

Dyeability of Nanofibers with Reactive, Vat and Disperse Dyes

Farooq Ahmed, Umair Ahmed Qureshi, and Zeeshan Khatri

Abstract—Colorful nanofibers were prepared through electrospinning technique followed by dyeing with different reactive dyes by comparing different dyeing techniques such as ultrasonic as well as conventional (padding method). Excellent color yield and color fastness were achieved through proper optimization conditions in ultrasonic treatment. Nanofibers exhibited smooth and bead free morphology. Two different polymers were selected for electrospinning, i.e. cellulose acetate and nylon-6. Preparation of cellulose nanofibers included electrospinning of cellulose acetate following deacetylation under alkaline conditions. Results suggested that dyes conferred improved color yield on the basis of K/S values. Deacetylation was also confirmed through FTIR. The resulting nanofibers can serve better choice for advanced apparel applications.

Index Terms—Padding, batch wise, dyed nanofibers.

I. INTRODUCTION

Nanofibers are drawing intense research interests because of ease of fabrication and wide variety of polymers used for electrospinning. They find wide variety of applications such as filters [1], biosensors [2], [3], wound healing [4], tissue scaffolds [5], drug delivery [6], [7], breathable membranes [8], [9] and nanocomposites [10]. Nanofibers are also considered as excellent water absorbents and offer greater flux for water vapors [11]. Different waterproof breathable nanofibers are reported [12]-[14]. Literature survey reveals broad application of nanofibers for apparel use but colorimetric properties are rarely discussed. The fundamental technique for production of colored nanofibers is to dye the nanofiber sample after electrospinning and color yield is the main criterion in selecting best quality of nanofiber. Therefore, present research focuses on the production of colored nanofibers after post electrospinning treatment through different techniques such as conventional as well as ultrasonic. In present work we have prepared two types of nanofibers, i.e. cellulose nanofibers and nylon-6 nanofibers followed by dyeing with reactive dyes and vat dyes. The dyeing procedure was compared through two techniques, i.e., conventional method and ultrasound assisted method. Different parameters such as color yield (K/S), color fastness to light and washing tests were assessed for dyed nanofibers. The characterization of resulting nanofibers was obtained by analytical techniques such as scanning electron microscopy (SEM) and FTIR.

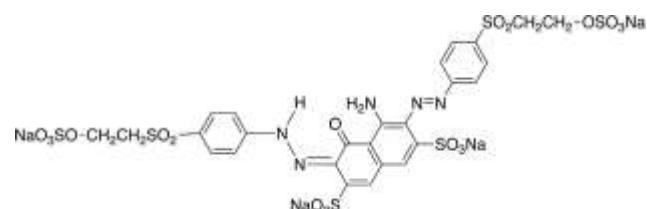
Manuscript received November 9, 2018; revised January 25, 2019.

The authors are with Centre of Excellence in Nanotechnology and Materials, Mehran University of Engineering and Technology, Jamshoro, Pakistan (e-mail: farooq.ahmed@faculty.muet.edu.pk, ahmedumair2011@gmail.com, zeeshan.khatri@faculty.muet.edu.pk).

II. EXPERIMENTAL

A. Materials

Following reagents were used in present work: Cellulose acetate (CA) and Nylon 6 (Sigma-Aldrich USA). CI reactive black 5 (RB 5), CI disperse blue 167:1 (DB 167:1) and (Sumitomo, Japan, Archroma, Pakistan and Huntsman, USA respectively). The chemical structures of studied dyes are given in Fig. 1.



III. RESULTS AND DISCUSSION

Two different methods, i.e., conventional and ultrasonic methods were used for dyeing of nanofibers. UV Vis Spectrophotometer was used for measuring color yield values.

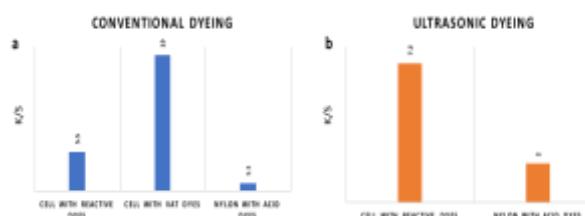


Fig. 2. Comparison of dyeing with (a) conventional and (b) US method.

A. Conventional Dyeing

From the Fig. 2(a), it is clear that cellulose nanofibers dyed with reactive dyes showed color yield of 5.5. The K/S values of cellulose nanofibers when dyed with vat dyes was 19 that is 3 times greater than former. The possible reason behind this can be higher molar extinction coefficient of vat dye than reactive. On the other hand, low K/S values were noticed with disperse dyes dyed on nylon-6 nanofibers owing to greater crystalline domain that inhibit their diffusion.

B. Ultrasonic Dyeing

Fig. 2(b) presents ultrasonically treated nanofibers using reactive and vat dyes. Contrary to reactive dyes, vat dye showed improved K/S value (7.2) on cellulose nanofibers. This may be due to ultrasonic cavitation generated due to sonication. Ultrasonically dyed nylon-6 nanofibers also showed greater K/S values (2) that was also better than conventional method.

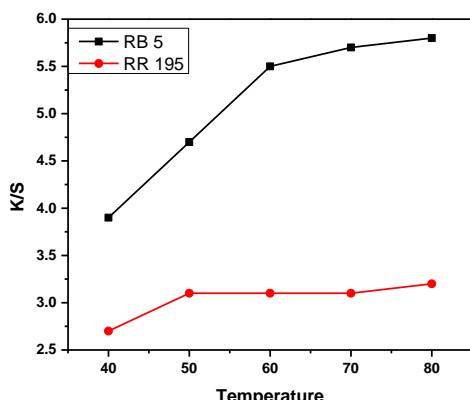


Fig. 3. Effect of dyeing temperature on color yield.

C. Effect of Temperature on Dyeing of Nanofibers.

As ultrasonic dyeing is reported for the very first time, therefore it was necessary to optimize dyeing parameter such as temperature. To begin with this, temperature was optimized using cellulose nanofibers at fixed time i.e. 80 min using C.I RB 5 and C.I RR 195. The color yield using RB% increased steeply from 40°C to 60°C that became constant on further rise in temperature as shown in Fig. 3. This could be due to substantivity ratio and hydrolysis of dye molecules on extremely higher temperatures. Irrespective to the dyeing temperature, the color yield of CI reactive black 5 obtained

higher than the CI reactive red 195. This may be due to the difference of molar extinction coefficient, affinity and reactivity between both dyes. On the other hand, dye uptake of CI reactive red 195 slowly increased from 40 °C to 60 °C and reached higher yield at 70 °C. This steady profile of CI reactive red 195 is due to lowering of substantivity ratio caused by increasing temperature. Whereas, for nylon nanofibers using disperse dyes the dyeing at fixed time (60 min), the maximum color yield obtained was at 80C beyond which the K/S values decreased due to either dye hydrolysis or migration of dye molecules back to solution phase from nanofiber phase.

D. Effect of Dyeing Time on Color Yield

Considering maximum dye uptake by cellulose nanofibers at 70 °C using RB5, impact of dyeing time on ultrasonic dyeing on cellulose nanofibers was investigated. RB5 shows steep rise in dye uptake with increase in time from 10 min to 20 min, further increase in time did not affect dye uptake and rendered a plateau beyond 20 min in the graph. This may be attributed to ultrasonic cavitation that breaks dye aggregates and tends to increase dye uptake. On the basis of these results 30 min were selected optimum for RB5 dyeing using cellulose nanofibers. Nylon-6 nanofibers also show similar behavior while using disperse dyeing. Whereas conventional dyeing rendered modest dye uptake and reached its maximum capacity at 60 min shown in Fig. 4. It is further suggested that sonication promotes significant mass transfer and transient cavitation near fiber surface are responsible for improved results.

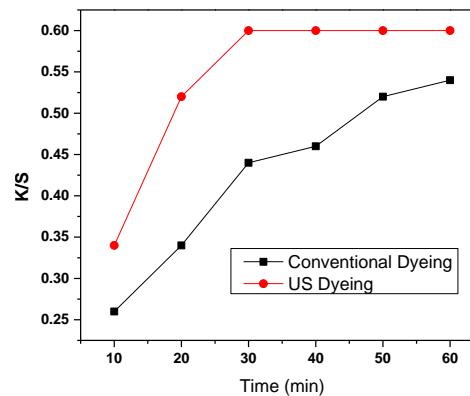


Fig. 4. Effect of dyeing time on color yield.

E. Color Fastness

Table I summarizes the the results of color fastness to light and washing. ultrasonically treated dyes showed better light fastness tests (4) compared to conventional. Vat dyes had better light fastness (7). This improvement on light fastness can be due to bulkier molecule size of vat dyes than the reactive. The observed light fastness in case of nylon 6 nanofibers was only 2 regardless of the dyeing technique. Generally, washing fastness of nanofibers was extremely excellent in performance. For instance, shade change of cellulose nanofiber was ¾ and 4 with reactive dyes, however, vat dye showed 4/5 better than the later. However, except cellulose nanofibers, the staining was 4/5 to 5 with other samples. Cellulose nanofibers dyed with reactive dyes presented staining 3 only. Sonication obviously does not

influence color fastness of the nanofibers. Color fastness to hot pressing was evaluated for each dyed nanofibers, the shade change and staining ratings obtained 4/5 for nanofibers dyed with CI Disperse Red 167:1. The nanofibers dyed by ultrasonic method did not show any difference than the nanofibers dyed by conventional method. Since the CI Disperse Red 167:1 is high energy level dye, it showed better fastness (hot pressing) results

TABLE I: COMPARISON OF LIGHT FASTNESS AND WASHING FASTNESS TESTS

Nanofiber	Dye	Light	Washing, Sh. Ch.	Washing Co. staining
Cell. nanofibers	RB5	3	3/4	3
US-Cell. nanofibers	RB5	4	4	5
Cell. nanofibers	Vat-Blue 4	7	4/5	4/5
Nylon 6 nanofibers	DR167:1	2	3/4	4/5
US-Nylon 6 nanofibers	DR 167:1	2	3/4	4/5

Shade Change: Sh Ch.; Cellulose: Cell. Cotton: Co.; Ultrasonic: US

F. Nanofibers Morphology

Fig. 5 reveals SEM images of dyed cellulose and nylon nanofibers. All nanofibers were smooth and bead free in morphology. It can also be observed that the diameter of cellulose nanofibers was greater (400 nm to 600 nm) than nylon-6 (80-150 nm). Dyeing procedure had no detrimental impact on nanofibers morphology. However, ultrasonic treatment caused a little detrimental impact.

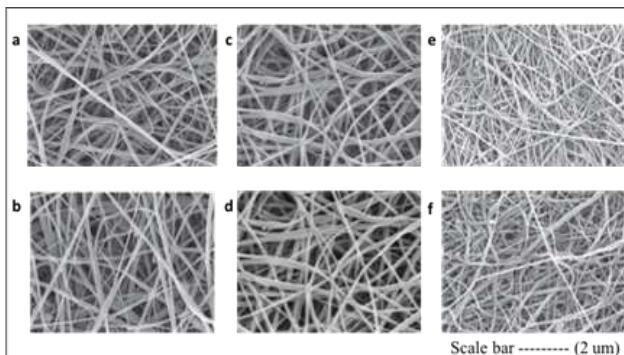


Fig. 5. SEM images of cellulose nanofibers (a) through conventional dyeing with reactive dye (b) through ultrasonic treatment (c) without dye cellulose nanofibers (d) Nylon-6 nanofibers conventionally dyed with vat dyes (e) conventional treatment of disperse dye(f) Ultrasonic treatment of nylon-6 nanofibers.

A. FTIR Characterization

The successful conversion of CA nanofibers into CNFs and subsequent dyeing was confirmed through FTIR as shown in Fig. 6. The disappearance of characteristic peaks from cellulose acetate i.e. 1745 due to C=O, 1375 due to C-CH₃, 1235 due to C-O-C confirms the successful conversion of cellulose acetate to cellulose. However, there was no significant change in the IR absorption bands of cellulose before and after dyeing that implies that ultrasonic treatment has no influence on chemical structure of cellulose.

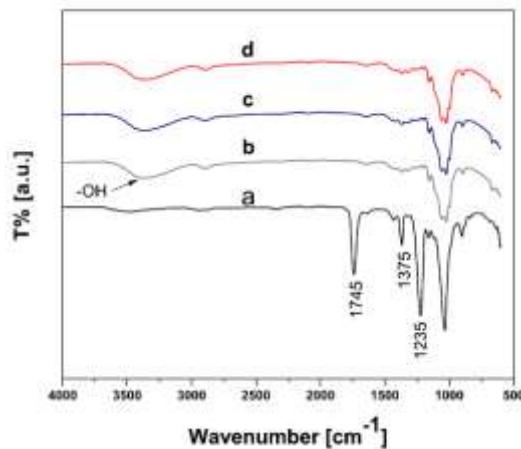


Fig. 6. FTIR analysis of (a) CA nanofibers, (b) CNFs (c) CNF dyed with RB 5 and (d) RR 195.

B. Mechanical Study of Nanofibers

Fig. 7 shows comparison of tensile strength between US dyed nylon-6 nanofibers and conventionally dyed nanofibers. Since cellulose nanofibers were not in condition and lost their strength after US dyeing, therefore, nylon-6 nanofibers were considered suitable for measuring mechanical properties. Nylon-6 nanofibers dyed with US technique showed a substantial improvement in mechanical strength (3 to 3.5 N tensile strength) in contrast to the conventional dyeing. The probable reason behind this can be cavitation during ultrasonic dyeing that imparted stiffness to the nylon-6 nanofibers. To confirm the influence of dye class on mechanical strength of nylon-6 nanofibers the nanofibers were subjected to US in water referred as blank. It was observed that dyeing class had no impact in imparting mechanical strength. Their greater stiffness and tensile strength can trigger its applications as surgical apparel.

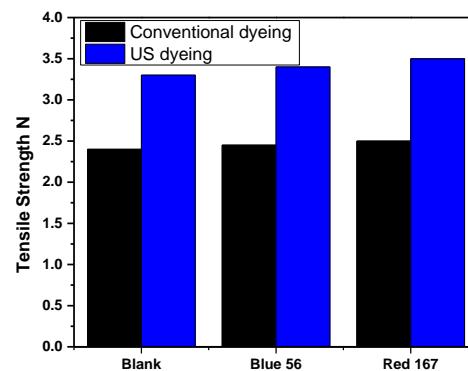


Fig. 7. Comparison of tensile strength of nylon-6 nanofibers dyed through US and conventional method.

IV. CONCLUSION

Cellulose and nylon-6 nanofibers were successfully prepared and dyed using different dyes. Excellent color yield was obtained using cellulose nanofibers than nylon-6. US dyeing of nanofibers showed better color yield than conventional dyeing. US dyeing completes within at 30 min, which is half of the conventional dyeing, which demonstrates substantial time reduction. Irrespective to the dye class used, the US dyeing showed a significant increase in %F as compared to conventional dyeing, however, the %F

decreased upon dye concentration increased. Dyeing of nylon-6 nanofibers with conventional method showed low K/S values, however similar dyeing with ultrasonic method improved its color yield. SEM images confirmed smooth and beadles nanofibers. On the basis of the color fastness and light fastness tests, it can be suggested that nanofibers can be effectively used for apparel applications. Color fastness tests indicate good dye fixation based on good to very good rating in color fastness to washing and hot pressing. The nanofibers dyed with US dyeing method showed a significant increase of tensile strength in comparison to conventional dyeing method.

ACKNOWLEDGMENT

The authors are grateful to Mehran University of Engineering and Technology Jamshoro Pakistan for providing lab and chemicals. The authors also pay gratitude to Prof. Ick Soo Kim from Shinshu University Japan for providing characterization facilities

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Farooq Ahmed is currently serving as a professor in Textile Engineering Department, Mehran University of Engineering and Technology. He obtained his B.Sc in engineering from National Textile University, Faisalabad, Pakistan in the year 1996 and secured doctorate degree in textile Engineering from Mehran University of Engineering and Technology, Jamshoro Pakistan in the year 2013. He joined Mehran University in the year 1998. His research interests include nanofibers, nanomaterials, environmental concerns regarding textile, Textile testing and quality control. He has published more than 25 publications in SCI-SCI expanded Journals.

Umair Ahmed Qureshi is a lecturer in chemistry at Government Boys Degree College Qasimabad Hyderabad, Pakistan. He is doing post doctorate research in Centre of Excellence in Nanotechnology and Materials Mehran University of Engineering and Technology Jamshoro Pakistan. He obtained his BS degree in organic chemistry in the year 2008 from University of Sindh Jamshoro Pakistan and obtained PhD in analytical chemistry in 2015 from same University. He was also awarded split PhD scholarship sponsored by scientific and technological research council of Turkey in the year 2013-2014. His research interests include nanofibers, electrospinning, environmental analytical chemistry, chromatographic separations and determinations of endocrine disrupting compounds.

Zeeshan Khatri is a professor at Department of Textile Engineering, Mehran University Jamshoro. He started his professional career in the year 2000 after graduating from (94 batch) Mehran University Jamshoro. He has 17 years academic and industrial experience. After spending 8 years in textile industry, he joined Mehran University as a lecturer in the year 2009 and did his ME in textile engineering. He then pursued for doctorate degree and completed within 2.5 years from Shinshu University Japan in September 2013. He also owns professional titles CCol ASDC (UK) and CText ATI (UK) and PE (Pak). In 2004, SDC awarded him a President's Diploma of Honor on his most meritorious performance in ASDC examinations

Dr. Khatri is a principal investigator of *Nanomaterial Research Group*, comprising of eminent scientist around globe. He has 38 international publications with cumulative impact factor of 130.0 and 2 book chapters published by Springer. Dr. Khatri has been a national speaker at various conferences, seminars and workshops and participated more than 100 national and international conferences. Dr. Khatri is a lead guest editor of annual issue in *Journal of Nanomaterials* (impact factor 1.7). He is inventor of various nanofibers membranes, on his credit are 2 Japanese patent, 1 US Patent and 6 patents have been filed. Dr. Khatri is a co-founder of nano CLO and CEO of MuTech (Pvt) Ltd