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Dyes and Pigments 70 (2006) 251–258
DYES and PIGMENTS
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Effect of D-isomer concentration on the coloration properties of poly(lactic acid)

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Received 24 April 2005; accepted 18 May 2005
Available online 9 August 2005

Abstract

Poly(lactic acid) (PLA) fibre is derived from annually renewable crops, it is 100% compostable and its life cycle potentially reduces the earth's carbon dioxide level. In this work PLA fabrics containing variable concentrations of the D- and L-isomers have been studied to ascertain their dyeability, the characteristics of those dyed polymers, and their subsequent performance and properties. Comparison of poly(lactic acid) fabrics with varying D-isomer content revealed differences in melting temperature; by virtue of a higher D-isomer concentration, 'high D-' fibres have greater fibre entropy which causes a decrease in melting temperature. As a result of greater fibre entropy, high D- fibres have more amorphous and less crystalline regions in the polymer, with respect to low D- fibres, hence, high D- fabrics display greater dye exhaustion and colour strength in comparison with their low D- counterpart in all dyes and all concentrations. In application of a dye mixture for a black shade, high D- fibres are able to be dyed to an excellent black shade, whereas low D- fibres appear very brown, due to lower exhaustion of the blue component of the mix. In terms of wash fastness, there is very little difference between high D- fibres and low D- fibres; this is because the glass transition temperature for both fibres is very similar.

Keywords: Poly(lactic acid); Coloration; Isomer; Entropy; Melting temperature; Amorphous

1. Introduction

Poly(lactic acid) (PLA) is a linear aliphatic thermoplastic polyester derived from 100% annually renewable sources such as corn and sugar beet; the polymer is compostable [1,2]. However, most initial uses were limited to biomedical applications such as sutures [3] and drug delivery systems [4], due to availability and cost of manufacture. More recently, NatureWorks LLC (USA) has developed large-scale operations for the economic production of PLA polymer used for packaging and fibre applications. It is important that such fibres are used in fabric for apparel applications for several reasons: polyesters currently used for apparel applications, mainly poly(ethyleneterephthalate) (PET), account for over 40% of world textile consumption (second only to cotton) and their use is constantly increasing; production of such polyesters consumes fossil fuel resources and disposal of the polymer adds to landfill sites as they are non-biodegradable and are not easily recycled; PLA fibre is derived from annually renewable crops, it is 100% compostable and its life cycle potentially reduces the earth's carbon dioxide level.

PLA is produced through the milling of an annually renewable resource, such as corn, separating starch, from which dextrose is processed and then subsequently

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0143-7208/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2005.05.011

converted to lactic acid through fermentation [5,6]. Chemically synthesized lactic acid gives the racemic mixture (50% D- and 50% L-), however, fermentation is very specific, allowing the production of essentially one major stereoisomer; fermentation derived lactic acid consists of 99.5% of the L-isomer and 0.5% of the D-isomer. The polymer is formed either by direct condensation of lactic acid or via the cyclic intermediate dimer (lactide), through a ring opening process (Fig. 1) [2]. The production of PLA uses 20–50% less fossil resources than comparable petroleum-based fibres [6]. Lactic acid can exist in two optically active forms L-lactic acid and D-lactic acid, and production of the cyclic lactide dimer results in three potential forms: the D,D-lactide (called D-lactide), L,L-lactide (called L-lactide) and L,D- or D,L-lactide (*meso*-lactide) [7] (Fig. 2). *Meso*-lactide has different properties from D- and L-lactide; D- and L-lactide are optically active, *meso*- is not. Before polymerization, the lactide stream is split into a low D-lactide stream and a high D-/*meso*-lactide stream. Ring-opening polymerization of the optically active types of lactide can yield a 'family' of polymers with a range of molecular weights by varying the amount and the sequence of D-lactide in the polymer backbone. Polymers with high L-lactide levels can be used to produce crystalline polymers, while the higher D-lactide materials (>15%) are more amorphous. By controlling the purity of the lactide it is possible to produce a wide range of molecular weights and by varying the amount and sequence of D-lactic units in the polymer backbone, the product properties can be changed [2]. Furthermore, production of a melt blend containing high proportions of both the D- and L-isomer can produce a PLA stereocomplex that has a significantly higher melting point than the standard D- or L-polymers alone [7], which has application where an elevated melting point is required.

Fischer et al. [8] studied the effects of the D/L composition on the polymer crystallization using PLA polymers consisting of a wide range of D/L ratios or varying optical purity (OP) of the lactic acid units. Tsuji and Ikada [9] reported that the crystallinity and melting temperature (T_m) of PLA lowered with decreasing OP while the glass transition temperature (T_g) was not significantly affected. The degree of crystallinity of fabrics depends on many factors, such as molecular weight, thermal and processing history, and temperature and time of annealing treatments [10–13].

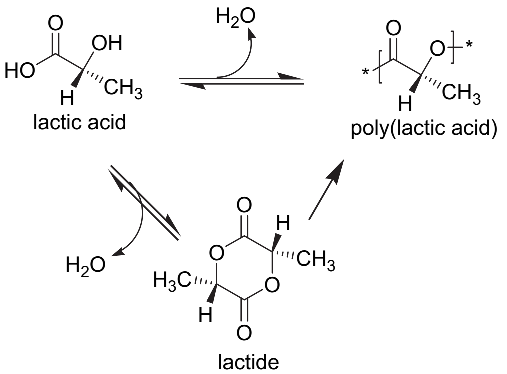


Fig. 1. Polymerisation routes to poly(lactic acid).

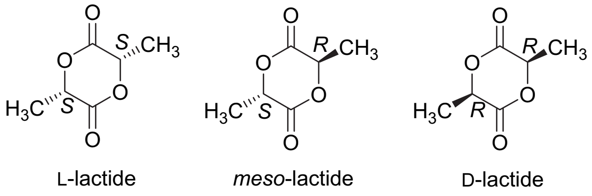


Fig. 2. Dimeric lactide isomers.

It is very important that, as the use of polyesters is increasing rapidly, the dyeability of a compostable fabric derived from renewable resources is understood; if a dyed fibre such as PLA can be used for apparel (and other undyed applications such as nonwovens, fibrefill, furnishings and industrial textiles), it will ease the pressure on fossil fuel resources and landfill sites. In order for PLA fibres to be substituted for PET and other aromatic fibres an improved understanding of dyeing behaviour is required, since the main applications in textiles require coloration. Some work has been carried out and fibres of poly(lactic acid) have been successfully dyed with disperse dyes [2,7,14–16], but there are very little data available on the effects of OP (D/L ratio) on dyeing behaviour.

Commercial Ingeo™ (Ingeo is a trademark of NatureWorks LLC) fabrics mainly comprise L-lactide, with a small concentration of the D-isomer blended to reduce crystallinity and improve processing. In this work commercial poly(lactic acid) fabrics containing two different D- and L-isomer ratios have been studied to ascertain their dyeability, the characteristics of those dyed polymers, and their subsequent performance and properties.

2. Experimental

2.1. Materials

Six poly(lactic acid) fabrics (Table 1; a–f) from different manufacturing sources were supplied (all PLA resin was supplied to the manufacturers by NatureWorks LLC). Two levels of D-isomer concentration were used in this study (1.4% and 2.0%), these being the two current commercial forms of the resin available to fibre manufacturers. Samples of the disperse dyes *Dianix Blue XF* (*BXF*) (C.I. Disperse Blue 284; **1**, see Scheme 1, *Dianix Yellow Brown XF* (*YBXF*) (C.I. Disperse Brown 19) and *Dianix Deep Red SF* (*DRSF*) were supplied by DyStar. Dyeing auxiliaries *Levegal DLP* (leveling agent)

Table 1
DSC results of PLA fibres a–f

Fabric	Construction	D-isomer content (%)	T_m[a] (°C)	ΔH_m[a] (J g^{-1})	T_g[b] (°C)
a	Spun jersey	1.4	171.06	50.85	62.75
b	Spun jersey	2.0	165.46	45.88	61.71
c	Filament	1.4	170.88	47.68	63.29
d	Filament	2.0	165.34	52.03	61.06
e	Spun interlock	1.4	169.62	48.88	62.09
f	Spun interlock	2.0	164.55	51.16	60.91

[a] From first scan.
[b] From second scan inflection point.

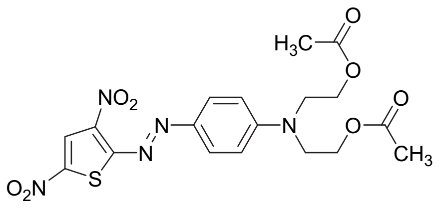
and *Ludigol AR* (anti-reducing agent) were supplied by Lanxess and BASF, respectively. All other chemicals were of general laboratory grade supplied by Aldrich.

2.2. Dyeing process

Fabric samples (5 g) were dyed in a laboratory-scale *Roaches Pyrotec 2000* dyeing machine in stainless steel, sealed dye pots, using a liquor:fibre ratio (LR) of 10:1, according to the recommended method by the dye manufacturer (Fig. 3) [17]. The six fabrics a, b, c, d, e and f were dyed with *BXF*, *YBXF* and *DRSF* at concentrations of 1%, 3% and 5% omf (on mass of fibre), respectively. A recipe recommended by DyStar for a black shade (*Dianix Blue XF* 3.64% omf and *Dianix Yellow Brown XF* 1.98% omf) was also used on each fabric. Prior to dyeing, all fabrics were scoured using 2 g dm^{-3} sodium carbonate and 1 g dm^{-3} non-ionic detergent using a 20:1 liquor ratio at 60 °C for 15 min. Reduction clearing was carried out after dyeing using 1.5 g dm^{-3} sodium carbonate and 2 g dm^{-3} sodium hydrosulfite using a 20:1 liquor ratio at 60 °C for 15 min.

2.3. Colour measurement

After drying, samples were measured using a *Datacolor SF600 Spectraflash* colour spectrophotometer connected to a personal computer using *DCI Colour Tools* software. From reflectance values (R) at a specified wavelength (λ) of the dyeings, the colour strength (K/S) of the sample was calculated using the Kubelka–Munk equation (Eq. (1)) [18].



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Scheme 1.

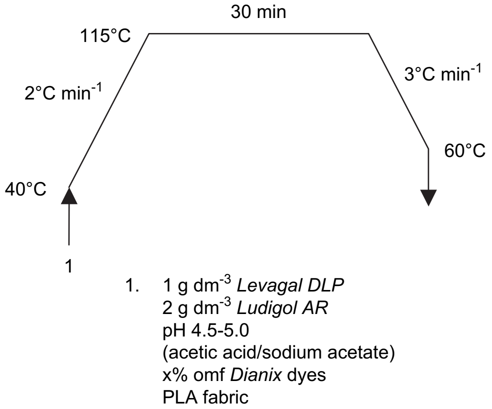

Fig. 3. DyStar recommended dyeing method for Dianix dyes on PLA.

$$K/S = \frac{(1 - R_\lambda)^2}{2R_\lambda} \quad (1)$$

The colour strength function, f_k, is the sum of weighted K/S values in the visible region of the spectrum and was developed to give a better correlation between measured and visual assessment. The f_k value is calculated using Eq. (2), where $\bar{x}_{10,\lambda}$, $\bar{y}_{10,\lambda}$ and $\bar{z}_{10,\lambda}$ are the colour matching functions for the 10° standard observer at each wavelength measured.

$$f_k = \sum_{\lambda=400}^{\lambda=700} (K/S)_\lambda \left[\bar{x}_{10,\lambda} + \bar{y}_{10,\lambda} + \bar{z}_{10,\lambda}\right] \quad (2)$$

2.4. Wash fastness testing

After dyeing the samples were subjected to the ISO 105: C06/B2S wash test [19] (50 °C) using SDC multifibre fabric as adjacent multifibre strips were visually assessed using grey scales according to the ISO 150: A03 test protocols [19] to determine the degree of cross-staining. The grey scale ranges from 5 for no staining, down to 1 for a severe staining, with half points in between.

2.5. UV/visible spectrophotometry

The exhausted dyebaths were measured using a *Perkin–Elmer Lambda 9* UV/Visible/NIR spectrophotometer in the visible region of the spectrum (400–700 nm), at 20 nm intervals. Concentrations were calculated from calibration graphs at the wavelength of maximum absorption (λ_{max}). The residual dye solution was diluted using 50/50 v/v acetone/water and measured at λ_{max} and percentage dyebath exhaustion (E%) calculated using Eq. (3), where A_0 and A_1 represent absorbance of dye solution before and after dyeing, respectively.

No difference in the shape of the absorption spectrum before and after dyeing was noted.

$$E\% = 100\left(1 - \frac{A_1}{A_0}\right) \tag{3}$$

2.6. Differential scanning calorimetry

The melting temperature (T_m), the enthalpy of crystal fusion (ΔH_f) and glass transition temperature (T_g, DSC) of the polymers were determined by Differential Scanning Calorimetry (DSC) on a *TA Instruments Thermal Analysis 2000 System* and *910 Differential Scanning Calorimeter* cell base. The DSC cell was calibrated with indium; heating rate, 20 °C min^{-1}; nitrogen atmosphere at 50 $\text{cm}^3\,\text{min}^{-1}$; sample size 4–6 mg. The as received sample was heated to 200 °C in the first scan and rerun after quenching in the second scan, under the same conditions. T_m (the major peak melting point) and ΔH_f were determined from the first scan, while T_g (inflection point of the glass transition step) was determined from the second scan.

3. Results and discussion

3.1. Thermal properties

The melting curves for all the six samples (as received) are shown in Fig. 4 and thermal analysis data tabulated in Table 1. As expected, the D-isomer content affects the melting temperature, T_m. Fabrics with the higher D-isomer content b, d and f have a lower T_m (around 165 °C) than the lower D-isomer a, c and e (170–171 °C).

This can be explained by the first law of thermodynamics. The free energy of fusion of the polymer, ΔG_m, can be expressed as:

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{4}$$

where ΔH_m and ΔS_m are the enthalpy and entropy of fusion, respectively. At the equilibrium melting temperature (T_m°), $\Delta G_m = 0$ and, therefore:

$$T_m^{\circ} = \frac{\Delta H_m}{\Delta S_m} \tag{5}$$

By virtue of a higher D-isomer concentration, 'high D-' fibres have greater fibre entropy (greater disorder), hence, by application of Eq. (5), an increase in entropy causes a decrease in melting temperature; this was observed experimentally.

It can also be observed from Fig. 4 that all the samples show a double melting behaviour at the peak temperatures (T_m). This two-peak endothermic melting event is quite common in fibres due to processing conditions, several papers have been published on this [20,21]. Mezghani et al. found that high speed melt spinning of PLA produced fibres with a double melting peak; they proposed that this was due to the presence of two different populations of crystals in the filaments with the second possibly being formed during heating in the DSC scan. Another possibility for the double peak is that a different additional crystalline form is produced during final heat treatment (heat setting) of the fabric. In order to establish if this is the case, an attempt was made to reproduce sample heat treatments and show how this can influence the shape of a DSC scan. Separate samples of fabric b (2.0% D-isomer) were heated to 200 °C and held for 2 min, then cooled down at 5 K min^{-1} to 20 °C (to produce semi-crystalline samples as in the case of fibres). The different samples were then annealed at 135 °C, 140 °C and 145 °C for 2 min in a pre-heated DSC cell, cooled and rescanned (Fig. 5). The sample heat treated at 145 °C shows a shoulder very similar to the as received fabrics, indicating that PLA fabrics used in this study could have been heat treated at this temperature.

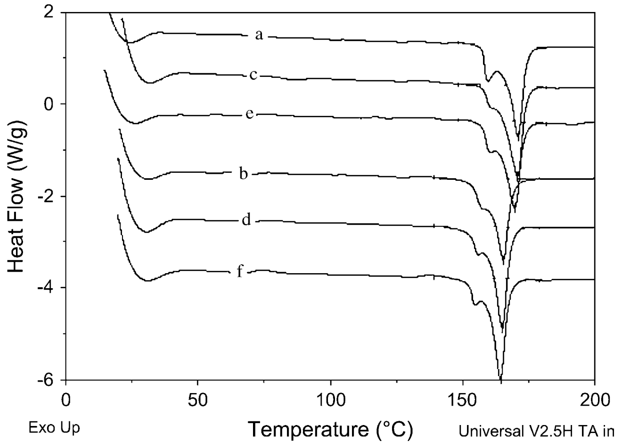

Fig. 4. DSC heating curves of fabrics a–f.

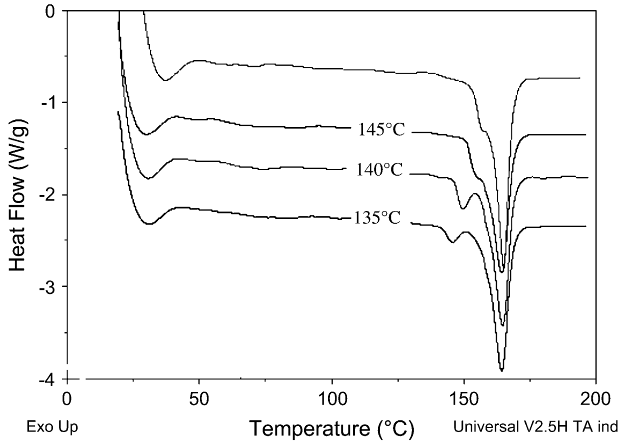

Fig. 5. Annealing experiment of high D-isomer (original sample b top curve).

Typically, DSC scans of quenched samples (Fig. 6) show a glass transition step (T_g) "cold" crystallization [20,21] and melting. From the quenched scans of the samples, it appears that the T_g of low D- fabrics are slightly higher than high D- fabrics by about 1–2 °C. There are different reports about T_g changing with optical purity; Tsuji and Ikada [9] pointed out that T_g does not change very much with the change in D-isomer content; both Fukuzaki et al. [22] and Urayama et al. [23] reported that T_g became higher with increased OP. In our work, due to very small difference in D-isomer content (only 0.6%), the slight T_g change tends to support Fukuzaki and Urayama's opinion, but the difference is so small that no strong conclusion can be made.

3.2. Dye exhaustion and colour yield

Exhaustion (E%) and colour strength (f_k) data for the dyeings on the six fabrics are shown in Figs. 7 and 8, respectively; in general it is observed that as application concentration increases E% decreases for the different dyes used. However, there are differences in the magnitude of the decrease; with *BXF*, E% decreases significantly as application increases for all fibres, whereas dyeings with *YBXF* vary little with increasing concentration, and the exhaustion decrease for *DRSF* is intermediate between the two extremes. We propose that these observations are related to the affinity of the dye for the fibre; PLA is a hydrophobic fibre, hence, dyes with greater hydrophobicity have higher affinity for the fibre. It is known that *YBXF* is very hydrophobic, *DRSF* in moderately hydrophobic, and *BXF* is relatively hydrophilic [24], hence explaining the observed differences in fibre exhaustion with increasing application concentration.

From the data, it is observed, in general, that high D- fabrics (b, d and f) have higher E% with respect to low D- fabrics (a, c and e) for all dyes and at all concentrations. It was noticed that high D- fabrics have significantly higher E% than low D- fabrics when dyeing with *BXF*, particularly when higher concentrations were employed, but this effect is not as pronounced when dyeing with *YBXF*; intermediate trends are observed for dyeings with *DRSF*. Dyes only diffuse into the amorphous regions of polymer substrates to which they are applied, hence, these observed differences in dye exhaustion for the two PLA fibre types can be explained in terms of the proportion of amorphous regions in the fibre. It would be expected that as D- content increased the crystallinity of the polymers would decrease, as the D-isomer content would create greater disorder and, hence, a greater proportion of amorphous regions. This increase in the amorphous regions in the high D- fibres leads to greater dye exhaustion, compared to the low D- fibres.

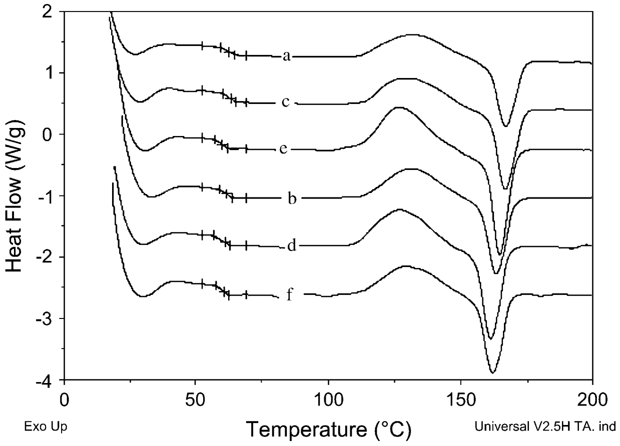

Fig. 6. Quenched samples showing T_g.

What is very interesting to note is that at a concentration of 3% omf *BXF*, the high D- fabrics (b, d and f) have nearly double E% in comparison with low D- fabrics (a, c and e). At 5% omf all exhaustions decreased to a very low degree. The observed differences are related to the polymer microstructure; disperse dyes will only diffuse in areas of free volume between polymer chains in the amorphous regions [25], hence, the significant variation in E% between high D- and low D- fibres for *BXF* (when E% difference for *YBXF* is very small) must be related to the relative sizes of the adsorbing and diffusing species (the dye) and the free volume available. Because this is observed markedly for *BXF*, this may be explained by the proposal that *BXF* dye molecules aggregate in solution when the application concentration is around 3% omf. It seems that 3% omf is a critical value and at this concentration the aggregated *BXF* dyes are able to diffuse into high D- fibres due to greater free volume in the amorphous regions in the fibre, as a result of the greater disorder caused by a higher D-isomer content, but are unable to diffuse as easily into the low D- fibres. At 5% omf *BXF* the E% for both high and low D- fibres is reduced through a combination of aggregation and the hydrophilicity of the dye molecules. Theory of PET coloration [25] teaches that only monomolecular disperse dye may diffuse into a thermoplastic polymer, and this is contrary to the proposals made here. However, the authors believe that it may be possible to achieve adsorption and diffusion of dimers, trimers, etc., of disperse dyes into PLA, which may explain the theories proposed. As a result, further research, including a detailed thermodynamic and kinetic study on the dyes used, is currently being conducted to explain the observed phenomena.

Colour strength (f_k) is compared in Fig. 8 and the trends are similar to E%, due to the fact that f_k is directly proportional to E%; high D- fibres have higher f_k values than low D- fibres. It is worth noting that high D- fibres dyed with 3% *BXF* do not show as much

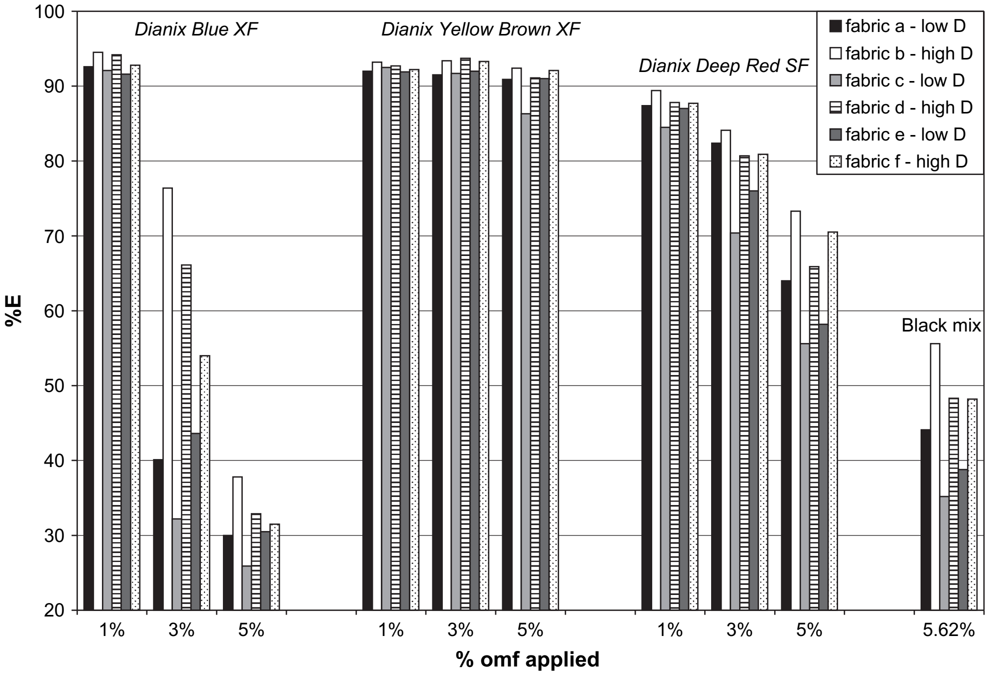

Fig. 7. Comparisons of exhaustions among six PLA fabrics of varying D-Isomer content.

difference in f_k values versus low D- fibres as the differences in $E\%$. This may be because the *BXF* that has diffused is in an aggregated form, which would result in a reduction in colour strength as aggregated dye particles show less interaction with light in comparison with single molecules; this is also currently being investigated.

The dye mixture for black comprises 3.64% omf *Dianix Blue XF* and 1.98% omf *Dianix Yellow Brown XF*. The high concentration of *BXF* in the recipe explains why the $E\%$ for the black is relatively low on all fabrics. What is more interesting is that high D- fibres are able to be dyed to an excellent black shade, whereas low D- fibres appear very brown. This can be explained by the examination of the full colour strength spectrum of the black recipe on the two fibres (Fig. 9). High D- fibres show higher colour strength in the range from 560 to 600 nm, as a result of a higher adsorption of

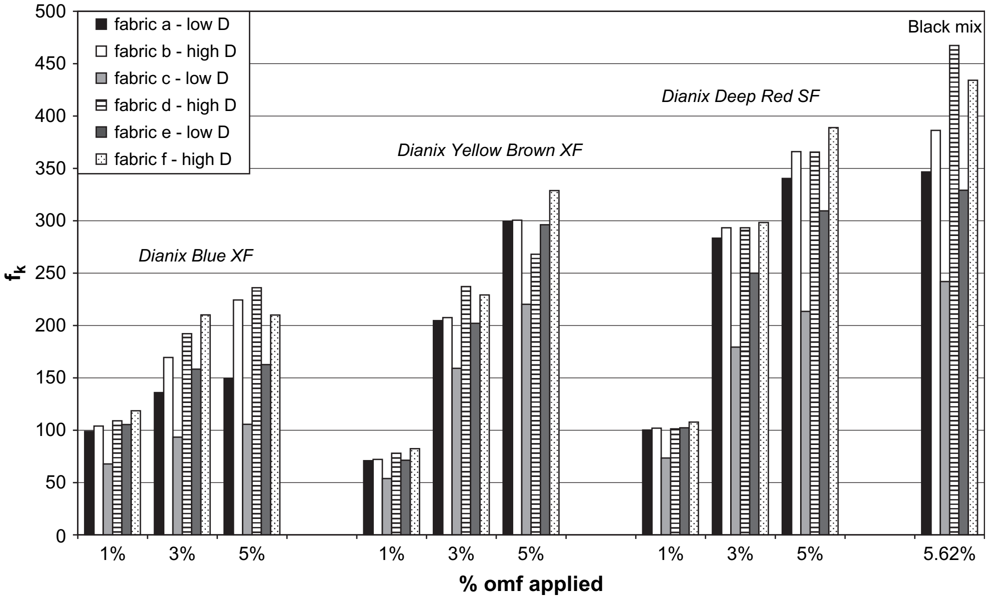

Fig. 8. Comparisons of colour strength among six PLA fabrics of varying D-isomer content.

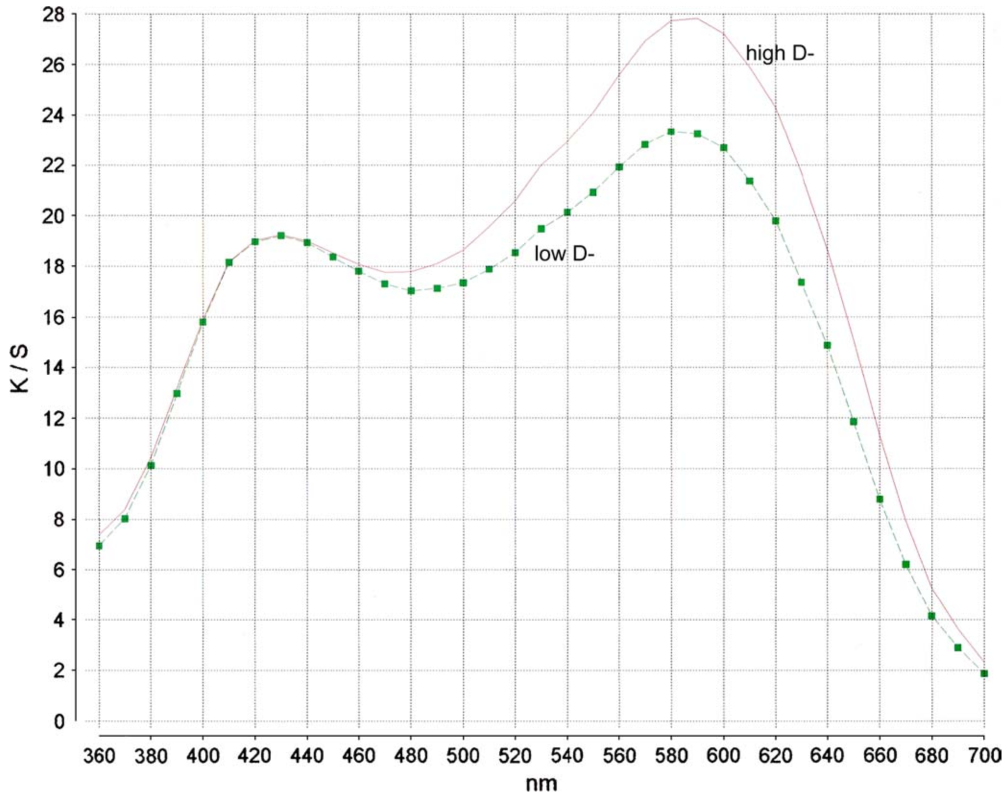

Fig. 9. K/S values over full visible spectrum for high D- and low D-fibres dyed with mixed Dianix dyes for black shade.

BXF. However, exhaustion of *YBXF* is more consistent for the two fibres, hence the two fibres display very similar colour strength at 420 nm, and hence the lack of blue adsorption for low D- fibres results in a brown appearance. Black is an extremely important colour, so from a commercial point of view the high D- fibre is very important, not only because in general colour strength is higher for all dyes, but also that a very good black shade can be achieved.

3.3. Colour fastness

In Table 2, 50 °C wash fastness results are listed; it can be seen that there is very little difference, in terms of staining of adjacent polyester, between high D- fibres and low D- fibres. This is because the glass transition temperature (T_g) for both fibres is very similar (60–62 °C). Wash fastness is directly related to T_g, hence very similar T_g values for the two fibre types results in very similar wash fastness performance.

4. Conclusions

Comparison of poly(lactic acid) fabrics with two different levels of D-isomer content revealed differences in thermal behaviour; high D- fibres have more amorphous and less crystalline regions in the polymer, with respect to low D- fibres, as a result of greater entropy from increased D- content, this is evidenced through observations that high D- fibres have lower melting point than low D- fibres. Upon examination of dyeings on the different PLA fabrics it was observed, in general, that high D- fabrics have greater exhaustion with respect to low D- fabrics in all dyes and all concentrations. High D- fibres have more amorphous and less crystalline regions in the polymer, with respect to low D- fibres, due to greater disorder caused by increased D-lactide concentration; this increase in the amorphous regions in the high D- fibres leads to greater dye exhaustion, with respect to the low D- fibres. As colour strength is directly proportional to exhaustion, high D- fibres have higher colour strength than low D- fibres. In application of

Table 2
Staining of polyester portion of SDC multifibre adjacent, subsequent to washing of PLA dyeings according to ISO 105: C06/B2S wash test (50 °C)

Fabric	*BXF*			*YBXF*			*DRSF*			Black
	1%	3%	5%	1%	3%	5%	1%	3%	5%	
a	5	5	5	5	4/5	3/4-4	5	4/5	3/4-4	4/5
b	5	5	5	5	4/5	3/4-4	5	4/5	3/4-4	4/5
c	5	5	5	5	4/5	3/4-4	5	4/5	3/4-4	4/5
d	5	5	5	5	4/5	3/4-4	5	4/5	3/4-4	4/5
e	5	5	5	5	4/5	3/4-4	5	4/5	3/4-4	4/5
f	5	5	5	5	4/5	3/4-4	5	4/5	3/4-4	4/5

a dye mixture for a black shade high D- fibres are able to be dyed to an excellent black shade, whereas low D- fibres appear very brown, due to less exhaustion of the blue component of the mix. In terms of wash fastness, there is very little difference between high D- fibres and low D- fibres; this is because the glass transition temperature for both fibres is very similar.

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