Effect of Nonionic Surfactant and Heat on Selected Properties of Polyester

HOWARD L. NEEDLES, ROY S. BERNS, WEN-CHU LU, and KENNETH ALGER, *Division of Textiles and Clothing, University of California, Davis, California 95616* and D. S. VARMA,* *Textile Technology Department, Indian Institute of Technology, Delhi, India*

Synopsis

The effect of heat treatment in the presence and absence of a nonionic surfactant (Triton X-100) on selected properties of polyester fabric was studied over the temperature range 180–220°C. Although significant heat-induced area shrinkage was evident (4.9–9.5%) in the treated polyester fabrics, stiffness, wrinkle recovery, tensile properties, moisture regain, and density of the fabrics showed only slight changes. The moisture-related properties of surfactant/heat-treated polyester were greatly improved compared to untreated control polyester or polyester subjected to heat treatment alone. Oligomer formation on the surface of surfactant-treated polyester was altered as a result of the presence of surfactant on heating compared to polyester heated alone at 180–220°C. Polyester heat treated in the presence and absence of surfactant showed increased dye uptake and more depth of color with 1,4-substituted anthraquinone dyes than untreated polyester, and these effects increased with increasing treatment temperature.

INTRODUCTION

In a recent study,[1] we examined the effect of surfactants and heat (150°C) on selected dyeing and physical properties of cotton, nylon, and polyester. It was apparent from this study that the surfactant treatment of polyester followed by heating at 150°C was not sufficient to cause major changes in the properties of polyester, because the treatment was well below the softening temperature of polyester. It is known that surfactants in aqueous solutions are adsorbed by the polyester fiber, but that such adsorption is reversible and the surfactant is desorbed when the surfactant solution is replaced by water.[2–6] Kissa and Dettre[6] have shown that heating of thermoplastic fibers such as polyester containing surfactant on the fiber surface to near the softening point of the fiber (220°C) causes the surfactant to become permanently adsorbed on and attached to the fiber. Also, Derminot, Hagege, and Jacquemart[7] have demonstrated that at temperatures of 150–230°C oligomeric materials in the polyester migrate to the fiber surface and crystallize with maximum oligomer migration occurring at 170–190°C. Therefore, heating of surfactant-treated polyester at temperatures approaching 200°C might be expected to cause both simultaneous fixation of surfactant and migration of oligomers to the fiber surface. In order to gain a better understanding of these coexisting processes and their mutual effect on the dyeing and physical properties of polyester, we have heat treated polyester at 180, 200, and 220°C for 5 min in the presence and absence of a nonionic surfactant (Triton X-100). The effect of heat alone and heat plus surfactant on the properties of the polyester are considered in depth.

* Visiting professor, University of California, Davis, 1979–1980.

Journal of Applied Polymer Science, Vol. 25, 1737–1744 (1980)

0021-8995/80/0025-1737$01.00

EXPERIMENTAL

Fabric Treatment

The spun polyester (Dacron 54W) fabric [Style 760 (0.123 kg/m^2)] was obtained from Test Fabrics, Inc. Untreated control fabric samples were washed in hot (60°C) water and distilled water and then dried at 100°C. Untreated control fabrics were used and tested without further treatment, whereas heated control fabrics were heated at 180 ± 5 °C, 200 ± 5°C, or 220 ± 5°C in a flatbed press (U.S. Testing, model 6584) for 5.0 min, followed by washing in hot water (60°C) and distilled water and drying at 100°C. Surfactant/heat-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. The treated fabric was then heated at 180, 200, or 220°C for 5 min and rinsed and dried as described above.

Dyeing and Color Measurement Procedures

Fabric samples were dyed for 1 hr at 100°C using 2% on weight of fabric (owf) anthraquinone disperse dyes (Eastman reagent grade) at a liquor ratio of 115:1. After dyeing, the fabrics were thoroughly rinsed in hot water (60°C) 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.[8] The color of the dyed fabrics is expressed in x, y, and Y color coordinates and was determined using a Gardner Color Difference Meter, model XLDGM.

Test Procedures

The test procedures used are listed in our earlier paper[1] and are based on standard AATCC and ASTM test methods. Density measurements were conducted employing a Techne TC-1 density gradient column using a xylene–carbon tetrachloride mixture. Scanning electron microscopy (SEM) was performed on small samples cut from the center of fabrics and coated with silver. A Cambridge Stereoscan Mark II instrument operating in the secondary mode at 5 kV was employed. Differential scanning colorimetry (DSC) was performed on a Mettler model TA 2000 under nitrogen at a scan speed of 10°C/min.

RESULTS AND DISCUSSION

The effect of heat (180, 200, and 220°C) on polyester in the presence and absence of a nonionic surfactant (Triton X-100) was studied with particular reference to oligomer formation. The effects of heating alone and surfactant plus heating on selected physical properties (Tables I and II) and on the dyeing and color properties (Table III) of the polyester were considered. Scanning electron microscopy was used to examine the effect of heat versus heat plus surfactant on oligomer formation and migration (Fig. 1).

The effect of heat treatment at various temperatures (180, 200, and 220°C) in the presence and absence of nonionic surfactant Triton X-100 had only a limited effect on selected physical properties of the polyester fabric including shrinkage, stiffness, wrinkle recovery, and tensile properties (Table I). The area shrinkage of the polyester increased with increasing treatment temperature, and

TABLE I
Effect of Surfactant and Heating on the Physical Properties of Polyester

Treatment		Area shrinkage,	Stiffness, cantilever,	Wrinkle recovery,	Tensile Properties			
Temperature, °C	Surfactant	%	nN m	Monsanto Warp (deg)	Breaking strength, N	Elong. at break, %	Energy to break, mN m	Density kg/m³
—	—	—	7.7	143	8.12 ± 0.88	30 ± 2	90.4 ± 13.9	1382
180	No	4.9	9.8	146	9.06 ± 0.88	30 ± 2	105.3 ± 16.4	1392
180	Yes	6.2	5.6	145	8.70 ± 0.95	32 ± 3	106.5 ± 19.2	1396
200	No	6.7	12.5	146	9.16 ± 0.55	31 ± 2	109.5 ± 12.2	1401
200	Yes	6.9	7.9	145	8.46 ± 1.23	29 ± 2	95.7 ± 20.7	1403
220	No	9.5	13.1	145	8.28 ± 0.75	30 ± 3	96.9 ± 15.7	1410
220	Yes	9.0	10.5	141	8.88 ± 0.77	31 ± 2	104.3 ± 15.6	1412

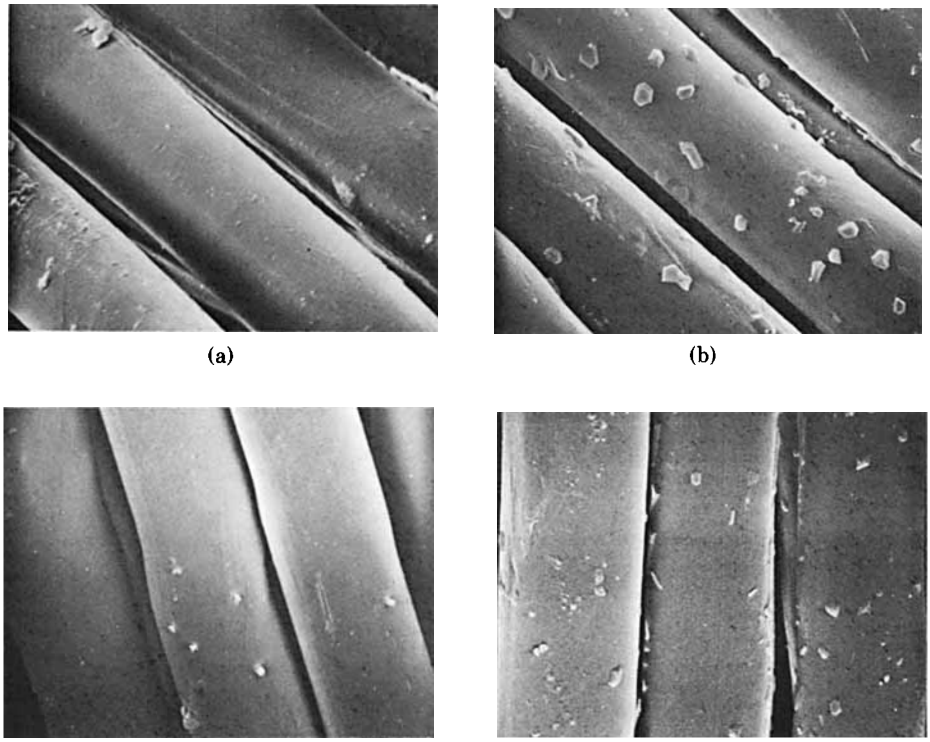
TABLE II
Effect of Surfactant and Heat on the Moisture-Related Properties of Polyester

Treatment		Regain,	Drop			
Temperature, °C	Surfactant	Moisture, %	absorbency time, min	Wicking height, cm 1 min	5 min	10 min
—	—	0.42	>30	1.3	3.4	4.0
180	No	0.47	>30	1.2	2.9	3.6
180	Yes	0.55	2.8	3.4	3.8	7.9
200	No	0.53	>30	1.2	2.8	3.4
200	Yes	0.56	0.0	3.6	6.8	8.5
220	No	0.50	>30	1.6	3.0	3.7
220	Yes	0.53	0.0	3.5	6.4	8.0

the surfactant had little effect on the overall degree of heat-induced shrinkage. The polyester fabric became somewhat stiffer as the temperature of heat treatment was increased, whereas surfactant treatment tended to moderate the degree of increased stiffness observed. Dry wrinkle recovery values or tensile properties for the polyester were essentially unaffected either by heat alone or by surfactant and heat treatment, although the treated samples appeared somewhat stronger and had higher energies to break than untreated control fabric. The density of the treated polyesters increased progressively with increasing heat-treatment

TABLE III
Effect of Temperature and Surfactant on the Dyeing and Color Properties of Polyester with Substituted Dyes

Treatment		Dye uptake,	Color		
Temperature, °C	Surfactant	mg/g	x	y	Y
		1,4-diaminoanthraquinone			
—	—	1.5	0.282	0.208	33.5
180	No	2.0	0.278	0.200	35.4
180	Yes	2.9	0.276	0.184	28.7
200	No	2.5	0.278	0.192	32.1
200	Yes	3.3	0.272	0.171	24.4
220	No	5.0	0.276	0.167	21.4
220	Yes	7.2	0.265	0.159	13.0
		1-amino-4-hydroxyanthraquinone			
—	—	10.8	0.453	0.230	5.9
180	No	8.3	0.450	0.235	7.7
180	Yes	12.5	0.470	0.235	5.5
200	No	10.8	0.466	0.235	6.2
200	Yes	13.3	0.472	0.236	6.7
220	No	15.6	0.478	0.241	4.9
220	Yes	17.1	0.470	0.241	4.5
		1,4-dihydroxyanthraquinone			
—	—	5.9	0.490	0.418	39.5
180	No	—	—	—	—
180	Yes	6.7	0.499	0.424	39.9
200	No	7.5	0.503	0.425	39.4
200	Yes	8.3	0.517	0.420	35.5
220	No	7.8	0.517	0.421	35.4
220	Yes	8.8	0.514	0.421	36.9



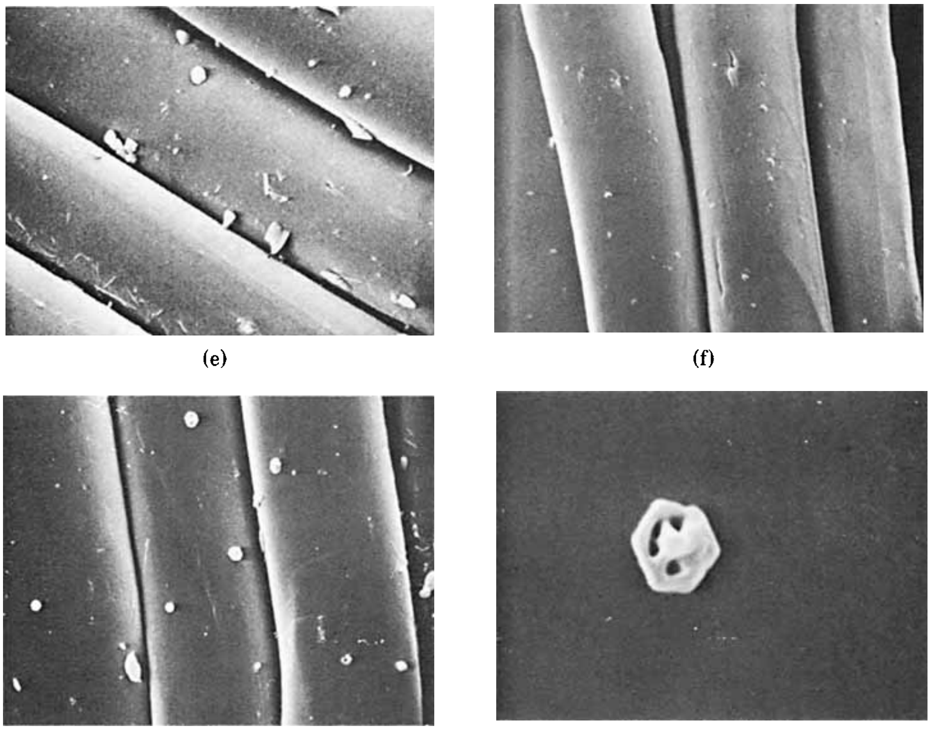
(a) (b)

(c) (d)

Fig. 1. Scanning electron micrographs of polyesters treated by heating (180–220°C) in the presence and absence of surfactant (Triton X-100). (a) Untreated polyester (2100×). (b) Polyester heated at 180°C for 5 min (2000×). (c) Polyester treated with surfactant and heated at 180°C (2000×). (d) Polyester heated at 200°C (2100×). (e) Polyester treated with surfactant and heated at 200°C (2050×). (f) Polyester heated at 220°C (2050×). (g) Polyester treated with surfactant and heated at 220°C (2100×). (h) Same as (g) (10,500×).

temperature. Surfactant/heat-treated polyester had somewhat higher densities than the corresponding samples that had been heat treated in the absence of surfactant. The small changes in these physical properties over the temperature range studied and in the presence and absence of surfactant can be attributed to low level heat-induced shrinkage within the constrained polyester fabrics under restraint within the press.

The moisture regains, drop absorbencies, and wicking action of the treated and control fabrics were measured in order to establish the effect of heat alone and surfactant plus heat on the moisture related properties of polyester (Table II). The moisture regain values for the heat-treated polyester are essentially the same as for untreated polyester, whereas the surfactant/heat-treated samples exhibited a dramatic improvement in drop absorbency and wicking behavior. Heat treatment alone slightly increased the moisture regain of the polyester compared to the untreated control, although the heat-induced increase in density would be expected to decrease the moisture regain. Migration of oligomer to the fiber surface would be expected to increase regain without decreasing fiber density. All surfactant/heat-treated fabrics wet out immediately and wicked water over two times more effectively than samples that have been heated in the



(e) (f)

(g) (h)

Fig. 1. (*Continued from previous page.*)

absence of surfactant. These data suggest that heat alone had little effect on these moisture-related properties, whereas residual surfactant fixed on the polyester greatly improved surface wetting and wicking of the polyester. Since the moisture regains are only slightly affected by surfactant/heat-treatment, the internal structure of the polyester is apparently essentially unchanged by the treatment, whereas the polyester surface is much more hydrophilic in character. Differential thermal analysis showed no changes in the polyester as a result of surfactant and/or heat-treatment. The above findings are consistent with the observations of Kissa and Dettre,[6] who observed that nonionic surfactants were irreversibly absorbed only on the surface of polyester if the polyester was heated above 180°C. The net effect observed was attributed to migration of the hydrophobic tail of the surfactant onto the surface of the heated polyester. On cooling, the hydrophobic tail of the surfactant was "locked" into the polyester and the hydrophilic head of the surfactant resided on the surface, providing easy surface wetting and limited swelling.

Scanning electron micrographs (SEMs) of the heated samples in the presence and absence of surfactant (Fig. 1) showed the effect of temperature and the presence of surfactant on the polyester surface. Untreated polyester [Fig. 1(a)] had small amounts of residual materials on the fiber surface although the fabric was prewashed prior to examination. These residual materials may be spin finishes that were not completely removed by the washing procedure. Polyester heated at 180°C [Fig. 1(b)] showed the presence of hexagonal crystals of oligomeric materials on the fiber surface. Such products have been observed previously,[7,9] and the maximum formation of such oligomers on polyester surfaces were observed in the 170–190°C range.[7] Heating of the fiber at higher temperatures (200 and 220°C) [Figs. 1(d) and 1(f)] led to progressively less oligomer present on the polyester surface with heating at 220°C, resulting in essentially no deposition of oligomer although deformation of the polyester owing to the high heating temperature can be seen. It is presumed that the reduced oligomer deposition at higher temperatures is due to diffusion and vaporization of oligomer from the polyester to the surroundings.

When the polyester was pretreated with nonionic surfactant and heated at 180°C [Fig. 1(c)], very little oligomer was found on the fiber surface. Surfactant-treated polyester heated at 200°C [Fig. 1(e)] showed more extensive oligomer formation, but the oligomer deposited in irregular shapes with only limited hexagonal crystal formation. Surfactant-treated polyester heated at 220°C had about the same level of oligomer formation as observed at 200°C, but the oligomer formed more regular hexagonal crystal structures [Fig. 1(g)], although the crystals are not completely formed. An incompletely formed hexagonal structure in higher magnification is seen in Figure 1(h). These data suggest that the nonionic surfactant on the surface of the polyester either retarded migration of oligomer to the surface of the polyester or interfered with hexagonal crystal formation of oligomer on the fiber surface. It is also possible that nonionic surfactant aided in removal of oligomer from the fiber surface during the washing step following heating, but this seems unlikely because of the temperature dependence of the amount of residue oligomer formed and the variation in crystal structure with heating temperature.

The dyeing properties of untreated and treated polyesters were studied using three related 1,4-substituted anthraquinone dyes, 1,4-diaminoanthraquinone (CI Disperse Violet 1), 1-amino-4-hydroxy-anthraquinone (CI Disperse Red 15), and 1,4-hydroxyanthraquinone (quinizarin) (Table III).

In general, the heat-treated and surfactant/heat-treated polyesters dyed to deeper shades than the untreated polyester. The polyesters generally had a greater affinity for 1-amino-4-hydroxyanthraquinone than for 1,4-dihydroxyanthraquinone, which in turn had a greater affinity for polyester than 1,4-diaminoanthraquinone under the dyeing conditions used. The total uptake of dye in the polyester increased progressively as the polyester annealing temperature increased. Surfactant/heat-treated polyester showed a similar increase in dye uptake as the annealing temperature was increased and had an overall higher uptake of the dyes than polyesters that were annealed in the absence of surfactant.

Although 1,4-diaminoanthraquinone had the lowest dye uptake on the treated and untreated polyesters, heat alone or heat and surfactant greatly and progressively increased the uptake of this dye on the polyester. The progressive increases in dye uptake with annealing temperature were much smaller for 1-amino-4-hydroxyanthraquinone than for 1,4-diaminoanthraquinone, and for 1,4-dihydroxyanthraquinone the dye uptakes were smallest. Although these dyes all show some degree of intramolecular hydrogen bonding,[10] the relative acidities and basicities of these dyes would still be expected to influence dye diffusion and overall dye uptake. These data suggest that heat alone and surfactant plus heat increase the accessibility of the polyester to these dyes, and that the acid dye sites within the polyester greatly influence the increased uptake of the dyes containing basic amino groups. Dumbleton, Bell, and Murayama[11] have carried out an extensive study of the effect of heat and drawing of the dyeing characteristics of polyester using 1-amino-4-anthraquinone. They found that the rate of dye uptake as well as the saturation value for dye uptake increased with increasing temperature for drawn fibers. This is consistent with our findings.

The color of the dyed, treated, and untreated polyesters was measured and expressed as x, y, and Y color coordinates (Table II). The progressive shifts in the color coordinates x, y as the polyesters dyed more deeply reflect progressive deepening of the shades as the dye uptake increased. The fabrics became darker as the dye uptakes increased, as reflected in progressively lower Y values, although the change in Y values did not correlate directly with increased dye uptake in all cases. Such effects could be due to differences in the location and degree of aggregation of the dyes within the polyester.[12]

CONCLUSION

Heating of polyester fabric in the presence and absence of the nonionic surfactant (Triton X-100) at 180, 200, and 220°C for 5 min caused limited fabric shrinkage and had only small effects on the stiffness, wrinkle recovery, tensile properties, and density of the fibers in the fabric. The moisture regain of the polyester was unaffected by heat alone in the absence of surfactant, whereas surfactant/heat treatment improved the wettability and wicking properties of the polyester. Scanning electron microscopy showed that oligomer present on the fiber surface decreased as the heat treatment temperature was increased, and surfactant on the fiber either retarded oligomer migration or interfered with oligomer crystal formation on the fiber to the fiber surface. Heat treatment alone or in the presence of surfactant increased the overall dye uptake and depth of dyeing of the polyester using 1,4-diamino-, or 1-amino-4-hydroxy-, and 1,4-dihydroxyanthraquinone disperse dyes, with the increases being greatest at 220°C and in the presence of surfactant and improved dye uptake being greatest for the more basic amino-substituted anthraquinones.

References

1. H. L. Needles et al., *Text. Chem. Color.*, **11**, 35 (1979).
2. C. F. Jelinek and R. L. Mayhew, *Text. Res. J.*, **24**, 765 (1954).
3. W. M. Linfield, J. C. Sherrill, G. A. Davis, and R. M. Rasche, *J. Am. Oil Chem. Soc.*, **35**, 590 (1958).
4. H. Kolbel and K. Horig, *Angew. Chem.*, **171**, 691 (1959).
5. B. E. Gardon and W. T. Shebs, *Proceedings of the International Congress on Surface Active Agents*, Vol. III, Barcelona, Supp. 1968, p. 155.
6. E. Kissa and R. H. Dettre, *Text. Res. J.*, **45**, 773 (1975).
7. J. Derminot, R. Hagege, and J. Jacquemart, *Bull. Sci. ITF*, **5**, 355 (1976).
8. H.-D. Weigmann, M. G. Scott, A. S. Ribnick, and L. Rebenfeld, *Text. Res. J.*, **46**, 574 (1976).
9. R. D. Van Veld, G. Morris, and H. R. Billica, *J. Appl. Polym. Sci.*, **12**, 2709 (1968).
10. R. S. Sinclair and E. McAlpine, *J. Soc. Dyers, Colour.*, **91**, 399 (1975).
11. J. H. Dumbleton, J. P. Bell, and T. Murayama, *J. Appl. Polym. Sci.*, **12**, 2491 (1968).
12. R. Kuehni, *Text. Chem. Color.*, **7**, 112 (1975).

Received October 29, 1979
Revised December 14, 1979