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The clearing of poly(lactic acid) fibres dyed with disperse dyes using ultrasound: Part 2 – fastness

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Abstract

Of the three types of clearing processes (water, ECE detergent and reduction clearing) applied to dyeings of six disperse dyes on PLA, water had little effect on fastness to both rubbing and repeated washing; reduction clearing was slightly more effective than ECE detergent in improving wash fastness whilst the detergent imparted higher levels of rub fastness. Both wash and rub fastness were higher when aftertreatment was carried out at 60 °C rather than at 50 °C. Ultrasound enhanced the effectiveness of both reduction clearing and ECE detergent in terms of rub fastness and enabled a modified reduction clearing process to be used that employed lower amounts of alkali and reducing agent. This offers the potential for reducing the BOD, COD, TOD and amount of suspended solids that are generated during the reduction clearing of disperse dyes from dyed PLA. The colour of the five times washed dyeings was unaffected by the aftertreatment used.

Keywords: Ultrasound; Disperse dyes; PLA fibre; Dyeing; Fastness

1. Introduction

Differences exist between the dyeability of the aliphatic, thermoplastic polyester, poly(lactic acid) (PLA) and that of it's more famous and far more well-established polyester similitude, poly(ethylene terephthalate) (PET). Owing to the marked hydrolytic sensitivity and the lower T_m of PLA fibres (~170 °C for PLA versus 250–260 °C for PET), the dyeing conditions that are commonly used for the application of disperse dyes to PET (high temperature dyeing at 125/130 °C and thermofixation at ~210 °C) cannot be employed for PLA. Consequently, dyeing conditions of 110–115 °C for 15–30 min at pH 4.5–5 have been recommended for PLA fibres [1]; the use of higher temperatures, longer times of dyeing at 110–115 °C or higher pH can lead to fibre hydrolysis. As in the case of PET which has been dyed with disperse dyes, a reduction clearing treatment is needed to remove surplus dye and auxiliaries from dyed PLA. However, the greater hydrolytic sensitivity and lower T_g of PLA (55–65 °C for PLA versus 80–90 °C in the case of PET) dictate that more weakly alkaline conditions (Na_2CO_3 rather than NaOH) [1,2] and lower temperatures (60 °C for PLA versus 60–80 °C for PET) [1,2] for 15 min [1,2] be employed for PLA which has been dyed with disperse dyes.

In the context of the susceptibility of PLA to hydrolysis, it was decided to establish whether or not a less severe clearing treatment (in terms of temperature and chemicals) could be devised for PLA via the well-known ability of ultrasound to enable the attainment of similar/improved results under less extreme conditions. In the first part of this paper [3], three types of clearing processes namely water, ECE detergent and reduction clearing were used to aftertreat six disperse dyes on PLA fibre. While reduction clearing imparted the greatest changes to both the colour strength and colour of the dyeings, treatment with ECE detergent also removed surplus dye and improved the chroma of the dyeings; treatment with water had very little effect on the colour strength and colour of dyeings, even in the presence of ultrasound. It was

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found that both depth of shade reduction and colour change were greater when aftertreatment was carried out at 60 °C rather than at 50 °C and that ultrasound neither impaired nor overly enhanced the effectiveness of either the ECE detergent or the reduction clearing processes.

This part of the paper concerns the effect of the three clearing processes (water, ECE detergent and reduction clearing) on the fastness of the six disperse dyes on PLA fibre to repeated washing and to rubbing.

2. Experimental

2.1. Materials

Scoured, poly(lactic acid) knitted fabric (which was obtained from NatureWorks LLC) described earlier [3] was used. Commercial samples of the six disperse dyes shown in Table 1 were generously supplied by DyStar and Clariant; the dyes were used without purification. All other chemicals were of general laboratory grade supplied by Aldrich.

2.2. Dyeing

Using the equipment described earlier [3] following the method shown in Fig. 1, 2% omf depths of shade were produced; the pH was adjusted using acetic acid/sodium acetate buffer.

2.3. Clearing treatments

Each of the 2% omf dyeings was subjected to the various treatments listed in Table 2, using the equipment and following the methods shown in Figs. 2 and 3, as described previously [3]. A Grant MXB22 ultrasound bath was used.

2.4. Colour measurement

All measurements were carried out using the equipment and procedures described earlier [3].

2.5. Wash fastness

The wash fastness of the dyed samples was determined using the ISO CO6/B2S (50 °C) test method [4] but was modified in that dyeings were subjected to five, consecutive wash tests and, at the end of each wash test, the washed sample was rinsed thoroughly in tap water (but was not dried) and a fresh sample of SDC multifibre strip was used to assess the extent of staining for each of the five wash tests.

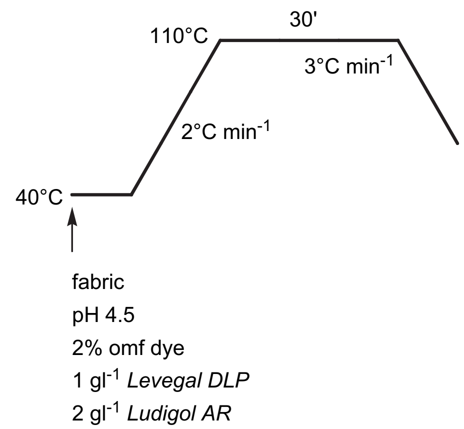

Fig. 1. Dyeing method.

2.6. Rub fastness

Both the dry and wet rub fastness of the dyed PLA samples were determined using the ISO 105:X12 test method [4].

3. Results and discussion

Six dyes were selected for use on the basis that they provided two representatives of low, medium and high energy classes of disperse dye; a 2% omf depth of shade was used as this provided typical medium depth dyeings. A repeated wash fastness protocol was employed, rather than a single wash test, as it was considered to more accurately reflect the progressive nature of the removal of dye and the redeposition of vagrant dye that occurs during domestic washing.

Table 3 shows the extent of staining, by vagrant dye, of multifibre strip that occurred during the five, consecutive wash tests as well as the shade change obtained during repeated washing in the case of C.I. Disperse Blue 56. It is clear that the non-aftertreated dyeing displayed moderate fastness to repeated washing at 50 °C, as evidenced by the high level of staining of the adjacent multifibre strip imparted by dye which

Table 1
Dyes used

Commercial name	C.I. generic name	Energy level	Supplier
Foron Brilliant Red E-2BL 200	Disperse Red 60	Low	Clariant
Foron Blue E-BL 200	Disperse Blue 56	Low	
Foron Yellow SE-FL	Disperse Yellow 42	Medium	
Foron Rubine S-GFL 150	Disperse Red 167:1	High	
Dianix Yellow Brown CC	None ascribed	Medium	DyStar
Dianix Crimson SF	None ascribed	High	

Table 2
Clearing treatments used

	Treatment	Temp. (°C)
None		
Absence of ultrasound	ECE detergent	60
	‘Standard’ reduction clear	
Presence of ultrasound	ECE detergent	60
	Modified reduction clear	
	Water	50
	ECE detergent	
	Modified reduction clear	

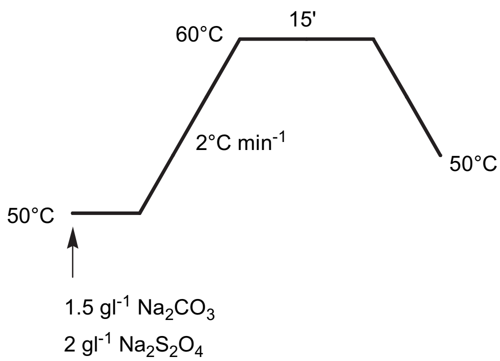

Fig. 2. Reduction clearing method.

had been removed from the dyeing during washing. The high extent of staining obtained for the adjacent nylon 6,6 fibre and the moderate staining of the polyester and diacetate components can be attributed to the higher substantivity of the dye towards these fibre types while the lower extent of staining observed for the adjacent cotton, acrylic and wool components arises from the inherent lower substantivity of the disperse dye towards such fibre types. It is apparent that the extent of staining achieved at the end of the first wash test was much worse than that obtained at the end of the third and fifth wash test and, also, that the extent of staining decreased as the number of wash tests increased. In view of the well-known, progressive nature of the removal of dye and the redepostion of vagrant dye that commonly occurs during washing, these findings were expected and can be attributed to a clearing treatment having not been carried out to remove surplus dye, which was then removed during successive washing.

Table 3 shows that the aftertreatment of the dyeings with both ECE detergent and reduction clearing at 60 °C in the absence of ultrasound improved, markedly, the fastness of the dye, as reflected by the lower staining of adjacent materials, especially in the case of the first wash test. Reduction clearing was slightly more effective during the first three wash tests, especially in terms of the staining of adjacent fibres, which can be attributed to the greater severity of the hydrosulfite/Na_2CO_3 process. However, there was no difference in the effectiveness of the two aftertreatments at the end of the five repeated wash tests, in terms of the levels of staining achieved.

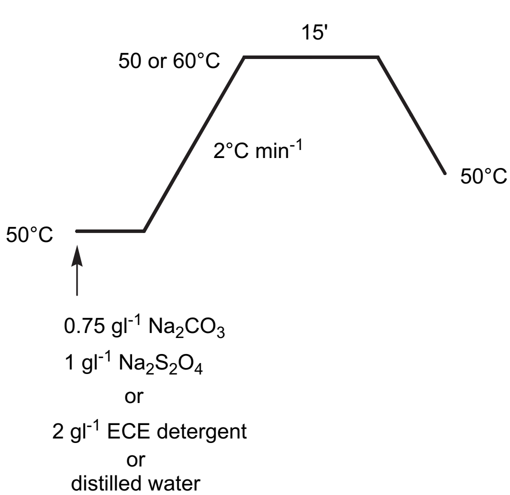

Fig. 3. Clearing methods.

As the aim of this work was to determine whether or not ultrasound could be used to intensify the reduction clearing process and enable similar/improved results to be attained under less extreme conditions, clearing was carried out in the presence of ultrasound, at 60 °C, using ECE detergent (Table 2) and a modified reduction clear process that used half the standard reduction clearing concentrations (i.e. using 1 g l^{-1} $Na_2S_2O_4$ and 0.75 g l^{-1} Na_2CO_3 rather than 2 g l^{-1} $Na_2S_2O_4$ and 1.5 g l^{-1} Na_2CO_3; Table 2). In the case of the dyeings of C.I. Disperse Blue 56, aftertreatment in the presence of ultrasound at 60 °C (Table 3) improved the fastness of the dyeing, as shown by the reduced levels of staining of adjacent materials obtained, using both the detergent and the modified reduction clear treatments. Once again, as observed when the two aftertreatments had been carried out in the absence of ultrasound, the extent of the improvement in fastness imparted by reduction clearing was slightly greater than that secured using the detergent in the presence of ultrasound during the first three wash tests. However, there was no difference in the effectiveness of the two aftertreatments at the end of the five repeated wash tests, in terms of the levels of staining achieved. When the results obtained for the two aftertreatments in the presence of ultrasound at 60 °C are compared with those secured in the absence of ultrasound at 60 °C (Table 3), it is apparent that there was little, if any, difference between the levels of staining observed. In the case of the ECE detergent, ultrasound did not enhance the ability of the detergent to remove surplus dye whereas, in the case of reduction clearing, as the aftertreatment that had been carried out in the presence of ultrasound used reduced concentrations of $Na_2S_2O_4$ and Na_2CO_3, it can be concluded that ultrasound enhanced the effectiveness of the hydrosulfite-based clearing treatment.

To further establish if ultrasound might enhance the clearing process, it was decided to use the lower temperature of 50 °C for aftertreatment of the dyeings. For this part of the work, both ECE detergent and the modified reduction clearing treatments (the latter employing half the standard reduction clearing concentrations) were used. It was also decided to aftertreat the dyed PLA fibre with water at 50 °C in the presence of ultrasound to determine if ultrasound would enable surplus dye to be removed from the dyeing using a ‘zero chemical’ clearing treatment. The corresponding fastness results obtained for C.I. Disperse Blue 56 (Table 3) show that aftertreatment with water at 50 °C in the presence of ultrasound had no effect on the fastness of the dyeing; the levels of staining achieved were identical to those obtained for the untreated dyeing. However, both the detergent and the modified reduction clearing treatments improved the fastness of the dye, as shown by the reduced levels of staining obtained. As observed when the two aftertreatments had been employed at 60 °C in the presence of ultrasound, the extent of the improvement in fastness imparted by reduction clearing was slightly greater than that secured using the detergent during the first three wash tests. There was, however, once again,

Table 3
Fastness of C.I. Disperse Blue 56 dyeings

Clearing treatment		Temp. (°C)	No. of washes	Change in shade	Diacetate	Cotton	Nylon	Polyester	Acrylic	Wool
None		–	1	4–5	2–3	4–5	1–2	3–4	5	4
			3	4–5	4–5	5	4	4–5	5	5
			5	4–5	5	5	4–5	5	5	5
Absence of ultrasound	ECE detergent	60	1	5	3–4	4–5	2–3	4	5	4–5
			3	5	4–5	5	4	5	5	5
			5	5	5	5	4–5	5	5	5
	Reduction clear		1	4–5	4–5	4–5	4	4–5	5	5
			3	4–5	5	5	4–5	4–5	5	5
			5	4–5	5	5	4–5	5	5	5
Presence of ultrasound	ECE detergent	60	1	5	3–4	4–5	2–3	4–5	5	5
			3	5	5	5	4	5	5	5
			5	5	5	5	4–5	5	5	5
	Modified reduction clear		1	5	4–5	4–5	4	4–5	5	5
			3	5	5	5	4–5	5	5	5
			5	5	5	5	4–5	5	5	5
	Water	50	1	4–5	2–3	4–5	2	3–4	5	4–5
			3	4–5	4–5	5	4	4–5	5	5
			5	4–5	5	5	4–5	5	5	5
	ECE detergent		1	5	3–4	4–5	2–3	4	5	5
			3	5	4–5	5	3–4	4–5	5	5
			5	5	5	5	4–5	5	5	5
	Modified reduction clear		1	5	4–5	4–5	3	4–5	5	5
			3	5	4–5	5	4	4–5	5	5
			5	5	5	5	4–5	5	5	5

no difference in the effectiveness of the two aftertreatments at the end of the five repeated wash tests, in terms of both the levels of shade change and staining achieved. When the results obtained using the reduction clear and the detergent in the presence of ultrasound at both 50 °C and 60 °C are compared, it is apparent that the fastness of the dyeings was slightly higher during the first three wash tests when aftertreatment had been carried out at 60 °C, in the cases of both detergent and reduction clearing. However, after five repeated wash tests, there was no difference in the fastness of the dyeings

Table 4
Fastness of C.I. Disperse Red 60 dyeings

Clearing treatment		Temp.(°C)	No. of washes	Change in shade	Diacetate	Cotton	Nylon	Polyester	Acrylic	Wool
None		–	1	5	2–3	5	1–2	4	5	4–5
			3	5	4–5	5	4–5	5	5	5
			5	5	5	5	5	5	5	5
Absence of ultrasound	ECE detergent	60	1	5	4	5	3	4–5	5	5
			3	5	5	5	4–5	5	5	5
			5	5	5	5	5	5	5	5
	Reduction clear		1	5	4–5	5	4–5	5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
Presence of ultrasound	ECE detergent	60	1	5	4	5	3	4–5	5	5
			3	5	5	5	4–5	5	5	5
			5	5	5	5	5	5	5	5
	Modified reduction clear		1	5	4–5	5	4–5	5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
	Water	50	1	5	3–4	5	2–3	4–5	5	5
			3	5	4–5	5	4–5	5	5	5
			5	5	5	5	5	5	5	5
	ECE detergent		1	5	3–4	5	3	4–5	5	5
			3	5	4–5	5	4–5	5	5	5
			5	5	5	5	5	5	5	5
	Modified reduction clear		1	5	4	5	3–4	5	5	5
			3	5	5	5	4–5	5	5	5
			5	5	5	5	5	5	5	5

Table 5
Fastness of C.I. Disperse Yellow 42 dyeings

Clearing treatment		Temp. (°C)	No. of washes	Change in shade	Diacetate	Cotton	Nylon	Polyester	Acrylic	Wool
None		–	1	4–5	3–4	3–4	1–2	4–5	5	5
			3	4–5	5	5	4–5	5	5	5
			5	4–5	5	5	5	5	5	5
Absence of ultrasound	ECE detergent	60	1	5	5	5	3–4	5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
	Reduction clear		1	5	5	5	4–5	5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
Presence of ultrasound	ECE detergent	60	1	5	5	5	3–4	5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
	Modified reduction clear		1	5	5	5	4–5	5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
	Water	50	1	4–5	4	4–5	2	5	5	5
			3	4–5	5	5	5	5	5	5
			5	4–5	5	5	5	5	5	5
	ECE detergent		1	5	5	5	3–4	5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
	Modified reduction clear		1	5	5	5	4	5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5

achieved at 50 °C and 60 °C in the presence of ultrasound (Table 3).

In the cases of the five other dyes used in this work (Tables 4–8), similar findings were obtained in terms of the effects of the various clearing treatments and two different temperatures. Whilst aftertreatment with water had no effect on the fastness of the dyeings, treatment with the ECE detergent and reduction clearing in both the absence and presence of ultrasound, improved, markedly, the fastness of each of the dyes, as reflected by the lower staining of adjacent

Table 6
Fastness of *Dianix Yellow Brown CC* dyeings

Clearing treatment		Temp. (°C)	No. of washes	Change in shade	Diacetate	Cotton	Nylon	Polyester	Acrylic	Wool
None		–	1	5	2–3	5	3	4–5	5	4–5
			3	5	4–5	5	5	5	5	5
			5	5	4–5	5	5	5	5	5
Absence of ultrasound	ECE detergent	60	1	5	4	5	4	5	5	4–5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
	Reduction clear		1	5	4–5	5	4–5	5	5	4–5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
Presence of ultrasound	ECE detergent	60	1	5	4	5	4	5	5	4–5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
	Modified reduction clear		1	5	4–5	5	4–5	5	5	4–5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
	Water	50	1	5	3	5	3–4	4–5	5	4–5
			3	5	4–5	5	5	5	5	5
			5	5	5	5	5	5	5	5
	ECE detergent		1	5	3–4	5	4	5	5	4–5
			3	5	4–5	5	5	5	5	5
			5	5	5	5	5	5	5	5
	Modified reduction clear		1	5	4	5	4	5	5	4–5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5

Table 7
Fastness of C.I. Disperse Red 167:1 dyeings

Clearing treatment		Temp. (°C)	No. of washes	Change in shade	Diacetate	Cotton	Nylon	Polyester	Acrylic	Wool
None		–	1	4–5	3	4–5	1–2	3	4–5	4–5
			3	4–5	5	5	5	5	5	5
			5	4–5	5	5	5	5	5	5
Absence of ultrasound	ECE detergent	60	1	5	4–5	4–5	3–4	4–5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
	Reduction clear		1	5	5	5	4–5	5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
Presence of ultrasound	ECE detergent	60	1	5	4–5	5	3–4	4–5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
	Modified reduction clear		1	5	5	5	5	5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
	Water	50	1	5	3–4	4–5	2	3–4	4–5	4–5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
	ECE detergent		1	5	4–5	4–5	3–4	4–5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
	Modified reduction clear		1	5	5	5	4	5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5

materials, especially in the case of the first wash test. The extent of the improvement in fastness imparted by reduction clearing was slightly greater than that secured using the detergent during the first three wash tests although there was no difference in the effectiveness of the two aftertreatments at the end of the five repeated wash tests, in terms of the levels of staining achieved. When the results obtained for the two aftertreatments in the presence of ultrasound at 60 °C are compared with those secured in the absence of ultrasound at 60 °C, it is apparent that there was little difference between the levels of

Table 8
Fastness of *Dianix Crimson SF* dyeings

Clearing treatment		Temp. (°C)	No. of washes	Change in shade	Diacetate	Cotton	Nylon	Polyester	Acrylic	Wool
None		–	1	4–5	5	5	4–5	5	5	5
			3	4–5	5	5	5	5	5	5
			5	4–5	5	5	5	5	5	5
Absence of ultrasound	ECE detergent	60	1	5	5	5	5	5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
	Reduction clear		1	5	5	5	5	5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
Presence of ultrasound	ECE detergent	60	1	5	5	5	5	5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
	Modified reduction clear		1	5	5	5	5	5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
	Water	50	1	4–5	5	5	5	5	5	5
			3	4–5	5	5	5	5	5	5
			5	4–5	5	5	5	5	5	5
	ECE detergent		1	5	5	5	5	5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
	Modified reduction clear		1	5	5	5	5	5	5	5
			3	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5

Table 9
Colorimetric data for C.I. Disperse Blue 56 dyeings

Clearing treatment		Temp. (°C)	No. of washes	$L*$	$a*$	$b*$	$C*$	$h°$	$f(k)$
None		–	0	39.7	6.9	−39.4	39.8	280.0	50.1
			5	40.5	7.7	−40.5	41.2	280.7	47.0
Absence of ultrasound	ECE detergent	60	0	39.9	7.7	40.2	41.9	280.8	49.1
			5	40.4	8.0	−40.7	41.5	281.1	47.4
	Reduction clear		0	40.5	7.0	−39.6	40.2	280.0	46.9
			5	40.2	8.1	−41.0	41.8	281.2	48.1
Presence of ultrasound	ECE detergent	60	0	40.5	7.5	−40.4	41.1	280.5	47.2
			5	40.8	7.8	−40.7	41.5	280.9	46.2
	Modified reduction clear		0	40.7	7.4	−40.3	41.0	280.3	46.8
			5	41.3	7.7	−40.7	41.4	280.7	44.6
	Water	50	0	39.7	6.9	−39.2	39.8	280.0	49.7
			5	40.1	8.0	−40.7	41.5	281.1	48.5
	ECE detergent		0	40.7	7.4	−40.4	41.1	280.4	46.8
			5	40.7	7.8	−40.7	41.4	280.9	46.4
	Modified reduction clear		0	40.3	7.5	−40.3	41.0	280.7	47.7
			5	40.8	7.8	−40.7	41.8	281.1	46.9

Table 10
Colorimetric data for C.I. Disperse Red 60 dyeings

Clearing treatment		Temp. (°C)	No. of washes	$L*$	$a*$	$b*$	$C*$	$h°$	$f(k)$
None		–	0	55.4	59.1	12.3	60.4	11.8	34.1
			5	55.9	59.5	12.3	60.7	11.7	33.1
Absence of ultrasound	ECE detergent	60	0	56.1	59.4	12.2	60.6	11.7	32.6
			5	55.7	58.9	12.0	60.1	11.5	32.8
	Reduction clear		0	55.6	58.4	11.8	59.6	11.5	32.6
			5	55.9	59.6	12.4	60.1	11.5	33.3
Presence of ultrasound	ECE detergent	60	0	55.4	59.6	12.5	60.9	11.9	33.7
			5	56.1	60.0	12.6	61.2	11.8	33.2
	Modified reduction clear		0	55.8	58.9	12.1	60.1	11.6	33.5
			5	56.0	59.6	12.2	60.8	11.6	32.9
	Water	50	0	55.3	59.1	12.3	60.3	11.8	34.3
			5	55.7	59.0	12.1	60.2	11.6	33.2
	ECE detergent		0	55.4	59.3	12.4	60.6	11.8	33.5
			5	55.1	59.0	12.2	60.3	11.8	34.7
	Modified reduction clear		0	55.7	58.6	11.9	59.8	11.5	33.2
			5	56.0	59.5	12.3	60.8	11.7	32.8

Table 11
Colorimetric data for C.I. Disperse Yellow 42 dyeings

Clearing treatment		Temp. (°C)	No. of washes	$L*$	$a*$	$b*$	$C*$	$h°$	$f(k)$
None		–	0	66.6	31.3	55.1	63.4	60.4	34.4
			5	67.9	31.9	56.2	64.6	60.4	32.6
Absence of ultrasound	ECE detergent	60	0	67.8	31.5	56.1	64.3	60.6	32.7
			5	68.1	31.7	56.1	64.4	60.5	31.9
	Reduction clear		0	67.8	31.5	55.6	63.9	60.5	32.0
			5	68.0	31.9	56.1	64.6	60.4	32.2
Presence of ultrasound	ECE detergent	60	0	67.6	31.9	56.1	64.6	60.4	33.1
			5	68.2	31.6	56.1	64.4	60.6	31.9
	Modified reduction clear		0	67.5	31.4	55.9	64.1	60.6	33.1
			5	68.1	32.0	56.4	64.8	60.4	32.5
	Water	50	0	66.6	31.3	55.1	63.4	60.4	34.2
			5	67.9	31.6	55.9	64.2	60.5	32.1
	ECE detergent		0	67.4	31.7	56.1	64.5	60.5	33.6
			5	68.1	31.9	56.5	64.9	60.6	32.4
	Modified reduction clear		0	67.5	31.2	55.8	63.9	60.4	32.9
			5	68.1	31.8	55.9	64.3	60.4	31.6

Table 12
Colorimetric data for *Dianix Yellow Brown CC* dyeings

Clearing treatment		Temp. (°C)	No. of washes	L^*	a^*	b^*	C^*	$h°$	$f(k)$
None		–	0	59.8	40.9	70.9	81.8	60.0	108.0
			5	61.2	41.3	71.9	82.9	60.2	100.5
Absence of ultrasound	ECE detergent	60	0	60.4	41.6	71.9	83.0	59.9	107.7
			5	61.2	41.2	71.8	82.7	60.1	99.3
	Reduction clear		0	60.3	41.3	71.6	82.6	60.0	107.1
			5	60.9	41.5	71.8	82.9	60.0	102.7
Presence of ultrasound	ECE detergent	60	0	60.4	41.6	71.9	83.1	59.9	107.6
			5	60.3	41.8	71.9	83.2	59.8	108.8
	Modified reduction clear		0	60.4	40.9	71.5	82.4	60.2	105.0
			5	61.1	41.1	71.8	82.7	60.2	100.2
	Water	50	0	59.9	41.1	71.5	82.5	60.1	110.5
			5	60.9	41.5	71.5	82.6	59.8	101.1
	ECE detergent		0	60.4	41.5	72.1	83.2	60.1	108.1
			5	60.4	41.7	71.3	82.6	59.7	104.8
	Modified reduction clear		0	60.2	41.2	71.9	82.8	60.2	109.5
			5	60.8	41.4	72.1	83.1	60.1	104.6

Table 13
Colorimetric data for C.I. Disperse Red 167:1 dyeings

Clearing treatment		Temp. (°C)	No. of washes	L^*	a^*	b^*	C^*	$h°$	$f(k)$
None		–	0	40.6	53.9	26.0	59.8	25.8	125.6
			5	41.6	55.2	26.7	61.3	25.8	120.0
Absence of ultrasound	ECE detergent	60	0	41.2	55.0	26.9	61.3	26.1	124.8
			5	41.5	55.0	26.7	61.1	25.9	118.7
	Reduction clear		0	41.5	55.0	26.3	60.5	25.8	118.4
			5	41.9	55.2	26.9	61.4	26.0	117.8
Presence of ultrasound	ECE detergent	60	0	42.9	55.3	26.2	61.2	25.3	105.9
			5	43.1	54.9	25.8	60.7	25.1	102.7
	Modified reduction clear		0	42.7	54.8	25.8	60.6	25.2	105.0
			5	43.0	54.8	25.8	60.6	25.2	102.3
	Water	50	0	40.8	54.2	26.5	60.4	26.1	126.3
			5	41.3	54.9	26.6	61.1	25.9	122.2
	ECE detergent		0	41.1	54.7	26.8	60.9	26.1	125.2
			5	41.4	54.9	26.8	61.1	26.0	120.2
	Modified reduction clear		0	42.6	54.5	25.6	60.2	25.2	106.2
			5	43.3	54.9	25.8	60.7	25.2	100.8

Table 14
Colorimetric data for *Dianix Crimson SF* dyeings

Clearing treatment		Temp. (°C)	No. of washes	L^*	a^*	b^*	C^*	$h°$	$f(k)$
None		–	0	67.8	48.6	31.2	57.8	32.7	17.7
			5	69.1	49.6	31.6	58.8	32.5	16.6
Absence of ultrasound	ECE detergent	60	0	68.8	49.9	32.1	59.3	32.7	17.2
			5	69.1	50.0	32.0	59.4	32.6	16.9
	Reduction clear		0	68.6	49.6	31.8	58.9	32.6	17.2
			5	69.1	49.8	31.6	58.9	32.4	16.6
Presence of ultrasound	ECE detergent	60	0	68.8	49.7	32.1	59.1	32.9	17.2
			5	68.7	49.2	31.4	58.4	32.5	16.9
	Modified reduction clear		0	68.3	49.2	31.7	58.6	32.5	17.2
			5	68.9	48.9	31.1	57.9	32.5	16.4
	Water	50	0	68.5	48.8	31.4	58.0	32.7	17.0
			5	69.2	49.8	31.7	59.0	32.5	16.6
	ECE detergent		0	68.8	49.8	31.8	59.1	32.5	17.0
			5	69.0	49.7	31.6	58.9	32.4	16.7
	Modified reduction clear		0	68.7	48.8	31.7	58.2	33.6	16.9
			5	69.2	49.4	31.7	58.9	32.7	16.5

Table 15
Rub fastness results

Treatment		Temp. (°C)	Dry Staining	Dry Shade change	Wet Staining	Wet Shade change	Dry Staining	Dry Shade change	Wet Staining	Wet Shade change	Dry Staining	Dry Shade change	Wet Staining	Wet Shade change
			C.I. Disperse Red 60				C.I. Disperse Blue 56				C.I. Disperse Yellow 42			
None		–	2–3	3–4	5	4–5	2	3–4	4	4–5	3	4	4	4–5
Absence of ultrasound	ECE detergent	60	3	4	5	5	3	4	5	5	3–4	4–5	4–5	4–5
	'Standard' reduction clear		3–4	4	5	5	3	4	5	5	3–4	4–5	4–5	4–5
Presence of ultrasound	ECE Clearing	60	3–4	4–5	5	5	3–4	4–5	5	5	4	4–5	4–5	4–5
	Modified reduction clear		4	4–5	5	5	3–4	4–5	5	5	4	4–5	5	5
	Water Clearing	50	3	3–4	5	4–5	2–3	3–4	4–5	4–5	3	4	4	4–5
	ECE Clearing		3	4	5	5	3	4	5	5	3–4	4–5	4–5	4–5
	Modified reduction clear		3	4	5	5	3	4	5	5	3–4	4–5	4–5	4–5
			Dianix Yellow Brown CC				Disperse Red 167:1				Dianix Crimson SF			
None			2	3–4	4	4–5	2	3	4	4–5	4–5	4	5	4–5
Absence of ultrasound	ECE detergent	60	2–3	3–4	5	5	2–3	3–4	5	5	5	4	5	4–5
	'Standard' reduction clear		3	3–4	5	5	3	3–4	5	5	5	4	5	4–5
Presence of ultrasound	ECE Clearing	60	3–4	4	5	5	4	4	5	5	5	4–5	5	4–5
	Modified reduction clear		3	4	5	5	4	4	5	5	5	4–5	5	4–5
	Water Clearing	50	2–3	3–4	4–5	5	2–3	3–4	4	4–5	4–5	4	5	4–5
	ECE Clearing		2–3	4	5	5	2–3	4	4–5	5	5	4	5	4–5
	Modified reduction clear		2–3	4	5	5	3	3–4	5	5	5	4	5	4–5

staining observed. In terms of the use of ultrasound at 50 °C and 60 °C, it is clear that the fastness of the dyeings was slightly higher during the first three wash tests when aftertreatment had been carried out at 60 °C, in the cases of both detergent and reduction clearing. This can be attributed to a corresponding increase in the amount of dye removed from the dyeings as a result of the greater kinetic energy of the clearing treatments at the higher temperature. However, after five repeated wash tests, there was no difference in the fastness of the dyeings achieved at 50 °C and 60 °C in the presence of ultrasound.

Table 9 shows the corresponding colorimetric data for dyeings of C.I. Disperse Blue 56 before and after subjecting to five wash tests. The sometimes quite marked, reduction in depth of shade which the dyeings underwent as a consequence of repeated washing is clearly shown by the lower $f(k)$ values of the five times washed samples. However, despite the reduction in depth of shade that repeated washing imparted, it is evident that the colour (hue and chroma) of the five times washed dyeings was largely unaffected by the particular aftertreatment used. Tables 10–14 show that similar results were obtained for the five remaining dyes insofar as aftertreatment with the detergent and the reduction clear process lowered the depth of shade of the dyeings but the colour of the five times washed dyeings was similar, for each of the particular aftertreatment employed.

In the context of the effects of the various clearing treatments on rub fastness, Table 15 shows that each of the seven aftertreatments improved both the wet and dry fastness of the dyeings, except in the case of C.I. Disperse Red 60 and *Dianix Crimson SF*, for which the wet rub fastness of the untreated 2% omf dyeing was rated as 5 (the maximum rating) for both shade change and staining which, therefore, could not be improved upon by any clearing process. Table 15 reveals that the least effective aftertreatment was water alone at 50 °C in the presence of ultrasound, and the highest levels of rub fastness (especially fastness to dry rubbing), were secured using the modified reduction clear and ECE detergent treatments at 60 °C in the presence of ultrasound; interestingly, there was little difference between the effectiveness of the ECE detergent and the modified reduction clearing treatments at 60 °C in the presence of ultrasound. The finding that ultrasound improved the effectiveness of both the ECE detergent and reduction clearing treatments at 60 °C can be attributed to the well-known intensification effect of ultrasound.

Overall, the results obtained show that the use of ultrasound enabled the attainment of similar/improved results under less extreme conditions insofar as the use of ultrasound at 60 °C enhanced the effectiveness of both the reduction clear process and ECE detergent in terms of rub fastness. Whilst ultrasound did not enhance the effectiveness of the detergent in improving wash fastness, it's use enabled fastness results to be achieved using the modified reduction clearing process (in which half the standard reduction clearing concentrations of $Na_2S_2O_4$ and Na_2CO_3 were employed) that were comparable to those achieved using the standard reduction clearing

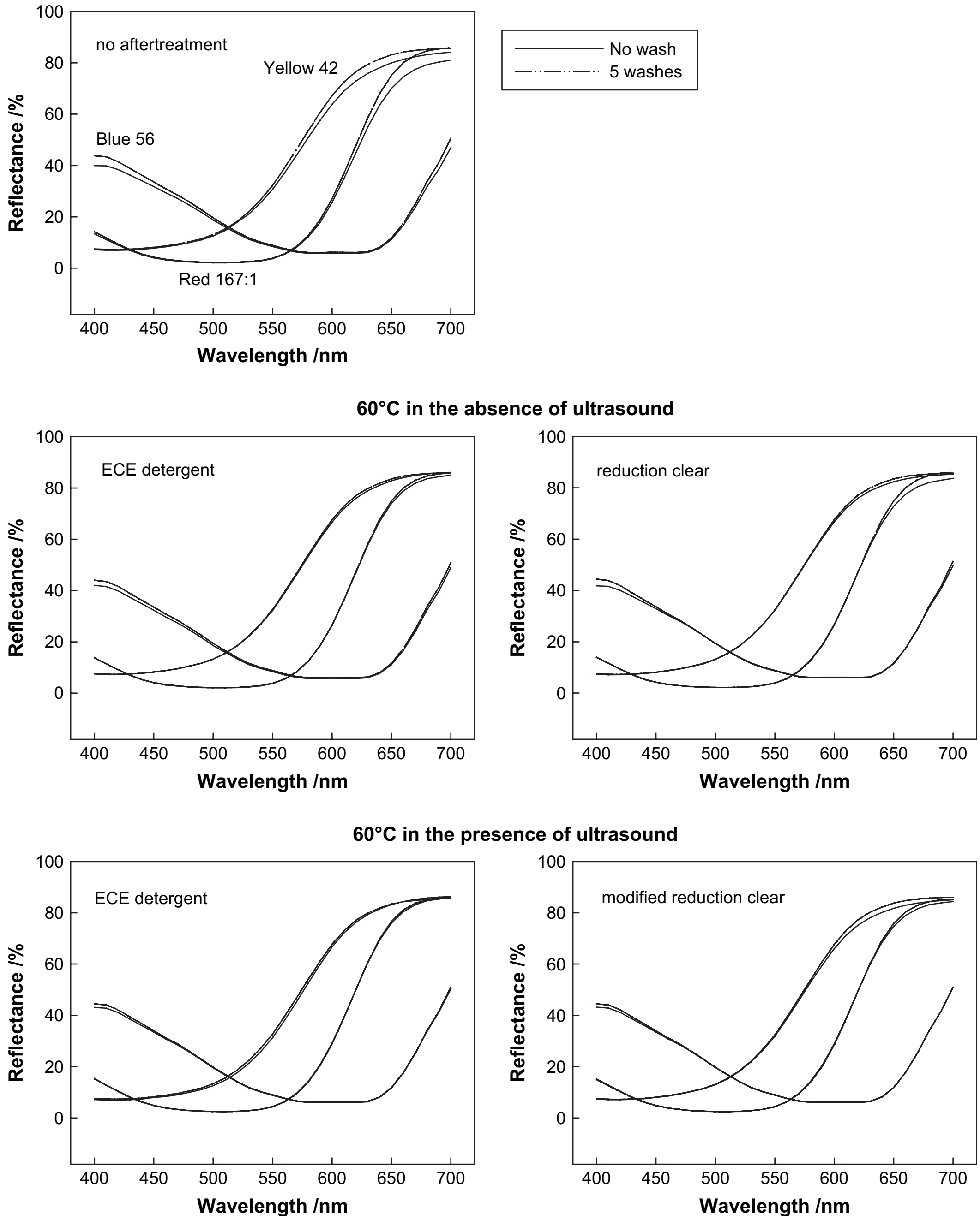

Fig. 4. Spectral data for C. I. Disperse Blue 56, C.I. Disperse Yellow 42 and C.I. Disperse Red 167.

process in the absence of ultrasound at 60 °C. Furthermore, aftertreatment at 60 °C in the presence of ultrasound had no effect on the colour and the λ_{max} of the respective dyeings, as shown in Figs. 4 and 5.

4. Conclusions

Of the three types of aftertreatments (water, ECE detergent and reduction clearing), water had little, if any, effect on the fastness to both rubbing and repeated washing; reduction clearing was slightly more effective than ECE detergent in improving wash fastness, especially in terms of the first three wash tests, whereas the detergent imparted higher levels of rub fastness. The findings that both the wash and rub fastness of the dyeings were higher when aftertreatment had been carried out at 60 °C rather than at 50 °C can be attributed to a corresponding increase in the amount of dye removed from the dyeings owing to the greater kinetic energy of the aftertreatments at the higher temperature. From the results obtained at 60 °C in both the absence and presence of ultrasound, it appears that ultrasound enhanced the effectiveness of both reduction clearing and ECE detergent in terms of

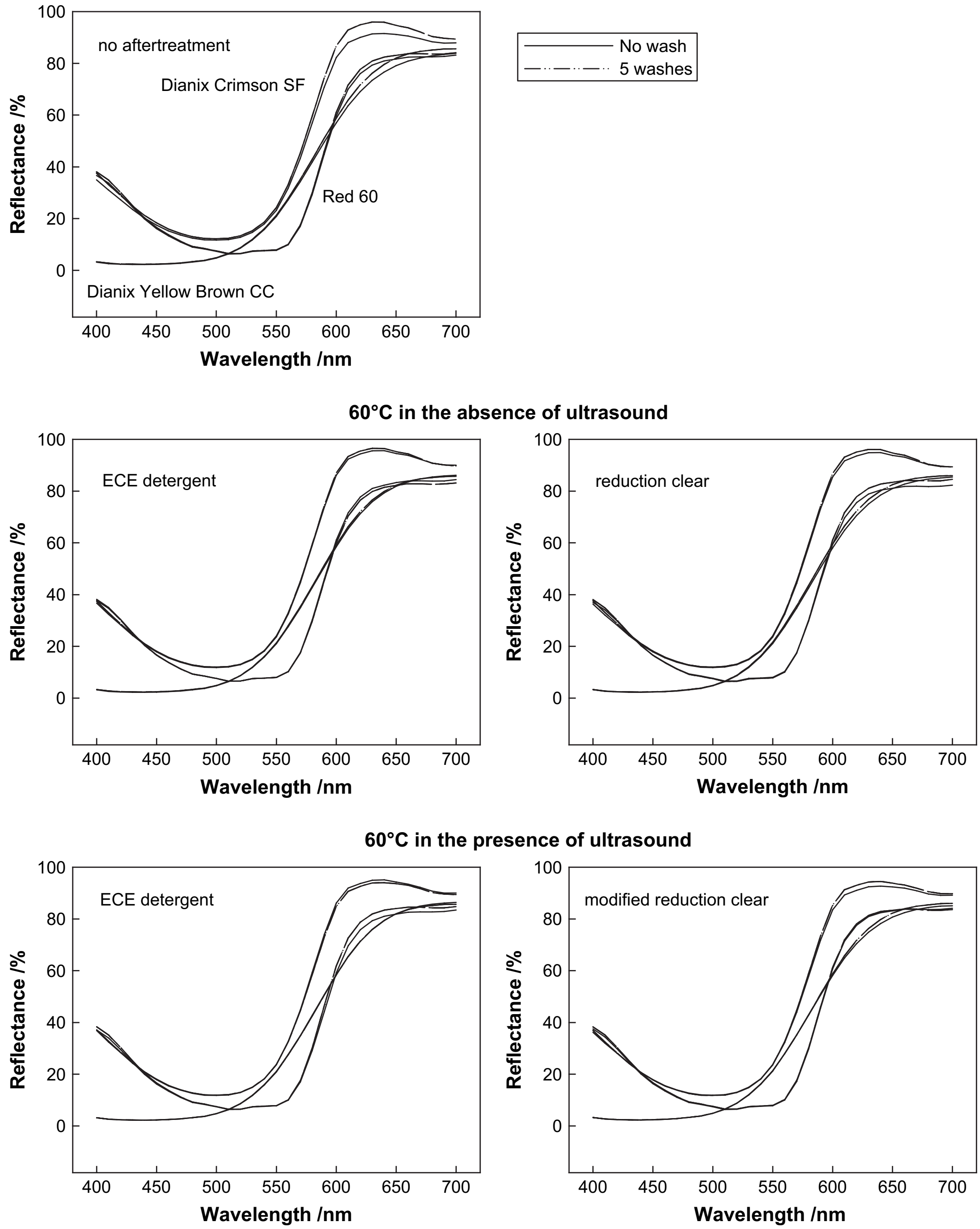

Fig. 5. Spectral data for C. I. Disperse Red 60, *Dianix Yellow Brown CC* and *Dianix Crimson SF*.

rub fastness and, although it did not enhance the effectiveness of the detergent in improving wash fastness, it's use enabled the modified reduction clearing process to yield fastness results that were comparable to those achieved using the 'standard' reduction clearing process in the absence of ultrasound. This finding not only means that the amounts of alkali and reducing agent used in reduction clearing can be lowered through the use of ultrasound, but also offers the potential for reducing the BOD, COD, TOD and amount of suspended solids that are generated during the reduction clearing of disperse dyes from dyed PLA. The colour of the five times washed dyeings was unaffected by the particular aftertreatment used.

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