Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Dyes and Pigments 77 (2008) 171−179
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

The clearing of poly(lactic acid) fibres dyed with disperse dyes using ultrasound. Part 1: Colorimetric analysis

S.M. Burkinshaw*, D.S. Jeong

The University of Leeds, Leeds LS2 9JT, UK

Received 3 August 2006; accepted 24 April 2007
Available online 6 May 2007

Abstract

Three types of clearing processes namely water, ECE detergent and reduction clearing were used to aftertreat the dyeings of six disperse dyes on PLA fibre. Reduction clearing imparted the greatest changes to the colour strength and colour of the dyeings while treatment with ECE detergent removed surplus dye and also 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. Both depth of shade reduction and colour change were greater when aftertreatment was carried out at 60 °C rather than at 50 °C due to a corresponding increase in the amount of removed dye as a result of greater kinetic energy at the higher temperature. Ultrasound neither impaired nor overly enhanced the effectiveness of either the ECE detergent or the reduction clearing processes.

Keywords: Ultrasound; Disperse dyes; PLA fibre; Reduction clearing

1. Introduction

Although WH Carothers first made poly(lactic acid) (PLA) in the early 1930s through direct condensation polymerisation of lactic acid, development of the polymer as a textile fibre was, at the time, abandoned owing to its low melting point and research efforts were focussed elsewhere, resulting in the introduction of the first commercially available, wholly synthetic textile fibre, *nylon 6,6*, in 1939. Nowadays, the thermoplastic polyester, PLA, is derived from annually renewable sources, such as corn and, in recent years, has enjoyed increasing commercial interest as an apparel fibre; although the linear, aliphatic nature of the polymer imparts susceptibility to hydrolysis, this particular characteristic allows the polymer to be industrially composted.

The dyeability of PLA [1−9] is akin to that of polyesters, such as poly(ethylene terephthalate) (PET) insofar as it is dyeable with disperse dyes, although differences exist between the two fibre types in terms of dye behaviour [6]. The lower T_m of PLA fibres (around 170 °C compared to 250−260 °C for PET) coupled with the hydrolytic sensitivity of the polymer means that neither elevated temperatures (125/130 °C) nor thermofixation (commonly 210 °C), which are commonly used to apply disperse dyes to PET, can be employed for PLA. Dyeing conditions of 110−115 °C for 15−30 min at pH 4.5−5 have been recommended for PLA [6]; the use of higher temperatures, longer times of dyeing at 110−115 °C or higher pH can lead to fibre hydrolysis.

As with disperse dyed polyester, a *reduction clear* treatment is needed to remove surplus dye and auxiliaries from PLA which has been dyed with disperse dyes. In the case of disperse dyes on polyester, reduction clearing comprises, typically, submitting the rinsed, dyed material to treatment for 20−30 min at 60−80 °C in an aqueous bath containing 2−3 $g\,l^{-1}$ NaOH, 2−3 $g\,l^{-1}$ $Na_2S_2O_4$ and, so as to restrain the washed-off dyes and auxiliaries from re-depositing on the dyed substrate, a surfactant; the reduction cleared substrate

* Corresponding author. Tel.: +44 113 343 3722; fax: +44 113 343 3740.
E-mail address: s.m.burkinshaw@leeds.ac.uk (S.M. Burkinshaw).

0143-7208/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2007.04.005

is then rinsed and, if necessary, neutralised with aqueous acetic acid. Reduction clearing relies on the marked hydrophobicity of the fibre preventing aqueous agencies from penetrating the substrate and also on the fact that the process is carried out at temperatures below the T_g (typically 80–90 °C in the case of PET), which means that not only will water and dissolved chemicals (NaOH and $Na_2S_2O_4$) not easily penetrate the dyed fibre but also dye molecules will not tend to migrate from the interior of the fibre to the surface during the reduction clearing treatment. In comparison to the reduction clearing of PET, that of PLA which has been dyed with disperse dyes employs more weakly alkaline conditions (Na_2CO_3 rather than NaOH) [6,10] and for a shorter time (15 min) [6,10] because of the greater alkali sensitivity of PLA and, as the T_g of PLA is in the range 55–65 °C, reduction clearing is undertaken, preferably at 60 °C [6,10,11].

In the context of the susceptibility of PLA to hydrolysis, and bearing in mind that such hydrolysis increases with increasing time, temperature and pH, 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 through reduced chemical usage. To this end, the decision was made to utilise the well-known abilities of ultrasound, videlicet, process acceleration and the attainment of similar/improved results under less extreme conditions (e.g. lower temperature, reduced chemical usage). Ultrasound (sound with a frequency above the upper limit of human hearing; >20 kHz), enjoys manifold applications, in fields as diverse as medical imaging, non-destructive testing and cleaning. The intensification of various wet textile processes using ultrasound is well-known and many papers have concerned the application of the technique to dyeing, as described in two comprehensive reviews [12,13]. Essentially, in textile wet processes such as dyeing, ultrasound influences mass transfer within the inter-yarn and intra-yarn regions of the substrate and it is generally considered that transient cavitation in the vicinity of the textile surface, rather than the ultrasound waves themselves, is responsible for the intensification observed [12–14].

This paper concerns the effect of ultrasound on the clearing of disperse dyed PLA fibre and the development of a hydrosulfite- and alkali-free clearing treatment; this part of the paper focusses on the effects of clearing on the colour of disperse dyeings on PLA.

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	

2. Experimental

2.1. Materials

Poly(lactic acid) knitted fabric (224.8 $g\,m^{-2}$), which was obtained from NatureWorks LLC, was scoured using 2 $g\,l^{-1}$ Na_2CO_3 and 1 $g\,l^{-1}$ *Sandozin NIN* (non-ionic surfactant; Clariant) using a 20:1 liquor ratio at 60 °C for 15 min. The scoured sample was rinsed thoroughly in tap water and allowed to dry in the open air. Commercial samples of the six disperse dyes shown in Table 1 were generously supplied by Dystar and Clariant; the dyes were used without purification. The six dyes were selected for use on the basis that they provided two representatives of low, medium and high energy classes of disperse dye. ECE detergent was sourced from the SDC. All other chemicals were of general laboratory grade supplied by Aldrich.

2.2. Ultrasound treatment

There are two methods of applying ultrasound namely *direct* and *indirect*. In the direct method, the solution of interest (in this case a reduction clearing solution) is placed directly in the ultrasound bath and the substrate (in this case, dyed PLA fibre) is immersed in the clearing bath. The advantages of this direct method of treatment are its simplicity of operation and its effectiveness; however, the removed dye and auxiliaries remain in the bath and, therefore, the reduction clear solution can be used only once; in addition, the highly alkaline solution can erode the ultrasound bath surface. The indirect method involves placing the reduction clearing solution and the dyed fibre in a container that is then placed inside the ultrasound bath. This method provides more flexibility and control over the ultrasound treatment; the removed dye and auxiliaries remain in the container and one or more solutions can be used at the same time.

In this work, the indirect method of ultrasound application was used.

2.3. Dyeing

A 2% omf depth of shade was used as this provided typical medium depth dyeings. Dyeing was carried out using a 10:1

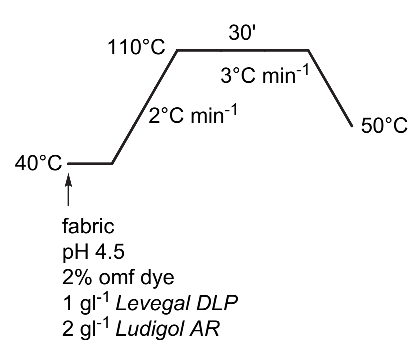

Fig. 1. Dyeing method.