Ultrasonics Sonochemistry 31 (2016) 350–354

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Ultrasonic dyeing of cellulose nanofibers

Muzamil Khatri [a], Farooq Ahmed [a], Abdul Wahab Jatoi [a,b], Rasool Bux Mahar [c], Zeeshan Khatri [a,b,*], Ick Soo Kim [b,*]

[a] Nanomaterial Research Group, Department of Textile Engineering, Mehran University of Engineering and Technology, Jamshoro 76062, Pakistan
[b] Nano Fusion Technology Research Group, Division of Frontier Fibers, Institute for Fiber Engineering (IFES), Interdisciplinary Cluster for Cutting Edge Research (ICCER), Shinshu University, Tokida 3-15-1, Ueda, Nagano Prefecture 386-8567, Japan
[c] US-PCASW at Mehran University of Engineering and Technology, Jamshoro 76060, Pakistan

ARTICLE INFO

Article history:
Received 25 December 2015
Received in revised form 19 January 2016
Accepted 20 January 2016
Available online 22 January 2016

Keywords:
Ultrasonic dyeing
Cellulose nanofibers
Electrospinning
Reactive dyeing
Color yield

ABSTRACT

Textile dyeing assisted by ultrasonic energy has attained a greater interest in recent years. We report ultrasonic dyeing of nanofibers for the very first time. We chose cellulose nanofibers and dyed with two reactive dyes, CI reactive black 5 and CI reactive red 195. The cellulose nanofibers were prepared by electrospinning of cellulose acetate (CA) followed by deacetylation. The FTIR results confirmed complete conversion of CA into cellulose nanofibers. Dyeing parameters optimized were dyeing temperature, dyeing time and dye concentrations for each class of the dye used. Results revealed that the ultrasonic dyeing produced higher color yield (*K*/*S* values) than the conventional dyeing. The color fastness test results depicted good dye fixation. SEM analysis evidenced that ultrasonic energy during dyeing do not affect surface morphology of nanofibers. The results conclude successful dyeing of cellulose nanofibers using ultrasonic energy with better color yield and color fastness results than conventional dyeing.

1. Introduction

Nanofiber for use in apparel has attained a great deal of interest recently due to its breathable characteristics, lighter in weight and ease of production via electrospinning. Apart from the intensive research on functional characteristics of nanofibers [1–5], the exploration of dyeability of nanofibers has also been initiated for obtaining aesthetic property. Since the past couple of years, dyeing of nanofibers by various methods has been reported. Most recent works include dyeability of cationic cellulose nanofibers with reactive dyes by batchwise method [6], dyeing of cellulose acetate (CA) nanofibers with disperse dye by pad-dry-bake method [7], cold-pad-batch dyeing method of nanofiber [8], dyeing of nanofibers by dual padding method [9] and dyeing of polyurethane nanofibers by pad-dry-bake method [10]. Despite consistent progress in this area, nanofiber dyeing remains a challenge due to lower color yield in comparison to conventional fibers. This is mainly due to higher surface to volume ratio that actually scatter more light and result into lower color yield values. Since this factor is out of dyer's control, the only possible way is to develop method that would be able to introduce more dye into nanofibers.

In our opinion, the color yield may improve if the nanofiber dyeing were assisted by ultrasonic energy, thanks to the sonication that breaks the dye aggregates. Later, this was proved through our experiments to be a better option to improve color yield. Ultrasonic assisted dyeing of cellulosic fibers has already proved to be a better choice among conventional dyeings. For instance, low temperature dyeing of knitted cotton fabric using ultrasonic energy [11], ultrasonic-assisted dyeing of bamboo fibers [12], ultrasound-assisted dyeing of cellulose acetate [13], cold-pad-batch dyeing of cotton fiber using ultrasonic energy [14], ultrasonic natural dyeing [15]; ultrasonic dyeing of cellulosic fabric [16], ultrasonic dyeing of cationized cotton fabric [17,18]. Dyeing of cotton fabrics with *Crocus sativus* using ultrasonic method [19], ultrasonic assisted dyeing of cationic cotton with lac natural dye [20]. Therefore, we attempted to optimize ultrasonic assisted dyeing method for cellulose nanofiber and report improvement in terms of color yield.

There has always been a choice for dyers to dye cellulosic fiber with reactive dyes, direct dyes, sulfur dyes and vat dyes [21]. We chose reactive dyes due to wide range of inexpensive brilliant colors with excellent color fastness to washing [22]. The cellulose nanofibers were dyed with CI reactive black 5 and CI reactive red 195 by ultrasonic-assisted batchwise dyeing method. The

* Corresponding authors at: Nanomaterial Research Lab, Department of Textile Engineering, Mehran University of Engineering and Technology, Jamshoro 76060, Pakistan (Z. Khatri).
E-mail addresses: zeeshan.khatri@faculty.muet.edu.pk (Z. Khatri), kim@shinshu-u.ac.jp (I.S. Kim).

http://dx.doi.org/10.1016/j.ultsonch.2016.01.020
1350-4177/

ultrasonic dyeing parameters optimized were dyeing temperature, dyeing time, dye concentrations and color fastness properties. The optimized results of conventional dyeing have also been presented in the article. The morphologies of optimum samples were investigated under scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

Cellulose acetate, CA (39.8% acetyl content having an average Mw = 30 kDa), was obtained from Sigma–Aldrich Chemical Co. and used without further purification. Two dyes used were namely, CI reactive black 5 (bis-sulphatoethylsulphone) (Mw = 991.82 g/mol) and CI reactive red 195 (Aminochlorotriazine-sulphatoethyl sulphone) (Mw = 1136.32 g/mol), supplied by the Sumitomo Chemical Co., Ltd., Japan; the corresponding dye structures are shown in Scheme 1. Sodium carbonate and sodium sulphate used were of Analar grade.

2.2. Preparing cellulose nanofibers

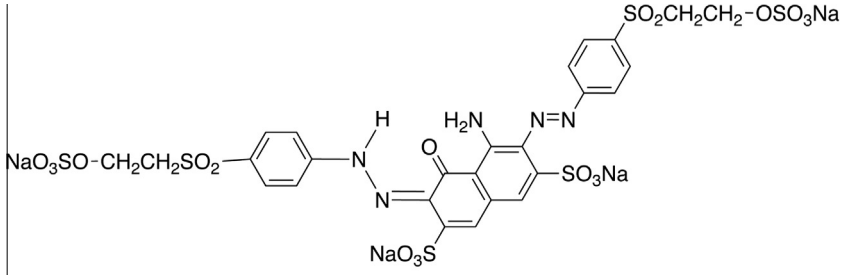
For cellulose nanofiber preparation, cellulose acetate (CA) was electrospun followed by deacetylated to remove acetyl group. Our previous method [14] was followed for electrospinning of CA nanofibers. A 17% of CA solution was prepared using acetone: DMF solvents (2:1) and electrospun using a high-voltage power supply (Har-100*12, Matsusada Co., Tokyo, Japan). The voltage applied was 12.5 kV and 15 cm distance from needle-tip to collector was fixed. The nanofibers were then dried in air for 48 h. For deacetylation, conversion of CA into cellulose, the CA nanofiber samples were soaked for 30 h in 0.05 M NaOH followed by rinsing with distilled water till neutral pH of cellulose nanofibers was obtained. Before ultrasonic dyeing, all cellulose nanofibers were dried at 50 °C for 4 h.

2.3. Dyeing of cellulosic nanofibers

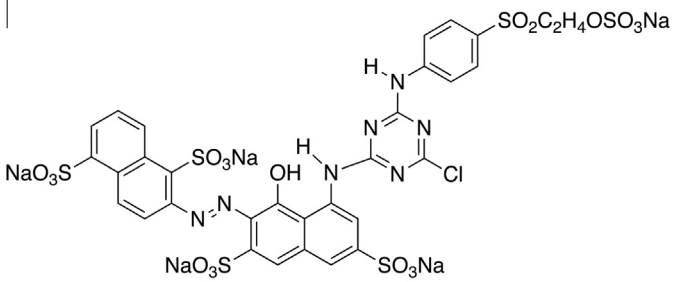
All nanofiber webs were dyed by batchwise method using Ultrasonic equipment (Model: Elmasonic E30H, Elma, Germany) with precise control of time and temperature. The dyeing was carried out at 320 W power output using fixed frequency of 37 kHz. The internal area of the bath was $24 \times 13.7\ cm^2$. The ultrasonic intensity to the dye bath was $0.97\ W/cm^2$ (Intensity = Power/ bath area; 320/328). At low ultrasonic intensities less than $3\ W/cm^2$, forms stable cavitation bubbles, which breaks dye aggregates at nanofibers surface as a result, dye diffusion is enhanced. The ratio of dye liquor to the mass of nanofibers was maintained at 20:1. Nanofibers dyeing was carried out to investigate the effect of dyeing temperatures (40–80 °C), effect of dyeing times (10–70 min) and effect of dye concentrations (2–6% on mass of web, omw) on color yields of dyed nanofibers. After dyeing, each sample was finally given a gentle rinse separately with warm then cold water followed by soaping-off with anionic detergent. The wash was continued until no dye bleeding was observed. In order to compare ultrasonic dyeing with conventional dyeing of nanofibers, we selected optimum dyeing conditions based on our previous work [6]. Briefly, conventional dyeing of cellulose nanofibers was carried out without using ultrasonic energy at 70 °C for 60 min. The dye concentration selected was 3% omw for each dye.

2.4. Measurement of color

The *K*/*S* values that determine the color yield of dyed nanofibers, were assessed for each dyed sample using Datacolor Spectrophotometer. The relative color yields (*K*/*S* values) were calculated using Eq. (1):



CI Reactive Black 5



CI Reactive Red 195

Scheme 1. Chemical structures of reactive dyes.