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Characterization of dimethyl sulfoxide-treated wool and enhancement of reactive wool dyeing in non-aqueous medium

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Abstract

Wool pretreated with dimethyl sulfoxide (DMSO) was characterized and its dyeing behavior in non-aqueous green solvents was investigated. Reactive dyeing of wool in deep shades is challenging because the mandatory alkaline after-treatment to match the fastness of mordant dyes inevitably causes damage to wool keratin. The current study showed that the colorfastness-integrity dilemma could be solved by replacing water with organic solvents as the dyeing medium. Covalent fixation is predominantly favored in solvent dyeing so that excellent colorfastness is achievable at any given shade without alkali aftertreatment. Compared with aqueous dyeing, solvent dyeing was found to give 30% higher covalent fixation on average, which translated to better colorfastness (0.5–1 grade) at higher color depth ($\Delta K/S = 1.3$ –4.9). In addition, scanning electron microscopy, X-ray diffraction and attenuated total reflection-infrared spectroscopy results indicated that DMSO pretreatment induced morphological and structural changes of wool in favor of dyeability. The findings are crucial to the phasing-out of metal-containing dyes for eco-friendly wool dyeing.

Keywords: wool keratin fiber, reactive dyeing, dimethyl sulfoxide, morphology, covalent anchoring

Wool is unparalleled by other fibers in terms of comfort in wear due to the fact that it has been engineered by evolution over millions of years to be worn next to an animal's skin.¹ Wool is traditionally dyed with acid mordant dyes and metal-complex dyes, whose usage had declined as a result of the growing environmental pressure against discharging heavy metals. Reactive dyes are becoming increasingly important as a metal-free alternative to mordant dyes.^{2,3} In order for reactive dyes to match the level of shade and fastness to mordant dyes, an alkali aftertreatment is obligatory.⁴ Considering the increasing possibility of keratin fiber damage under alkaline conditions, further research is required to find new ways to maximize wet fastness of wool fabrics reactive dyed to deep shades.^{5,6}

The splitting of the covalent bonds between dye and fiber is an unfavorable process requiring high energy.¹ In the ideal case where all dyes are covalently bonded,⁷ the wet fastness of reactive dyed wool fabric should be exceptionally good. However, under the typical conditions for dyeing wool fabric with reactive dyes, fixation via the labile columbic interaction is unavoidable. Two strategies can be used to minimize ionic interactions. One is the alkaline aftertreatment, which selectively removes the ionically bonded dyes by reversing the surface potential. The other is to lower the ionizing power of the dyeing medium, so that fixation via ion exchange is suppressed during dyeing.

Our laboratory has successfully developed a recyclable non-aqueous procedure to dye cotton with vinylsulfone

(VS) dyes in a mixture of two green solvents, namely dimethyl sulfoxide (DMSO) and dimethyl carbonate (DMC).^{8,9} In an effort to expand the scope to dye cotton/wool blends, the method was tried on reactive dyeing of wool fabrics. Preliminary results showed that good colorfastness in deep shades was achievable. The favorable results were supposed to be resulting from the lower ionizing power of the DMSO/DMC mixture used as the dyeing medium. Moreover, early investigations by Friedman and Keonig¹⁰ and Koenig and Friedman¹¹ claimed that DMSO was a good swelling solvent and penetration enhancer for wool. Both features are essential for a qualified dyeing medium. However, DMSO has never been reported as a dyeing medium for wool. The effect of DMSO on dyeability of wool has not been systematically investigated either. If DMSO was used instead of water in the reactive dyeing of wool, the following benefits might emerge: diffusion of the dye across the intercellular lipids in wool would be enhanced; excellent wet fastness in dyeing deep shades would be achievable without alkaline aftertreatment; adjusting pH during dyeing would no longer be necessary; unevenness caused by strong ionic interactions between the dye and fiber would be alleviated; and one-bath solvent dyeing of a cotton-wool blend would be possible.¹² Replacing processing water with the much more costly solvents inevitably raises concerns about the cost of the solvent dyeing process. At the current stage, even when all solvents are considered recyclable, the cost to reclaim solvents through distillation is still more than the cost of fresh water. However, the overall cost of the solvent dyeing process can be compensated by savings on dyes, chemicals and waste treatment or disposal. Therefore, the solvent dyeing process has the potential to be economically practical.

In this paper, scanning electron microscopy (SEM), X-ray diffraction (XRD) and attenuated total reflection-infrared (ATR-IR) analysis were used to study the effect of DMSO pretreatment on the morphology and structure of wool. The treated wool was then subjected to reactive dyeing in a DMSO/DMC mixture. The effect of DMSO/DMC ratio on color depth was studied. Dyeing results showed that solvent dyeing offered better colorfastness and higher color yield compared to aqueous dyeing. The observed enhancement was interpreted to be caused by a shift in the dyeanchoring mechanism in favor of covalent bonding.

Experimental details

Materials

Fabric. The wool serge fabric (2/2 twill, botany serge) was kindly supplied by Yingchun Woollen Textile Co., Ltd

(Shanghai, China) and used as is. The multifiber adjacent fabric used for colorfastness assessment was purchased from Testfabrics Inc.

Chemicals. DMC DMSO, acetone, chloroform, methanol, sodium chloride (NaCl), hydrochloric acid (HCl), anhydrous sodium sulfate (Na₂SO₄) and sodium carbonate (Na₂CO₃) were of reagent grade and were purchased from Sino Reagent Co. and used as received. C.I. Reactive Blue 19 (RB19), Reactive Orange 16 (RO16), Reactive Black 5 (RBK5) and Reactive Yellow 201 (RY201) were purchased from Shangyu Shunlong Chemical Co., Ltd (Zhejiang, China). All dyes were in the unactivated β -sulphatoethylsulphone form and were converted to the corresponding VSs and purified before use.

General procedure to prepare VS dyes

The appropriate dye in its β -sulphatoethylsulphone form (30 mmol) was dissolved in 50 mL of deionized (DI) water. The pH of the solution was adjusted to 8.5 by adding sodium carbonate. The solution was then heated to and maintained at 60°C with stirring. The progress of the β -sulphatoethylsulphone elimination reaction was monitored by thin layer chromatography (TLC) on silica using a 9:1.5:1 mixture of chloroform, methanol and acetone as the eluent. For all four dyes studied, the reactions were completed in 1 h. The pH of the reaction mixture was then brought down to 7 by adding HCl. NaCl (50 g) was added to the reaction mixture to precipitate out the VS product. The crude product was extracted with acetone. Insoluble salts were removed by filtration. The extracts were combined and dried and the solvents were evaporated using a rotovap to yield the VS dyes. Nuclear magnetic resonance (NMR) and high-performance liquid chromatography (HPLC) analysis of the purified dyes showed that they all had purity greater than 95%. Structures of the VS dyes prepared are shown in Figure 1.

Pretreatment of wool fabrics

The wool fabrics were cut into pieces of approximately 3 g, and soaked in DMSO or deionized (DI) water for 1 h at 25°C. For morphological and structural characterization, the soaked fabric was placed in a glass vial, dried at 50°C, 10 mbar for 2 h, and conditioned at 25°C, 65% humidity for 24 h. For dyeing, the soaked samples were centrifuged at 2600 rpm for 5 min on an Allegra 25R Centrifuge equipped with a TA-14-50 rotor.

Figure 1. Chemical structures of the reactive dyes in their vinylsulfone form investigated in this study.

General procedures for reactive dyeing of wool in solvents and in water

Solvent dyeing. The pretreated wool sample (3 g) was transferred to a vessel containing dyeing liquor consisting of 0.09 g of the appropriate dye (VS form) dissolved in 18 mL DMC and 27 mL DMSO. (DMSO:DMC = 3:2, liquor ratio = 15:1). The vessel was sealed, heated at a rate of 2°C/min and maintained at 85°C for 3 h with 60 rpm mechanical agitation. The vessel was cooled to room temperature and the sample was removed from the dyebath and centrifuged at 2600 rpm for 5 min.

Aqueous dyeing. The presoaked wool sample (3 g) was introduced to 45 mL (liquor ratio = 15:1) of aqueous solution containing 0.09 g of the appropriate VS dye. The pH of the dyebath was adjusted to 4.5 using a 0.25M aqueous acetic acid solution.¹² The dyebath was heated to and maintained at 85°C for 60 min mechanical agitation at 60 rpm. The vessel was cooled to room temperature and the sample was removed from the dyebath and centrifuged at 2600 rpm for 5 min.

For different research purposes, two methods were applied to the dyed samples to remove unfixed dyes. For determination of percentage fixation, the samples were stripped three times with boiling 25% (vol. /vol.) pyridine/water for 15 min at the liquor ratio of 1:20. The procedure was developed by Lewis and Smith¹³ to remove all unfixed and ionically anchored dyes. For colorfastness measurement, the samples were soaped with 2 g/L aqueous detergent solution at 95°C and the liquor ratio of 1:20 for 15 min followed by two rinses with 45 mL cold DI water. Samples that underwent either rinsing process were dried

under reduced pressure at ambient temperature to constant weight.

Determination of dye uptake and relative dye fixation

Percentage dye uptake. The concentration of the dyes in solution before (C_0) and after (C_1) dyeing was measured spectroscopically using a Shimadzu UV-1800 spectrophotometer and was used to determine the percentage uptake of dye by the wool fabrics. Dye uptake was calculated according to Equation (1) assuming dye decomposition could be ignored under the dyeing conditions:

$$\text{Uptake\%} = \frac{C_0 - C_1}{C_0} \times 100\% \quad (1)$$

Relative dye fixation. Relative dye fixation (F_{rel}), that is, the proportion of covalent dye to adsorbed dye, was calculated as the quotient of average K/S values after the pyridine stripping process by the value before stripping (Equation (2)):

$$F_{rel} = \frac{\overline{K/S}_{after}}{\overline{K/S}_{before}} \times 100\% \quad (2)$$

$$\overline{K/S} = \frac{1}{n} \sum_{i=1}^n (K/S)_{i,\lambda_{max}} \quad (3)$$

$\overline{K/S}$ is the arithmetic mean of K/S values of an individual sample from six measurements. The K/S values were determined by a Datascolor 650 benchtop spectrophotometer using the Kubelka–Munk equation (Equation (4)).

Measurements were done at maximum absorption wave lengths ($\lambda_{\max}$), which were 595nm for RB19-VS, 370nm for RY201-VS, 490nm for RO16-VS and 600nm for RBK5-VS respectively.

$$K/S = \frac{(1 - R_{\min})^2}{2R_{\min}} \quad (4)$$

where K and S are spectral absorption and scattering coefficients, respectively, and $R_{\min}$ is the minimum spectral reflectance ratio.

Materials characterization

ATR-IR spectroscopy. Samples for infrared (IR) spectra were measured on a Nicolet Nexus-670 FTIR spectrometer equipped with a SMART iTR diamond accessory in the spectral scanning frequency range of 650–4000 cm^{-1} at the spectral resolution of 4 cm^{-1} .

XRD measurements. Fibers were randomly withdrawn from a wool fabric sample and their XRD spectra were taken with a Rigaku D/MAX-2400 XRD analyzer. The test conditions were as follows: voltage = 46 kV, current = 100 mA, Cu K_{α} radiation, $\lambda = 1.54050 \text{ \AA}$, scanning scope $2\theta = 0\text{--}60^\circ$, step = 0.02° and scanning speed = $4^\circ/\text{min}$.

SEM measurements. Fibers were randomly withdrawn from a wool fabric and the morphology of their surfaces was examined with a Hitachi TM-1000 scanning electron microscope at an accelerating voltage of 15 kV. The sample surfaces were coated with thin layers of gold before the observation.

Assessment of colorfastness. Colorfastness to laundering was determined according to AATCC test method 61-1986(2 A) using a Darong SW-12 washing colorfastness tester. Dry and wet colorfastness to crocking was examined according to AATCC test method 8-1988 using an Atlas AATCC Mar Tester CM-5.

Tensile strength. For the tensile strength tests, yarn specimens were withdrawn from the wool fabrics. Tests of the specimens were conducted according to ASTM method D-5035 on a Sintech universal mechanical tester with a load cell weighing 1113N (250 lb). The gauge length used was 5 cm and the crosshead speed was set to be 50 mm/min. For each fabric sample, no fewer than 20 yarns were withdrawn and tested. Data generated were subjected to analysis of variance (ANOVA) using Microsoft Excel 2010. A p -value of less than 0.05 was considered statistically significant.

Results and discussion

Effect of DMSO on wool structure

In our previous investigations on solvent reactive dyeing of cotton, it was found that DMSO was the best swelling solvent among all non-nucleophilic polar solvents investigated.⁹ Results of an investigation by Friedman and Koenig¹⁰ suggested that DMSO was also an effective swelling solvent for wool at ambient temperatures. Therefore, all wool fabrics subjected to solvent dyeing were pre-soaked in DMSO for 1 h at room temperature to allow sufficient swelling. The effects of the DMSO pretreatment on morphological and structural properties of wool were investigated using SEM, XRD and ATR-IR analysis.

Figure 2 shows the scanning electron microscopic images of the wool fibers untreated and pretreated in water and in DMSO, respectively. The images clearly showed that wool fibers lost the sharp and round scale edge after the pretreatment in DMSO. The observation suggested that the wool scales had been partially removed by DMSO, possibly because DMSO is a good solvent for the lipidic intercellular cement holding the cuticle cells together. In contrast, the surface of the water-treated sample remained essentially unchanged. The scales, or cuticle cells, constitute the outermost surface of the wool fiber and are crucial in controlling the accessibility of the inner wool fiber. Partial removal of the scales facilitated the transportation of dyestuff across the cuticle layer and would consequently lead to improved dyeability.

The results of XRD of the preswollen wool in DMSO and in water are shown in Figure 3. The XRD of an untreated control is also included for comparison. All samples showed the typical diffraction patterns of the α -helix and the antiparallel β -sheet structures with peaks centered at $2\theta = 9.1^\circ$, $d = 9.72 \text{ \AA}$ and $2\theta = 20.2^\circ$, $d = 4.40 \text{ \AA}$, respectively. A decrease in the intensity of the $2\theta = 9.1^\circ$ peak relative to the $2\theta = 20.2^\circ$ peak was observed for the sample pretreated with DMSO. A similar effect was not observed for water pretreatment. The change could be interpreted as partial collapsing of the α -helix caused by the disturbance of wool structural integrity on the longer range order.¹⁴ The crystallinity of untreated and solvent-pretreated wool was 23.80% and 22.80%, respectively. The essentially invariant overall crystallinity suggested that the DMSO treatment caused α -helices to transform to β -sheets rather than to amorphous strands. Similar effects of DMSO on human stratum corneum keratin have been reported.^{15,16}

The ATR-IR spectra of the wool samples are compared in Figure 4(a). No noticeable change was observed for the two protein amide peaks at 1645 cm^{-1} (C=O stretching) and 1532 cm^{-1} (N-H bending) after either pretreatment in

Figure 2. Scanning electron microscope images of the (a), (b) untreated; (c), (d) water-treated; and (e), (f) dimethyl sulfoxide-treated wool keratin fibers.

DMSO or in water. The C-H deformation vibration peak at 1452 cm^{-1} was also invariant. By examining the difference IR spectra shown in Figure 4(b), it was found that swelling of wool by water did not cause evident chemical changes on the functional groups of wool. However, wool swollen by DMSO showed a significant decrease in O-H and N-H stretching intensities at 3458 and 3212 cm^{-1} , respectively. This might be due to the disruption of the internal H-bonding network in wool keratin from the incorporation of DMSO molecules.

The above results suggested that DMSO pretreatment could lead to dyeability enhancement by disintegrating the cuticle layer and disrupting the internal H-bonding network of wool. DMSO is also known to be a powerful penetration enhancer for both hydrophilic and lipophilic permeants through human stratum corneum keratin.¹⁷ Similarly, it could promote the penetration of reactive dyes across wool keratin and be suited as the dyeing medium for wool.

Optimal conditions for solvent dyeing of wool with RB19-VS

As suggested by our IR and XRD results, DMSO disrupts the internal hydrogen bonding of wool keratin and causes the collapse of the wool helical structure. The changes have no noticeable adverse effect on physical properties of the wool at ambient temperature. However, preliminary results showed that under prolonged heating conditions typically required for wool dyeing, pure DMSO as

Figure 3. X-ray diffraction of the wool keratin untreated and pre-treated in water and solvent.

the dyeing solvent led to marked shortening of wool. Using a less polar cosolvent, such as DMC, could alleviate wool from the shrinkage. The effects of DMC content on the dimensional stability and dye uptake of wool fabrics were studied. The study was done at 85°C , which was reported to be necessary for fixation of VS dyes on wool under neutral conditions.¹⁸

The results are plotted in Figure 5. From Figure 5, increasing DMC content had an overall negative effect on

Figure 4. (a) Attenuated total reflection-infrared (ATR-IR) spectra of wool fabrics untreated and swollen in water and solvents. (b) Difference ATR-IR spectra in swollen and untreated wool.

dye uptake. This trend is the opposite of what was observed for reactive dyeing of cotton in DMSO/DMC, where better exhaustion was achieved at higher DMC content.⁹ Adding DMC has two counteracted effects on dye uptake. On one hand, DMC is a poor solvent for RB19-VS. Therefore, increasing DMC content would destabilize the dye in the dye-bath and facilitate dye sorption. On the other hand, a less polar dyeing media would slow down the rate of the fixation reaction. It is apparent that the effect on dye fixation overwhelms the effect on sorption in determining dye uptake for reactive wool dyeing. Based on the change in wool dimensions with varying DMC contents, a minimum of 40% DMC by volume is required to keep

Figure 5. Effects of dimethyl carbonate (DMC) content on area shrinkage and dye uptake of wool fabrics (dyeing temperature = 85°C, liquor ratio = 1:15, initial RB19-VS concentration = 2 g/L).

Figure 6. Fixation (K/S after stripping) kinetic curves at dyeing temperatures of 45°C, 65°C, 85°C, and 100°C (dimethyl carbonate/ dimethyl sulfoxide = 40:60, liquor ratio = 1:15, initial RB19-VS concentration = 2 g/L).

the shrinkage of wool within an acceptable range. Therefore, the optimal DMC content was decided to be 40% and used in the further investigations.

Dye fixation kinetics in the solvent dyeing system was investigated in terms of variation in K/S values as affected by dyeing time at the dyeing temperatures of 45°C, 65°C, 85°C, and 100°C. The samples were stripped¹³ so that only covalently fixed dyes were considered. As shown in Figure 6, a maximum K/S of about 22 was achieved at the dyeing

temperatures of 85°C and 100°C in 3 and 2 h, respectively. In contrast, 6 h, and 12 h were required to reach maximum dye fixation at 65°C and 45°C, respectively. The maximum color depths achieved at lower temperatures were also significantly lower ($K/S = 16$ for dyeing at 65°C and $K/S = 12$ for dyeing at 45°C). Considering that dyeing at 100°C did not show any advantage over dyeing at 85°C in terms of achievable depth of color, it was decided to use 85°C for the rest of the investigation. Safety-wise, 85°C is preferable because it is below the boiling point of both DMC

and DMSO. If 100°C was used, the process would become pressurized. Higher temperature should also be avoided to minimize wool damage from dyeing.

Comparison of solvent dyeing to aqueous dyeing

Figure 7 compares the sorption and fixation curves of RB19-VS on wool in solvent and aqueous dyeing systems. Aqueous dyeing gave higher sorption throughout the monitored time interval. The rate of dye sorption was also faster in aqueous dyeing. Maximum sorption was achieved within 1 h in aqueous dyeing. Meanwhile, dye sorption continued to increase in solvent dyeing. At the initial stage of dyeing, the aqueous-dyed sample displayed higher dye fixation. However, the solvent-dyed sample overtook after 2 h. It is worth to mention that the relative dye fixation ($F_{rel}\%$) of the solvent-dyed sample was much higher than that of the aqueous-dyed sample (87% versus 62%).

Essentially, reactive dyes are acid dyes with reactive groups. As displayed in Figure 8, the adsorbed reactive dye (RB19-VS) can be attached to the surface of wool via either ionic or covalent bonding. Water promotes ionization of both wool keratin and the dye ($-\text{SO}_3\text{Na}$), facilitating ionic anchoring through ion exchange. In mixed solvents of DMSO/DMC, both the sulfonic group of the dye and the pending groups on wool are involved in tight ion-pairing. Therefore, the surface of wool fabrics displayed completely different characteristics in DMSO/DMC than in water under the dyeing conditions applied. Since ion exchange is significantly suppressed with tight ion-pairs, the likelihood of dye anchoring through ionic interactions is almost nonexistent in DMSO/DMC.

From Figure 7, it was also observed that dye sorption equilibrated much faster in water, which also agreed with

Figure 7. Sorption and fixation curves of RB19-VS on wool in solvent and aqueous dyeing systems. (Dyeing: temperature = 85°C, liquor ratio = 1:15, initial dye concentration = 2 g/L; dimethyl carbonate/dimethyl sulfoxide = 40:60 for solvent dyeing. Stripping: 25% (wt./vol.) boiling aqueous pyridine, 15 min, 3 times, liquor ratio = 1:20.)

Figure 8. Illustration of dye-anchoring mechanisms (a) in aqueous and (b) in solvent wool dyeing.

Figure 9. (a) Build-up properties of RB19-VS on wool in solvent dyeing and aqueous dyeing (dyeing temperature = 85°C, liquor ratio = 1:15, dyeing time = 3 h, dimethyl carbonate/ dimethyl sulfoxide = 40:60 for solvent dyeing, K/S were measured after pyridine stripping). (b) Tensile strength of yarns withdrawn from untreated, solvent-dyed and aqueous-dyed/alkali-treated wool fabrics. Data points with different symbols indicate statistically significant difference.

the switch in the dye-anchoring mechanism. Time to reach equilibrium is much shorter for the ion-exchange process compared with the formation of covalent bonds. Sorption driven by ionic attractions is very sensitive to pH change. Therefore, aqueous reactive dyeing of wool usually relies on careful manipulation of the dyebath pH to achieve appropriate shade and levelness. In contrast, sorption is driven by solvophobic interactions in solvent dyeing. It is easier to achieve levelness and no pH adjustment is needed, although the rate is slower.

Dye fixation was represented by K/S values of samples before and after stripping with hot aqueous pyridine. Stripping with hot pyridine was meant for removing ionically but not covalently adsorbed dyes.¹⁹ Higher dye fixation of the solvent-dyed wool samples can be understood considering covalent anchoring dominated in solvent dyeing. It is widely accepted that the ionic-bonded dyes could be removed through ion exchange during the washing process.²⁰ Therefore, a higher percentage of covalent fixation translates to higher colorfastness. The difference would be more pronounced when dyeing in deep shades.

The build-up properties of RB19-VS in solvent and aqueous dyeing systems are compared in Figure 9(a). Based on the data, solvent dyeing gave color depth comparable to aqueous dyeing when the initial concentration was less than 2.7 g/L. Beyond that point, the color depth of aqueous-dyed wool leveled off at a K/S value of 21. The K/S of the solvent-dyed wool continued to increase and finally leveled off at 28. The higher maximum color depth achieved with solvent dyeing resulted from the intrinsic lower ionizing power of the medium. The available dye sites on the wool surface were essentially all occupied by covalently anchored dye molecules on dyed wool fabric. In contrast, a significant fraction of them were taken by

Table 1. Color depth and fastness properties of wool fabrics dyed with selected vinylsulfone dyes.^a

Reactive dye		K/S	Color Change	Fastness to laundering		Fastness to crocking	
				Staining ^b		Dry	Wet
RB19-VS	Solvent	23.9	5	5	5	4–5	4–5
	Aqueous	21.9	4–5	4–5	4–5	4–5	4
RO16-VS	Solvent	30.5	5	5	5	4–5	4–5
	Aqueous	25.6	4	4–5	4	4–5	4
RY201-VS	Solvent	24.3	5	5	5	4–5	4–5
	Aqueous	21.9	4–5	4–5	4	4–5	4
RBK5-VS	Solvent	27.3	5	5	5	4–5	4–5
	Aqueous	23.9	4–5	4–5	4–5	4–5	4

a. Dyeing temperature = 85°C, liquor ratio = 1:15, initial dye concentration = 2 g/L, all samples were soaped prior to measurements.

b. Results for other stain fabrics were all grade 5 and not listed.

ionically bonded dyes later removed during stripping in aqueous dyeing. Blue19-VS exhibits good build-up properties in solvent dyeing, which enables achieving color depth unattainable in aqueous dyeing.

The mechanical properties of untreated, solvent-dyed and aqueous-dyed/alkali-treated wool fabrics are compared in Figure 9(b). Based on ANOVA of the results, the difference in tensile strength of untreated and solvent-dyed wool was insignificant (p -value = 0.454). On the other hand, aqueous-dyed and alkali-treated wool fabrics was found to suffer from a noticeable loss of tensile strength (0.15N on average, p -value = 0.0007). The results clearly demonstrate that solvent dyeing causes less damage to wool compared with the combined aqueous dyeing and alkali treatment.

The difference in solvent and aqueous dyeing of wool was further compared in terms of colorfastness using four VS dyes featuring different chromophores and different numbers of sulfate groups. The results are shown in Table 1. For all four dyes investigated, solvent-dyed samples showed higher K/S values after one soaping. The difference was measured to be as high as 4.9 in the case of RO16-VS. Despite having higher color depth, solvent-dyed samples displayed washing and wet crocking fastness half to one grade better than the aqueous-dyed counterpart. The soaping procedure used here was not as efficient as pyridine stripping in removing ionically bonded dyes. Therefore, the remaining ionically anchored dyes fell off in the following colorfastness tests. The observed differences agreed with the fact that solvent-dyed wool hardly contains ionically bonded dyes.

Conclusions

In this paper, the effect of DMSO pretreatment on wool was investigated using SEM, XRD and ATR-IR. Results indicated the pretreated wool underwent substantial morphological and structural changes in favor of its dyeability. The cuticle layer was disintegrated, the α -helices were partially converted to β -sheets and the internal hydrogen bonding system was disrupted. Reactive dyeing of the treated wool in a mixture of DMSO and DMC was demonstrated to give excellent colorfastness in deep color shades. The appreciable improvement was due to the prevalence of covalently bonded over ionically bonded dye in solvent-dyed wool samples. On average, solvent dyeing enjoyed 30% higher covalent fixation compared with aqueous dyeing. Results from dyeing wool with four more different VS dyes showed that solvent-dyed samples all had higher color depth ($\Delta K/S$ = 1.3–4.9) yet better colorfastness (0.5–1 grade) compared with the aqueous-dyed controls. There was also no need for stringent control of pH in solvent dyeing. The favorable findings indicate that the

colorfastness-integrity dilemma in reactive dyeing of wool could be solved using the solvent dyeing technique. At the current stage, the process needs further improvement in that an extra pretreatment of the wool is mandatory, longer dyeing time is required and reclamation of solvent could be costly. Nevertheless, with further improvement solvent dyeing could lead to phasing-out of metal-containing dyes for eco-friendly wool dyeing.

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