated fabric tended to shrink more than untreated nylon at most temperatures. The stiffness of the fabric increased slightly on heat treatment both in the presence and absence of surfactant with surfactant/heat treatment causing greater increases. Recovery of the heat-treated fabrics from dry bending deformation as evidenced by Monsanto wrinkle recovery values showed that heat treatment alone at 125°C or above gave increased wrinkle recovery, whereas the presence of surfactant tended to cause decreased wrinkle recovery except at 175°C. The tensile properties of the nylon were not significantly affected by heat treatment even when surfactant was present. Small changes in tenacity and elongation at break owing to heat treatment in the 100–175°C range have been observed previously.[3,4]

Heat treatment in the presence and absence of surfactant caused a small but detectable increase in the density of the nylon, with the density increasing with increasing treatment temperature. The presence of surfactant appeared to have little effect on this increase in density. The progressive increase in density of the nylon suggests that heat-induced crystallization of the nylon has occurred which has resulted in a slight increase in the order within the fiber. Small steady increases in density and increases in the degree of crystallinity with rising heating temperature have been observed previously for nylon 6,6 (refs. 3 and 4) in the 100–175°C temperature range. In summary, heat treatment of the nylon 6,6 both in the presence and absence of nonionic surfactant has only a limited effect on the overall physical properties of the nylon.

The effect of heat treatment in the presence or absence of surfactant is more evident in the moisture-related properties of the nylon (Table II). Although the apparent moisture regains for the treated nylons do not change much because of heat treatment, the regain values tended to decrease as the heat treatment temperature increased with surfactant having no effect on the regain of samples. Two parameters relating to the wettability of the fiber surfaces, drop absorbency time and wicking height, show the overall effect of surfactant combined with heat treatment on the nylon. Whereas nylon samples heated in the 100–175°C range show an increase in time necessary for water to wet the surface and a lower rate of wicking, surfactant and heat-treated nylon samples show sharply decreased drop absorbency times and greatly improved rates of wicking. These observations suggest that the effect of heat alone, as well as surfactant plus heat treatment, is confined to the surface of the nylon. Whereas heat treatment alone decreases the wetting of the nylon fabric surfaces, surfactant plus heat increases the overall wetting of the nylon presumably because of residual surfactant permanently fixed to the nylon. These findings are consistent with our earlier study[1] on the effect of surfactants and heat treatment at 150°C on the moisture-related properties of nylon.

It became evident that as the heating temperature increased, the color of the heat-treated samples changed significantly both in the presence and absence of surfactant. The color differences (ΔE) between untreated and treated nylons and between heat-treated samples in the presence and absence of surfactant were determined (Table III). As the heat treatment temperature was increased, the

TABLE I
Effect of Surfactant and Heat on the Physical Properties of Nylon

Treatment		Area shrinkage, %	Stiffness cantilever, nM m	Wrinkle recovery Monsanto Warp (deg)	Tensile properties			
Temperature, °C	Surfactant				Breaking strength, N	Elongation at break, %	Energy to break, mN m	Density, kg/m^3
—	—	—	7.1	132	9.54 ± 1.26	43 ± 4	168.2 ± 31.6	1148
100	No	0.4	8.1	126	8.44 ± 1.18	47 ± 6	144.7 ± 37.1	1152
100	Yes	1.3	14.2	123	9.18 ± 1.78	42 ± 5	184.8 ± 68.7	1152
125	No	0.5	8.6	140	9.19 ± 1.22	43 ± 5	166.6 ± 36.4	1153
125	Yes	1.4	10.1	124	9.42 ± 1.43	44 ± 6	173.8 ± 54.3	1153
150	No	0.5	9.4	138	9.09 ± 1.21	42 ± 5	160.9 ± 34.9	1154
150	Yes	1.4	8.1	121	9.45 ± 1.39	40 ± 6	156.8 ± 53.0	1154
175	No	1.4	8.2	138	9.30 ± 1.32	44 ± 9	165.7 ± 48.8	1157
175	Yes	1.4	16.5	135	9.42 ± 1.23	46 ± 11	182.4 ± 67.9	1156

TABLE II
Effects of Surfactant and Heat on the Moisture-Related Properties of Nylon

Treatment		Regain, moisture,	Drop absorbency	Wicking height,		
Temperature, °C	Surfactant	%	time, min	1 min	5 min	10 min
—	—	3.3	20.5	0.0	0.9	2.0
100	No	3.2	>30	0.0	0.1	0.3
100	Yes	3.2	0.8	3.3	5.9	8.7
125	No	3.2	>30	0.0	0.3	0.6
125	Yes	2.9	0.6	3.3	9.3	9.3
150	No	2.9	20.3	0.0	0.8	1.1
150	Yes	3.0	0.6	3.2	6.4	8.3
175	No	2.9	>30	0.0	0.3	1.0
175	Yes	2.9	0.5	3.3	6.5	8.6

samples became progressively more yellow in character and less reflective, and the values of color differences between control and treated samples became progressively larger. Color differences (ΔE) between samples heated at the same temperature in the presence and absence of surfactant were very small, and surfactant seemed to have little effect on color change. Overall, the color changes observed were small and would not be expected to interfere with or significantly alter the color of dyed samples.

In order to determine the effect of heat treatment alone and in the presence of nonionic surfactant on the dyeing and resultant color properties of the nylon, the due uptake of three 1,4-disubstituted anthraquinone disperse dyes on the nylons, as well as the resultant color and color differences ΔE, were measured (Table IV). Previous studies have shown that heat treatment of nylon 6,6 in the 100–175°C temperature range leads to decreased dyeability and dye uptake with selected acid and disperse dyes.[2,4] The 1,4-disubstituted anthraquinone disperse dyes selected (1,4-diamino, 1-amino-4-hydroxy-, and 1,4-dihydroxy anthraquinone) exhibit differing acidities and have been used previously in

TABLE III
Effect of Surfactant and Heat on the Color of Nylon

Treatment		Color			Color difference (ΔE)	
Temperature, °C	Surfactant	x	y	Y	Compared to untreated control	Compared to sample at same temperature
—	—	0.311	0.319	68.9	—	—
100	No	0.311	0.320	67.8	0.5	0.2
100	Yes	0.311	0.320	68.4	0.2	
125	No	0.311	0.320	67.4	0.7	0.3
125	Yes	0.311	0.320	68.7	0.2	
150	No	0.312	0.321	68.0	1.0	0.5
150	Yes	0.313	0.322	67.7	1.5	
175	No	0.314	0.324	67.7	2.1	0.5
175	Yes	0.314	0.323	68.2	1.8	

TABLE IV
Effect of Surfactant and Heat on the Dyeing and Color Properties of Nylon with Substituted Anthraquinone Dyes

Treatment		Dye uptake,	Color			Color difference (ΔE)	
Temperature, °C	Surfactant	mg/g	x	x	Y	Compared to untreated control	Compared to sample at same temperature
			1,4-diaminoanthraquinone				
—	—	4.8	0.256	0.146	5.0	—	—
100	No	6.6	0.255	0.141	4.0	3.4	2.7
100	Yes	6.3	0.255	0.138	3.2	2.4	
125	No	7.5	0.256	0.139	3.8	3.9	3.2
125	Yes	5.5	0.255	0.141	4.6	1.9	
150	No	6.3	0.255	0.143	4.2	2.9	1.6
150	Yes	7.2	0.256	0.142	3.8	4.3	
175	No	5.8	0.256	0.142	4.3	2.4	2.2
175	Yes	6.4	0.254	0.143	4.1	3.7	
			1-amino-4-hydroxyanthraquinone				
—	—	11.7	0.388	0.223	4.2	—	—
100	No	11.2	0.392	0.221	4.2	1.3	4.3
100	Yes	8.8	0.392	0.215	4.6	5.2	

125	No	11.3	0.393	0.220	4.3	2.5	1.1
125	Yes	10.2	0.394	0.218	4.1	2.6	
150	No	10.5	0.389	0.220	4.4	1.2	1.2
150	Yes	9.1	0.390	0.217	4.4	3.3	
175	No	8.6	0.387	0.218	4.8	4.2	11.5
175	Yes	4.7	0.329	0.190	5.8	14.2	
			1,4-dihydroxyanthraquinone				
—	—	4.8	0.474	0.397	29.8	—	—
100	No	3.8	0.470	0.391	27.0	4.9	1.3
100	Yes	3.1	0.470	0.389	26.5	5.7	
125	No	3.8	0.470	0.390	26.9	5.0	0.2
125	Yes	2.6	0.470	0.391	27.0	4.8	
150	No	3.7	0.468	0.395	28.8	2.9	4.9
150	Yes	3.0	0.464	0.385	26.5	7.7	
175	No	2.3	0.465	0.392	29.5	3.7	4.3
175	Yes	2.6	0.464	0.384	26.7	7.8	

studies relating the effect of substrates, including nylon, on the ultraviolet spectra of these dyes.[6] In our study, the substitution on the anthraquinone had a marked effect on the dyeability of the treated and untreated nylons and in some cases on the color of the resultant dyed fabrics. The specific findings are outlined below.

With 1,4-diaminoanthraquinone, heat treatment alone caused a greater dye uptake than untreated nylon, with the increased uptake being greatest at a heat treatment temperature of 125°C. Heat treatment in the presence of surfactant showed a similar effect with the greatest increase being observed at 150°C. This finding is contrary to a previous study using other disperse dyes[2] in which the disperse dye decreased the dye uptake with increasing temperature of heat treatment. The difference in dye uptake may be explained by the difference in the structure and basicity of this dye compared to the dyes used in the previous study. Color measurements confirm that the treated nylons dyed to deeper shades and were somewhat more purple in character than untreated nylon. Significant color differences (ΔE) of similar magnitudes were found when comparing treated versus untreated nylon and heat-treated nylons in the presence versus the absence of surfactant.

Dyeing of treated and untreated nylons with 1-amino-4-hydroxyanthraquinone showed that heat treatment alone caused a decrease in the dye uptake with increasing treatment temperature. Nylons heat treated in the presence of surfactant exhibited a lower dye uptake than nylon heat treated alone, with the largest difference occurring at 175°C. The treated nylons tended to dye more red in character than untreated nylon. The color difference was most pronounced for surfactant heat-treated nylon at 175°C, which was much more blue in character compared to untreated nylon or nylon heat treated in the absence of surfactant at 175°C. Heat alone as well as surfactant in the presence of heat decreased the uptake of this dye on the nylon, and the effects of surfactant and heat in decreasing the dye uptake were additive. The dye 1-amino-4-hydroxyanthraquinone showed greater affinity for the nylon than 1,4-diamino- or 1,4-dihydroxyanthraquinone.

Heat treatment alone caused a decrease in the uptake of 1,4-dihydroxyanthraquinone on the nylon, and the presence of surfactant tended to depress the dye uptake further. With increasing heat treatment, the nylons dyed more blue in character and were less reflective, although less dye was present on the fiber. Color differences between samples heat treated at the same temperature in the presence and absence of surfactant were larger at higher treatment temperatures (150 and 175°C).

Whereas uptake of 1,4-diaminoanthraquinone on the nylon increased with heat treatment alone, uptake of 1-amino-4-hydroxyanthraquinone and 1,4-dihydroxyanthraquinone decreased on heat treatment of the nylon. The presence of surfactant depressed the dye uptake further in most cases. The above findings suggest that heat treatment alone permits greater access to carboxyl groups within the fiber permitting greater uptake of the basic 1,4-diaminoanthraquinone on the fabric. The nonionic surfactant Triton X-100 reduced dye uptake at most heat-treatment temperatures except for 1,4-diaminoanthraquinone at 150 and 175°C where it slightly increases dye uptake.

Scanning electron microscopy and differential scanning calorimetry were used as methods to detect changes in nylon caused by heat treatment in the presence and absence of nonionic surfactant. Scanning electron microscopy showed little change in the surface of any of the treated samples, and differential scanning calorimetry showed little change between treated and untreated nylons. These findings suggest that heat treatment in the 100–175°C range in the presence and absence of surfactant have little effect on the morphology of the fibers.

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