

Interaction of Dyes Used for Foods with Food Packaging Polyester Fibers

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SYNOPSIS

The effect of pH, temperature, dye concentration, and additives on the absorption of the dyes FD & C (Food, Drugs and Cosmetics) Blue 1 and Blue 2 upon poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) subjected to different draw ratios (and, thus, resulting in different percentage crystallinities determined with DSC and wide-angle X-ray diffraction patterns) was investigated and a correlation between these parameters and the dye uptake was suggested. The absorption kinetics of the dyes on the polyesters were studied and a mechanism based upon the development of hydrogen bonds between the dyes and the end groups (—COOH, —OH) of the polyesters and the swelling of the network was proposed. Finally, an indirect measurement of the T_g values of the polyesters was suggested based upon the different dyeing diffusion rates. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The promotion and the consumption of a food product is closely linked to its appetizing appearance, which is usually, in turn, connected to its food-packaging material. Polymeric materials usually defined as “plastics” are extensively used in food-packaging applications. To date, poly(ethylene terephthalate) (PET), with its improved clarity, is expected to take a growing portion of the glass replacement in the future.¹

The following properties of polyesters² give them a dominant role in the packaging industry:

- (a) hydrophobic nature (< 1% w/w);
- (b) excellent resistance to organic solvents, light and weathering conditions;
- (c) indifference to microorganisms;

- (d) good recovery from bending and stretching;
- (e) low creep and considerable retention of properties at elevated temperatures;
- (f) low gas permeability; and
- (g) transparency.

Depending on the country of PET production, PET is known under a variety of different names, such as Mylar (USA), Melinex (UK), Luminar (Japan), and Terphane (France).^{3,4} Similarly to PET films, PET fibers are also known under various trade names, the most well known of which are Terylene (UK) and Dacron (USA).

Both natural and synthetic dyes are used for dyeing the polymers either superficially or throughout their entire mass. Although, nowadays, there exists a strong trend toward the utilization of natural dyes, advocating their biodegradability and the consumers' health, synthetic dyes continue to prevail over the natural dyes because of their lower price. The synthetic dyes (for foods, drugs, and cosmetics applications) could be concisely described as acid dyes of low molecular weight that contain one or more sulfonic groups in their molecules.⁵⁻⁷ The

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eventually undesirable effects of dye migration from foods to polyamide-packaging materials has been observed and several publications have dealt with it. This migration was attributed to interactions between the amine/amide groups and the sulfonic groups.^{5,7,8}

The dyeing properties of polyester fibers are strongly influenced by many of the processing conditions to which the fiber may be subjected during manufacture. Of the various means for the conversion of polymers to fibers, only one (melt-spinning) is of present-day importance for polyester fiber manufacture.

The undrawn or partially oriented yarns produced by melt spinning and cooling the polymer are easy to dye. Drawn materials, on the other hand, are dyed much more slowly. During the process of drawing, stresses are developed in the structure that tend to align some of the molecular chain segments [previously being in the amorphous state, Fig. 1(a)] in the direction of stress and cause stress-induced orientation [Fig. 1(b)]. The resulting structure is termed uniaxial orientation,⁹ i.e., the chain axes of the crystals are oriented toward the machine direction, whereas the plane of the amorphous rings tends to be oriented parallel with the fiber surface; ca. 10–20% of the structure is in the crystalline phase [Fig. 1(c)].

Thus, determination of the relationship between draw ratio and the dyeing parameters for disperse dyes on polyester fibers indicates that both the equilibrium absorption A_∞ and the diffusion coefficient decrease with increasing draw ratio. This is due to the increased crystallization of the fiber matrix together with a slightly increased orientation, which results in a decrease in the accessibility to penetrating molecules.^{10,11}

Consequently, the increase in the percentage crystallinity (%K) of the polyesters, measured with

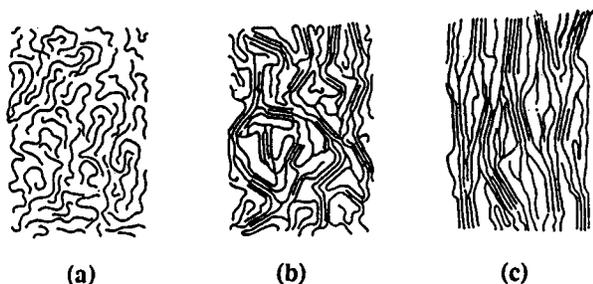


Figure 1 Fringed micelle model of PET and PBT¹⁷: (a) randomly oriented chains in the amorphous quenched state; (b) randomly oriented semicrystalline structure; (c) uniaxially oriented semicrystalline structure.

DSC and wide-angle X-ray diffraction patterns, depends greatly on the draw ratio and on the temperature and time of the hot-drawing stage. Analogously, high draw ratios, high temperatures ($T_g < T < T_m$), and prolonged annealing times improved substantially the perfection of the crystals of polyamides and also induced an increase in their T_g 's.^{7,12–15}

In addition to our previous work on dye absorption on polyamide food packaging materials,⁷ we have undertaken this study in order to examine the mechanism and the conditions under which a dye migration from food to polyester packaging can occur. This attempt was made in order to correlate the draw ratios and the % crystallinity and some structural features, e.g., T_g , and the amount of end groups —COOH, —OH of polyesters with the dye absorption. The effect of pH value, temperature, dye concentration, and presence of additives on dye absorption was also studied. An indirect measurement of T_g values, based upon the differences in the diffusion dyeing rates, was suggested and compared to the results obtained with differential scanning calorimetry (DSC) and dynamic mechanical thermal analyzer (DMTA). The results of polyester dyeing (due to migration from foods) were compared to those of polyamides⁷ and similarities/differences in the two cases were pinpointed.

MATERIALS

Polyesters-Substrates

Polyester fibers were prepared by melt extrusion at spinning speed 3000 rpm. Polyesters as spun fibers were subsequently hot drawn (at $T = T_g + 20^\circ\text{C}$, i.e., at 86°C for PET and 42°C for PBT) at various draw ratios $\lambda = 0$ –3.

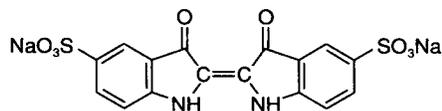
The substrates consisted of standard 5 g samples of the polyester fibers that were exposed to solutions of the dyes. The polyesters were purchased from Ciba-Geigy. The draw ratio was attained using an apparatus elsewhere described¹⁶ placed in a chamber of controlled temperature. The amorphous polyesters were heated to about 20°C above T_g (at 86 and 42°C for PET and PBT, respectively) where the polymer molecules acquire sufficient thermal energy and molecular mobility, allowing the fiber to be drawn by a factor 3–4 in the machine direction.¹⁷

Dyes

Dyes were purchased from a commercial company in the powder form as their sodium salts (Warner Jenkinson, St. Louis, MO). Stock solutions were

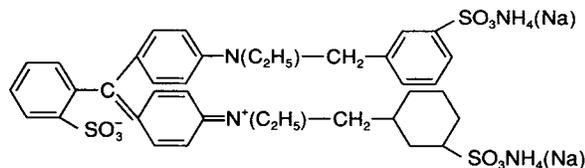
prepared in distilled water at concentration of 1000 ppm. The following two dyes were used:

(a) C.I. Food Blue 1 73015¹⁸:



[2 sulfonic groups] (I)

(b) C.I. Food Blue 2 42090¹⁸:



[3 sulfonic groups] (II)

Apparatus

Differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) measurements were carried out with a Perkin-Elmer DSC-2 (10°C/min = heating rate) and PL-DMTA (Mark II) (2.5°C/min and 1 Hz were heating rates and frequency, respectively) described in detail in previous publications.¹²⁻¹⁴ A Philips 1020PW diffractometer was used to record the wide-angle diffraction patterns and the traces were analyzed as previously described.¹²⁻¹⁴

pH Variation

The pH of the solutions (40 ppm) was subjected to 1 unit increments within a range from 1 to 8, slightly lower than the pH of most foodstuffs.² The pH adjustments were made using 2.0M benzoic acid or sodium hydroxide solutions. Substrates were exposed to the dye solutions for a period of 72 h under controlled temperature (65 and 100°C for PET and PBT, respectively).

Concentration Variation

The range of concentrations used was 10–60 ppm. Six concentrations (10, 20, 30, 40, 50, and 60 ppm) of dye solution were used in total as the most commonly used in beverage drinks.⁵ The solutions were adjusted to pH 2 with 2.0M benzoic acid. Exposure time and temperature of these substrates to the above-mentioned six solutions were 72 h and 65 and 100°C for PET and PBT, respectively.

Temperature Effect

It was studied at the following temperatures:

PBT -20, -10, 0, 5, 10, 20, 25, 30, 40, 50, 60, 70, 80, 90, and 100°C

PET 0, 20, 30, 40, 50, 60, 70, 75, 80, 84, 88, 90, 92, 94, 96, 98, and 100°C

The concentration of the dye solutions was 40 ppm and the exposure time for all of them was 72 h.

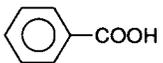
Determination of the Dye Migration Rate

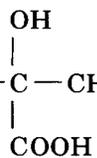
Solutions of dye (Brilliant Blue, No. 1) of 20 ppm concentration were adjusted to pH 2 using a 2.0M benzoic acid solution. Substrates of PET and PBT were exposed to the dye solutions at 10, 20, 30, 40, 50, 60, 70, and 80°C (for PBT) and at 20, 40, 50, 60, 70, 80, 90, and 100°C (for PET) at various time intervals for the time range 24, 48, 72, 96, 130, and 154 h. The action of the dye absorption was stopped by immersing the substrates into liquid nitrogen recipients.

Determination of the Dye Migration Mechanism

Seven solutions of 20 ppm Blue No. 1 were prepared from the stock solution. The pH of each solution was adjusted to 2.0 with one of the following acids¹⁹:

(a) CH₃COOH pK_a = 4.74

(b)  pK_a = 4.2

(c)  pK_a = 3.13

(d) ClCH₂COOH pK_a = 2.86

(e) Cl₂CHCOOH pK_a = 1.26

(f) Cl₃CCOOH pK_a = 0.64

(g) H₂SO₄ first pK_a = -5.2

Exposure time and temperature of the polyester (PET and PBT) substrates were 72 h and 100°C, respectively.

Effect of Additives on Dye Migration Rate

Solutions of 20 ppm dye were prepared from stock solutions and the pH of each solution was adjusted to pH 2.0 with 2.0M benzoic acid. Sodium chloride

(NaCl), sodium sulfate (Na_2SO_4), and several sugars such as glucose, fructose, and sorbitol were added to produce solutions within the concentration range 0.1–1.0M.

RESULTS AND DISCUSSION

pH Effect

The pH of dye (I) and (II) solutions was varied within relatively wide range (1–8). Although it was previously reported that the pH has a pronounced effect upon the migration of the dye to packaging polyamides,^{7,20} in the case of polyesters, the pH effect is not so intense in absolute values (compared to polyamides), although it seems to be in relative values (Figs. 2–3). The low dye migration to polyester packaging was attributed to their rigid structures and their lack of reactive dyesites, whereas the high number of $-\text{NH}_2$ end groups was held responsible for the hydrogen bonding between the dyes and the polyamide sites.⁷ Hydrophobic fibres, such as polyester, cannot be dyed with dyes of high aqueous solubility, as the case with acid dyes is, because the ionization (and thus strongly polar behavior) in water of the dyes produces adverse interactions with the fiber. Apart from size hindrance, which is encountered with most ionic dyes and makes penetration of these dyes difficult, electrical repulsion of anionic dyes takes place due to the high negative surface potentials exhibited by hydrophobic fibers

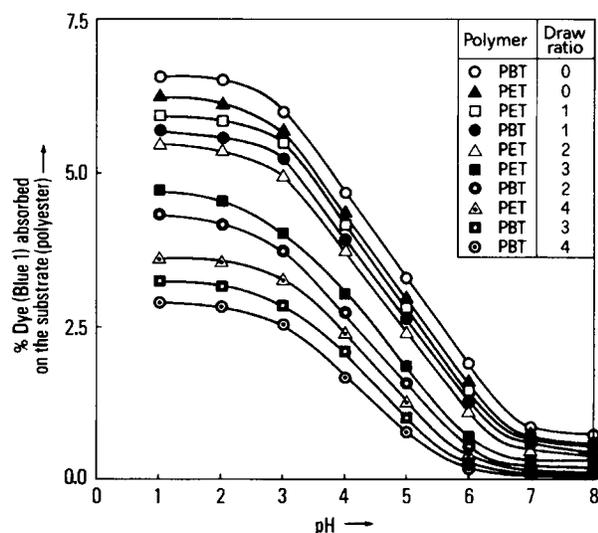


Figure 2 Effect of the pH on the absorption of Blue 1 on PET and PBT previously subjected to various draw ratios at 100°C after 72 h (exposure time).

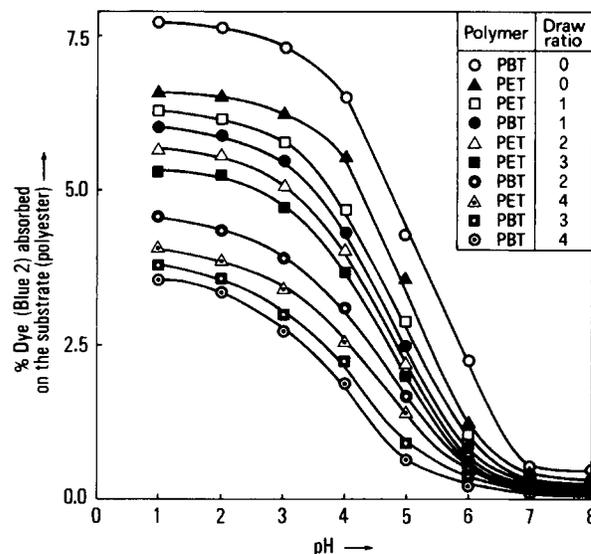


Figure 3 Effect of the pH on the absorption of Blue 2 on PET and PBT, previously subjected to various draw ratios, at 100°C after 72 h (exposure time).

in contact with aqueous solutions.¹⁰ However, a low level of dye absorption is observed for both PET and PBT, especially at high pH's (Figs. 2 and 3). This could be attributed to the following reasons:

- i. Development of hydrogen bonding between the carboxyl and hydroxyl end groups of the polyester fiber and the imino-, alkylimino-, and carboxy-groups of the dye molecules. Table I gives the average carboxyl²¹ and hydroxyl²² end groups of the polyesters involved in this study.
- ii. The benzoic acid present in the dye solution may have a "carrier" action by increasing swelling of the fiber and loosening of the fiber structure⁹ at low pH values (Table II).

The absorption of the dye upon the polyester fiber is favored at low pH values, especially when these are attained with high benzoic acid contents. Figure 4 shows that, if the same pH is attained by both strong and weak acids, it is the latter which promote a greater dye absorption upon the polyester fibers.

Possible action of chlorinated hydrocarbon solvents used recently in the dyeing of "difficult" materials (such as polyesters)²³ has also been studied by adding dichlorobenzene to the dye solution. The use of an organic solvent in the dyeing process for polyester fibers may be considered to be a variant of the carrier dyeing process. Figure 5 shows that the higher the dichlorobenzene content, the higher the percentage of the absorbed dye upon the polyester fiber.

Table I Carboxyl²¹ and Hydroxyl²² End Groups and Percentage Crystallinity (%K) Determined with DSC and Wide-angle X-ray Diffraction Patterns of the Polyester Samples ($x \pm SD$: Average and Standard Deviation Determined from Five Measurements)

	Draw Ratio	Carboxyl End Groups Equiv — COOH/ \bar{M}_n	Hydroxyl End Groups Equiv — OH/ \bar{M}_n	% Crystallinity	
				DSC	X-rays
PET	0	0.45	0.62	0	0
	1	0.43	0.58	3 ± 0.3	4 ± 0.5
	2	0.46	0.61	8 ± 1.0	11 ± 1.3
	3	0.44	0.60	14 ± 1.2	15 ± 1.3
	4	0.45	0.61	19 ± 1.5	23 ± 1.4
PBT	0	0.34	0.49	0	0
	1	0.38	0.50	5 ± 0.4	8 ± 0.9
	2	0.36	0.52	12 ± 1.0	15 ± 1.2
	3	0.35	0.49	20 ± 1.5	22 ± 1.4
	4	0.36	0.50	26 ± 2.1	31 ± 2.2

Correlation Between the Dye Uptake and the Polyester Structure

The observed significant differences at the level of the dye uptake between the PET and the PBT could be attributed to their structural features and, in particular, to flexibility/stiffness of the polymeric chain that can facilitate the access to the dye molecules. PBT has four methylene groups (compared to two of the PET) and it is therefore more flexible than PET. The T_g of amorphous PBT is $\approx 22^\circ\text{C}$,

whereas the T_g of amorphous PET was found to be approximately $65\text{--}69^\circ\text{C}$.^{4,24,25} The level of the absorbed dye upon the PBT fiber was found to be, generally speaking, higher than PET at various temperatures due to the higher accessibility (greater flexibility), higher number of —COOH and —OH end groups, and easier penetration of the PBT network (Figs. 6 and 7). However, in both cases (PET and PBT), the equilibrium was achieved after considerably longer time than that for polyamides, i.e., many hours/days compared to several minutes/hours, thus making clear the greater difficulty that

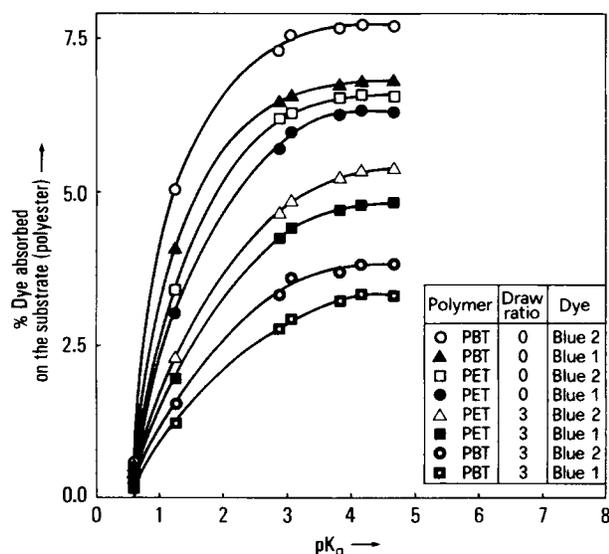


Figure 4 Effect of pK_a (weak/strong acids) on the absorption of dyes (Blue 1 and Blue 2) on PET (draw ratio = 0) and PBT at pH 1, at 100°C after 72 h (exposure time).

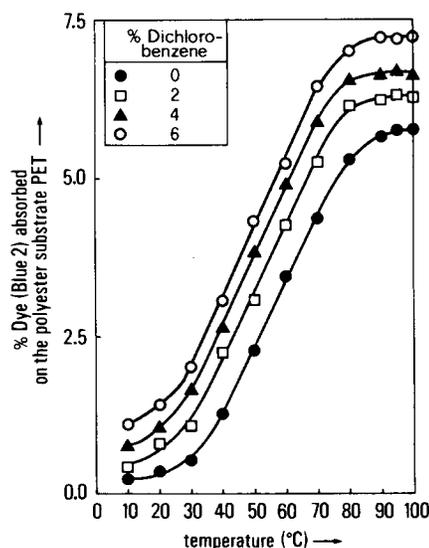


Figure 5 Effect of dichlorobenzene content on the dye (Blue 2) absorption on PBT vs. temperature at pH 1.

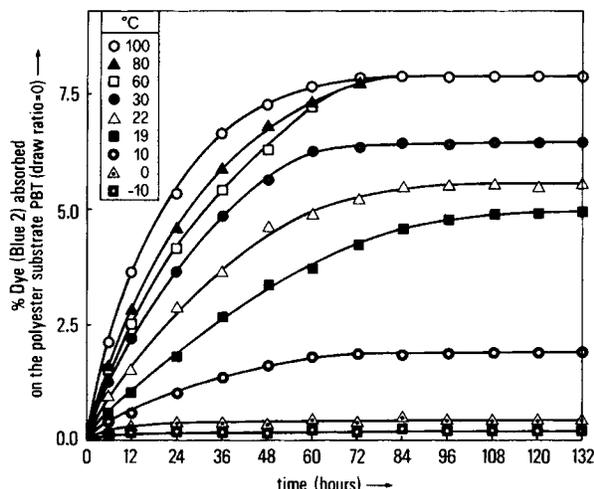


Figure 6 Effect of temperature on the absorption of Blue 2 on PBT (draw ratio = 0) vs. time.

the dye encounters on its migration to the polyester substrate (Figs. 6 and 7).

The percentage crystallinity of the substrate was also studied because it was shown in previous publications that the diffusion of the dye increases in the amorphous regions, whereas it is rather difficult to penetrate in the highly crystalline materials.^{7,10,26,27} In an effort to induce considerable differences in the percentage crystallinity that would enable us to speculate about its effects on the level of absorbed dye, the polyester samples were subjected to various drawing ratios at temperatures higher than their T_g for 72 h. Table I gives the values of the developed percentage crystallinity (%K) with the draw ratio, temperature, and time. Several previous articles have described the orientation distri-

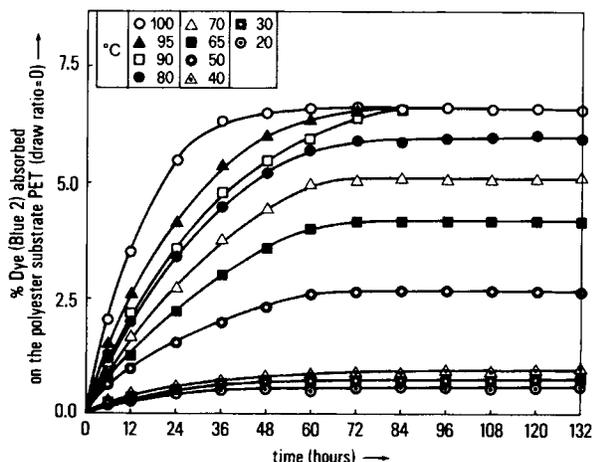


Figure 7 Effect of temperature on the absorption of Blue 2 on PET (draw ratio = 0) vs. time.

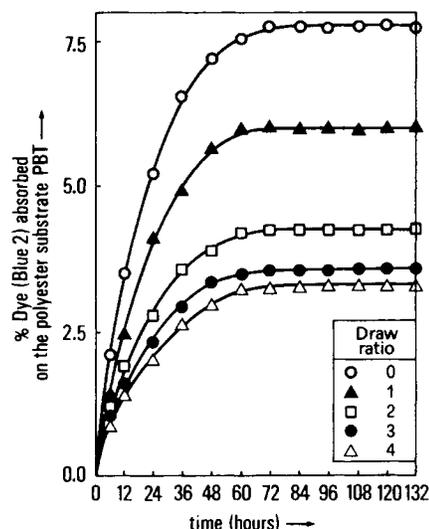


Figure 8 Effect of draw ratio (from 0 to 4) on the absorption of Blue 2 on PBT (at pH 1 and 100°C) vs. time— isothermal absorption studies.

bution of free crystallites in PET.²⁸⁻³⁴ However, paracrystallite formation in uniaxially oriented PET has also been reported including rotation with increasing ratio.³⁵ The influence of the draw ratio on the dye absorption of the polyester substrate is evident from the Figures 8 and 9, which show that the higher the draw ratios and/or the longer the annealing time the lower the amount of the absorbed dye for PET. A comparison between PBT and PET shows that drawing is more effective in the case of PBT, because of its higher $-\text{CH}_2-$ content, thus

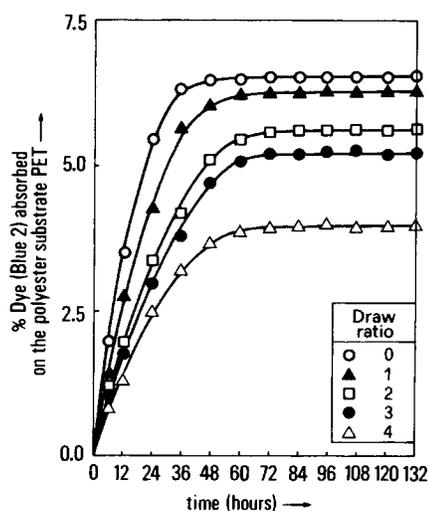


Figure 9 Effect of draw ratio (from 0 to 4) on the absorption of Blue 2 on PET (at pH 1 and 100°C) vs. time— isothermal absorption studies.

resulting in shorter times in higher percentage crystallinities (%K) (Table I). Allomorphs that undergo a unique reversible transformation at low levels of applied stress have been reported for PBT.³⁵ One phase (α) is always present in an unstressed oriented state and transforms to a different phase (β) when the material is stressed, reverting back to the original α -phase when the stress is released.³⁶ This behavior is attributed to a conformational change of the tetramethylene chain from a relaxed *gauche-trans-gauche* to a stretched all-*trans* form and involves a small change in enthalpy and volume. Both phases have been characterized as having a triclinic unit-cell structure.³⁵⁻³⁸ The crystal structure of PET has also a triclinic unit cell that has been determined by wide-angle X-ray diffraction³⁵ (Figs. 10 and 11).

The crystallization kinetics of PBT involve higher rates than that of PET; they do not require nucleating agents³⁹ as in PET (talc, graphite, MgO, calcium benzoate, etc.¹¹), but they have been only partially

investigated.^{40,41} PET crystallizes slowly and therefore is best used for applications where crystallinity and strength can be enhanced through mechanical orientation. On heating amorphous PET above T_g ($\approx 70^\circ\text{C}$), larger crystals and spherulites are formed, resulting usually in brittle samples.⁹ Therefore, the significantly higher dye absorption of PBT (to PET), shown in Figures 12 and 13, could be attributed to its higher crystallization rates, initiated by drawing, resulting in the obstruction of the dye molecules, whereas the same phenomenon is of less importance for the PET because of its lower crystallization rates.

Determination of T_g

The T_g 's may be defined from dyeing experiments as midpoints of the transitions from the nearly undyed state, in which diffusion of the dye molecule

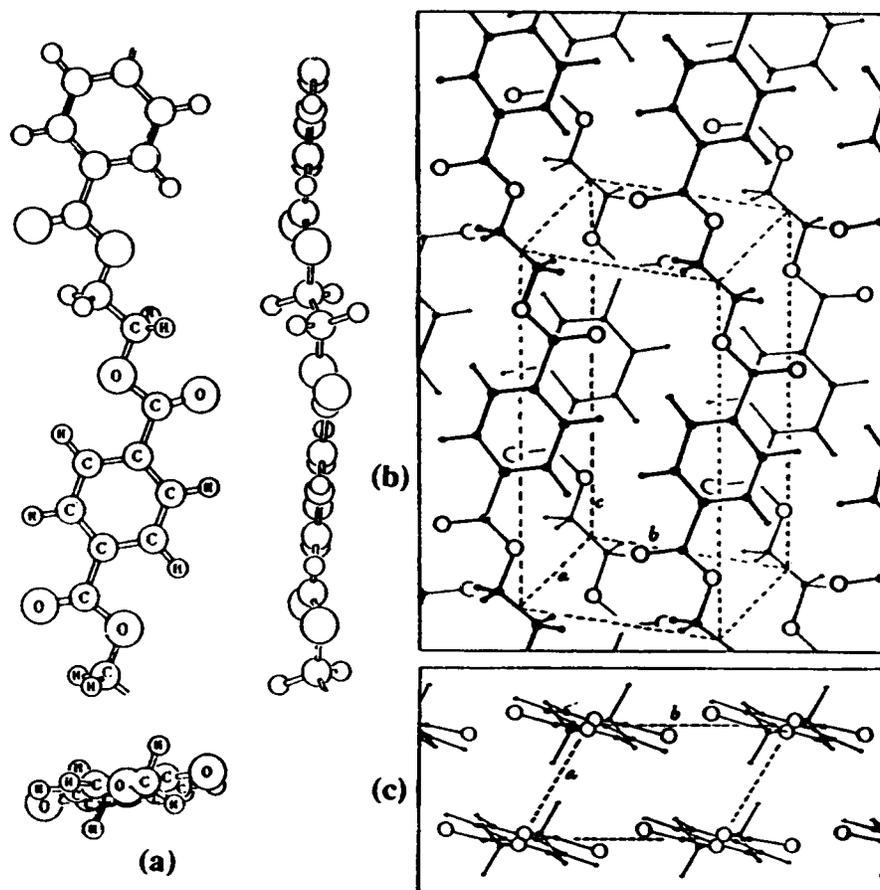


Figure 10 Configuration of PET molecule³³: (a) Arrangement of molecules in crystal: above, projection normal to 010 plane; (b) below projection along c axis (c). Larger dots, carbon; smaller dots, hydrogen; open circles, oxygen.

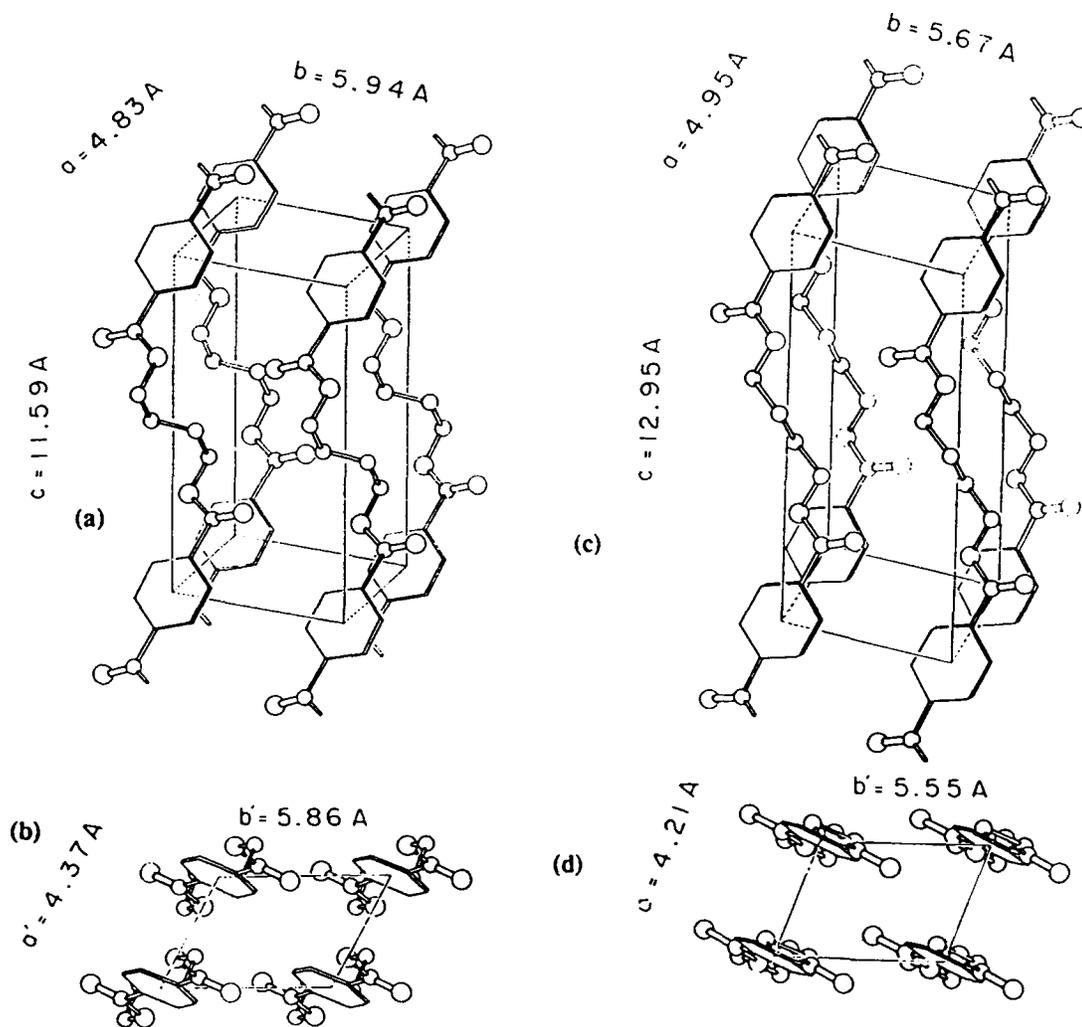


Figure 11 Arrangements of molecules in crystal of the α and β form of poly(butylene terephthalate)³⁶: above, projections normal to the 010 plane for α and β forms [(a) and (c), respectively]; below, projection of α and β crystals along the c axis [(b) and (d), respectively].

through the substrate is extremely slow, to the nearly equilibrium dyed state at which the dye diffusion rates are substantially higher.⁴² However, it should be mentioned that the actual T_g values determined in this way are dependent both on the nature of the dye molecule and on the structural properties of the polyesters. Table III summarizes the T_g values obtained with this method, with DSC and with DMTA measurements. Table III shows that the T_g values obtained from the DSC (midpoint of the change in heat capacity), DMTA (defined as the loss modulus peak), and the dyeing diffusion rates (midpoint of transition) are in satisfactory agreement (differences 2–4°, i.e., deviation 10–15%, which lies within the margin of experimental errors predicted for every

method. The observed increase in T_g with the increase in percentage crystallinity (% K), at various draw ratios, is attributed to the restrictive influence of the developed crystallites on the surrounding noncrystalline (amorphous) material (Table III) and is in agreement with the results of previous investigations on the polyamides,⁴² isotactic polystyrene, poly(ethylene oxide), and poly- ϵ -caprolactone.⁴³ However, exactly the opposite trend was observed (higher draw ratios induced lower T_g 's) for a number of polymers such as isotactic polypropylene and poly-4-methyl-1-pentene among others,^{44–46} which makes apparent the need for further investigation on the effect of annealing and/or draw ratio upon the T_g of polymers.

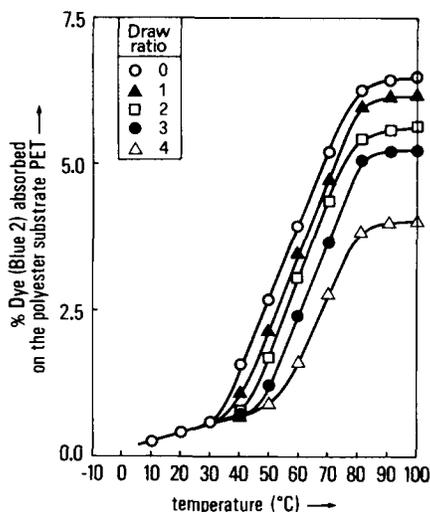


Figure 12 Effect of draw ratio (from 0 to 4) on the absorption of Blue 2 on PET vs. temperature (at pH 1).

Dye Concentration Effects

The influence of the concentration of the dye solutions (Blue 1 and Blue 2) on the dye absorption upon the substrates (PET and PBT) was studied and the results are shown in Figure 14. Figure 14 shows that even at very low dye concentrations (10^{-4} mol/L) the dye uptake for both dyes on the polyester fiber is very low ($\leq 7.5\%$ in most cases). The dye uptake is favored by higher amounts of $-\text{COOH}$ and $-\text{OH}$ end groups as it had happened in previous investigation of polyamides where the end groups were $-\text{NH}_2$ and $-\text{COOH}$ groups.⁷ However, the limited importance of hydrogen bonding

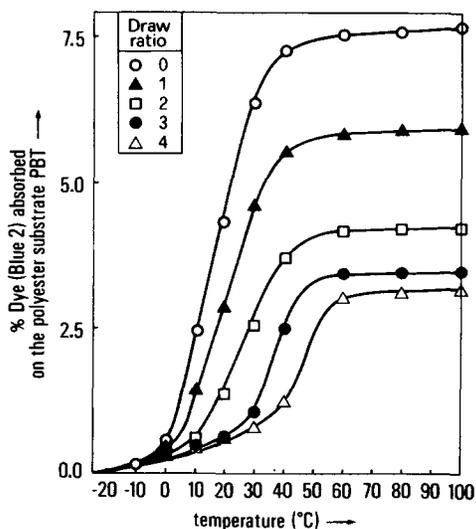
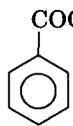
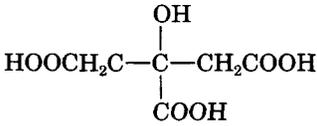


Figure 13 Effect of draw ratio (from 0 to 4) on the absorption of Blue 2 on PBT vs. temperature at pH 1.

Table II Acids Used for the pH Adjustment and their pK_a

Acid	pK_a
CH_3COOH	4.74
	4.2
	3.13
ClCH_2COOH	2.86
Cl_2CHCOOH	1.26
Cl_3COOH	0.64
H_2SO_4	-5.2

for the dye absorption results in the above low dye uptake values on both PET and PBT.

Temperature Effect

The influence of temperature on the dye absorption of the polyesters was studied for Blue 1 and amorphous and semicrystalline PBT and PET (Table IV). Figures 6 and 7 show that the dye absorption increases with an increase in temperature, which is in agreement with the results of similar studies on polyamides.^{5,7,27} At very low temperatures, i.e., -20 ,

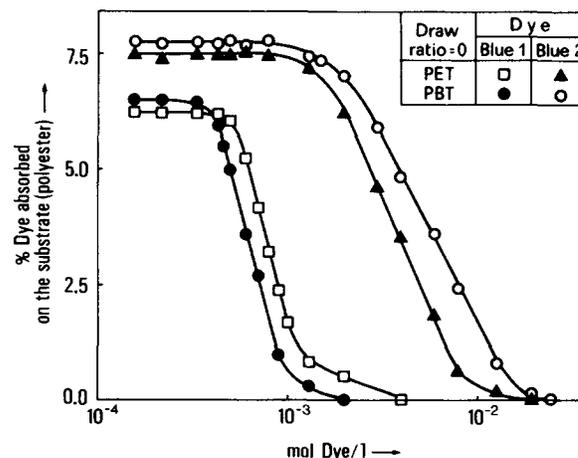


Figure 14 Effect of dye concentration (mol/L) on the absorption of dyes (Blue 1 and Blue 2) on PET and PBT at pH 1, at 100°C and after 72 h (exposure time).

Table III Glass Transition (T_g) Values Determined with DSC, DMTA, and Dyeing Diffusion Rates

Draw Ratio	Glass Transitions (°C)					Dyeing Diffusion Rates
	DSC	DMTA				
		E''^a	E'^b	$\tan \delta^c$		
PET	0	57.5 ± 2.1	60.2 ± 3.2	56.4 ± 1.8	63.2 ± 2.3	60.5
	1	63.0 ± 2.5	62.7 ± 2.1	60.1 ± 2.3	66.8 ± 2.4	64.0
	2	64.3 ± 1.8	65.1 ± 2.4	61.9 ± 2.4	70.3 ± 3.0	66.0
	3	68.1 ± 2.3	70.3 ± 2.5	64.5 ± 2.6	74.8 ± 1.4	69.0
	4	70.2 ± 3.1	72.4 ± 1.9	67.9 ± 2.5	78.9 ± 2.1	71.0
PBT	0	18.6 ± 1.3	20.4 ± 1.8	17.1 ± 2.1	22.8 ± 1.7	19.0
	1	21.4 ± 2.0	24.7 ± 2.1	19.0 ± 1.4	27.9 ± 2.0	23.0
	2	30.2 ± 1.7	28.2 ± 1.5	24.6 ± 1.6	33.5 ± 3.2	30.0
	3	38.7 ± 1.6	39.3 ± 1.4	32.7 ± 2.0	42.4 ± 2.3	40.0
	4	47.9 ± 1.8	48.7 ± 2.0	41.2 ± 1.8	52.3 ± 1.8	50.0

^a E' = storage modulus.^b E'' = loss modulus.^c δ : $\tan \delta = E''/E'$.

-10, and 0°C, there was no measurable dye absorption on the polymer substrate. The effect of temperature on the dye absorption was also studied at different draw ratios for PET and PBT (Figs. 12 and 13). Figure 12 shows that at temperatures < 30°C, Blue 2 uptake on PET is insignificant for all the draw ratios applied, whereas on PBT, even at low temperatures (> 0°C), a slight dye absorption is observed mainly for draw ratios 0-2 (Fig. 13).

Finally, the effect of temperature on the dyeing rate of PET and PBT for the dye Blue 2 was studied and the results are given in Table V. Table V shows that for a given draw ratio half-dyeing time increases with increasing temperature, since the A_∞ values are increasing, as has already been mentioned.

Determination of Dye Absorption Rate

Several hyperbolic and exponential equations have been suggested in the past for determining the

dyeing rates.^{7,27,47-49} However, their applicability to the determination of dyeing rates both for polyamides⁷ and polyesters with Blue 1 and Blue 2 was found to be very limited. Therefore, the determination of half-dyeing time has been suggested as a convenient method for providing numerical values. Half-dyeing time ($t_{1/2}$) is the time required for the fiber to absorb half as much dye as it will absorb in the equilibrium state. The dyeing rate is described in terms of sigmoid time absorption isotherms. The method for describing $t_{1/2}$ and the percentage of absorbed dye (A) was to measure first the equilibrium exhaustion (Figs. 8 and 9) and then to determine from the curve the time at which the $A/2$ absorption

Table IV Half-dyeing Times ($t_{1/2}$) for PET and PBT by Blue 1 at 100°C

PET		PBT	
Draw Ratio	$t_{1/2}$ (h)	Draw Ratio	$t_{1/2}$ (h)
0	11	0	14
1	14.5	1	18.5
2	21	2	20
3	18	3	18.5
4	22	4	23

Table V Half-dyeing Times ($t_{1/2}$, h) for PET and PBT by Blue 2 at Different Temperatures at Draw Ratio = 0

PBT		PET	
(°C)	$t_{1/2}$	(°C)	$t_{1/2}$
-10	5	20	15.0
0	9	30	17.0
10	37.5	40	18.0
19	33.0	60	20.0
22	24.0	65	22.0
30	21.0	70	21.0
60	22.5	80	21.0
80	19	90	22.0
100	13.5	95	16.5
		100	10.5

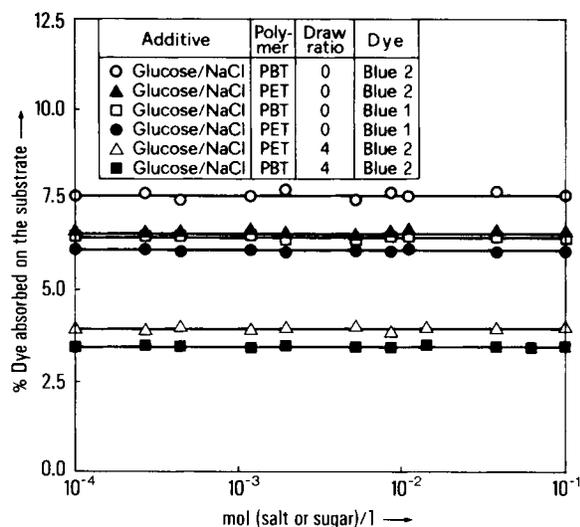


Figure 15 Effect of additives (glucose, sodium chloride) on the absorption of dyes (Blue 1 and Blue 2) on PET and PBT at pH 1 at $T = 100^{\circ}\text{C}$.

occurred. Tables IV and V give the half-dyeing times ($t_{1/2}$) for various draw ratios of PET and PBT. It is evident that the half-dyeing times are longer for high draw ratios (both for PET and PBT), which means that the dyeing rates reach equilibriums lower than the substrates subjected to low draw ratios. Long half-dyeing times ($t_{1/2}$) for high draw ratios could be attributed to the perfection of crystallites both at the levels of molecule and network.

In addition, PBT showed longer dyeing times than did PET both at low and high draw ratios, which could be attributed to the higher amount of end groups in PET and faster development of crystallinity in PBT³⁹ (Table I), respectively.

Effect of Additives

The influence of the addition of a sugar (glucose, sucrose) or a salt (NaCl) solution on the absorption of Blue 1 and Blue 2 was investigated and is shown in Figure 15. No alteration in the dye absorption rate of the polyester (PET and PBT) was observed, as was the case with polyamides⁷ and polycaprolactam.⁵

CONCLUSIONS

Polyester fibers (PET, PBT), which could eventually come in contact with dyes, might present staining problems only after the following conditions:

- amorphous polyesters not previously monoaxially or biaxially drawn or annealed at temperatures above their T_g ;
- pH 1–3;
- high number of $-\text{COOH}$ and $-\text{OH}$ end groups; and
- storage temperatures considerably higher than their T_g 's ($\geq 22^{\circ}\text{C}$ and $\geq 68^{\circ}\text{C}$ for amorphous PBT and PET, respectively).

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