Dyeing of Electrospun Nanofibers

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Contents

Abstract

Dyeing and colorimetric properties on different types of nanofibers is promising for potential apparel applications. Apart from the functional properties electrospun cellulose acetate nanofibers, cellulose nanofibers, Nylon 6 and Nylon 6,6

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nanofibers, Polyester nanofibers, and polyurethane nanofibers are being widely studied recently for dyeing with different dyes and techniques. In general, the polymers solution prepared and converted into nanofibers using electrospinning. The prepared nanofibers are continued to obtain a web thickness varied between 10 um and 100 um, depending on the type of polymer being electrospun. The nanofiber web is then dyed with specific dyes by either batch wise or padding method. We also report using ultrasonic energy in dyeing process to enhance color strength (K/S) values and efficiency of process. This chapter covers range of nanofibers that can be dyed with different dyes and techniques with achieving enough color strength, color fastness values with unaltered morphology, and chemistry of nanofibers. The dyed electrospun nanofibers can potentially be considered for advanced apparel applications.

Keywords
Nanofibers · Dyeing · Dyes · K/S · Color · Apparel · Textile · Electrospinning

Introduction

The dyeing of electrospun nanofibers is an integral part of advance apparel textiles. Nanofiber-based nonwoven fabrics have intensive research interest because of consistent production and availability of polymers and dyes in variety. Nanofibers have broad application spectrum specifically for apparel applications such as lighter weight and waterproof breathable membranes. Some recent studies showed a very good performance of nanofibers in terms of their waterproofing, vapor permeability with better breathability; this research trend confirms that nanofiber can potentially be used as advanced apparel applications [1].

However, the aesthetic properties of nanofibers in terms of color appearance remain an important parameter to be considered for the smart and functional apparel. Therefore, dyeing of nanofibers opens a new door to explore coloring and dyeability of nanofibers. Dyeing and colorimetric properties on different types of nanofibers such as electrospun cellulose acetate nanofibers, cellulose nanofibers, Nylon 6 and Nylon 6,6 nanofibers, Polyester nanofibers, and polyurethane nanofibers are being widely studied these days using different dyes and techniques [2–13]. There are several kinds of dyes which can be used on different types of fiber, either by affinitive properties play role or the fiber surface is functionalized (cationized or anionized) according to application of respective dyes on nanofibers substrate. Dyeing on electrospun cellulose nanofibers has achieved vital enhancements, basically cellulose nanofibers are being made from precursor of cellulose acetate nanofibers. Cellulose acetate nanofibers can be prepared by electrospinning method which is given in Fig. 1. Mainly two solvents Acetone and Dimethylformamide are used with 2:1 for making polymer solution of cellulose acetate with 17%. The nanofibers are collected on negatively charged collector and peeled in the form of non-woven web. Cellulose acetate is then converted into cellulose by using deacetylation process; ultrasonic deacetylation is used as rapid deacetylation process

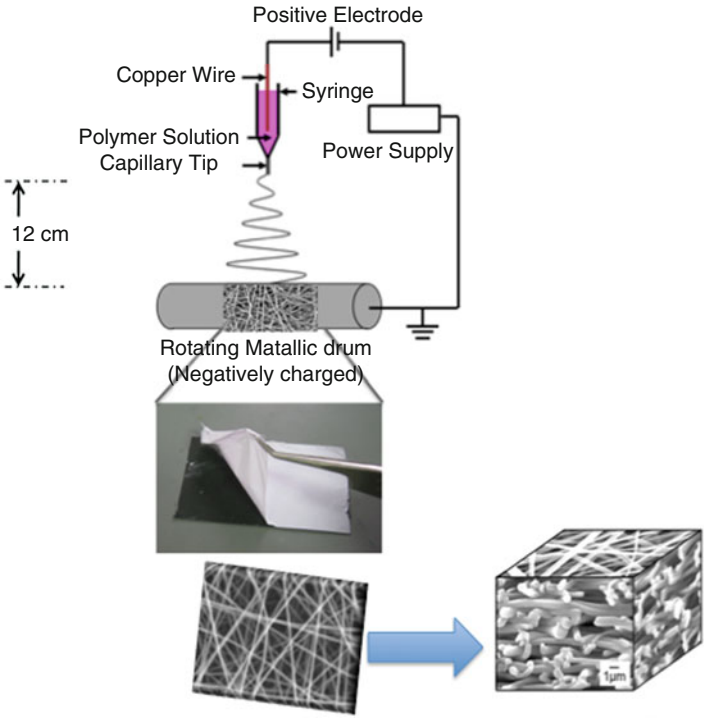

Fig. 1 Electrospinning setup

these days which can be carried in only 1 h [14]. Deacetylation is the process in which acetate is removed from cellulose acetate in alkali solution where NaOH is used as alkali with 0.05 molar in the solution for deacetylation. After deacetylation, the electrospun nanofibers are carried under either dyeing process or either surface functionalization process.

Cellulose nanofibers are dyed with reactive dyes using different techniques such as: Cellulose nanofibers are cationized and can be dyed with reactive dyes, which have significance to enhance the color yield values of around 76% with excellent color fastness properties. Cellulose nanofibers dyed with reactive dyes using because of dye uptake in order to obtain higher color strength values, cellulose nanofibers were dyed dual pad method. The cold-pad-batch method offers economy since there no temperature involved during dyeing process. On the other hand, dyeing of cellulose nanofibers with assisted with ultrasonic energy show better color yield and fixation values.

Ultrasonic energy produces cavitation within the molecules of any fluid or liquid to enhance the efficiency of any chemical process or chemical reaction. Ultrasonic energy in dyeing process is used to enhance color strength (K/S) values and efficiency of process. Ultrasonic energy also saves the temperature comparing to conventional dyeing process. Ultrasonic dyeing also includes dyeing of Nylon

6 nanofibers with acid dyes; nylon nanofibers can also be dyed conventionally with acid dyes, but the color strength K/S can be attained less than the ultrasonication. Polyurethane nanofibers can by dyed ultrasonically or conventionally using disperse dyes where ultrasonically dyed polyurethane can attain more K/S values compared to conventional method.

Cellulose acetate nanofibers and polyester nanofibers can also be dyed by using disperse dyes with sufficient color strength values. Polyester nanofibers were dope dyed. Doping is a technique in which dye is directly mixed with polymer solution and electrospun on electrospinning machine to fabricate colored nanofibers directly during electrospinning. In nanofiber dyeing processes, first dyeing parameters are optimized such as dyeing temperature, dyeing time and dye concentration, and color build up values. K/S color strength values can be measured by using data color spectrophotometer. This measures the wavelength of visible range color by reflectance principle.

This chapter deals with different polymers and techniques being used for dyeing of polymeric nanofibers and advantages associated with them. The dyed electrospun nanofibers are then carried under different characterizations to know actual physical and chemical properties such as Fourier transform infrared spectroscopy, X-ray Photoelectron spectroscopy, and Raman Spectroscopy for chemical and Scanning electron microscopy, transmission electron microscopy, water contact angle, wicking behavior, tensile strength, and thermodynamics studies for physical characterizations.

Dyeing of Electrospun Cellulose Nanofibers

Cellulose nanofibers after electrospinning have been dyed with reactive dyes and vat dyes. Since these dyes have the affinity towards cellulosic nanofibers, the cellulose nanofibers were dyed with dyes using batchwise method. In particular, two different class of vat dyes viz. CI vat blue 4 (VB4) and CI vat green 1 (VG1) were selected for dyeing cellulose nanofibers. The influence of dyeing temperature on color yield (K/S) while using VB4 and VG1 dyes were investigated as shown in Fig. 2. Color yield of VG1 showed rapid increase with increasing dyeing temperature from 40 °C to 50 °C and slow increments were observed in color yield between dyeing temperature from 50 °C to 60 °C, whereas dyeing temperature of 70 °C show no

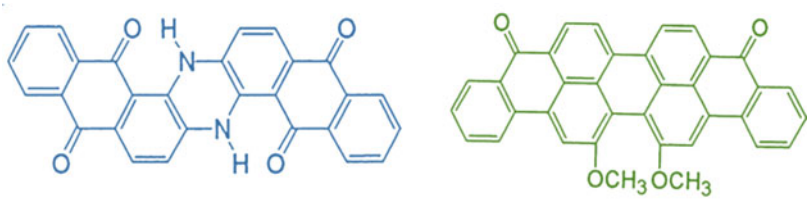

Fig. 2 Chemical structures of vat dye blue and vat dye green

significant increment in color yield. Dyeing temperature optimized at 60 °C because it showed maximum color yield at constant time and dye concentration. Similarly, influence of time was investigated using optimum temperature and 1% dye concentration. The maximum color yield was obtained when the dyeing carried out for 50 min, after which, no further increase in color yield was observed. Similar trend was observed for the cellulose nanofibers dyed with VB4.

Color build-up property of both VB4 and VG1 on cellulose nanofibers were investigated using different dye concentrations (1%, 1.5%, 2%, 2.5%, and 3%) using optimized time and temperature 50 min and 60 °C, respectively. The dye VG1 resulted higher K/S values than the dye VB4; it is mainly due to higher molar extinction coefficient of VG1. VB4 dye resulted 20.5 K/S at 3% dye concentration, which is twice as higher than 1% dye concentration. Similarly, VG1 dye resulted 22.5 K/S at 3% dye concentration, which is also twice as higher than 1% dye concentration. Since K/S values are continuously increased with increasing dye concentrations of both vat dyes as shown in Fig. 3 Thus, the vat dyes have good color build up properties for cellulose nanofibers.

Staining in washing fastness test for VB4 obtained high ratings because it indicated no color bleed, which is evidence of good dye fixation. The staining observed on VB4 dyed nanofibers obtained more than half of the fastness ratings compared to cellulose nanofibers dyed using VG1 due to different molar extinction coefficient of vat dyes. Color change rating in case of both vat dyes is 4/5, which is very good rating for washing fastness test. Results of color fastness to light were assessed against blue wool scale (1–9), 1 being very poor and 9 being excellent. Light fastness of dyed cellulose nanofibers also shows 7 blue wool scale ratings, which considered to be excellent. The overall color fastness performance and dyeability of cellulose nanofibers with vat dyes showed very good as per given Table 1 (Fig. 4).

In another study, influence of ultrasonic dyeing of cellulose nanofibers using Reactive Red 195 and Reactive Black 5 dyes was observed and compared to

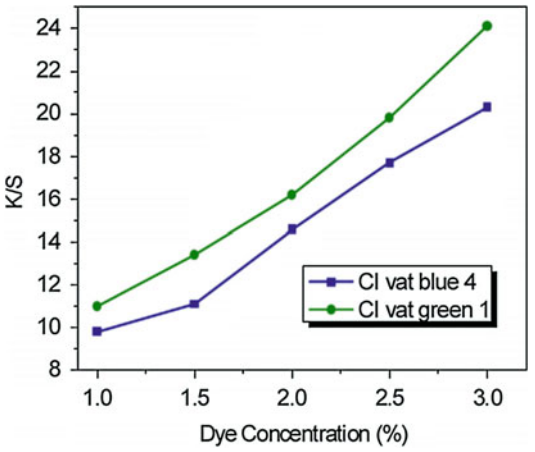

Fig. 3 Effect of dye concentrations on color yield (dyeing time 50 min; dyeing temperature 60 °C)

Table 1 Color fastness to washing test ISO 105-C10:2006 and color fastness to light test ISO 105-BO2

Dye conc. (1%)[1]	Light fastness (20 h)[2]	Washing fastness (Change of shade)[3]	Washing fastness (Staining on multifiber)[4]					
			CT	CO	PA	PES	PAC	Wo
VB4	7	4/5	5	4/5	5	5	5	5
VG1	7	4/5	5	4/5	5	5	5	5

[1]Dyeing conditions: Dyeing temperature 60 °C and time 50 min
[2]Blue wool scale 1–9, being 1 is poor and being 9 is excellent
[3]Grey scale 1–5, being 1 is poor and being 9 is excellent
[4]*CT* cellulose triacetate, *CO* cotton, *PA* polyamide, *PES* polyester, *PAC* polyacrylic, *Wo* wool

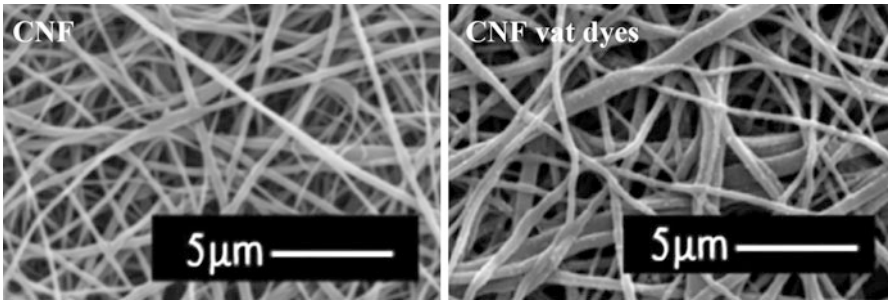

Fig. 4 Morphology of cellulose nanofibers before and after vat dyeing

conventional dyeing [16]. Ultrasonic assisted dyeing of cellulosic fibers has already proved to be a better choice among conventional dyeing. Like other parameters, the color yield of CI reactive black 5 increased gradually with increasing dyeing temperature from 40°C to 60°C with a slower increase from 60 °C to 70 °C. The color yield at higher dyeing temperature (80°C) remained same. This may be due to higher dyeing temperature that lowers the substantivity ratio of the dye and lead to accelerate dye hydrolysis [14, 15]. For CI reactive black 5, a notably higher increase in color yield can be observed from 10 to 20 min thereby maximum color yield obtained until 30 min of dyeing time. This may be due to ultrasonic cavitation that breaks the dye aggregates and helps to increase dye uptake [16]. The color yield of nanofibers dyed with CI reactive red 195 also increased from 10 to 20 min with substantial increase and higher color yield at 30 min. Comparison of ultrasonic dyeing and conventional dyeing of cellulose nanofibers has been given in Fig. 5.

The results show ultrasonic dyeing show higher color yield than the conventional dyeing for both dyes. Color yield of nanofibers dyed with CI reactive black 5 by ultrasonic dyeing showed 20.35% higher than the nanofiber dyed by conventional dyeing, whereas CI reactive red 195 showed 14.53% higher color yield. The higher K/S value with ultrasonic supported dyeing may be attributed to breaking of dye aggregates at nanofiber surface by ultrasonic energy and establishment of resultant equilibrium in a shorter time period. After analyzing color fastness to washing tests

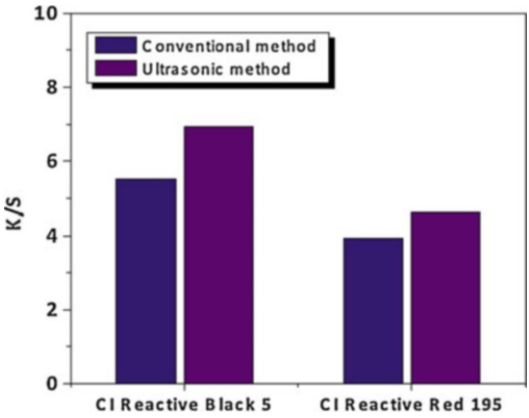

Fig. 5 Comparison of color yield between ultrasonic dyed nanofibers and conventional dyed nanofibers (dye conc. 3%)

and light fastness tests, cellulose nanofibers dyed with 3% dye concentrations of C.I reactive red 195 and CI reactive black 5 at optimum conditions. The staining in washing fastness test for CI reactive black 5 has attained maximum rating, which indicates no color bleeding and therefore good dye fixation as given in Table 2. The staining of CI reactive red 195 demonstrates half rating less than the CI reactive 5 dyes obtained. The color changes were observed to be very good rating of 4/5 for both dyes. The light fastness results on the other hand, demonstrated average ratings. The cellulose nanofibers dyed with.

CI reactive black 5 has shown better light fastness than the cellulose nanofibers dyed with CI reactive red 195. The fastness to light of a dyed fiber depends on many factors. The probable reason to this may be due to the inherent stability of the dye chromogen of CI reactive black 5 (Fig. 6).

Besides ultrasonic treatment, other methods are also reported for dyeing of nanofibers that are briefly discussed here. Dual pad method [6]: in this method, the nanofiber web samples were dyed by padding (two dip-two nip, 100% wet pick-up) through a padding liquor. The padding liquor containing dyes of known concentration, 25 g/L sodium carbonate (30 g/L in case of higher dye conc.), 50 g/L Urea and 2 g/L sodium alginate. The samples were air dried followed by baking and soaping off. Dyeing experiments were followed by two sequences: first, single padding of white nanofibers and, second, dual padding of dyed nanofibers. In addition to K/S values, the colorimetric values (L*, a*, b*, C* and ho) were measured for each dye concentration. As expected, the lightness value L* decreased as the dye concentration was increased indicating the dyed nanofibers became darker; the results are well in agreement with the K/S obtained. The negative a* designate for the greenness and positive for the redness. In this case, consistently decreasing negative a* with increasing dye concentration showed that a tone of dyed nanofibers shifting towards a redder region. In addition to K/S values, the reflectance (%R) were measured for each dual padded nanofiber sample and compared to their corresponding single paddings. The CI reactive black 5 gives two reflectance values, one broad and low in the wavelength region between 360 and

Table 2 Color fastness to washing test ISO 105-C10:2006 and color fastness to light test ISO 105-BO2

Dye conc. (1%)[1]	Light fastness (20 h)[2]	Washing fastness (Change of shade)[3]	Washing fastness (Staining on multi-fiber)[4]					
			CT	CO	PA	PES	PAC	Wo
CI reactive black 5	3/4	4/5	5	5	5	5	5	5
CI reactive red 195	2	4/5	4/5	4/5	4/5	4/5	4/5	4/5

[1]Dyeing conditions: Dyeing temperature 70 °C and time 30 min
[2]Blue wool scale 1–9, being 1 is poor and being 9 is excellent
[3]Grey scale 1–5, being 1 is poor and being 9 is excellent
[4]*CT* cellulose triacetate, *CO* cotton, *PA* polyamide, *PES* polyester, *PAC* polyacrylic, *Wo* wool

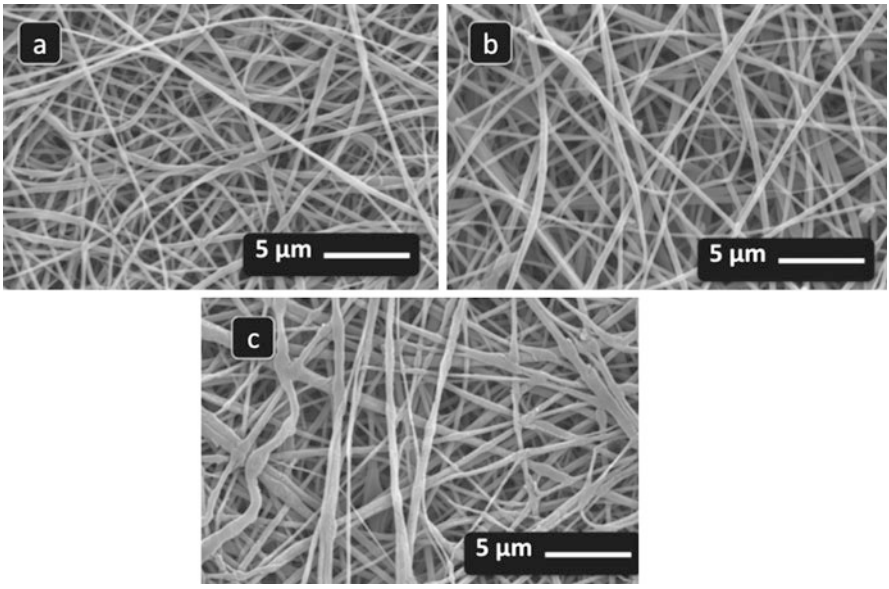

Fig. 6 (**a**) undyed cellulose nanofibers (**b**) dyed with reactive black 5, and (**c**) dye with reactive red 195

500 nm and second sharp and high in the wavelength region between 700 and 750 nm. In comparison to single paddings, all dual paddings show same reflectance profile with lower %R values over the wavelength (360–750 nm). This indicates that the dual paddings exhibit deeper shade than the shades obtained by single paddings. In the work reported [2], Single padding with 20 g/L shows a very good shade change and staining ratings among all other samples. The higher concentration of single padding with 80 g/L affected just half rating on shade change. The washing fastness results for dual paddings were encouraging despite of very high dye concentrations were used. The acceptable ratings for shade change and staining on

multi fibers strip indicate that the dye fixation was reasonably good. The light fastness, on the other hand, was found to be very poor for all dyed nanofibers; this may be due to the small diameter of nanofibers than the conventional nanofibers, the light can easily penetrate into the interior of nanofibers that lead to more photo-fading of dye [17].

Other method known as cold pad batch (CPB) [8]; Dyeing of cellulose nanofibers was carried out by CPB method to study the effect of batching time and dye concentrations on the final color yield, since the dwell time greatly affects the color yield and dye fixation. Prolonged dwell time increases the chance of dye hydrolysis, which results in poor dye fixation. All samples were padded with two dip two nip at 70% wet pick-up using a Rapid laboratory horizontal padding mangle. The padding liquor contained dyes of known concentration, 20 g/L sodium carbonate, 20 g/L NaOH (38 ^{o}Be') and 150 g/L urea. Soon after the padding, each sample was wrapped in a polyethylene bag and batched for a predetermined time. Upon completion of the batching time, the dyed samples gently rinsed with warm and then cold water. The wash was carried out in a water bath and continued until no dye bleeding was observed. Dyed nanofibers were then dried at 120°C for 10 min in a laboratory mini dryer. The effects of batching time on color yield and dye fixation for cellulose nanofibers dyed with CI Reactive Red 195 showed that increasing the batching time from 2 to 8 h, the color yield increased sharply and increased slightly at a batching time of 12 h. This may be due to having a better substantivity than the CI Reactive Black 5. The optimum %F (percent fixation) for CI Reactive Red 195 obtained at 8 h batching time was 80%, whereas at 12 h batching time, the K/S values decreased slightly, which may be due to dye hydrolysis at prolonged batching. Similarly, for CI reactive blue 19, the color yield obtained for CI Reactive Blue 19 linearly increased with increasing batching time, while the %F increased until 8 h of batching and remained at around 80% dye fixation at 12 h batching; this may be due to the dye hydrolysis for prolonged batching.

To investigate the buildup property of a dye, the effect of dye concentrations on color yield and dye fixation was studied for each dye. The cellulose nanofibers were dyed using dye concentrations of 20, 40, 60 and 80 g/L and each batched for 8 h. It was observed that there was a significant increase in color yield for CI Reactive Black 5 when the dye concentration was increased from 20 to 80 g/L, indicating very good build up. The color yield of cellulose nanofibers dyed with CI Reactive Red 195 increases gradually until 60 g/L and increased rapidly at 80 g/L. In comparison to CI Reactive Black 5, CI Reactive Red 195 demonstrated better dye build up, particularly at a higher dye concentration of 80 g/L. Similarly, CI Reactive Blue 19 demonstrated a very good build up property; If the color yield at a dye concentration of 80 g/L for each dye is compared, the maximum yield (K/S) obtained is in the order of 3.5, 3.25 and 2.5 for CI Reactive Black 5, CI Reactive Red 195 and CI Reactive Blue 19, respectively.

The color fastness results showed that the CI Reactive Red 195 and CI Reactive Black 5 had moderate 3/4 wash fastness results with maximum staining on cotton with a rating of 3. The acceptable ratings for shade change and staining on a multifiber strip indicate that the dye fixation was reasonably good. The washing

fastness results were encouraging despite the very high dye concentrations used. The light fastness, on the other hand, was found to be very poor for all dyed nanofibers except the nanofibers dyed with the CI Reactive Blue 19, which shows the better results as compared to CI Reactive Red 195 and CI Reactive Black 5.

Dyeing of Electrospun Cellulose Acetate Nanofibers

The dyeing properties of a cellulose acetate nanofibers with disperse dyes have been investigated to produce colored nanofibers for apparel use [7]. Cellulose acetate nanofibers were electrospun from polymer solution and the nanofiber webs were dyed with disperse dyes using the pad–dry–bake method. The dyed nanofibers were evaluated for color yield (K/S), colorimetric values, color fastness, tensile properties and scanning electron microscopy (SEM) analysis. The nanofiber web samples were dyed by padding (two dip–two nip, 100% liquor pick-up) with 30 g/L dye in a dye bath with a pH of 5 (adjusted using acetic acid)]. The samples were air-dried at an ambient temperature of ca. 35 °C using a fan for 20 min, followed by baking on a Rapid laboratory mini-dryer for 60 s, and were finally given a gentle rinse with warm then cold water. The wash was given in a water bath and continued until no dye bleeding was observed. Dyeing were carried out to study the effect of variation in the magnitudes of baking temperature (80–180 °C), baking time (0–120 s) and dye concentration (10–50 g/L). The dyeing of cellulose acetate nanofibers can effectively be carried out with disperse dyes by the pad–dry–bake method. The dyeing results were mainly dependent on the baking temperature and the dye class used. It was generally observed that the high-energy level dye, CI Disperse Red 167:1, had better color yield and color fastness results than the low energy level dye, CI Disperse Blue 56. Besides successful dyeability and good color fastness results (washing, light and hot pressing), Young's modulus of dyed nanofibers increased around three times in comparison to the undyed cellulose acetate nanofibers, therefore suggesting that the colored nanofibers are worth considering for use in aesthetically pleasing apparel, as well as for use in casual apparel [17].

Dyeing of Electrospun Nylon Nanofibers

Both nylon 6 and nylon 66 nanofibers have been utilized for the dyeing purpose. Nylon 66 regular fiber (1 denier) and nanofiber (approximately 0.003 denier), were used in the dyeing experiment [3]. The samples were dyed with three high molecular mass acid dyes i.e., CI Acid Orange 67, CI Acid Red 336 and CI Acid Blue 260. Effects of dyeing temperature, pH of the dye bath, and dye concentration on dyeing properties were examined. X-ray diffraction and DSC were performed for measurement of degree of crystallinity. Water absorption and amino end group of nylon fibers were analyzed in order to study their effects on dyeing properties. Nanofiber starts to absorb C.I Acid Red 336 dye at lower temperature and gets dyed at a rapid rate as compared with regular fiber. The extent of exhaustion of

regular fiber is in the range of 92–87% that of nanofiber is 95–89% as shown in Fig. 7. It appears that the extent of exhaustion of nanofiber is slightly higher.

Furthermore, pH effect of three dyes on both regular and nanofibers was observed. It was observed that acidic pH hindered the active sites by protonation on both regular and nanofibers. The authors correlated this behavior with number of end amino groups on both regular and nanofibers. The nanofiber had about 40% of amino end group in comparison with regular fiber, the decrease of the protonated amino group on fiber surface by increasing pH was less than regular fiber. The remarkable difference in K/S value between regular fiber and nanofiber is clearly seen, originating from the difference in the specific surface area. The greater extent of surface reflection that ensues from the greater surface area of nanofiber makes the dyed nanofiber visually lighter in shade than regular fiber dyed at the same dye concentration. As dye concentration increases, K/S value of the dyed regular fiber increases, but it increases a little above 5% on weight of fabric (owf) K/S value of the dyed nanofiber increases very slowly with dye concentration, but it increases gradually up to 11% owf, suggesting that very high dye concentration is required to give deep color to nanofiber. Light fastness results showed that nylon 66 nanofibers had inferior light fastness (grade 1) due to larger surface area.

In other case, a new method based on ultrasound-assisted dyeing was proposed using nylon 6 nanofibers [3]. Two disperse dyes were selected (disperse red 167 and disperse blue 57). Different parameters were optimized using nanofiber to liquor ratio 1:100 using pH 6. Ultrasonic assisted dyeing was carried out at output power of 180 W and at 38 kHz frequency. For temperature optimization, Nylon-6 nanofiber samples were dyed with CI Disperse Blue 56 for 60 min using 0.5% dye concentration. The dyeing was carried out with and without sonication. The color yield for ultrasonic assisted dyeing rapidly increases from 50 °C and rises to maximum K/S value of 0.6 at 80 °C, whereas, for conventional dyeing without sonication the K/S values modestly increased and reached highest value of 0.55 at 90 °C. Based on the results 80 °C for ultrasonic assisted dyeing and 90 °C for conventional dyeing were

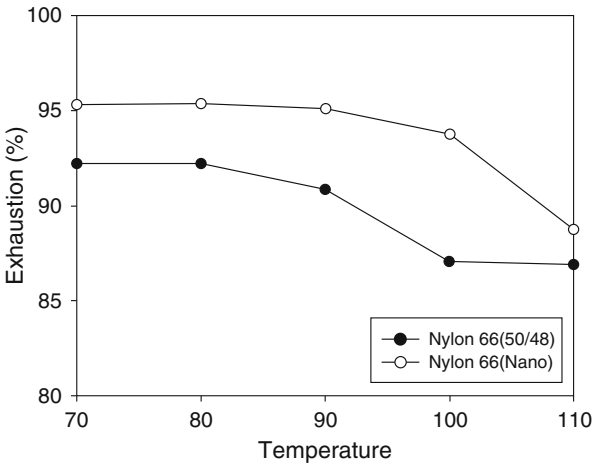

Fig. 7 The extent of exhaustion of regular fiber and nanofiber as a function of dyeing temperature. (Reproduced from Ref. [3])

decided as optimum dyeing temperatures. For ultrasonic assisted dyeing, a rapid increase in color yield is observed from 10 to 20 min rendering maximum color yield of 0.6 at 30 min dyeing time. Whereas in conventional dyeing the dye uptake property increased modestly with increasing dyeing time and reached highest dye uptake of 0.55 at 60 min of dyeing time. Based on the results 30 and 60 min were decided as optimum dyeing time in ultrasonic assisted and conventional dyeing respectively. 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 than CI Disperse Blue 56.

Dyeing of Electrospun Polyester Nanofibers

Recently due to hydrophobic nature of disperse dyes, the hydrophobic Polyethylene terephthalate (PET) nanofibers have been prepared [7]. The uniqueness of work lies in the fact that instead of pure PET granules, PET based waste bottles were used as precursor for developing nanofibers through electrospinning technique. In this study, sufficient data was achieved to investigate the thermodynamic parameters and isotherm parameters of dyeing. Two types of disperse dyes i.e., C.I disperse red 167 (DR-167:1) and CI disperse blue 56 (DB-56) were used. The influence of temperature was observed at fixed time (30 min) and concentration of dye (2% shade on weight of nanofibers) respectively during dyeing. The color yield of both dyes gradually increased with increasing dyeing temperature from 50 °C to 90 °C and 90 °C was found optimum. The standard affinity increases with increasing temperature for both dyes. The standard affinity of DB-56 dye is higher than DR-167:1 dye. This finding reveals that the tendency of Blue dye is higher than the Red dye to PET nanofibers. The enthalpy change of dye bath containing DB-56 is greater than the DR-167:1; i.e., the bond strength of DB-56 dye was greater than DR-167:1. It is concluded that DB-56 molecules are more embedded to PET nanofibers than the DR-16 7:1 because of their smaller molecular size. Whereas, the entropy change of DR167 was lower than DB-56 that suggested DR167 molecules were less strained in PET nanofibers than DB-56 molecules.

In order to gain higher color yield and observe the optimum dyeing time, dyeing of PET nanofibers was carried out at optimum temperature 90 °C using 2% shade of both dyes. It was observed that color yield increased with increase in time and beyond 30 min no color increment was achieved. Figure 8a shows rapid increased color yield as compared to DR-167:1 and this is because disperse blue have low energy level and smaller molecular size. Figure 8b shows that dyeing rate of DB-56 was greater than DR-167:1.

Both dyes showed very good results in the light fastness in dyed nanofibers webs and are being rated 7 on the blue wool reference scale. The DR-167:1 showed slightly better results in hot pressing than the nanofibers dyed with DB-56. The washing test was done to check the color fastness properties of dyed nanofibers.

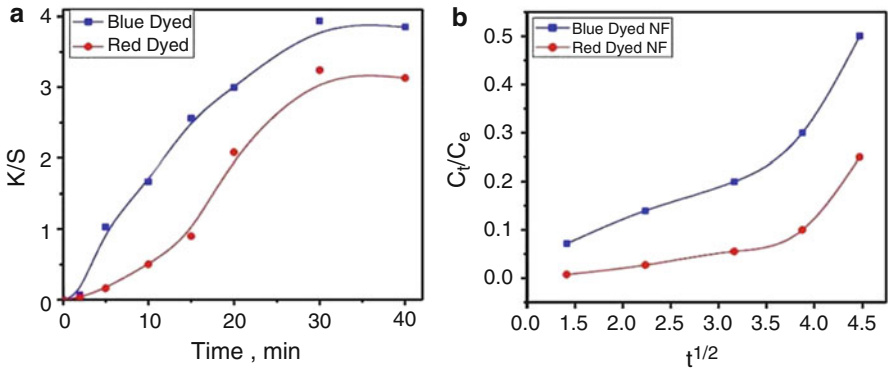

Fig. 8 (**a**) Effect of color yield on dyeing time, and (**b**) diffusion plots of DB-56 and DR-167:1. (Reproduced from Ref. [10])

The nanofibers dyed with DB-56 and DR- 167:1 showed good to excellent grade, respectively, using gray scale.

In another study carried by similar group [10], a new modified method was used named doped dyeing method compared to batch dyeing. The dyes used were same as mentioned above (i.e., disperse red 167 and disperse blue 57). This method was followed to prevent generation of waste dye effluent and environmental contamination. Different polymer concentrations using fixed dye as well as using optimum polymer concentration with varying dye concentration were investigated to achieve optimum composition for better color yield and fastness tests. Firstly, influence of dye coloration on different polymeric concentration was observed using fixed dye concentration 2% (0.006 g). Figure 9 shows that 15% were found to be optimum polymer concentration. Further dye concentration optimization was carried out using 15% polymer concentration and 3% dye was found optimum beyond which no nanofiber formation was noticed. This demonstrates PET nanofibers exhibit a very good ability to color build-up properties. Both dyes showed very good results in the light fastness in dyed nanofibers and rated at 7 on the blue wool reference scale. The nanofibers dyed with both DB 56 and DR 167 showed good grade with respect to gray scale.

Dyeing of Electrospun Polyurethane Nanofibers

In this study, pure electrospun polyurethane nanofibers were dyed with disperse dyes using pad–dry–cure method [12]. The influence of temperature had a positive impact on nanofiber dyeing. The optimum curing temperature was found 120 °C. The color strength increased with increasing baking time up to 90 s for DR-167:1 and up to 60 s for DB-56. The maximum color strength of DB-56 was achieved earlier than that of DR-167:1. The effect of dye concentration (10–30 g/L) using optimum temperature and time showed increase in color strength but further increase in dye amount (from 30 to 40 g/L) did not significantly alter the color strength.

The Commission on Illumination (CIE) colorimetric evaluation revealed that the color strength, depth (L*), and saturation (C*) values of the webs dyed with DR-167:1 were slightly higher than those of the webs dyed with DB-56. From the photographic images of undyed and dyed polyurethane nanofibers; it is clear that these nanofibers can generate excellent color build up and can be used as casual, fashion and sports apparel (Fig. 10).

The hot pressing of web dyed with CI Disperse Red 167:1 was generally better than that of web dyed with DB-56. The overall washing fastness of DR-167:1 was very good, and that of DB-56 was fair.

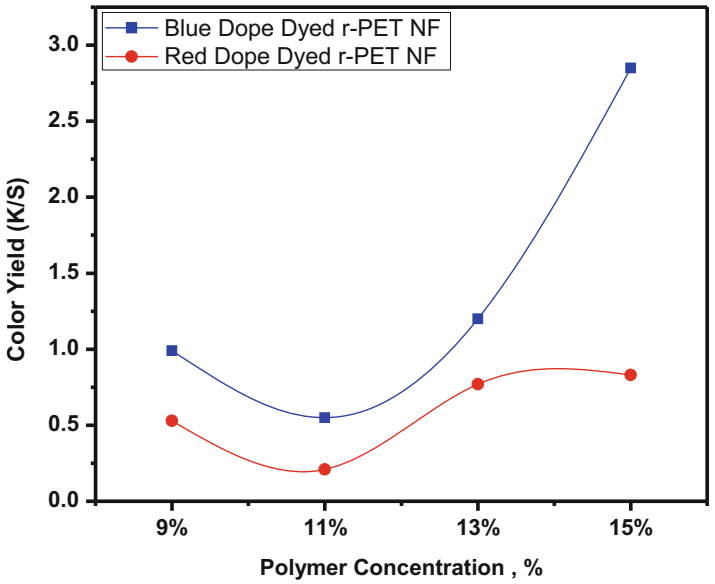

Fig. 9 Effect of polymer concentration on dope dyed nanofibers. (Reproduced from Ref. [10])

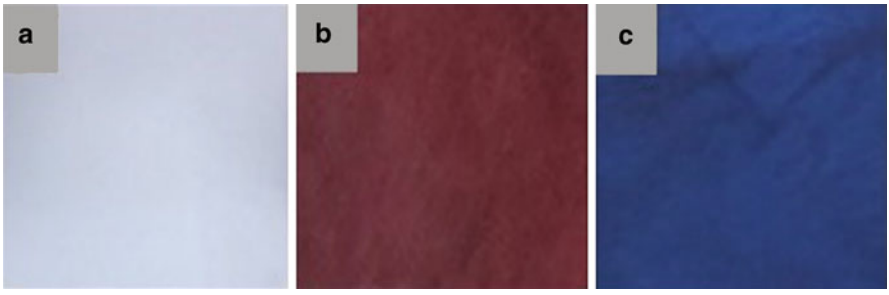

Fig. 10 Photographic images of PU mats: (**a**) undyed; (**b**) dyed with CI Disperse Red 167:1; (**c**) dyed with CI Disperse Blue 56. (Reproduced from Ref. [12])

The PU nanofibers were fabricated by electrospinning process and were subsequently dyed following exhaust method using sonication. The two disperse dyes selected were a low-energy disperse dye (DB-56) and a high-energy disperse dye (DR-167:1). The ultrasonic energy was used to achieve higher color build-up on PU nanofibers. The temperature/time (T/T) diagram of proposed dyeing process has been suggested; dyeing time and dyeing temperature were optimized. Color build-up properties (measured in terms of K/S values), dye fixation (%), and color fastness properties were studied in detail. The samples were characterized by scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and mechanical strength measurements. The results show 70 °C and 40 min as optimum dyeing temperature and time, respectively. The SEM, FTIR, and XRD results did not show any significant effect of ultrasonic dyeing on morphology, chemical, and crystallographic structure of PU nanofibers. Color fastness results revealed excellent light fastness, very good washing, and hot pressing fastness of both dyes.

Conclusion and Future Directions

Dyeing of nanofibers is possible with various dyestuff and that depends on dye affinity and type of polymeric nanofibers. To date, cellulose, cellulose acetate, polyurethane, nylon 6, nylon 66, and polyester nanofibers, whereas the dyestuff studied so far include reactive, vat, disperse, and acid dyes. The color yield increases with increase dye concentration and color fastness properties in general are very good, however, except few dyed nanofiber, light fastness properties of dyed nanofibers are fair to good. The dyeability of nanofibers is possible by any method include conventional batchwise, pad dry cure and cold pad batch methods. The ultrasonic dyeing of nanofibers show better color yield values than conventional dyeing methods. The tensile properties of nylon, polyester and polyurethane nanofibers were found to be better than the cellulose and cellulose acetate.

Since last decade, reports on dyeing of nanofibers have been increasing substantially. Almost all researcher report the color attributes of dyed nanofibers and claim good dyeability with different dyestuffs. The nanofibers are thought to be one step ahead than microfibers, because products made of microfibers have already proven to be better than conventional fibers in terms of their dyeability and mechanical strength. Although research on the dyeing of nanofiber is already at its pace, the mechanical strength of nanofibers is too weak for them to be used in apparel or garment directly. Until now, a few polymeric nanofibers have been reported such as cellulose, cellulose acetate, polyester, polyurethane, and nylon nanofibers, but there are still many polymeric nanofibers that need to be explored with respect to their dyeing properties as well as their color fastness properties. The prospective work can also be explored by using ultrasonic and microwave assistance dyeing that will help reduce energy with reduced impact on environment. Another area that requires researcher's attention is dope dyeing. The dyes are mixed with polymers solutions before electrospinning of nanofibers as a result, nanofibers produced colored directly. We can foresee the future apparel made up of colorful dyed nanofibers.

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