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The clearing of poly(lactic acid) fibres dyed with disperse dyes using ultrasound: Part 3

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Abstract

The effectiveness of an ultrasound-assisted, ECE detergent-based aftertreatment was found to be little improved by the use of temperatures higher than 60 °C, durations longer than 5 min and detergent concentrations greater than 2 g l^{-1}. As little difference was found between the effectiveness of the detergent aftertreatment and that of the traditional reduction clearing process, it appears that, in terms of fastness and colour, the Na_2CO_3 and $Na_2S_2O_4$ used in the reduction clearing of disperse dyed PLA fibre can be replaced with a treatment using 2 g l^{-1} ECE detergent in the presence of ultrasound. This alternative aftertreatment of dyed PLA may offer a reduced risk of hydrolytic damage to the fibre as well as reduced chemical consumption and also generate a more environmentally acceptable effluent than reduction clearing.

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

1. Introduction

A reduction clearing treatment is needed to remove surplus dye and auxiliaries from poly(lactic acid) (PLA) which has been dyed with disperse dyes. Owing to the hydrolytic sensitivity and T_g of PLA, reduction clearing comprises, typically, of submitting the rinsed, dyed material to treatment for 15 min at 60 °C in an aqueous bath containing 1.5–2 g l^{-1} Na_2CO_3 and 2 g l^{-1} $Na_2S_2O_4$ [1,2]. However, the use of sodium dithionite produces environmentally unfriendly effluent which, in the case of azo disperse dyes, may also contain aromatic amines [3]. In this latter context, together with the susceptibility of PLA to hydrolysis, it was decided to establish whether or not a clearing treatment could be developed for dyed PLA which offered a low risk of hydrolytic damage and which constituted a more environmentally friendly approach as well as reduced chemical usage. To this end, the decision was made to determine if the well-known abilities of ultrasound (process acceleration and the attainment of similar/improved results under less extreme conditions) would enable both the Na_2CO_3 and $Na_2S_2O_4$ used in reduction clearing to be replaced by an aftertreatment with a common detergent formulation.

In the first part of this paper [4], three types of clearing process namely water, reduction clearing and ECE detergent, were used to aftertreat six disperse dyes on PLA fibre. Although 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 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. The second part of the paper [5] revealed that reduction clearing was slightly more effective than ECE detergent in improving wash fastness whilst ECE detergent imparted higher level of rub fastness; water had little effect on fastness to both rubbing and repeated washing. Both wash and rub

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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	

fastness were higher when aftertreatment had been 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 final part of the paper concerns the effects of varying the amount of ECE detergent used as well as different times and temperatures of aftertreatment on the fastness of three disperse dyes to both rubbing and repeated washing.

2. Experimental

2.1. Materials

Scoured, poly(lactic acid) knitted fabric (which was obtained from NatureWorks LLC) described earlier [1] was used. Commercial samples of the three disperse dyes shown in Table 1 were generously supplied by Clariant and were used without purification; the three dyes were selected for use on the basis that they were representative of contemporary disperse dyes. ECE detergent was obtained from the Society of Dyers and Colourists; all other chemicals were of general laboratory grade supplied by Aldrich.

2.2. Dyeing

Dyeings of 1% and 2% omf were produced, using the equipment described earlier [1] following the method shown in Fig. 1; the pH was adjusted using acetic acid/sodium acetate buffer. The dyeings were rinsed thoroughly in tap water and allowed to dry in the open air.

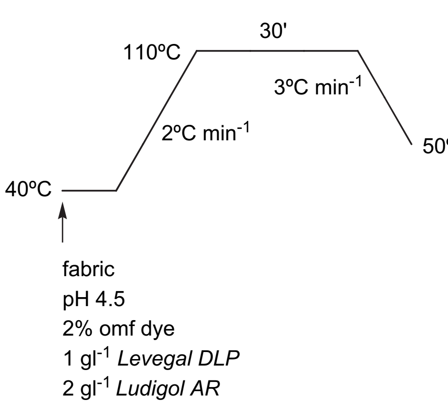

Fig. 1. Dyeing method.

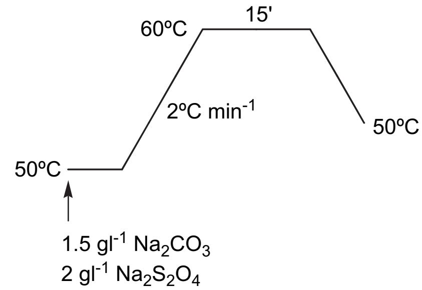

Fig. 2. Reduction clearing method.

2.3. Aftertreatments

2.3.1. Reduction clearing

Dyeings were reduction cleared, in the absence of ultrasound, using the equipment described earlier [2] following the method shown in Fig. 2.

2.3.2. ECE detergent

Dyeings were treated using 2, 4 and 8 $g\,l^{-1}$ ECE detergent, at 60, 70 and 80 °C for 5, 15 and 30 min, using the method shown in Fig. 3, employing the equipment described before [2] in the presence of ultrasound provided by a Grant MXB22.

2.4. Colour measurement

All measurements were carried out using the equipment and procedures described earlier [1].

2.5. Wash fastness

The wash fastness of the dyed samples was determined using the ISO CO6/B2S (50 °C) test method but was modified such 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 [2].

2.6. Rub fastness

The dry and wet rub fastness of the dyed PLA samples were determined using the ISO 105:X12 test method [2].

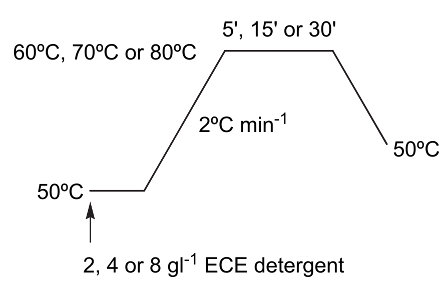

Fig. 3. Aftertreatment using detergent.

Table 2
Effect of temperature on wash fastness of 2% omf dyeings (15 min; 2 g l^{-1} ECE detergent)

Dye	Temp. (°C)	No. of washes	Change in shade	Diacetate	Cotton	Nylon	Polyester	Acrylic	Wool
C.I. Disperse Red 60	60	1	5	4	5	3	4–5	5	5
		5	5	5	5	5	5	5	5
	70	1	5	4	5	3–4	4–5	5	5
		5	5	5	5	5	5	5	5
	80	1	5	3–4	5	3	4–5	5	5
		5	5	5	5	5	5	5	5
C.I. Disperse Blue 56	60	1	5	3–4	4–5	2–3	4–5	5	5
		5	5	5	5	4–5	5	5	5
	70	1	5	3–4	4–5	2–3	4–5	5	5
		5	5	5	5	4–5	5	5	5
	80	1	5	3–4	4–5	2	4–5	5	5
		5	5	5	5	4–5	5	5	5
C.I. Disperse Yellow 42	60	1	5	5	5	3–4	5	5	5
		5	5	5	5	5	5	5	5
	70	1	5	5	5	3–4	5	5	5
		5	5	5	5	5	5	5	5
	80	1	5	5	5	3	5	5	5
		5	5	5	5	5	5	5	5

3. Results and discussion

Dyeings of 2% omf were aftertreated with three concentrations (2, 4 and 8 g l^{-1}) of ECE detergent for three different times (5, 15 and 30 min) and at three temperatures (60, 70 and 80 °C) and the effects of these treatments on the colour, rub fastness and fastness to repeated washing at 50 °C were assessed.

Table 2 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 cases of the three disperse dyes. It is evident that each of the three dyes displayed different levels of fastness to repeated washing at 50 °C, as measured in terms of the levels of staining of the adjacent multifibre strip imparted by dye which had been removed from the dyeing during washing. In this context, lowest fastness was obtained for 2% omf dyeings of C.I. Disperse Blue 56, as shown by the high extent of staining obtained for the adjacent nylon 6,6 fibre and the moderate staining of the diacetate, polyester and cotton components; such staining can be attributed to the higher substantivity of the dye towards these fibre types while the lower extent of staining observed for the adjacent acrylic and wool components arises from the inherent low 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 fifth wash test. In view of the well-known, progressive nature of the removal of dye and the redeposition of vagrant dye that commonly occurs during washing, these findings were expected and can be attributed to the detergent aftertreatment having not removed all surplus dye, which was then removed during successive washing.

In terms of the effect of the temperature used for aftertreatment on wash fastness, it is clear that for each of the three dyes used, there was very little difference in the fastness of the dyeings after the first wash test. Furthermore, it is clear that the level of fastness achieved after the fifth wash test, for each of the three dyes used (as judged by the staining of adjacent fibres), was unaffected by the temperature at which aftertreatment with the detergent had been carried out. Table 3 reveals that the rub fastness of the C.I. Disperse Blue 56 and C.I. Disperse Yellow 42 dyeings were very slightly lower when aftertreatment had been carried out at 60 °C and that there was no difference between the results obtained for aftertreatments at 70 and 80 °C. The corresponding colorimetric data for the dyeings (Table 4) which had been subjected to five wash tests in the presence of ultrasound using 2 g l^{-1} ECE detergent, shows that repeated washing lowered the depth of shade of each of the dyeings, as shown by the lower $f(k)$ values of the five times washed samples; this is attributable to the wash tests having removed surface dye from the dyeings. Also, it is

Table 3
Effect of temperature on rub fastness of 2% omf dyeings (15 min; 2 g l^{-1} ECE detergent)

Temp. (°C)	Dry		Wet		Dry		Wet		Dry		Wet	
	Staining	Shade change	Staining	Shade change	Staining	Shade change	Staining	Shade change	Staining	Shade change	Staining	Shade change
	C.I. Disperse Red 60				C.I. Disperse Blue 56				C.I. Disperse Yellow 42			
60	3–4	4–5	5	5	3–4	4–5	5	5	4	4–5	4–5	4–5
70	3–4	4–5	5	5	4	4–5	5	5	4–5	5	5	5
80	3–4	4–5	5	5	4	4–5	5	5	4–5	5	5	5

Table 4
Effect of temperature on colorimetric data for 2% omf dyeings (15 min; 2 g l^{-1} ECE detergent)

Temp. (°C)	No. of washes	L^*	a^*	b^*	C^*	$h°$	$f(k)$	L^*	a^*	b^*	C^*	$h°$	$f(k)$	L^*	a^*	b^*	C^*	$h°$	$f(k)$
		C.I. Disperse Red 60						C.I. Disperse Blue 56						C.I. Disperse Yellow 42					
60	0	55.4	59.6	12.5	60.9	11.9	33.7	40.5	7.5	−40.4	41.1	280.5	47.2	67.5	31.9	56.1	64.1	60.6	33.1
	5	55.7	60.0	12.6	60.8	11.7	33.2	40.8	7.8	−40.7	41.5	280.9	46.2	68.2	31.6	56.1	64.4	60.6	31.9
70	0	55.4	58.7	12.3	60.0	11.9	33.9	41.1	7.3	−40.2	40.9	280.2	45.1	68.5	30.6	55.0	62.9	60.9	30.3
	5	55.5	58.8	12.2	60.1	11.7	33.6	41.5	7.4	−40.1	40.8	280.4	43.7	68.3	31.3	55.9	64.1	60.7	30.1
80	0	55.8	59.2	12.4	60.5	11.8	33.2	41.0	7.4	−40.3	41.0	280.4	45.4	68.6	30.7	55.0	63.6	60.9	29.7
	5	56.1	59.0	12.3	60.3	11.7	32.3	41.4	7.7	−40.5	41.2	280.4	44.1	68.9	30.8	55.4	63.4	60.9	29.5

Table 5
Effect of time on wash fastness of 2% omf dyeings (60 °C; 2 g l^{-1} ECE detergent)

Dye	Time (min)	No. of washes	Change in shade	Diacetate	Cotton	Nylon	Polyester	Acrylic	Wool
C.I. Disperse Red 60	5	1	5	3–4	5	2–3	4–5	5	5
		5	5	5	5	5	5	5	5
	15	1	5	4	5	3	4–5	5	5
		5	5	5	5	5	5	5	5
	30	1	5	4	5	3	4–5	5	5
		5	5	5	5	5	5	5	5
C.I. Disperse Blue 56	5	1	5	3	4	2	4	5	5
		5	5	5	5	5	5	5	5
	15	1	5	3–4	4–5	2–3	4–5	5	5
		5	5	5	5	4–5	5	5	5
	30	1	5	3–4	4–5	2–3	4–5	5	5
		5	5	5	5	4–5	5	5	5
C.I. Disperse Yellow 42	5	1	5	5	5	3–4	5	5	5
		5	5	5	5	5	5	5	5
	15	1	5	5	5	3–4	5	5	5
		5	5	5	5	5	5	5	5
	30	1	5	5	5	3–4	5	5	5
		5	5	5	5	5	5	5	5

Table 6
Effect of time on rub fastness of 2% omf dyeings (60 °C; 2 g l^{-1} ECE detergent)

Time (min)	Dry		Wet		Dry		Wet		Dry		Wet	
	Staining	Shade change	Staining	Shade change	Staining	Shade change	Staining	Shade change	Staining	Shade change	Staining	Shade change
	C.I. Disperse Red 60				C.I. Disperse Blue 56				C.I. Disperse Yellow 42			
5	3	4	5	5	3–4	4–5	5	5	4	4–5	4–5	4–5
15	3–4	4–5	5	5	3–4	4–5	5	5	4	4–5	4–5	4–5
30	3–4	4–5	5	5	4	4–5	5	5	4	4–5	4–5	5

Table 7
Effect of time on colorimetric data for 2% omf dyeings (60 °C; 2 g l^{-1} ECE detergent)

Time (min)	No. of washes	L^*	a^*	b^*	C^*	$h°$	$f(k)$	L^*	a^*	b^*	C^*	$h°$	$f(k)$	L^*	a^*	b^*	C^*	$h°$	$f(k)$
		C.I. Disperse Red 60						C.I. Disperse Blue 56						C.I. Disperse Yellow 42					
5	0	55.5	58.5	12.1	59.7	11.6	33.3	40.3	7.2	−39.9	40.6	280.3	47.7	68.0	30.7	54.7	62.7	60.6	30.6
	5	55.4	59.1	12.5	60.9	12.2	34.3	40.4	8.0	−40.6	41.4	281.6	47.2	68.2	31.6	56.2	64.5	60.7	32.0
15	0	55.4	59.6	12.5	60.9	11.9	33.7	40.5	7.5	−40.4	41.1	280.5	47.2	67.5	31.9	56.1	64.1	60.6	33.1
	5	55.7	60.0	12.6	60.8	11.7	33.2	40.8	7.8	−40.7	41.5	280.9	46.2	68.2	31.6	56.1	64.4	60.6	31.9
30	0	55.1	58.7	12.3	60.0	11.8	34.7	41.1	7.3	−40.3	41.0	280.2	45.1	68.2	30.8	55.0	63.1	60.7	30.6
	5	55.4	59.2	12.4	60.6	12.0	34.4	40.8	7.8	−40.6	41.3	280.8	45.9	68.3	31.4	55.9	64.1	60.9	31.4

Table 8
Effect of detergent concentration on wash fastness of 2% omf dyeings (60 °C; 15 min)

Dye	ECE detergent ($g\,l^{-1}$)	No. of washes	Change in shade	Diacetate	Cotton	Nylon	Polyester	Acrylic	Wool
C.I. Disperse Red 60	2	1	5	4	5	3	4–5	5	5
		5	5	5	5	5	5	5	5
	4	1	5	4–5	5	3	4–5	5	5
		5	5	5	5	5	5	5	5
	8	1	5	4–5	5	3–4	4–5	5	5
		5	5	5	5	5	5	5	5
C.I. Disperse Blue 56	2	1	5	3–4	4–5	2–3	4–5	5	5
		5	5	5	5	4–5	5	5	5
	4	1	5	4	4–5	2–3	4–5	5	5
		5	5	5	5	4–5	5	5	5
	8	1	5	4	4–5	2–3	4–5	5	5
		5	5	5	5	4–5	5	5	5
C.I. Disperse Yellow 42	2	1	5	5	5	3–4	5	5	5
		5	5	5	5	5	5	5	5
	4	1	5	5	5	4	5	5	5
		5	5	5	5	5	5	5	5
	8	1	5	5	5	4	5	5	5
		5	5	5	5	5	5	5	5

evident that repeated washing had little, if any effect on the colour (hue and chroma) of the dyeings. In terms of the effect of temperature of aftertreatment on the dyeings before wash testing, the data in Table 4 show that generally, colour strength decreased with increasing temperature, the colour of the dyeings was largely unaffected by a change in temperature at which the aftertreatment had been carried out.

In the context of the effects of the duration of the aftertreatment upon fastness, Table 5 shows that in the cases of C.I. Disperse Red 60 and C.I. Disperse Yellow 42, the staining of adjacent materials was the greatest when aftertreatment had been carried out for 5 min although identical levels of staining were obtained in the cases of 15 and 30 min treatment. Table 5 also shows that the level of fastness achieved after the fifth wash test, for each of the three dyes used (as judged by the staining of adjacent fibres), was unaffected by the duration of the aftertreatment. Table 6 reveals that the rub fastness of the C.I. Disperse Red 60 dyeing was slightly lower when aftertreatment had been carried out for 5 min but, significantly, there was no difference between the results obtained when aftertreatment had been carried out for 15 and 30 min, for each of the three dyes used. The corresponding colorimetric data for the dyeings (Table 7) show that the duration of aftertreatment had little, if any, effect on the depth of shade and colour of the dyeings, both before and after repeated wash testing in the cases of C.I. Disperse Red 60 and C.I. Disperse Yellow 42. The colour strength of dyeings of C.I. Disperse Blue 56 were reduced to a small extent by aftertreatment for 30 min, although the colour of the dyeings was unaffected by the duration of aftertreatment.

Increasing the concentration of ECE detergent from 2 to 4 $g\,l^{-1}$ slightly reduced the level of staining of adjacent materials achieved after the first wash test, for each of the three dyes used, but had no effect on the fastness of the five times washed dyeings (Table 8); further increase in detergent concentration to 8 $g\,l^{-1}$ had no effect on the fastness of either the first or fifth washed dyeings. Although an increase in the amount of detergent had no effect on rub fastness (Table 9), increased amounts of detergent lowered the colour strength of dyeings achieved for C.I. Disperse Yellow 42, both before and after repeated washing (Table 10).

As mentioned, because of the hydrolytic sensitivity and T_g of PLA, disperse dyeings on the fibre are reduction cleared for 15 min at 60 °C in an aqueous bath containing Na_2CO_3 and $Na_2S_2O_4$. The aims of this work were to establish whether or not an alternative aftertreatment to reduction clearing could be developed for dyed PLA which offered a low risk of hydrolytic damage, consumed few chemicals and which generated a more environmentally acceptable effluent. The colour and fastness results described thus far indicate that the effectiveness of the detergent-based aftertreatment was little improved, if at all, through the use of temperatures above 60 °C, times in excess of 15 min and detergent concentrations greater than 2 $g\,l^{-1}$; furthermore, in the context of the aims of this work,

Table 9
Effect of detergent concentration on rub fastness of 2% omf dyeings (60 °C; 15 min)

ECE detergent ($g\,l^{-1}$)	Dry		Wet		Dry		Wet		Dry		Wet	
	Staining	Shade change	Staining	Shade change	Staining	Shade change	Staining	Shade change	Staining	Shade change	Staining	Shade change
	C.I. Disperse Red 60				C.I. Disperse Blue 56				C.I. Disperse Yellow 42			
2	3–4	4–5	5	5	3–4	4–5	5	5	4	4–5	4–5	4–5
4	3–4	4–5	5	5	3–4	4–5	5	5	4	4–5	4–5	5
8	3–4	4–5	5	5	3–4	4–5	5	5	4	4–5	4–5	5

Table 10
Effect of detergent concentration on colorimetric data of 2% omf dyeings (60 °C; 15 min)

ECE detergent ($g\,l^{-1}$)	No. of washes	L^*	a^*	b^*	C^*	$h°$	$f(k)$	L^*	a^*	b^*	C^*	$h°$	$f(k)$	L^*	a^*	b^*	C^*	$h°$	$f(k)$
		C.I. Disperse Red 60						C.I. Disperse Blue 56						C.I. Disperse Yellow 42					
2	0	55.4	59.6	12.5	60.9	11.9	33.7	40.5	7.5	−40.4	41.1	280.5	47.2	67.5	31.9	56.1	64.1	60.6	33.1
	5	55.7	60.0	12.6	60.8	11.7	33.2	40.8	7.8	−40.7	41.5	280.9	46.2	68.2	31.6	56.1	64.4	60.6	31.9
4	0	55.8	59.0	12.2	60.3	11.7	33.2	40.5	7.7	−40.6	41.3	280.7	47.1	68.3	30.8	55.1	63.1	60.8	30.5
	5	55.7	58.8	12.3	60.0	11.8	33.0	40.9	7.8	−40.7	41.4	280.8	45.7	68.5	31.1	55.7	63.8	60.9	30.7
8	0	55.6	59.1	12.4	60.4	11.8	33.7	40.3	7.6	−40.4	41.1	280.7	47.0	68.1	40.0	55.3	63.4	60.7	31.0
	5	55.6	58.7	12.4	60.0	11.9	33.2	40.7	7.9	−40.6	41.4	281.0	45.7	68.6	31.1	55.9	64.0	60.9	30.6

the use of temperatures, times and concentrations of detergent other than 2 $g\,l^{-1}$ ECE detergent for 15 min at 60 °C would be disadvantageous from both cost and environmental viewpoints. Hence, the effectiveness of the ultrasound-assisted, detergent aftertreatment using 2 $g\,l^{-1}$ ECE detergent for 15 min at 60 °C was compared to that of a traditional reduction clearing process carried out in the absence of ultrasound.

Table 11 shows the fastness to repeated washing at 50 °C, of 1% and 2% omf dyeings which had been reduction cleared (in the absence of ultrasound) using 1.5 $g\,l^{-1}$ Na_2CO_3 and 2 $g\,l^{-1}$ $Na_2S_2O_4$ at 60 °C for 15 min, as well as dyeings which had been aftertreated using 2 $g\,l^{-1}$ ECE detergent (in the presence of ultrasound) for 15 min at 60 °C; results are also shown for dyeings which had received neither reduction clearing nor aftertreatment with ECE detergent. It is evident that for each of the three dyes used, the non-aftertreated dyeings displayed moderate/poor fastness to repeated washing at 50 °C, as evidenced by the staining of the adjacent multifibre strip imparted

Table 11
Wash fastness of 1% and 2% omf dyeings

Dye	Dye conc. (omf)	Clearing treatment	No. of washes	Change in shade	Diacetate	Cotton	Nylon	Polyester	Acrylic	Wool
C.I. Disperse Red 60	1	None	1	5	4	5	3–4	5	5	5
			5	5	5	5	5	5	5	5
		Reduction clear without ultrasound	1	5	5	5	4–5	5	5	5
			5	5	5	5	5	5	5	5
		ECE detergent[a] with ultrasound	1	5	4–5	5	4	5	5	5
			5	5	5	5	5	5	5	5
	2	None	1	5	2–3	5	1–2	4	5	4–5
			5	5	5	5	5	5	5	5
		Reduction clear without ultrasound	1	5	4–5	5	4–5	4	5	5
			5	5	5	5	5	5	5	5
		ECE detergent[a] with ultrasound	1	5	4	5	3	4–5	5	5
			5	5	5	5	5	5	5	5
C.I. Disperse Blue 56	1	None	1	5	3–4	4–5	2	4	5	4–5
			5	5	5	5	4–5	5	5	5
		Reduction clear without ultrasound	1	5	4–5	5	4	5	5	5
			5	5	5	5	4–5	5	5	5
		ECE detergent[a] with ultrasound	1	5	4–5	5	3–4	4–5	5	5
			5	5	5	5	4–5	5	5	5
	2	None	1	4–5	2–3	4–5	1–2	3–4	5	4
			5	4–5	5	5	4–5	5	5	5
		Reduction clear without ultrasound	1	5	4–5	4–5	4	4–5	5	5
			5	5	5	5	4–5	5	5	5
		ECE detergent[a] with ultrasound	1	5	3–4	4–5	2–3	4–5	5	5
			5	5	5	5	4–5	5	5	5
C.I. Disperse Yellow 42	1	None	1	4–5	4	4	2	4–5	5	5
			5	4–5	5	5	5	5	5	5
		Reduction clear without ultrasound	1	5	5	5	5	5	5	5
			5	5	5	5	5	5	5	5
		ECE detergent[a] with ultrasound	1	5	5	5	3–4	5	5	5
			5	5	5	5	5	5	5	5
	2	None	1	4–5	3–4	3–4	1–2	4–5	5	5
			5	4–5	5	5	5	5	5	5
		Reduction clear without ultrasound	1	5	5	5	4–5	5	5	5
			5	5	5	5	5	5	5	5
		ECE detergent[a] with ultrasound	1	5	5	5	4	5	5	5
			5	5	5	5	5	5	5	5

[a] ECE detergent 2 $g\,l^{-1}$; 60 °C; 15 min.

Table 12
Rub fastness of 1% and 2% omf dyeings

Dye conc. (omf)	Clearing treatment	Dry		Wet		Dry		Wet		Dry		Wet	
		Staining	Shade change	Staining	Shade change	Staining	Shade change	Staining	Shade change	Staining	Shade change	Staining	Shade change
		C.I. Disperse Red 60				C.I. Disperse Blue 56				C.I. Disperse Yellow 42			
1	None	3–4	4	5	5	3	4	4–5	4–5	4	4–5	4–5	4–5
	Reduction clear without ultrasound	4	4–5	5	5	3–4	4	5	5	4–5	5	5	5
	ECE detergent[a] with ultrasound	4	4–5	5	5	4	4–5	5	5	4–5	5	5	5
2	None	2–3	3–4	5	4–5	2	3–4	4	4–5	3	4	4	4–5
	Reduction clear without ultrasound	3–4	4	5	5	3	4	5	5	3–4	4–5	4–5	4–5
	ECE detergent[a] with ultrasound	3–4	4–5	5	5	3–4	4–5	5	5	4	4–5	4–5	4–5

[a] ECE detergent 2 g l^{-1}; 60 °C; 15 min.

by dye which had been removed from the dyeing during washing. It is also clear that the 2% omf dyeings displayed lower fastness, as expected, owing to the higher concentration of dye present. Table 11 also shows that the aftertreatment of the dyeings with both ECE detergent and reduction clearing improved, markedly in many cases, the fastness of the dyes, as reflected by the lower staining of adjacent materials, especially in the case of the first wash test. Although reduction

Table 13
Colorimetric data for 1% and 2% omf dyeings

Dye	Dye conc. (omf)	Clearing treatment	No. of washes	L^*	a^*	b^*	C^*	$h°$	$f(k)$
C.I. Disperse Red 60	1	None	0	58.7	59.7	12.4	61.0	11.8	27.4
			5	58.6	59.7	12.5	61.0	11.8	27.5
		Reduction clear	0	58.5	59.6	12.5	60.9	11.9	27.2
		without ultrasound	5	58.9	59.7	12.4	61.0	11.8	26.5
		ECE detergent[a] with	0	58.4	59.5	12.3	60.7	11.7	27.7
		ultrasound	5	58.8	59.4	12.2	60.6	11.6	26.6
	2	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	33.2
		Reduction clear	0	55.6	58.4	11.8	59.6	11.5	32.6
		without ultrasound	5	55.9	59.6	12.4	60.1	11.5	33.3
		ECE detergent[a] with	0	55.4	59.6	12.5	60.9	11.9	33.7
		ultrasound	5	56.1	60.0	12.6	61.2	11.8	33.2
C.I. Disperse Blue 56	1	None	0	45.8	5.8	−39.8	40.2	278.3	32.4
			5	46.5	6.2	−40.4	40.9	278.7	30.7
		Reduction clear	0	46.4	6.1	−40.1	40.3	278.3	31.0
		without ultrasound	5	46.8	6.0	−40.2	40.7	278.5	30.2
		ECE detergent[a] with	0	46.1	6.1	−40.1	40.6	278.6	31.6
		ultrasound	5	46.8	5.9	−40.0	40.5	278.4	30.1
	2	None	0	39.7	6.9	−39.8	39.8	280.1	50.1
			5	40.5	7.7	−40.5	41.2	280.7	47.0
		Reduction clear	0	40.5	7.0	−39.6	40.2	280.1	46.9
		without ultrasound	5	40.2	8.1	−41.0	41.8	281.2	48.1
		ECE detergent[a] with	0	40.5	7.5	−40.4	41.1	280.5	47.2
		ultrasound	5	40.8	7.8	−40.7	41.5	280.9	46.2
	1	None	0	68.5	28.0	53.0	60.0	62.2	27.6
			5	70.2	27.8	53.3	60.1	62.5	24.8
		Reduction clear	0	70.1	27.0	52.8	59.3	62.9	24.5
		without ultrasound	5	70.0	27.6	53.1	59.8	62.5	24.3
		ECE detergent[a] with	0	69.7	27.5	52.8	59.8	62.5	25.1
		ultrasound	5	70.1	27.9	53.6	60.4	62.5	25.2
	2	None	0	66.6	31.3	55.1	63.4	60.2	34.4
			5	67.9	31.9	56.2	64.6	60.4	32.6
		Reduction clear	0	67.8	31.5	55.6	63.9	60.5	32.1
		without ultrasound	5	68.1	31.9	56.1	64.6	60.4	32.2
		ECE detergent[a] with	0	67.6	31.9	56.1	64.6	60.4	33.1
		ultrasound	5	68.2	31.6	56.1	64.4	60.6	31.9

[a] ECE detergent 2 g l^{-1}; 60 °C; 15 min.

clearing was slightly more effective during the first wash test, which can be attributed to the greater severity of the hydrosulfite/Na_2CO_3 process, 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. Table 12 shows that, for each of the dyes used, the non-aftertreated dyeings displayed moderate/poor fastness to rubbing, especially dry rubbing, due to dye having not been removed from the dyeing by a subsequent aftertreatment. It is also apparent hat the 2% omf dyeings displayed lower rub fastness, as to be expected, owing to the higher concentration of dye present. Table 12 also reveals that both the detergent aftertreatment and the reduction clearing treatment improved the fastness of each of the three dyes to wet and dry rubbing and, also, that the detergent aftertreatment was slightly more effective, especially in the case of the 2% omf dyeings. The corresponding colorimetric data (Table 13) reveals that both the reduction clearing process and the detergent aftertreatment lowered the depth of shade of the dyeings, as shown by the lower $f(k)$ values of the cleared sample; this can be attributed to each of the aftertreatments for having removed surface dye from the dyeings. It is apparent that both reduction clearing and detergent aftertreatment imparted changes to the colour of the dyeings and that this was slightly more pronounced in the case of the reduction cleared samples.

The findings presented in Tables 11–13 show that there was little difference between the effectiveness of the ultrasound-assisted, detergent aftertreatment and that of the traditional reduction clearing process. Consequently, it appears that, in terms of fastness and colour, the Na_2CO_3 and $Na_2S_2O_4$ that are currently recommended for the reduction clearing of disperse dyes on PLA can be replaced with $2\ g\ l^{-1}$ ECE detergent in the presence of ultrasound.

4. Conclusions

The effectiveness of the ultrasound-assisted, detergent-based aftertreatment was little improved, if at all, through the use of temperatures $>60\ °C$, times >15 min and detergent concentrations $>2\ g\ l^{-1}$. As little difference was found between the effectiveness of the detergent aftertreatment and that of a traditional reduction clearing process, it seems that, in terms of fastness and colour, the Na_2CO_3 and $Na_2S_2O_4$ used in reduction clearing can be replaced with $2\ g\ l^{-1}$ ECE detergent. The alternative, ultrasound-assisted aftertreatment for dyed PLA may offer not only lower risk of hydrolytic damage to the fibre, but also reduced chemical consumption and the generation of a more environmentally acceptable effluent than reduction clearing.

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