Interrelation Between Dyeing and Thermal Properties of PET Fibers

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ABSTRACT: The interrelation between dyeing and the thermal properties of micro and conventional poly(ethylene terephthalate) fibers is studied with conventional and modulated differential scanning calorimetry. X-ray diffraction, density, and birefringence studies are used to confirm the obtained results. It is shown that three studied anthraquinone dyes, in contrast to three studied benzodifuranone dyes, act as plasticizers for the fibers. A comparison between fibers and partially crystallized bulk samples is made. The specific fiber morphology makes the fibers more susceptible to plasticization than are bulk samples. This ability of a dye to lower the glass transition of the fibers will influence the dye diffusion and this information is needed to optimize the dyeing process for a specific dye–fiber combination. Further, the presence of an anthraquinone dye in the fiber alters the melting endotherm by changing the stability of the original crystals. The onset of the melting and recrystallization process is lowered. Although still well above the dyeing temperature, this lowering may be critical for the dimensional stability of the fabrics during any subsequent high-temperature process. A first investigation of the effect of variations in the thermal properties on the obtained color strength after dyeing is reported. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 105–114, 2003

Key words: glass transition; fibers; dyes; thermal properties; differential scanning calorimetry

INTRODUCTION

Modulated differential scanning calorimetry (MDSC) has been shown to be an excellent technique to monitor the thermal properties of poly(ethylene terephthalate) (PET) fibers relevant to their further processing, allowing, for the first time, a fundamental understanding of the until now empirical experience in PET fiber dyeing.[1] Both the very broad and weak glass transition region of the fibers as well as the start of the melting and recrystallization process were shown to be key parameters for understanding the dyeing and preparatory heat-setting process, which could be well studied by MDSC. The melting profile of the fibers was studied mainly by conventional DSC.

So far, only "as-received" fibers (not yet dyed) have been investigated.[1] Although this already provided a valuable insight into the thermal parameters of importance for the dyeing process, it does not permit the understanding of possible differences in dyeing behavior between various disperse dye classes. Diffusion studies of anthraquinone and benzodifuranone dyes in PET fibers revealed a substantial difference in the diffusion behavior between both dye classes.[2,3] This necessitates the study of the interrelation of the dyeing process with the thermal properties of the dyed fibers, which should allow a better understanding and optimization of the dyeing process for a specific dye–fiber combination. The methodology for the determination of the thermal properties set up for as-received fibers[1] will be used on dyed fibers in this article.

To rationalize the findings of anthraquinone and benzodifuranone disperse dyes on the T_g region of PET fibers, the effect of these dyes on the T_g of bulk PET samples is first discussed. Whereas the glass transition of the fibers has been shown to be of direct relevance to the dye diffusion in the fabrics,[1] the onset of the melting and recrystallization may be equally important for the dyeing process (or any other high-temperature process) with regard to the dimensional stability of the fabrics. The dyes are thought to diffuse into the amorphous regions of the fiber only.[4–7] Thus, one does not expect the dyes to alter the crystalline phase, but the dyes may alter the melting behavior due to a solvent effect. As such, the effect of the dyeing process on the melting transition of the fibers was also studied. To obtain some indication of the dimensional stability, the fabric crimp during a dyeing process was measured. The start of melting and recrystallization was monitored after dyeing for a series of fabrics
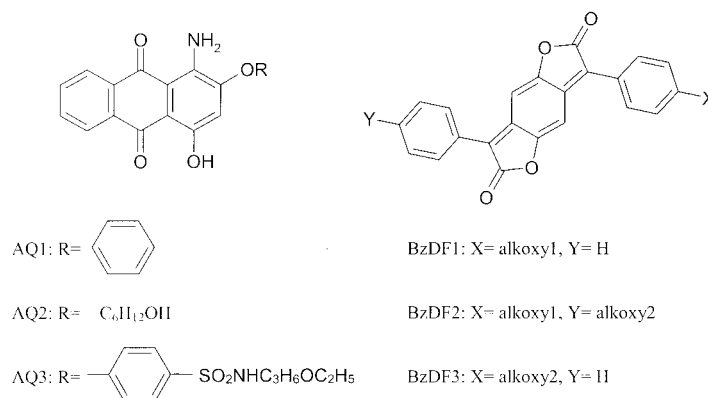
Figure 1 Dye structures.

heat-set at different temperatures, as this may be relevant for the dimensional stability during any high-temperature posttreatment. The original fiber morphology of the dyed and undyed fibers was determined with the aid of density and X-ray diffraction measurements. Finally, preliminary studies of the magnitude of the color buildup as a function of the thermal properties of the fabrics heat-set at different temperatures are given.

EXPERIMENTAL

Materials

The same PET fabric qualities, supplied by Sofinal (Waregem, Belgium), described in ref. 1 were used. Fabric quality 6460 is referred to as the conventional fiber fabric; quality 6145, as the microfiber fabric; and other fabric qualities, by their quality number.

Three anthraquinone dyes (AQ1, AQ2, and AQ3) and three benzodifuranone dyes (BzDF1, BzDF2, and BzDF3) were supplied by Dystar UK Ltd. (Cheadle, UK). They were all supplied both as a predispersed dye in the powder form and as a pure dye. The predispersed dyes are laboratory-optimized mixtures of a pure dye and a dispersing agent to achieve a stable dispersion during the dyeing process and to give the best performance on the fabrics. The structures of the dyes are shown in Figure 1.

All dyeings were performed in a Mathis Labomat BFA-8 lab dyeing machine, using sealed stainless-steel dye pots. Fabric samples of 3 g were dyed in 60-mL dyebaths, thus obtaining a liquor-to-goods ratio of 1:20. The dyebath pH was adjusted to 5 with an acetic acid buffer at the start of the dyeing process and checked to be within a pH range of 5 ± 0.2 at the end of the dyeing process. No substantial deviations of pH during the course of the dyeing process were observed. The temperature profile applied during the dyeing process is illustrated in Figure 2.

Analogous to most common industrial dyeing processes for PET fabrics, an isothermal step at 130°C of 1 h was taken as a standard dyeing process. Fabric samples were dyed with 1, 2, 4, 8, and 15% o.w.f. predispersed dye, with the concentration of dye in the dyebath (Cb) determined by percentage on weight of fabric (percent o.w.f.). All results reported here relate to fabrics dyed with predispersed dyes. However, to exclude the possible effect of the unknown dispersing agents in the dye dispersion, all dyes were also applied as pure dye in the dyebath to the conventional PET fibers. The results on these samples, although the concentrations of dye were lower and less reproducible, agree with the results of the dye dispersions and an effect of the dispersing agents on the conclusions can be excluded.

Although the same concentration of predispersed dye was added to the dyebaths for all six dyes, the fabrics did not contain similar concentrations of pure dye after dyeing (Cf) due to a different buildup behavior.[8] This is shown in Table I for AQ1 and BzDF1 on the conventional fiber and microfiber fabric, with the other anthraquinone and benzodifuranone dyes behaving similarly to AQ1 and BzDF1, respectively. Blank-dyed fabrics are obtained by exposing the fabrics to the dyeing process without any dye present in the dyebath.

As in ref. 1, the warp and weft yarns of the fabrics were separated before analysis with MDSC. Again, the figures relate to the weft fibers, unless otherwise
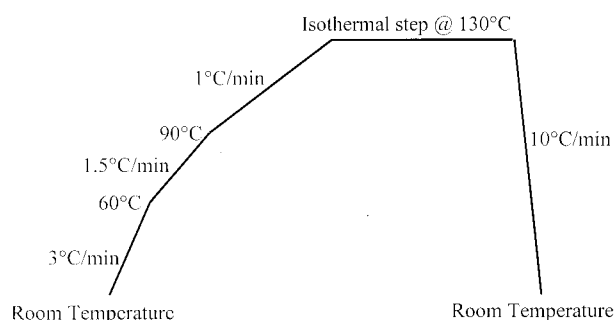

Figure 2 Temperature profile during the dyeing processes.

TABLE I
Dye Concentration in the Fiber (*Cf*) in Milligrams Pure Dye/Gram Fabric as a Function of the Dye Concentration in the Bath (*Cb*) in Percent o.w.f.

| | Cf (mg/g) | | | |
| | Conventional fiber | | Microfiber | |
Cb (% o.w.f.)	AQ1	BzDF1	AQ1	BzDF1
1	4.7	0.7	4.0	0.9
2	9.8	0.5	9.3	1.6
4	18.6	1.0	16.3	2.0
8	24.0	1.3	29.4	3.2
15	32.5	2.4	34.0	4.3

stated, but the warp fibers gave similar results and led to the same conclusions. The standard conventional fiber and microfiber fabric qualities were studied "as-received," blank-dyed, and dyed with the six different dyes. The supplementary fabric qualities 6645, 6447, and 5065 were studied as received, blank-dyed, and dyed with AQ1 and BzDF1 only.

To rationalize the findings on the dyed fibers, a series of bulk PET samples were investigated. The bulk PET samples were prepared in a similar manner as in ref. 1 by heating the weft fibers of the conventional fabric at 280°C for 5 min, quenching in liquid nitrogen, and annealing at 100°C.

DSC and MDSC

DSC and MDSC experiments were performed according to the methodology described in ref. 1. The experiments in the glass transition region on the as-received, blank-dyed, and AQ1-dyed conventional weft fibers were repeated at least five times, resulting in a standard deviation of 1.5°C for T_g and 0.015 J g^{-1} °C^{-1} for ΔCp at T_g. The weft conventional fibers dyed with the other five dyes, as well as all weft microfibers, were measured at least three times. The measurements of T_g and ΔCp at T_g for the other fibers (warp of the standard fabric qualities and both warp and weft of fabric qualities 6645, 6447, and 5065) were performed at least twice. The determination of the onset of melting and recrystallization was performed at least twice on all samples. All trends were reproducible.

Measurement of fabric crimp

The fabric crimp during dyeing is calculated as

$$FC = 100 \times (La - Ld)/La$$

where FC is the fabric crimp in percent La, a marked length on the as-received fabric, and Ld, the distance between the marks after dyeing.

Other analytical techniques

Wide-angle X-ray diffraction, density, and birefringence measurements were performed by Acordis Industrial Fibers Research (Arnhem, The Netherlands). X-ray diffraction measurements were performed on a Philips diffractometer equipped with a quartz monochromator, Soller slits, a divergence slit (1°), a scatter slit (0.2 mm), and a receiving slit (1°). The transmission technique was used with CuKα X-rays at a scanning rate of 1°/min. The PET fibers were wound very accurately on thin sample holders as to obtain a grid of densely packed parallel fibers. The overall density was determined in a gradient column. Further experimental details are described in refs. 9 and 10.

The birefringence (Δn) of PET fibers was determined via the compensation method according to deSénarmont on a Jena Pol microscope. Dibutylphthalate was used as the immersion liquid. Twenty fibers were measured and averaged. The amorphous orientation (Fa) may be determined from Δn as follows:

$$\Delta n = VcFc \, \Delta n_c + (1 - Vc)Fa \, \Delta n_a$$

where Vc is the crystalline volume fraction, and Fc, the crystalline orientation, determined from X-ray diffraction and density measurements. The intrinsic birefringence of the crystalline (Δn_c) and amorphous (Δn_a) fractions were taken as 0.220 and 0.275, respectively.

To quantify the color of the dyed fabrics, the diffuse reflectance spectra of the fabrics were measured on a Perkin–Elmer Lambda 900 spectrophotometer, equipped with a Spectralon Labsphere 150-mm integrating sphere sample accessory. A common 8/d measuring geometry was used (illumination: direct at 8° from the normal of the fabric; measured reflectance: diffuse). The spectra were collected from 400 to 700 nm with a data interval of 5 nm, a slit width of 5 nm, and an integration time of 0.2 s. All fabrics were folded four times as to be opaque and measured at the upper surface in three directions: warp horizontal, warp vertical, and warp at 45°. The mean reflectance spectrum was taken for further study and transformed into Kubelka–Munk units (K/S).[11,12] The color strength was determined as the area under the K/S curve.[8]

RESULTS AND DISCUSSION

Plasticizing effect of dyes on bulk PET samples

In ref. 1, the very broad and weak glass transition of PET fibers was rationalized by comparing it to the T_g of a series of semicrystalline bulk PET samples with increased crystallinity and rigidity of the amorphous phase, obtained by annealing amorphous PET for prolonged times. Comparable experiments were repeated to study the effect of dye on the glass transition in the bulk samples. This was obtained by preparing the bulk samples from fibers dyed with 15% o.w.f. AQ1
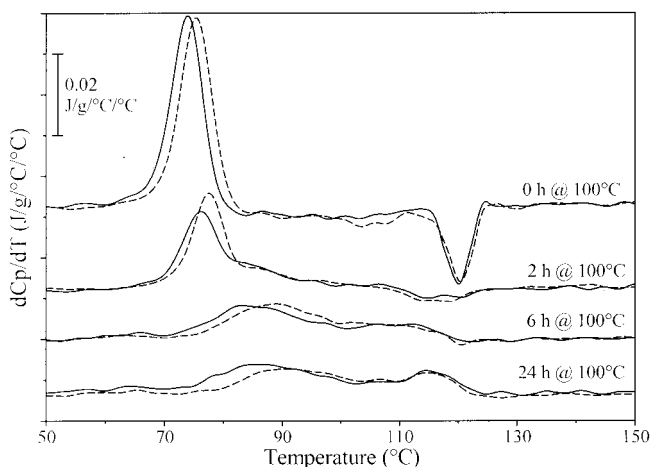
Figure 3 Variations in glass transition due to the presence of AQ1 in bulk PET samples annealed for prolonged times (0–24 h) at 100°C. MDSC.(—) Bulk samples prepared from fibers dyed with 15% o.w.f. AQ1; (----) bulk samples prepared from as-received fibers.

instead of as-received fibers. Figure 3 compares the derivative of the heat-capacity signal (dCp/dT), obtained by MDSC, for both series of bulk samples.

It can be observed that the presence of the AQ1 dye lowers the T_g of the PET samples. The decrease in T_g is larger with increasing annealing times. This is probably due to a higher effective concentration of dye in the amorphous regions as the dye is ejected from the crystals formed during annealing. The peak around 115°C in the dCp/dT signal, which is attributed to the start of the melting and recrystallization of unstable crystals formed during annealing,[1] is not affected by the presence of the dye.

To investigate the effect of increasing concentrations of dye in PET, several other series of bulk samples were prepared. As the maximum amount of pure dye in the PET fibers by a dyeing process is always limited (cf. Table I), the bulk samples were prepared by starting from as-received fibers and adding a known amount of pure dye before melting, quenching, and annealing the sample. Four series of samples were prepared: two with varying concentrations of the AQ1 dye and two with varying concentrations of the BzDF1 dye. For each dye, one series was investigated after quenching and one after annealing for 24 h at 100°C. Figure 4 shows the T_g of all samples, measured by MDSC.

The data confirm the plasticizing effect of the AQ1 dye on PET, which is increased with increasing dye concentration. Again, the lowering of T_g is more pronounced for the annealed samples compared to the quenched samples, due to a higher concentration of dye in the amorphous regions as discussed above. Figure 4 also shows that the plasticizing effect of the BzDF1 dye is smaller than that of the AQ1 dye. These results are used to improve the understanding of the
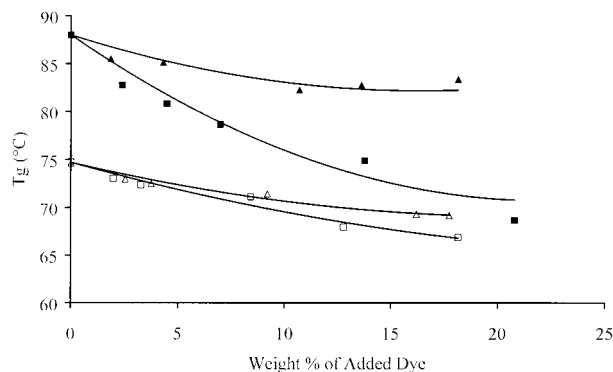

Figure 4 Glass transition temperature of bulk PET samples as a function of dye content: (□) amorphous bulk containing AQ1; (△) amorphous bulk containing BzDF1; (■) semi-crystalline bulk annealed for 24 h at 100°C containing AQ1; (▲) semicrystalline bulk annealed for 24 h at 100°C containing BzDF1. The trend lines are drawn as a guide to the eye.

effect of dyes on fibers, as the amount of dye in a fiber is limited (cf. Table I) and the fiber morphology leads to even weaker glass transitions than the bulk samples annealed for 24 h.[1]

Effect of the dyeing process on the glass transition of PET fibers

Figure 5 shows a typical example of the heat capacity and its derivative (Cp and dCp/dT signal), obtained by MDSC, for the weft fibers from the conventional fiber fabric. As-received, blank-dyed, and fibers dyed with 15% o.w.f. AQ1 are illustrated. Table II shows T_g, $T_{g_{onset}}$, $T_{g_{endset}}$, and ΔCp at T_g, measured on the Cp signal, for the fibers of the standard conventional fiber fabric and the standard microfiber fabric dyed with different dyes.

Although a substantial experimental error cannot be avoided, due to the very weak glass transition and the inherent practical problems of mounting fibers in a DSC pan (e.g., no reproducible sample-pan contact, which may even change during the DSC run), never-
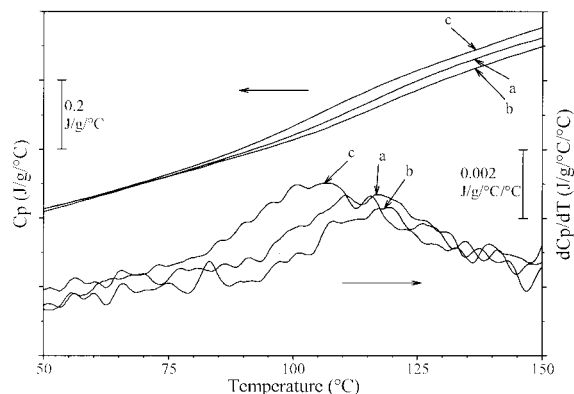

Figure 5 Glass transition region of dyed PET fibers. MDSC. (a) As-received fibers; (b) blank-dyed fibers; (c) fibers dyed with 15% o.w.f. AQ1.

TABLE II
Effect of Dyeing with Different Dyes on T_g, $T_{g_{onset}}$, and ΔCp at T_g of the PET Fibers

Sample	Dyeing process	$T_{g_{onset}}$ (°C)	T_g (°C)	$T_{g_{endset}}$ (°C)	ΔCp (J/g/°C)
Weft conventional fiber	As-received	96	112	130	0.21
	Blank-dyed	99	112	130	0.18
	15% o.w.f. AQ1	88	104	120	0.21
	15% o.w.f. AQ2	86	103	119	0.22
	15% o.w.f. AQ3	93	107	125	0.22
	15% o.w.f. BzDF1	101	111	128	0.18
	15% o.w.f. BzDF2	99	110	130	0.19
	15% o.w.f. BzDF3	97	109	128	0.20
Warp conventional fiber	As-received	102	114	130	0.17
	Blank-dyed	102	114	132	0.18
	15% o.w.f. AQ1	89	106	122	0.23
	15% o.w.f. AQ2	87	103	120	0.22
	15% o.w.f. AQ3	94	109	127	0.20
	15% o.w.f. BzDF1	101	114	131	0.18
	15% o.w.f. BzDF2	101	113	131	0.18
	15% o.w.f. BzDF3	99	113	131	0.19
Weft microfiber	As-received	96	109	126	0.20
	Blank-dyed	100	110	127	0.17
	15% o.w.f. AQ1	88	101	117	0.20
	15% o.w.f. AQ2	85	100	117	0.21
	15% o.w.f. AQ3	88	102	120	0.20
	15% o.w.f. BzDF1	100	110	125	0.16
	15% o.w.f. BzDF2	99	110	124	0.16
	15% o.w.f. BzDF3	95	108	124	0.18
Warp microfiber	As-received	98	111	127	0.17
	Blank-dyed	105	111	127	0.14
	15% o.w.f. AQ1	88	104	118	0.21
	15% o.w.f. AQ2	88	102	117	0.19
	15% o.w.f. AQ3	93	108	122	0.17
	15% o.w.f. BzDF1	105	112	124	0.13
	15% o.w.f. BzDF2	99	112	129	0.17
	15% o.w.f. BzDF3	101	112	126	0.14

theless, the following trends are meaningful: The data of the blank-dyed samples show that the dyeing process by itself does not influence the glass transition temperature of the fibers. All three anthraquinone dyes tested decrease the T_g of the fibers, while ΔT_g does not show an appreciable change. Dyeing with the three benzodifuranone dyes does not affect the fiber T_g significantly.

Table III shows the amorphous orientation (Fa) in the weft fibers of the conventional fiber fabric. Dyeing with AQ1 lowers the amorphous orientation, whereas the blank dyeing process or the dyeing with BzDF1 does not show a significant effect on the amorphous

orientation. This agrees with the plasticizing effect observed by MDSC.

Although the concentration of the benzodifuranone dyes in the fibers is much lower than that of the anthraquinone dyes, the lower plasticizing effect of the former dyes is confirmed by the results on bulk PET (cf. Fig. 4) where similar concentrations of both dye types can be used. It should also be noted that the plasticizing effect of AQ1 absorbed in the fibers, as a result of the dyeing process, is even larger than is the plasticizing effect of the same concentration of dye in the bulk PET sample annealed for 24 h at 100°C (T_g shift of ca. 5°C in bulk versus T_g shift of ca. 8°C in the

TABLE III
Effect of Dyeing on the Crystal Dimensions ($\Lambda 100$, $\Lambda 010$, $\Lambda 105$), the Crystalline Volume Fraction (Vc), and the Amorphous Orientation (Fa) of PET Conventional Weft Fibers

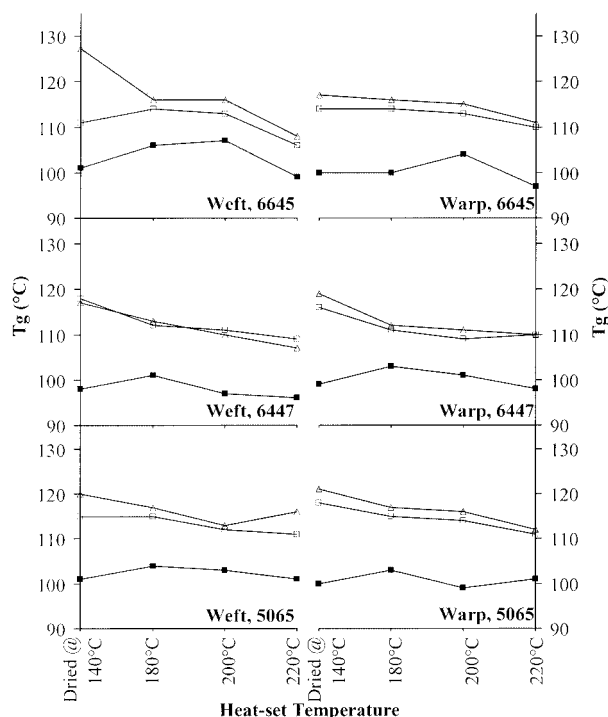| Sample	$\Lambda 100$ (nm)	$\Lambda 010$ (nm)	$\Lambda 105$ (nm)	Vc	Fa
As-received	4.5	6.4	8.2	0.41	0.475
Blank-dyed	4.5	6.4	8.0	0.41	0.470
15% o.w.f. AQ1	4.6	6.4	8.1	0.42	0.436
15% o.w.f. BzDF1	4.5	6.4	8.2	0.40	0.483

Figure 6 Effect of the dyeing process on the glass transition temperature for warp and weft of the PET fabric qualities 6645, 6447, and 5065 dried and heat-set at different temperatures: (□) as-received fibers; (△) blank-dyed fibers; (■) fibers dyed with 15% o.w.f. AQ1.

fibers). This agrees with the earlier observation (cf. Fig. 3) that the shift in T_g, due to the presence of AQ1, is larger with increasing annealing times. It can be explained by the ΔCp at T_g of the fibers being smaller than any of the annealed bulk samples,[1] resulting in a higher concentration of dye in the amorphous regions of the fibers. The specific fiber morphology, with its high molecular orientation, high crystallinity, and high rigidity of the amorphous fraction, thus leads to a higher susceptibility toward a possible plasticizing effect of dyes.

Further, ΔCp at T_g is not altered appreciably by the dyeing process. It is slightly reduced by a blank dyeing process or in the presence of benzodifuranone dyes and increased again in the presence of an anthraquinone dye to or even above the value of the as-received fibers. This may be attributed to a small reorganization of the amorphous fraction during the 1-h dyeing process at 130°C. As such, a small part of the amorphous fraction may become more rigid and not contribute to the measured Cp step around 110°C. The presence of an anthraquinone dye, acting as a plasticizer, will counteract this increase in rigidity. The changes in ΔCp at T_g are, however, small compared to the changes in T_g, induced by anthraquinone dyes, which clearly act as plasticizers.

Finally, the plasticizing effect of the AQ1 dye is confirmed in Figure 6, which shows the fiber T_g for as-received, blank-dyed, as well as AQ1-dyed fibers

for the fabric series heat-set at different temperatures. ΔT_g and ΔCp at T_g are not shown for these samples but they also confirm the trends observed in Table II, showing no significant variations in ΔT_g and only a small reduction in ΔCp at T_g due to the blank dyeing process, but an increase again after dyeing with AQ1. The dyeing with BzDF1 again induces no significant variations in the fiber T_g compared to the blank-dyed samples and is therefore not shown.

The T_g of the blank-dyed samples, which did not receive a heat-set treatment but only a drying step at 140°C, does not totally agree with the observation that the blank dyeing process does not have a major effect on the fiber T_g. The onset of melting and recrystallization measured on the as-received dried samples (cf. Table IV), however, is around or even lower than the dyeing temperature of 130°C. As such, the dyeing process will act as a wet annealing treatment. This will result in changes in fiber morphology (and thus also in fiber T_g) during the dyeing process that are different from those of fibers with an onset of melting and recrystallization above the dyeing temperature (all heat-set samples in this work).

The plasticizing effect of a dye on PET is important, as the dyeing temperature needs to be increased above the fiber T_g to allow appropriate dye diffusion into the fiber.[4-7] The dyeing with the anthraquinone dyes studied here will influence the dyeing process of PET fibers, as the diffusion of dye into the fiber will lower the T_g of the fiber, which may result in an even faster diffusion of dye in the fiber. This is in contrast to the benzodifuranone dyes studied.

MDSC gives us a technique to monitor this "autocatalytic" effect of any dye, which is of great relevance for the dyeing process as it may cause variations to the general, empirical process conditions. This substantially different diffusion and dyeing behavior between both dye classes is to be further reported and discussed elsewhere.[2,3,8]

Effect of the dyeing process on the melting transition of PET fibers

Figure 7 compares the melting region of the weft fibers of the conventional PET fabric dyed with 15% o.w.f. AQ1 to those of an as-received fabric as a function of the heating rate. Similar to the as-received fibers, the whole melting profile of the dyed fibers is shifted to higher temperatures with decreasing heating rates. The observed melting profile of the dyed fibers is thus also the result of a continuous melting and recrystallization process.[1]

The melting transition of the dyed fibers is, however, broadened and situated at a lower temperature compared to the as-received fibers. During the dyeing process, the dyes are thought to diffuse into the amorphous phase only, which is mobile at the dyeing temperature of 130°C.[4-7] The crystals in the as-received

TABLE IV
Effect of the Dyeing Process in Combination with the Heat-set Temperature on the Onset of Melting
and Recrystallization (the Nonreversing Signal), the Fabric Crimp (*FC*) of a Blank-dyed Sample,
and the Color Strength (Area K/S) of the Dyed Fabrics (Warp and Weft Not Separated)

| Fabric quality | Programmed heat-set temperature | Measured onset of melting and recrystallization (°C) | | | Fabric crimp (*FC*) (%) | Area K/S | |
		As-received	Blank-dyed	15% o.w.f.		15% o.w.f.	15% o.w.f. BzDF1
Weft, 6645	Dried at						
	140°C	108	151	151	9.2	1784	512
	180°C	173	173	168	1.3	1402	413
	200°C	195	194	191	0.4	1348	415
	220°C	208	209	203	1.1	1413	485
Warp, 6645	Dried at						
	140°C	146	150	154	6.7	—	—
	180°C	175	176	170	2.2	—	—
	200°C	195	193	189	1.6	—	—
	220°C	206	205	202	1.9	—	—
Weft, 6447	Dried at						
	140°C	128	150	150	11.0	2782	764
	180°C	173	172	164	3.7	2389	705
	200°C	190	191	186	2.3	2194	718
	220°C	196	197	194	1.9	2174	776
Warp, 6447	Dried at						
	140°C	130	150	150	10.8	—	—
	180°C	173	175	165	3.3	—	—
	200°C	189	195	184	2.4	—	—
	220°C	201	203	193	2.1	—	—
Weft, 5065	Dried at						
	140°C	150	153	154	10.6	2614	685
	180°C	169	173	162	2.1	1862	592
	200°C	190	189	183	1.1	1683	599
	220°C	215	217	210	0.3	1662	628
Warp, 5065	Dried at						
	140°C	115	150	150	13.2	—	—
	180°C	170	169	160	3.4	—	—
	200°C	186	187	182	2.8	—	—
	220°C	209	211	202	2.7	—	—

fibers are thus not expected to be altered. This is confirmed in Table III, which shows the crystal dimensions and crystalline volume fraction as the result of
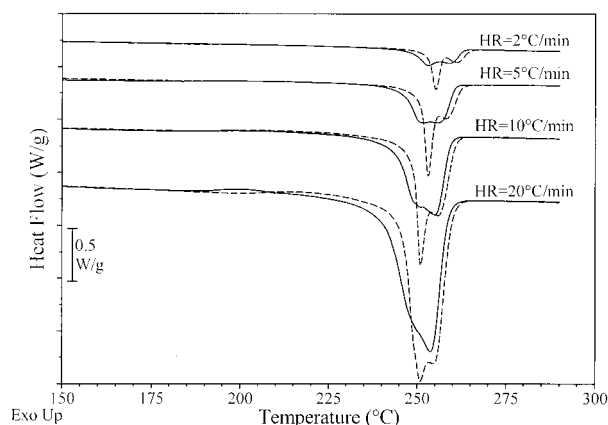

Figure 7 Melting region of conventional weft PET fibers. Conventional DSC with varying heating rates (HR): (—) fibers dyed with 15% o.w.f. AQ1; (----) as-received fibers.

X-ray diffraction and density measurements for as-received, blank-dyed, AQ1-dyed, and BzDF1-dyed fibers. No significant changes are observed.

However, the dyes present in the amorphous fraction may alter the stability of the polymer crystals and thus lower the melting temperature. This is confirmed in Figures 8 and 9, which show the effect of increasing concentrations of AQ1 on the melting of the weft fibers of the conventional fiber and the microfiber fabrics, respectively.

For both fiber types, increased concentrations of AQ1 led to an increased broadening of the melting profile. The peak temperatures are lowered and the relative importance of the different endotherms is altered as well.

For the conventional fibers, the lower-temperature endotherm is reduced in favor of the higher-temperature one, while the total peak area is relatively unaffected. As the presence of the AQ1 dye broadens the lower-temperature endotherm on the low-temperature side, a longer time interval is available for recrys-
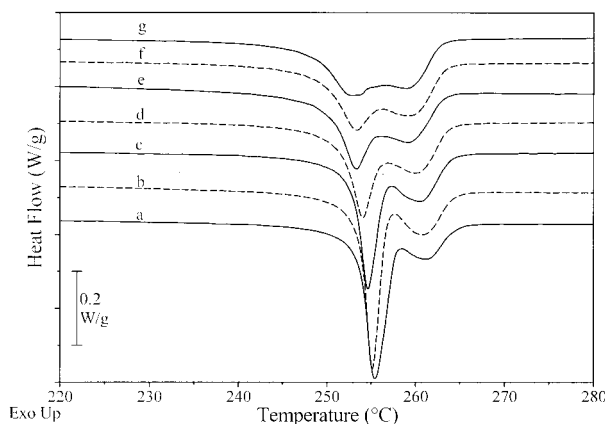
Figure 8 Melting region of PET conventional weft fibers, dyed with increasing concentrations of AQ1. Conventional DSC at a heating rate of 2°C/min: (a) as-received; (b) blank-dyed; (c) 1% o.w.f. AQ1; (d) 2% o.w.f. AQ1; (e) 4% o.w.f. AQ1; (f) 8% o.w.f. AQ1; (g) 15% o.w.f. AQ1.

Figure 10 Melting region of PET conventional weft fibers, dyed with different dyes. Conventional DSC at a heating rate of 2°C/min: (a) as received; (b) blank-dyed; (c) 15% o.w.f. BzDF1; (d) 15% o.w.f. BzDF2; (e) 15% o.w.f. BzDF3; (f) 15% o.w.f. AQ1; (g) 15% o.w.f. AQ2; (h) 15% o.w.f. AQ3.

tallization, which may explain the relative increase of the area of the high-temperature melting peak, although the peak temperature itself is lowered.

In contrast to the conventional fibers, the multiple melting is not as obvious in the as-received microfibers. A dominant endotherm at a temperature intermediate to the two endotherms of the conventional as-received fiber can be observed together with a weak higher-temperature endotherm, visible only as a shoulder. The earlier start of the melting process of the dyed microfibers leads to an extra shoulder or peak at the low-temperature side for the highest dye concentrations. Again, the longer time available for recrystallization or reorganization may explain the relative increase of the highest melting endotherm, although it remains weak.

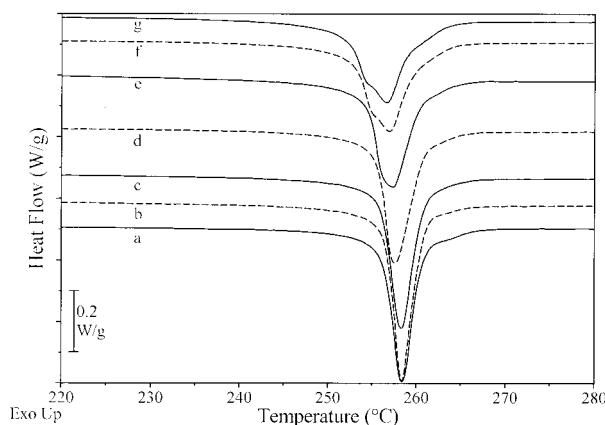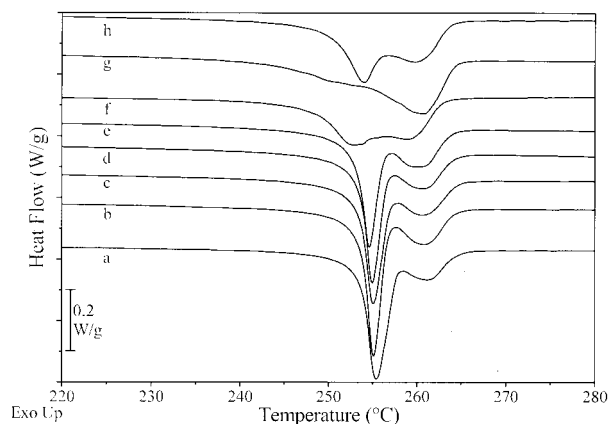The presence of the AQ1 dye will, by altering the stability of the crystals and the crystallization kinetics

during the melting and reorganization process, affect the melting profile of the dyed fibers. Figure 10 illustrates that the two other anthraquinone dyes have a similar effect, with the effect of the AQ2 dye being even more pronounced. In contrast, the three benzodifuranone dyes tested do not alter the melting behavior significantly.

It was indicated in a previous article[1] that the start of melting and recrystallization is triggered by the heat-set process and can be observed as an exotherm in the nonreversing heat-flow signal as well as a small step in the Cp signal or peak in the dCp/dT signal, obtained by MDSC. Figure 11 shows the nonreversing heat-flow signal and the dCp/dT signal for the as-received, blank-dyed, and AQ1-dyed weft fibers of fabric quality 6447 heat-set at 200°C. Both the nonreversing heat flow and the dCp/dT signal show a lower onset of recrystallization in the AQ1-dyed weft fibers heat-set at 200°C compared to the as-received fibers,

Figure 9 Melting region of PET weft microfibers, dyed with increasing concentrations of AQ1. Conventional DSC at a heating rate of 2°C/min: (a) as-received; (b) blank-dyed; (c) 1% o.w.f. AQ1; (d) 2% o.w.f. AQ1; (e) 4% o.w.f. AQ1; (f) 8% o.w.f. AQ1; (g) 15% o.w.f. AQ1.
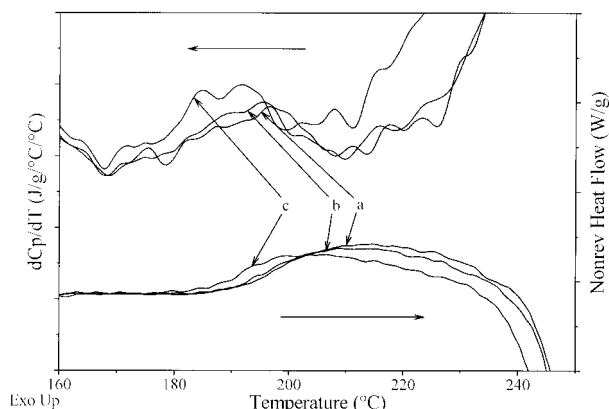

Figure 11 Variations in the onset of melting and recrystallization after dyeing for the weft PET fibers of fabric quality 6447 heat-set at 200°C. MDSC. (a) As-received fibers; (b) blank-dyed fibers; (c) fibers dyed with 15% o.w.f. AQ1.
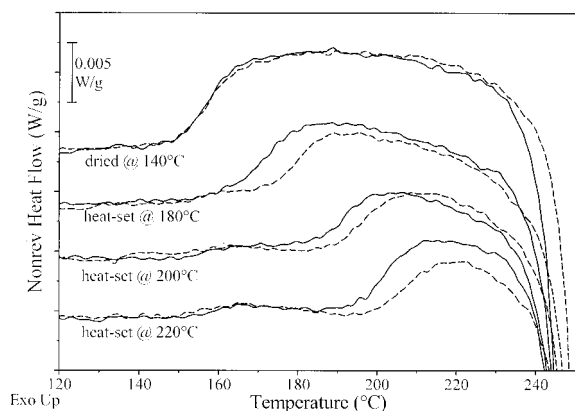
Figure 12 Effect of dyeing with 15% o.w.f. AQ1 on the onset of melting and recrystallization for the weft PET fibers of fabric quality 6447 with varying heat-set temperature. MDSC. (—) Fibers dyed with 15% o.w.f. AQ1; (---) blank-dyed fibers.

while the blank dyeing process itself has no major effect. Figure 12 and Table IV further confirm that the dyeing with AQ1 lowers the onset of melting and recrystallization for all heat-set temperatures. Note that this can also be observed in the highest heating rate curves obtained by conventional DSC (Fig. 7), although the exotherm is not as clear.

In contrast to the heat-set samples, the measured onset of melting and recrystallization for the dried samples is not lowered upon dyeing with an anthraquinone dye (Fig. 12). This can again be explained in terms of the low onset of melting and recrystallization of the as-received fabrics. The dyeing process will thus act as a wet annealing treatment for these dried samples and result in an increased onset temperature of melting and recrystallization for both the blank-dyed as well as the anthraquinone-dyed fabrics This agrees with the behavior of annealed bulk samples where the dye was also introduced prior to annealing (cf. Fig. 3).

The fibers dyed with 15% o.w.f. BzDF1 do not reveal any change in the start of melting and recrystallization (not shown). The onset temperature of melting and recrystallization was determined for the two standard fabric qualities dyed with the other anthraquinone and benzodifuranone dyes as well. This confirmed that all studied anthraquinone dyes behave according to AQ1, whereas all studied benzodifuranone dyes behave according to BzDF1.

In addition to the effect of the dyeing process on the onset of melting and recrystallization, Table IV illustrates the concomitant high fabric crimp (*FC*) during a blank dyeing process if the onset of melting and recrystallization of the as-received fabric is not sufficiently above the dyeing temperature. The dyeing with AQ1 results in no major differences in fabric crimp compared to the blank-dyed fabrics and these are thus not shown.

The lowering of the onset of the melting and recrystallization process by anthraquinone dyes may not be

of great importance for the dyeing process itself as long as the fabrics are appropriately heat-set. However, PET fabrics and microfiber PET fabrics, in particular, are often subjected to a heat-set posttreatment as part of a subsequent coating process at temperatures around 160–180°C. The lowering of the start of melting and recrystallization by certain dyes may very well be critical for the properties of the fabrics during these subsequent processes. Indeed, the process may be optimized, based on empirical findings, for a specific dye–fiber combination. When processing another dye–fiber combination, the optimization is usually not repeated, which may lead to serious problems if the dye lowers the onset of melting and recrystallization to a temperature below the process temperature.

Interrelation between the thermal properties and the color strength

In the literature,[5,9,13–16] the effect of the heat-set temperature on the color strength is usually suggested to be related to variations in the accessibility of the amorphous regions with the heat-set temperature. However, the glass transition region of the fibers was never studied in detail. Furthermore, the published results usually were related to the heat-set treatment of the fibers during their production, which is distinctly different from the heat-set conditions on the fabrics studied in this work.

Table IV illustrates the color strength, as the total peak area under the K/S curve,[8] of the different fabrics dyed with 15% o.w.f. AQ1 and 15% o.w.f. BzDF1. One can observe a substantial drop in color strength between the dried and heat-set samples. This is probably due to a macroscopic effect. The fabric crimp for the dried fabrics during dyeing is much higher than for the heat-set samples, as a result of their low-temperature onset of melting and recrystallization. This will result in a denser fabric after dyeing and concomitant higher color strength.

The variations in color strength between the fabrics heat-set at different temperatures cannot be explained by a macroscopic effect. The fabric structure is very similar for all heat-set temperatures, since the onset of melting and recrystallization is situated sufficiently above the dyeing temperature. For BzDF1, an increase in color strength is observed with the heat-set temperature, and this is especially obvious for the highest heat-set temperature of 220°C. The differences observed for AQ1 are much less. This may be interpreted in terms of the different diffusion kinetics of both dyes.

Indeed, BzDF1 itself does not affect the fiber T_g. Thus, the reduced fiber T_g with an increasing heat-set temperature will accelerate the diffusion kinetics for the dyeing with BzDF1. Since BzDF1 has not reached equilibrium yet at a dyeing time of 1 h,[8] the faster dye diffusion will show up in the resultant color strength.

This will be most obvious for the heat-set temperature of 220°C, since this also results in the most obvious reduction in fiber T_g. On the other hand, dyeing with AQ1 lowers the fiber T_g to a larger extent than do the differences introduced due to the varying heat-set temperature. Thus, due to its autocatalytic nature, the color strength of fabrics dyed for 1 h is much less affected by the original variations in the fiber T_g.

Only two dyes were tested in this study. Other dyes that, similar to BzDF1, do not reach equilibrium after a dyeing time of 1 h, but that show a higher color buildup than that of BzDF1 may very well be even more sensitive to variations in color strength due to relatively small differences in fiber T_g. Further, one may also expect an effect in color strength due to variations in ΔCp at T_g. The latter is a measure for the amount of the amorphous fraction available for dye diffusion. The recorded variations in ΔCp at T_g with the heat-set temperature are, however, small and subject to an appreciable standard deviation to allow for any conclusions on the interrelation with the color strength.

To better elucidate the interrelation between the color strength and the thermal properties of the fibers, further experiments are needed. But it can already be stated that the glass transition and the onset temperature of melting and recrystallization of the fibers are important parameters for the understanding of the different color strength as a result of a different heat-set temperature.

CONCLUSIONS

It was shown that the studied anthraquinone dyes tend to lower the glass transition temperature of the fibers, whereas the blank dyeing process itself or the dyeing with the studied benzodifuranone dyes had a measurable effect on the fiber T_g. The study of bulk samples with increasing concentrations of dye confirmed the higher plasticizing effect of the anthraquinone dyes compared to the benzodifuranone dyes.

Further, the analysis of bulk samples with varying morphology, as a result of increased annealing (cold-crystallization) times, revealed the high susceptibility of fibers to the plasticizing effect of anthraquinone dyes. This is probably due to the high molecular orientation, crystallinity, and mobility restriction of the amorphous regions of the fibers. The possibility of a dye to act as a plasticizer is of great relevance as it will induce an "autocatalytic" effect on the dyeing process. It was clearly shown that the thermal properties of the fibers are very important for their dyeing properties. Both are interrelated and may affect one another. As such, MDSC does not only serve in understanding the empirically determined dyeing temperatures, but it also gives insight into the driving forces of dye absorption for a specific dye–fiber combination.

DSC and MDSC also showed that the anthraquinone dyes altered the melting endotherm of the dyed fibers by lowering the stability of the original crystals and affecting the kinetics of the melting and recrystallization process. It was already shown that heat-setting the fabrics prior to dyeing triggers the start of melting and recrystallization.[1] The fabric crimp measurements due to a blank dyeing process confirmed the importance of an appropriate heat-set process to push the onset temperature of melting and recrystallization above the dyeing temperature. Dyeing with the anthraquinone dyes studied lowered the start of this process, whereas dyeing with the benzodifuranone dyes studied did not. This may cause serious problems during subsequent high-temperature textile processes, such as the application of a coating, as these are usually performed at temperatures only slightly below the heat-set temperature. Finally, it was shown that the differences in color strength as a result of variations in the heat-set temperature can be better understood by monitoring the glass transition and the onset of melting and recrystallization of the dyed fibers by MDSC.

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