Comparison of Disperse Dye Exhaustion, Color Yield, and Colorfastness Between Polylactide and Poly(ethylene terephthalate)

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ABSTRACT: Ten popular disperse dyes with different energy levels and chemical constitutions were used to compare their exhaustion, color yield, and colorfastness on polylactide (PLA) and poly(ethylene terephthalate) (PET). Only two out of the 10 dyes had exhaustions higher than 80% on PLA at 2% owf. Five out of the 10 dyes had exhaustions less than 50%. All 10 dyes had more than 90% exhaustion on PET, whereas six of them had exhaustions of 98% or higher. There was no obvious pattern as for which energy level or which structure class provided dye exhaustion better than that of others. Although PLA had lower disperse dye exhaustion than that of PET, it had higher color yield. Based on the 10 dyes examined, the color yield of PLA was about 30% higher than that of PET. This means that even with low dye uptake, PLA could have a similar apparent shade depth as that of PET if the same dyeing conditions are applied. Our study supported that the lower reflectance, or reflectivity, of PLA contributes to the higher color yield of PLA than that of PET. A quantitative relation between the shade depth of PLA and PET based on their dye sorption was developed. Disperse dyes examined had lower washing and crocking fastness on PLA than on PET. The differences in class were about 0.5 to 1.0. If the comparison was based on the same dye uptake, the differences might be larger. The differences in light fastness between the two fibers were smaller than that in washing and crocking fastnesses. The light fastness of disperse dyes on PLA is expected to be even better if the comparison is based on the same dye uptake on both fibers. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3285–3290, 2003

Key words: polyesters; dyes/pigments; colorfastness; dispersions; refractive index

INTRODUCTION

Similar to poly(ethylene terephthalate) (PET), polylactide (PLA), or poly(lactic acid), textiles are dyeable with disperse dyes. Like PET, the repeating units of PLA also are connected by ester linkages.

Because the dyeing behaviors of PET and its blends are well known, the comparison of the dyeing properties between PET and PLA will result in a better understanding of the performance of PLA. Such a comparison will provide information on the dyeing and performance properties of blends with PLA. This information will be very helpful for the design and development of final products containing PLA materials.

Some interesting comparisons of PLA and PET are their dye exhaustion, color yield, and colorfastness. Disperse dye exhaustion and colorfastness of some selected BASF dyes (Cheadle Julme, UK) were compared between PLA and PET by Lunt and Bone.[1] All nine dyes examined in their work had exhaustions of 80% or more under the appropriate dyeing conditions. Five of the nine had very similar percentages dye exhaustion to that of PET. However, a study published by Scheyer and Chiweshe[2] showed that seven of nine disperse dyes they studied had exhaustions below 80%, and four of these dyes had exhaustions below 50% at 2% owf (on the basis of fiber weight).

Dye exhaustion is a very important dyeing parameter, not just because it is directly related to dyeing cost and effluent control, but also because it is an indication of colorfastness. We examined 10 disperse dyes from four different dyestuff companies. The selection was based on their popularity, energy levels, and different chemical constitutions. All the dyes have C.I. names. The dye exhaustions on PLA and PET were compared, together with the colorfastness to accelerated home laundering, crocking, and light.

Lunt and Bone[1] stated that medium-energy dyes were the most suitable ones for PLA, based on the work of Scheyer and Chiweshe,[2] and based on their

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own study with selected medium-energy Dispersol and Palanil dyes. The dye exhaustion and colorfastness study of the 10 dyes we selected would provide some information on the effect of energy levels on PLA dyeing.

It was reported briefly that PLA had better color yield than that of PET.[3] Here, color yield means the shade depth based on a certain amount of dye sorption. The explanation was the higher refractive index of PLA than that of PET.

Based on Fresnel's reflection formulas (Feynman et al.[4]), reflectivity, or reflectance, for normal incidence is

$$R = [(n - 1)/(n + 1)]^2 \tag{1}$$

where n is refractive index and R is reflectance, or the fraction of light reflected.

The refractive indices of PLA and PET are 1.45 and 1.58, respectively.[3] From eq. (1), percentages of light reflected from the surface of PLA and PET are about 3.4 and 5.0%, respectively. A smaller fraction of reflected light from the surface of PLA compared to that of PET should make the PLA surface look darker than the surface of PET. However, the calculation is based on the undyed materials.

In this study, the quantitative relationship between the shade depth of PLA and PET, based on their dye sorption, is established. Such a relationship provides information on color matching and color comparison between the two fibers. From this relationship, the contribution of the reflectance of the fibers to the color yield also is discussed.

EXPERIMENTAL

Materials

Both the PLA and PET fabrics were double-knit jersey fabrics with a weight of 0.16 kg/m^2 (4.7 oz/yd^2). The fabrics were made of both filament and staple fiber yarns. The yarn sizes of the filament and the staple were 90 denier and 25 Ne, respectively. Before use, the fabrics were scoured with AATCC Standard Reference Detergent WOB (without optical brightener) according to AATCC Standard Test Method 124.

Ten disperse dyes were selected based on their popularity, pH sensitivity, energy levels, and chemical constitutions. Characteristics of these dyes are summarized in Table I.

TABLE I
Characteristics of Disperse Dyes

Dye	Energy level	Structure class
Disperse Blue 56	Low	Anthraquinone
Disperse Yellow 64	Low	Quinoline
Disperse Yellow 86	Low	Nitrodiphenylamine
Disperse Blue 60	Medium	Anthraquinone
Disperse Blue 73	Medium	Anthraquinone
Disperse Yellow 211	Medium	Monoazo
Disperse Orange 29	Medium high	Diazo
Disperse Blue 79	High	Monoazo
Disperse Red 82	High	Monoazo
Disperse Red 167	High	Monoazo

All dyeing experiments were performed without additional auxiliary chemicals except buffer solution for pH adjustment to evaluate dyeability without external interference. The pH values of the dyebath were adjusted by HAc/NaAc (pH 5). Acetone was used to dissolve dye in samples removed from the residual dye bath, so that measurement of percentage transmission could be performed.

Methods

Fabrics weighing 10.00 g were dyed with 2.00% owf of a disperse dye and a liquor-to-goods ratio of 15:1. The pH used for both PLA and PET dyeings was 5 adjusted by HAc/NaAc. Dyebath pH was measured before and after dyeing and found to be unchanged. Commercial dyes were used directly without further purification. The dyeing was performed in the Launder-Ometer, started at ambient temperature, and then ramped to the dyeing temperature at 2°C/min, and held for 90 min. Holding for 90 min was to exclude the possible effect of dyeing rate on exhaustion. After 90-min holding, dyeing was very close to equilibrium.[5] The dyeing temperatures for PLA and PET were 110 and 130°C, respectively. The temperature for PLA dyeing was recommended by Lunt and Bone[1]; the dyeing temperature for PET was a common PET dyeing temperature in the industry.

Two parallel dyeings were performed at each condition, with the average being reported in this study. At the end of the dye cycle, fabric samples were removed from the canisters and rinsed with cold tap water until no color bleeding was noticed. Fabric samples were centrifuged and air dried at room temperature.

Testing

The dried samples were evaluated for shade depth (K/S value); at the wavelength of the maximum absorbance ($\lambda_{\max}$), using a BYK Gardner spectrophotometer (Columbia, MD), according to AATCC Evaluation Procedure 6. K/S is a function of the reflectance R, as expressed in the following equation:

$$K/S = f(R) = \frac{(1 - R)^2}{2R} \tag{2}$$

Each sample was read in four different areas and the average value was recorded. All samples were read from the back of the fabric for consistency.

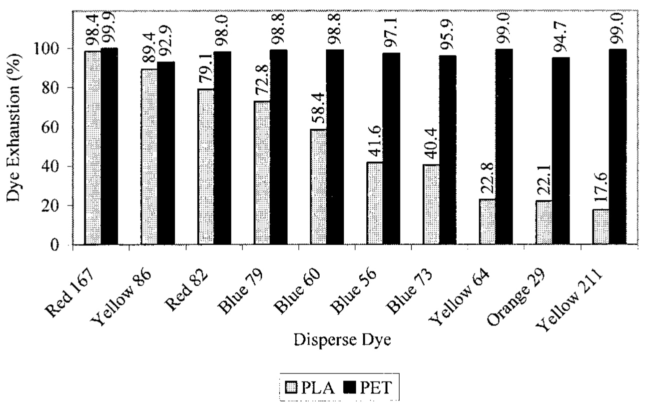

Figure 1 Comparison of % exhaustion of disperse dyes on PLA and PET fabrics. The fabrics were dyed with 2% owf dye at pH 5 with a liquor ratio of 15:1. PLA and PET were dyed at 110 and 130°C, respectively, with the same holding time of 90 min.

Dyebath samples after each dyeing were dissolved in a 50/50 acetone/water solution. The concentration of the dye in the bath was then measured by a spectrophotometer based on the Beer–Lambert law. The calibration curves for all the dyes had $r^2 > 0.9990$. From the concentration change of the dyes in the bath after dyeing, the percentage dye exhaustion was calculated.

Washfastness, crockfastness, and lightfastness tests were conducted according to AATCC Test Methods 61-2A, 8, and 16E, respectively.

RESULTS AND DISCUSSION

Dye exhaustion

Exhaustions of all 10 disperse dyes on both PLA and PET are illustrated in Figure 1. Only two of the 10 dyes, Disperse Red 167 and Yellow 86, had exhaustion values above or close to 90% on PLA, although all 10 dyes had higher than 90% exhaustion on PET. Five out of the 10 dyes had PLA exhaustion values below 50%.

Comparing the dye exhaustion values in Figure 1 and the energy levels and structure classes of the dyes in Table I showed no obvious pattern as to which energy level or which structure class provided the best dye exhaustion. For example, although Disperse Red 167 had a much higher exhaustion value (98%) than that of most of the other dyes and was a high-energy dye, the dye with the second best exhaustion value (89%), Disperse Yellow 86, was a low-energy dye. The medium-energy Disperse Yellow 211 had the lowest exhaustion value among all dyes examined, only 18%. Although three of the four dyes with exhaustion values higher than 70% were azo dyes, the two dyes with the lowest exhaustion values also had azo structures.

The information in Figure 1 and Table I did not provide any useful pattern between dye structural classes and exhaustion values. For example, both Disperse Red 167 and Yellow 211 were azo dyes, but one had the highest and the other had the lowest exhaustion value. A more thorough investigation, considering the detailed chemical structures of the dyes and with more dyes, is perhaps necessary to understand dye affinity to PLA.

Color yield

Color yield is a term used to describe color efficiency. In this study, it is used to describe the shade depths of PLA and PET dyed with a certain dye at a certain dye sorption value. Shade depth is represented by the *K/S* value.

To find the relationship of color yield between PLA and PET, the relationship between the ratio of *K/S*

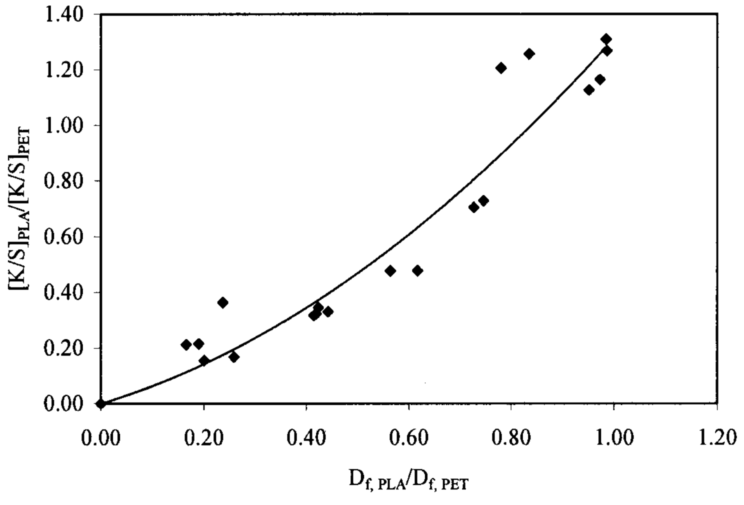

Figure 2 Correlation between shade depth (*K/S*) and dye sorption (D_f) on PLA and PET ($r^2 = 0.9214$).

TABLE II
Colorfastness to Laundering (AATCC Test Method 61-2A)

Disperse dye	% Dye exhaustion (2% owf)[a] (PLA/PET)	Gray scale for color change[a]	Gray scale for staining[a] (PLA/PET)					
			Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
Blue 56	42/97	5/5	2/3	4/4	2/2–3	4/4–5	4–5/5	2–3/4
Yellow 64	23/99	4–5/5	2–3/3–4	4/4–5	2–3/3–4	4/4–5	5/5	4–5/5
Yellow 86	89/93	4–5/5	2–3/2–3	5/5	3–4/4	5/5	5/5	4–5/4–5
Blue 60	58/99	5/5	4/4–5	4–5/5	4/5	5/5	5/5	5/4–5
Blue 73	40/96	5/5	2/3	4/4–5	2/2–3	3/4–5	5/5	3/4
Yellow 211	18/99	5/5	3/3	5/5	3–4/3–4	4–5/5	5/5	4–5/4–5
Orange 29	22/95	5/5	3/3–4	3–4/4	2–3/3	4/5	5/5	4–5/5
Blue 79	73/99	5/5	2–3/3–4	3–4/4	3/3	3–4/4	4–5/4–5	4–5/4–5
Red 82	79/98	5/5	2/2–3	4/4–5	2–3/3	3–4/3–4	4–5/5	3/3–4
Red 167	98/100	5/5	2–3/3	3–4/3–4	2–3/3	3/4	4–5/5	3/4

[a] First part of each value is for PLA and the second part is for PET. For example, color changes of Yellow 86 of 4–5/5 means that the color change of PLA is 4–5 and that of PET is 5.

and the ratio of dye sorption of the two fibers was explored, and is depicted in Figure 2. The correlation between the ratio of K/S and the ratio of dye sorption was obtained from the regression of the data in Figure 2 and expressed in the following equation:

$$\frac{[K/S]_{\mathrm{PLA}}}{[K/S]_{\mathrm{PET}}} = 0.755\left[\frac{D_{f,\mathrm{PLA}}}{D_{f,\mathrm{PET}}}\right]^2 + 0.558\left[\frac{D_{f,\mathrm{PLA}}}{D_{f,\mathrm{PET}}}\right] \quad (3)$$

where D_f is the dye concentration on fabric after dyeing (mg dye/g fabric).

The correlation coefficient r^2 of the data in Figure 2 by eq. (3) was 0.9214, indicating a satisfactory fit of the equation to the experimental results.

Equation (3) could be used to estimate the dye uptake required on PLA for the development of the same shade depth as that of PET if the dye sorption on PET is known. This is useful for the development of a dyeing recipe for PLA if the recipe for PET is known. Using eq. (3) could save some work in color matching for PLA-containing materials.

From eq. (3), the color yield of PLA compared to that of PET also could be estimated. Assuming that the dye sorption on PLA is the same as that on PET, eq. (3) reduces to

$$[K/S]_{\mathrm{PLA}} = 1.313[K/S]_{\mathrm{PET}} \quad (4)$$

This means that color yield on PLA is about 30% higher than on PET. Although disperse dye exhaustion on PLA is lower than that on PET, eq. (4) indicates that the apparent shade depth of PLA should be comparable to that of PET.

Shade depth of a dyed fabric is a function of the reflectance of the fabric $f(R)$, as expressed in eq. (2). The reflectance of the dyed fabric is a function of the reflectance of the fiber; the amount of the sorbed dyes; the structure of the dye agglomerates on the fiber; the dye distribution in the fiber; and, of course, the fiber, yarn, and fabric structures. Therefore, the main difference between the color yields of PLA and PET should be from these differences. The contribution of a lower reflectance of PLA (3.4%) than of PET (5.0%) to the high color yield can be calculated as follows:

$$\frac{f(R)_{\mathrm{PLA}}}{f(R)_{\mathrm{PET}}} = \frac{[(1-R)^2/2R]_{\mathrm{PLA}}}{[(1-R)^2/2R]_{\mathrm{PET}}} = \frac{[(1-0.034)^2/2\times 0.034]}{[(1-0.050)^2/2\times 0.050]} \approx 1.52 \quad (5)$$

This means that if all the other factors are identical, PLA should look 50% darker than PET. Equation (4) indicates only a 30% difference in shade depth. The 20% deficit from the calculation based on pure PLA and PET , and the actual measurement of the dyed fabrics was possibly the result of differences of the two fibers in dye distribution, the physical structures of the dye particles, and the fiber, yarn, and fabric structures. Based on the calculations, it is probably appropriate to say that the lower reflectance or reflectivity value of PLA than that of PET contributes to the higher color yield of PLA.

Colorfastness

Colorfastness to accelerated home laundering is compared in Table II. Listed with the colorfastness ratings are the percentage dye exhaustion, given that the colorfastness rating is directly related to the amount of dyes sorbed on the test fabrics. As shown in Table II, except for Disperse Blue 60, all the other dyes examined had 0.5 to 1.0 class lower fastness to staining for PLA than for PET. Considering the much lower dye sorption on PLA than on PET, for many dyes examined, the colorfastness for PLA would be even lower if the comparison was based on the same dye sorption. Table II also indicates that the medium-energy dyes (cf. Table I) were not necessarily better than the high- or low-energy dyes, with respect to either the dye exhaustion or colorfastness to laundering.

The data presented in Table II are from the fabrics rinsed only with water after dyeing. Our study also indicated that reduction-cleaning could effectively improve the washfastness of PLA. An improvement of 0.5 to 1.5 classes is achievable if appropriate reduction-cleaning is applied. Detailed research on this topic will be discussed in a separate study.

Colorfastness to crocking of PLA and PET is compared in Table III. Crockfastness of the disperse dyes on PLA was much better than washfastness, although there were still 0.5 to 1.0 class lower crockfastness of PLA than of PET for five of the 10 dyes. The other five dyes that had the same crockfastness on PLA as on PET were the ones that had 40% or less dye exhaustion values. It is very possible that these dyes will have lower crockfastness on PLA than on PET if the comparison is based on the same dye exhaustions.

Colorfastness to light of disperse dyes on PLA and PET is compared in Table IV. Five of the 10 disperse dyes had 0.5-class lower lightfastness on PLA than on PET. Four of the 10 dyes had the same lightfastness on both fibers. Only Disperse Orange 29 had a much lower lightfastness on PLA (Class 5) than on PET (Class 8). Different from most of the colorfastnesses, lightfastness increased with increasing dye concentration on the fabric. One of the reasons of the very low light fastness of Disperse Orange 29 on PLA was perhaps attributable to the much lower dye exhaustion on PLA (22%) than on PET (95%). However, the dye concentration on the fabric should not be the only reason for the relatively low lightfastness of some disperse dyes on PLA. For example, Disperse Yellow 211 had only 18% exhaustion on PLA, but 99% exhaustion on PET. The lightfastness of the dye was very similar on both fibers, Classes 8–9 for PLA and 8 for PET. The interaction between the dye and fiber, the distribution of the dye in the fiber, and the dye crystallization and agglomeration all play important roles in lightfastness.

TABLE III
Colorfastness to Crocking (AATCC Test Method 8)

Disperse dye	% Dye exhaustion[a] (2% owf) (PLA/PET)	Gray scale rating for dry crockfastness[a] (PLA/PET)	Gray scale rating for wet crockfastness[a] (PLA/PET)
Blue 56	42/97	4–5/4–5	4/4
Yellow 64	23/99	4–5/4–5	4/4
Yellow 86	89/93	4–5/5	4–5/5
Blue 73	58/99	4–5/5	4/4–5
Blue 60	40/96	4–5/4–5	4–5/4–5
Yellow 211	18/99	4–5/4–5	4–5/4–5
Orange 29	22/95	4–5/4–5	4/4
Blue 79	73/99	4–5/5	4–5/4–5
Red 82	79/98	4/4–5	3–4/4–5
Red 167	98/100	4–5/4–5	3–4/4–5

[a] First part of each value is for PLA and the second part is for PET. For example, a gray scale rating of Yellow 86 of 4–5/5 means that the crocking fastness of PLA is 4–5 and that of PET is 5.

TABLE IV
Colorfastness to Light (AATCC Test Method 16E)

Disperse dye	% Dye exhaustion (2% owf)		Colorfastness to light	
	PLA	PET	PLA	PET
Blue 56	42	97	6	6
Yellow 64	23	99	5	5
Yellow 86	89	93	5–6	7
Blue 73	40	96	4–5	5
Blue 60	58	99	8	8
Yellow 211	18	99	8–9	8
Orange 29	22	95	5	8
Blue 79	73	99	4–5	5
Red 82	79	98	5–6	6
Red 167	98	100	5–6	5–6

CONCLUSIONS

Based on the dyes examined, PLA had relatively lower disperse dye affinity than did PET. Only two out of the 10 dyes had exhaustion values higher than 80% on PLA at 2% owf. Five of the 10 dyes had exhaustion values less than 50%. All dyes had more than 90% exhaustion on PET, with six of those having exhaustions of 98% or higher. There was no obvious pattern as to which energy level or which structure class provided better dye exhaustion.

PLA had higher color yield than that of PET. Based on the regression study of all dyes examined, the color yield of PLA was about 30% higher than that of PET. Lower reflectance, or reflectivity of PLA, contributed to the higher color yield of PLA than of PET. This means that, although PLA may have lower dye uptake, it can still be dyed with the similar apparent shade depth to that of PET. A quantitative relation between the shade depth of PLA and PET and their dye sorption was developed.

Colorfastness to accelerated home laundering indicated that PLA had lower washfastness than that of PET. Compared at the same 2% owf, washfastness of disperse dyes on PLA was about 0.5 to 1.0 class lower than that on PET.

Crockfastness of PLA was closer to that of PET than washfastness. Five of the 10 dyes had their crockfastness 0.5 to 1.0 class lower on PLA than on PET. If the comparison was based on the same dye uptake rather than the same initial dye concentration, the crocking fastness on PLA probably would be worse.

Colorfastness to light of PLA was very close to that of PET. Five of the 10 dyes had 0.5-class lower lightfastness on PLA than on PET. Four of the 10 dyes had the same lightfastness on both fibers. Only Disperse Orange 29 had a substantially lower light fastness on PLA (Class 5) than on PET (Class 8).

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