Disperse dyes as structure probes for a modified polyester film

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(Received 15 September 1988; revised 22 June 1989; accepted 27 June 1989)

Six azo and anthraquinone disperse dyes were used as probes to study changes in the morphology of a polyester film modified by treatment with aqueous 5% sodium hydroxide, 70% ethylamine, or 70% *N,N*-dimethylformamide (DMF) solutions. Aqueous sodium hydroxide-treated polyester was less accessible to these dyes and dyed to different shades than untreated polyester suggesting that the non-crystalline content of the film surface is slightly greater than that of the interior of the film. Aqueous ethylamine and DMF-treated polyester tended to dye to deeper and different shades than untreated polyester demonstrating that these treatments provide greater access to the non-crystalline regions within the polyester depending on the particular treatment and the dye used.

(Keywords: polyester film; disperse dyes; film modification; structure probes; dyeing properties; colour properties; scanning electron microscopy; morphology; colour and shade differences)

INTRODUCTION

Chemical and solvent treatments of polyester fibre and films have a marked effect on the dyeing and colour properties of these substrates[1–9]. Kuwahara[5] examined the dyeing characteristics of moderately crystalline solvent-treated polyester films using Disperse Red 15. He found that the saturation values for Disperse Red 15 on the pretreated polyester films increased linearly with the amorphous contents and with the pretreatment temperature of the films. Rao and Dweltz[9] studied the dyeing characteristics of uniaxially drawn polyester films using Disperse Blue 7. They found that there was no unique relationship between dye uptake and orientation or crystallization of the polyester films, although drawing temperature, draw ratio, and tension affected dye uptake. These studies demonstrate that disperse dyes can be used as sensitive probes of changes in the amorphous or non-crystalline morphology of moderately crystalline polyester. No studies using a series of disperse dyes as structure probes for modified polyester films are reported in the literature.

In this study we have examined the nature of chemical and solvent-induced changes in a polyester film using a series of six disperse dyes of differing structures. The dyeing and colour characteristics of this film modified with aqueous sodium hydroxide, ethylamine, or *N,N*-dimethylformamide were markedly different than those for the untreated polyester film. The effect of dye structure on the dyeing and colour characteristics of the modified and untreated polyester film samples was also examined.

EXPERIMENTAL

Materials

A biaxially-oriented Mylar polyester film of 0.258 μm thickness was used. The film had a glass transition temperature (T_g) of 77.1°C and a melting temperature (T_m) of 261°C by thermal mechanical analysis and differential thermal analysis, respectively.

Wide angle X-ray scattering (WAXS) of the film specimens was carried out on a Dian-XRD 800 diffractometer giving 50 kV CuKα radiation at 15 mA. Scanning was performed from 12 to 32° at 1.6 degrees/min. Wide angle X-ray scattering (WAXS) showed that the 010 spacing at 25.9° predominated over the $\bar{1}$10 spacing at 22.8° and over the lesser 010 spacing at 17.9°. All chemicals were reagent grade from domestic sources. The dyes were from commercial sources.

Film modification

Polyester film was reacted with either 5% aqueous sodium hydroxide (NaOH) at 100°C for 5 h, with 70% aqueous ethylamine ($EtNH_2$) at 30°C for 4 h, or with 70% aqueous *N,N*-dimethylformamide (DMF) at 108°C for 0.5 h at liquor ratios of 100:1 to 200:1. The samples were all thoroughly rinsed with warm water, dried, and conditioned at 21°C and 65% RH prior to dyeing. NaOH-treated polyester sustained a 10.7% loss in mass, while ethylamine and DMF-treated polyester lost 1.0 and 2.9% in mass, respectively. WAXS diagrams for the modified fibres are essentially the same as the WAXS diagram for the untreated film. Scanning electron microscopy (SEM) was performed on gold-coated film samples of untreated and treated films on a ISI DS-130 scanning electron microscope using a lab 6 filament at 10 kV (*Figure 1*). Treatments caused a significant change in surface morphology as evidenced by SEM.

Dyeing procedure and colour measurement

Treated and untreated samples were dyed from an infinite dyebath at 100°C for 6 h at a liquor ratio of 100:1. The dyed film samples were thoroughly rinsed in warm water, dried, and conditioned prior to colour measurement. The colour (L^*, a^*, b^*), differences in depth of shade (ΔL^*) and shade ($\Delta a^*, \Delta b^*$), and overall colour differences (ΔE) of the samples were measured on a MacBeth MS-2000 colour spectrophotometer using the Cielab system and illuminant C (*Tables 1* and *2*). Undyed untreated and undyed treated films had very similar L^*, a^*, b^* values.

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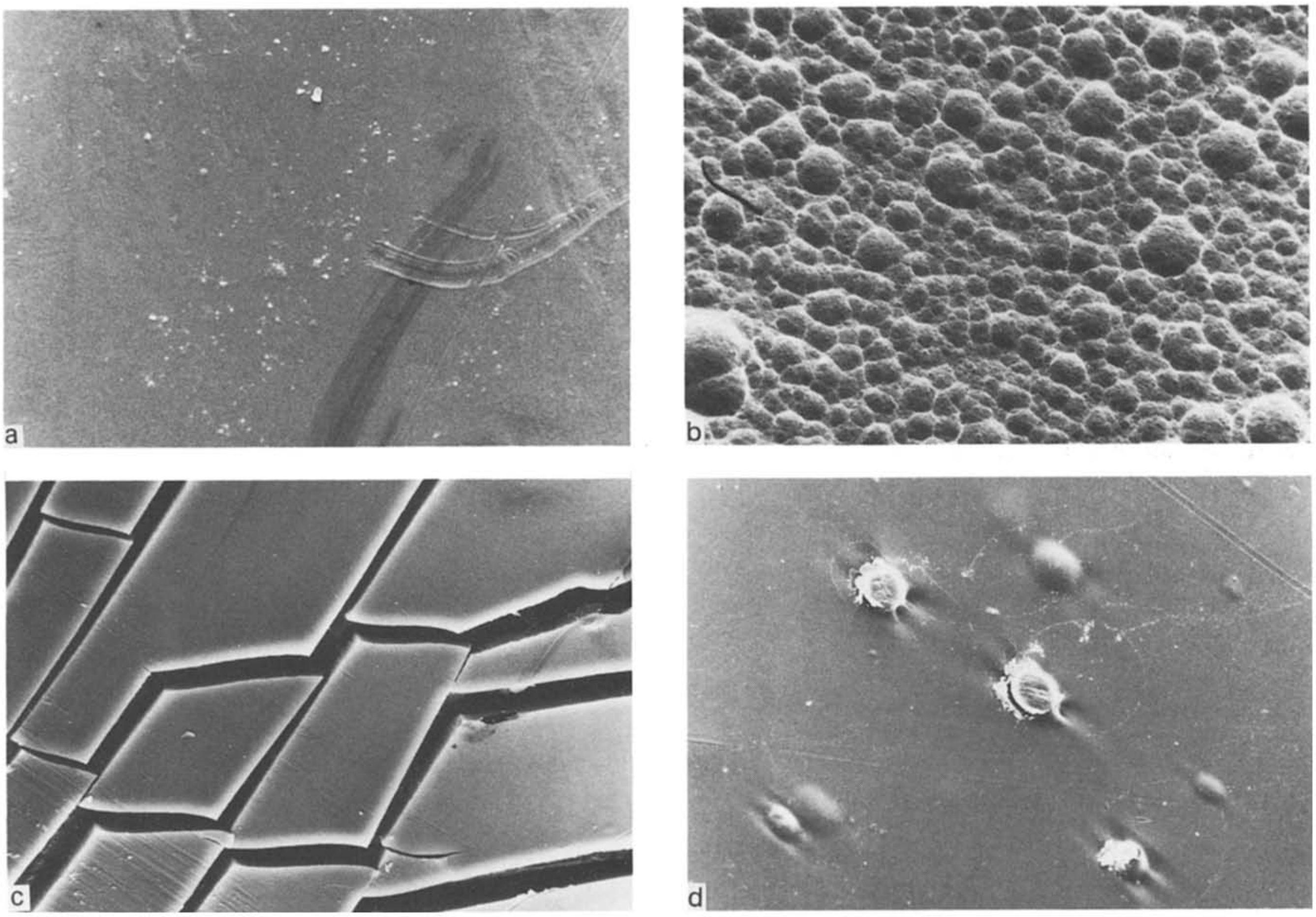

Figure 1 (a) Untreated polyester film (×1350); (b) NaOH-treated film (×1340); (c) $EtNH_2$-treated film (×1905); (d) DMF-treated film (×930)

Table 1 Colour of dyed untreated polyester samples

	Colour		
Dye	L^*	a^*	b^*
Disperse violet 1	12.1	28.4	−19.5
Disperse red 15	27.6	39.1	16.3
Pigment violet 12	69.3	33.3	107.7
Solvent yellow 7	74.2	13.2	96.2
Disperse orange 3	49.4	53.0	74.7
Disperse red 19	53.1	54.6	83.1

RESULTS AND DISCUSSION

Film modification and characterization

A biaxially-oriented polyester film was modified and characterized as follows. The film was modified by surface hydrolysis using 5% aqueous sodium hydroxide (NaOH) or by a combined surface and internal treatment using hydrolysis with 70% aqueous ethylamine ($EtNH_2$) or by solvent-induced modification with 70% aqueous *N,N*-dimethylformamide (DMF). The untreated and modified films were examined by scanning electron microscopy (SEM) and wide angle X-ray scattering (WAXS). Hydrolysis of the NaOH removed 10.7% of the polyester, while treatments with $EtNH_2$ and DMF removed 1.0 and 2.9% by mass of the film. WAXS showed that the untreated and treated films were nearly identical.

Although untreated film displays little surface morphology other than small occasional scratches (*Figure 1a*), the modified films show extensive modification in surface morphology (*Figure 1b–d*). NaOH-treated film shows extensive regular surface pitting due to surface hydrolysis (*Figure 1b*) appearing as a continuum of craters. Sanders and Zeronian[10] also found that NaOH treatment of polyester caused similar surface pitting with an increased accessibility to the hydrophilic groups on the film surface. Aqueous $EtNH_2$-treated polyester film shows extensive

Table 2 Colour differences for dyed, treated polyester films

Dye	Treatment	ΔL^*	a^*	b^*	ΔE
Disperse Violet 1	NaOH	14.9	−12.1	5.5	20.0
	$EtNH_2$	0.5	−17.5	13.5	22.0
	DMF	6.5	− 2.7	3.8	8.0
Disperse Red 15	NaOH	5.9	− 6.4	− 4.0	9.6
	$EtNH_2$	1.2	−22.4	− 3.6	22.7
	DMF	− 2.4	6.3	−21.1	22.2
Pigment Violet 12	NaOH	4.4	− 1.2	−26.0	26.4
	$EtNH_2$	− 4.7	5.5	−11.7	13.8
	DMF	− 2.4	6.3	−21.1	22.2
Solvent Yellow 7	NaOH	3.0	− 0.8	− 9.1	10.4
	$EtNH_2$	0.0	1.0	− 6.9	6.9
	DMF	− 1.9	0.8	5.2	5.6
Disperse Orange 3	NaOH	5.8	− 5.8	−23.6	25.0
	$EtNH_2$	− 8.3	− 0.2	−23.2	24.7
	DMF	− 5.3	− 0.7	−25.0	25.6
Disperse Red 19	NaOH	6.2	− 6.3	−27.1	28.5
	$EtNH_2$	−15.4	4.2	−34.4	37.9
	DMF	− 5.2	1.9	−20.7	21.5

surface crazing (*Figure 1c*). Sekine and coworkers[11] have found similar changes to the surface morphology of $EtNH_2$-treated moderately crystalline polyester films. They also found that the more crystalline the specimen the lower the weight loss that occurred. Aqueous DMF-treatment caused slight surface cavitation of the polyester film (*Figure 1d*). In summary, these aqueous treatments all cause significant but highly different changes to the surface morphology of polyester.

Dyeing properties and colour characteristics of the films

Untreated and treated polyester film samples were dyed with six disperse dyes of differing structures to demonstrate the effect of the treatments on the dyeing and colour characteristics of the films (*Tables 1* and *2*). The chemical and solvent-modified films dyed to markedly different shades and depths of shade than untreated polyester film, demonstrating that these dyes are sensitive to changes in the morphology caused by these treatments.

NaOH-treated polyester consistently dyed to much lighter shades and markedly different shades than untreated polyester. These differences were much greater than can be accounted for by the decrease in film mass and thickness caused by hydrolysis of the film surface. These findings suggest that there is less dye adsorbed and that the non-crystalline content of the film surface is greater than that of the film interior. Removal of the film surface decreases the non-crystalline content and therefore the dyeability of the film.

Ethylamine-treated polyester dyed to similar or deeper shades and markedly different shades than untreated polyester. Ethylamine-induced modification of the surface and interior non-crystalline morphology of the polyester film tends to increase the accessibility of the dyes to the non-crystalline morphology of the polyester film through aminolysis in the polyester.

DMF-treated polyester samples dye to deeper shades and to much different shades than untreated polyester. DMF treatment provides additional non-crystalline content in the film through void formation and improves the accessibility of amorphous areas in the film.

Specific dye structures are particularly sensitive to changes in the amorphous structure caused by the chemical or solvent treatments. However, there appears to be little or no correlation between dye structure and differences in the depth of shade and shade for the dyed modified film samples compared to untreated film.

CONCLUSION

Disperse dyes are extremely sensitive indicators of chemical and solvent-induced changes in the non-crystalline morphology of polyester film with the modified films dyeing to markedly different shades and depths of shade compared to untreated film. However, the colour differences on the dyed films caused by the chemical or solvent treatment cannot be related to dye structure.

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