

# Dyeing Behaviors of Ionic Liquid Treated Wool

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**ABSTRACT:** In this article, a new class of “green” solvent—ionic liquid (IL) was employed to improve the dyeability of wool. The physical and chemical properties of the IL-treated wool, such as surface morphology, wettability, and tensile strength were first analyzed, and then the dyeing properties of IL-treated wool were investigated in terms of dyeing rate, dyeing exhaustion at equilibrium, color depth, and color fastnesses. The scanning electron microscope (SEM) images showed eroded marks on IL-treated wool fiber surfaces. The water contact angle of the fabric treated with IL at 100°C decreased from 118.6° to 106.4°. The tensile

strength of IL-treated wool fibers was slightly decreased when the treating temperature was less than 100°C. Dyeing kinetics experiments revealed that the IL treatments greatly increased initial dyeing rate, shortened half-dyeing time, and time to reach dyeing equilibrium. The final exhaustion and color depth of IL-treated wool were also increased accompanying with slightly decreased color fastness. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2278–2283, 2010

**Key words:** ionic liquid; wool; dyeing; modification; adsorption

## INTRODUCTION

As a natural protein fiber, wool has a complex physical and chemical structure. The scales on the surface produce some undesired effects such as the barrier of dye diffusion and felting.<sup>1</sup> Modifications of wool are commonly conducted by chemical degradation of the scales such as chlorination and oxidation.<sup>2,3</sup> Although these methods are effective to improve the dyeability of wool, the effluents including chloro-organic compounds from antifelt finishing and dyeing processes pollute the environment and water resources.

To replace the chlorination treatment, some new eco-friendly methods, such as liquid ammonia treatment, low-temperature plasma modification, and microbial enzyme treatment have been developed recently.<sup>4–10</sup> Liquid ammonia treatment, which is traditionally employed in the processes of cotton-based materials processing is useful for improving dyeing properties of wool.<sup>4</sup> But the toxicity of ammonia, the high pressure and low temperature of liquid ammonia treatment restrict its application in textile industry. Low-temperature plasma treatment is a dry process, which can make significant amount of efforts in

surface modification of wool, including improving wetting, adhesion, and dyeing properties.<sup>5,6</sup> However, plasma treatments would generate a rather harsh handle and there are serious obstacles, such as costs, compatibility, and capacity, which greatly restrict the application of the technique in textiles.<sup>7</sup> Enzyme treatments have been considered as appropriate alternatives because they can replace harsh chemicals, work under mild conditions, and are biodegradable.<sup>8</sup> Much research has shown that protease treatment can improve the dyeability and shrink-resist of wool.<sup>9</sup> However, the existence of F-layer (a hydrophobic layer, which is mainly composed of fatty acids) in the wool surface prevents the protease from attacking wool fibers. Therefore, oxidative pretreatments are still needed to modify the wool surface. Furthermore, wool fibers are frequently damaged after oxidative pretreatment because protease preferentially attacks the highly swellable cell membrane complex (CMC) by penetrating cuticular scales, causing stripping and weakening of the wool fibers.<sup>10</sup> The limitations of these methods promoted us to develop a new modification method for wool fibers.

Recently, a new class of keratin solvent—1-butyl-3-methylimidazolium chloride ([Bmim]Cl) has been reported. It can dissolve unmodified wool keratin fiber, making subsequent modifications of wool in this solvent attractively possible.<sup>11</sup> [Bmim]Cl belongs to ionic liquids (ILs), which are often fluid at room temperature, and consist entirely of ions, in contrast to conventional solvents comprised of covalent molecules.<sup>12</sup> Compared with conventional organic solvents, ILs have many fascinating properties

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including negligible volatility, high thermal stability, low melting point, and strong solubility for many organic and inorganic substances.<sup>13,14</sup> Furthermore, they can be recycled and are eco-friendly. Therefore, ILs have gained increasing attention as media for the processing of biological macromolecules.<sup>15–17</sup>

In this article, [Bmim]Cl is employed to modify the wool surface before dyeing with an acid dye. The effects of IL treatment on wool dyeing properties have been studied including dyeing rate, equilibrium exhaustion, dyeing kinetics, and color fastnesses. In addition, the wettability and surface morphology of IL-treated wool are also discussed.

## EXPERIMENTAL

### Materials and chemicals

Wool fibers (the average diameter is about 25  $\mu\text{m}$ ) and 2/1 twill wool fabrics (45 ends  $\text{cm}^{-1}$ , 36 tex; 25 picks  $\text{cm}^{-1}$ , 36 tex) were kindly supplied by Xiexin Group Co., (Wuxi, China). They were scoured with acetone for 3 h using Soxhlet extraction. Then, the solvent-scoured wool samples were washed twice with deionized water, followed by drying at 50°C for 1 h and then air drying.

A commercial acid dye C.I. Acid Red 249 supplied by Dystar Co., (Wuxi, China) was used for wool dyeing without further purification. [Bmim]Cl was supplied by Henan Lihua Pharmaceutical Co., (Anyang, China). All other chemicals used in this study were of analytical grade unless exceptional explanation.

### IL treatment

The wool samples were separately treated with [Bmim]Cl in 250 mL-conical flasks at different temperatures (80  $\pm$  1°C, 100  $\pm$  1°C or 120  $\pm$  1°C) for 10 min. Then the samples were washed three cycles with ethanol at 45°C. This is because ethanol has a good solubility for [Bmim]Cl and it is also easy for IL recycle.<sup>18</sup> Finally, the samples were rinsed twice with deionized water and air dried.

### Surface morphology observation

The surface morphologies of wool fibers were visualized using a Quanta 200 Scanning Electron Microscope (FEI, Holland), operating at a typical accelerating voltage of 10 kV. The samples were positioned and gold-sputtered under vacuum before observation.

### Wettability test

The wettability of the wool fabric was characterized in terms of wetting time (in min) and contact angle.

The wetting time of wool samples was determined according to the drop test (AATCC Test Method 39-1980). Contact angle of each sample was measured with the Drop Shape Analysis System DSA 100 (Krüss, German). This method used distilled water with a drop size of 0.02 mL as test liquid. Data of contact angle were recorded after 20 s of contact. Ten measurements were taken on the different places of the fabrics.

### Tensile strength test

The tensile strength of wool fibers was determined using an electronic single fiber strength tester YG001A (Darong Textile Instrument, China). Testing condition is as follows: initial distance between clamps was 1 cm, stretching speed: 20 mm/min, pretension: 0.50 cN. The samples were balanced at 25°C and a relative humidity of 60% for 24 h before testing. The results were given as the arithmetic means of 50 different samples.

### Dyeing process

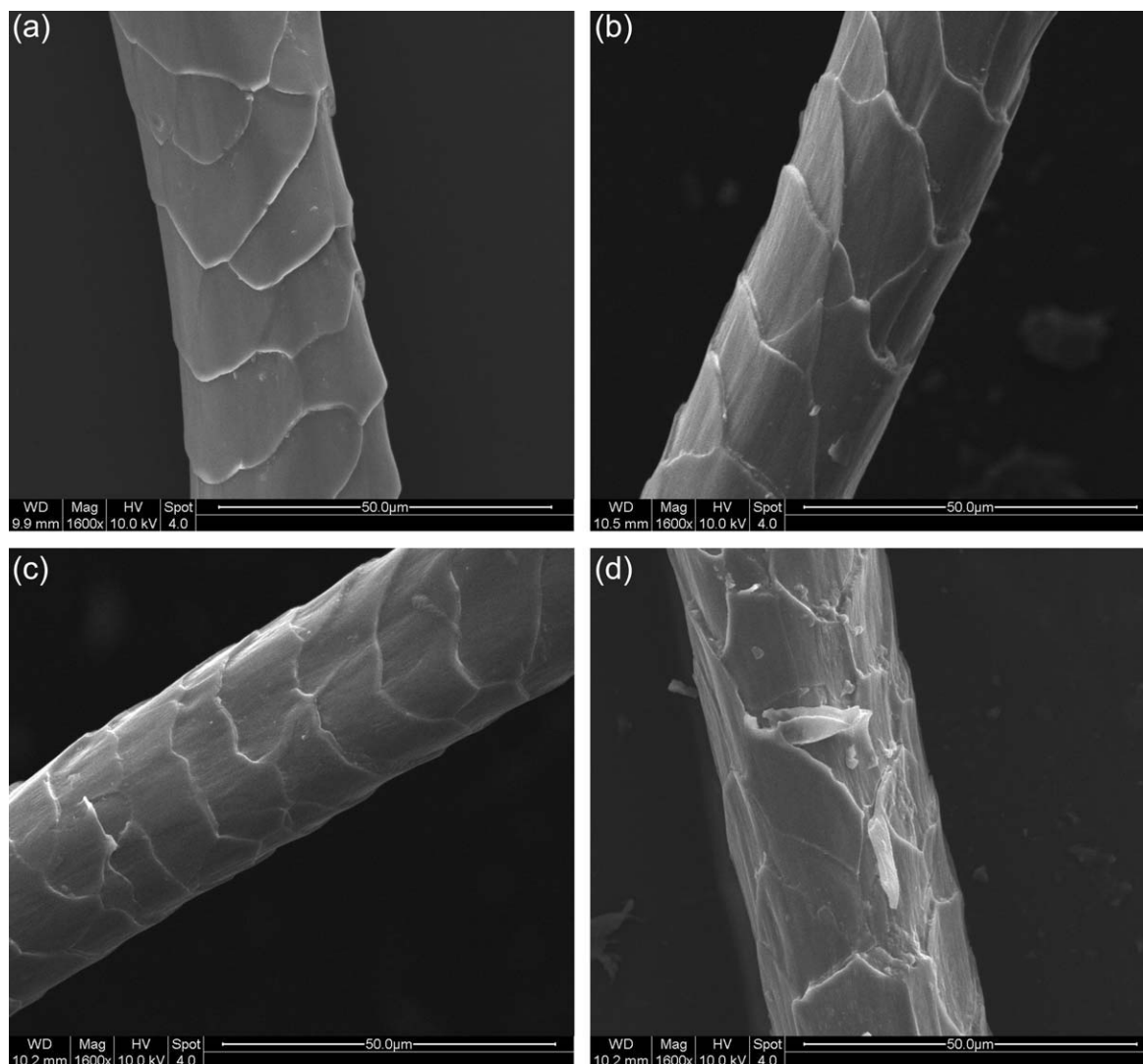
The dyeing process was carried out in a Rapid lab-scaled oscillating dyeing machine (Xiamen, China). Wool samples were dyed with 2% owf (on weight of fabric) C.I. Acid Red 249 and 1 g/L  $\text{Na}_2\text{SO}_4$  at boiling temperature for 2 h with a liquid-to-goods ratio of 100 : 1. The dyeing system was maintained at pH 4 with acetic acid. The dyeing exhaustion was determined by measuring the light absorbency of the original and exhausted dye bath solutions at different time of dyeing. The light absorbency was measured with a UV-2100 Spectrophotometer (Unico, America) at the wavelength of maximum absorbance ( $\lambda_{\text{max}}$ ) of the dye used. All measurements of the dye solution were conducted at room temperature and the exhaustion was calculated according to the following equation:<sup>19</sup>

$$E = \left( \frac{A_0 - A_t}{A_0} \right) \times 100\% \quad (1)$$

Where  $E$  is exhaustion percentage at  $t$  min,  $A_0$  and  $A_t$  are the absorbance of the dye bath before and after dyeing at  $\lambda_{\text{max}}$  of the dye used, respectively.

### Color depth and color fastness measurement

The apparent color depth ( $K/S$  value) was measured with a spectrophotometer Color-Eye 7000A (Gretag Macbeth, USA). Color fastnesses were tested according to the AATCC Test Methods 107-1997 (Color Fastness to Water Washing) and 120-1994 (Color Change to Flat Abrasion).



**Figure 1** SEM pictures of the wool fibers after different treatments. (a) untreated; (b) IL-treated at 80°C; (c) IL-treated at 100°C; (d) IL-treated at 120°C.

## RESULTS AND DISCUSSION

### Surface morphology

The surface morphologies of wool fibers are characterized by the scales, which play a critical role in controlling dye diffusion during wool dyeing. The SEM micrographs of wool fibers after different treatments are shown in Figure 1.

Figure 1(a) shows the surface morphology of the untreated wool fiber. It can be observed that the intact scales on the fiber surface overlap one another like tiles on a roof. In general, the scale is consisted of epicuticle, exocuticle, endocuticle, and intercellular cement.<sup>20</sup> The epicuticle, which is located at the surface of wool scales, is hydrophobic and thus produces a considerable impact on the wettability and dyeing behaviors of wool.

The SEM micrographs of IL-treated wool samples [Fig. 1(b–d)] reveal visible deterioration to the wool

scales compared with the untreated one. For the IL-treated fibers at 80°C, as shown in Figure 1(b), it can be seen that most of the scales are still completed except that the outer surface is slightly eroded. When the treating temperature increased to 100°C, although the cuticular scales are clearly visible on the wool surface, the scale edges have been eroded and become rounded [Fig. 1(c)]. After the sample was treated with IL at 120°C, most of the scales are dissolved out and some fibrils emerge from the damaged parts [Fig. 1(d)]. It could be concluded that processing temperature plays an important role in IL treatment according to the SEM pictures. It has been reported that only 4 wt % wool keratin could be dissolved in [Bmim]Cl at 100°C, but the solubility could reach up to 11 wt % at 130°C.<sup>11</sup> These changes in the surfaces of wool scale caused by IL treatments would damage the diffusion barrier, thus enhancing dye diffusion.

**TABLE I**  
Wetting Properties of the Wool Fabrics

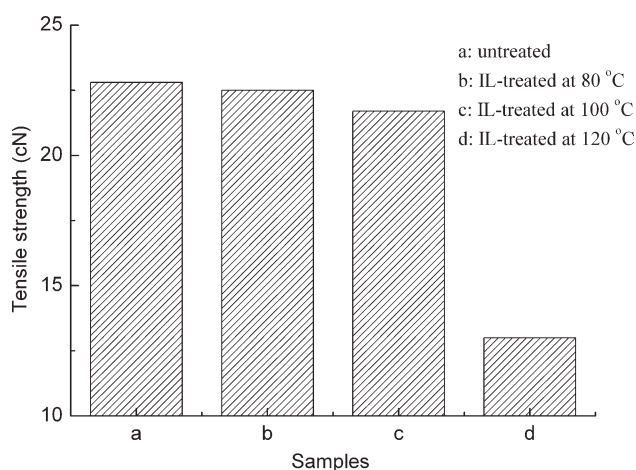
Samples	Contact angle (°)	Wetting time (s)
Untreated	118.6	>1800
IL-treated at 80°C	115.4	>1800
IL-treated at 100°C	106.4	1418
IL-treated at 120°C	80.9	88

### Wettability

The contact angles and wetting time of wool fabrics are listed in Table I. As shown in Table I, it is clear that through IL treatment, the water contact angle and wetting time of IL-treated wool fabrics are decreased quickly with the increase of treatment temperature. This might be due to better water absorption and faster diffusion into the IL-treated fiber as a result of IL modification. For the untreated wool fibers, the epicuticle has a thickness of 5–7 nm and is chemically composed of an external fatty acid monolayer (F-layer) and a protein layer with hydrophilic groups.<sup>21</sup> It had been demonstrated that F-layer is mainly composed of C<sub>21</sub> fatty acid, which is oriented away from the fiber, thus making the surface hydrophobic. After IL treatment, some scales were eroded, so that the fatty acids, which are chemically bound to the scales were removed together. The exposure of underlying proteins improved the hydrophilicity of the wool surface.

### Mechanical properties

Figure 2 shows the tensile strength of the untreated and IL-treated wool fibers. The tensile strength of IL-treated wool fibers is lower than that of the untreated one. The strength retention of the wool fibers treated at 100°C is 95.2% as compared to the untreated wool, which is acceptable in wool process-



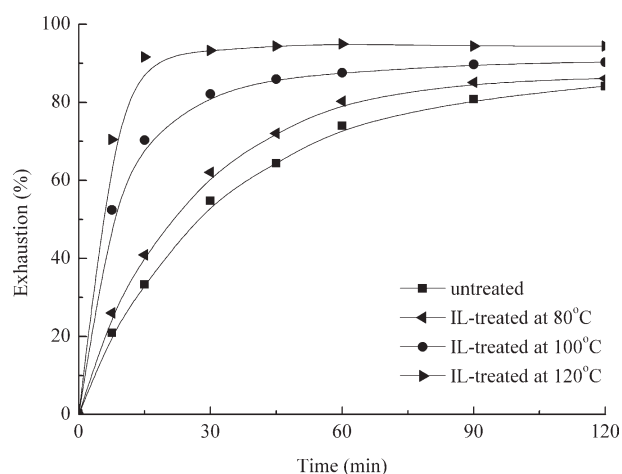
**Figure 2** Tensile strength of wool fibers after different treatments.

ing. However, a remarkable decrease in tensile strength happened when the wool fibers were treated at 120°C. This result reveals that IL treatment merely functions on the surface of wool fibers at a lower treatment temperature, which leads to a weak decrease in strength. However, ILs can easily penetrate into the interior of the wool fibers due to their lower viscosity at high temperature,<sup>22</sup> which will result in the degradation to the cortical cells.

### Dyeing behaviors

Figure 3 shows the percentage exhaustion curves of IL-treated wool fibers dyed with C.I. Acid Red 249. The characteristics of a dyeing system can be determined according to the variation of dye bath concentration against time. As shown in Figure 3, IL treatment has a considerable impact on the dyeing rate and the ultimate exhaustion of acid dye.

Firstly, the initial dyeing rate of IL-treated wool fibers was much higher than that of the untreated sample during the first stage of the dyeing process, i.e. within the first 15 min. In this stage, only 33.3% of dyes were adsorbed by untreated wool fibers, while 40.9% of dyes were adsorbed by the sample treated with IL at 80°C. When the treatment temperature was increased to 100°C, the percentage exhaustion of dyes onto wool fibers rapidly increased to 70.3%. This indicates that IL-treated wool fibers have better adsorption abilities than the untreated sample. In addition, the time to reach the dyeing equilibrium for IL-treated wool fibers is also shorter than that for the untreated one. Usually, the half-dyeing time ( $t_{1/2}$ ), which refers to the time taken in minutes to adsorb 50% of the dyes amount that it will adsorb at equilibrium under the same condition, is used to quantify the dyeing rate in a dyeing system of textiles. From the results of  $t_{1/2}$  in Table II, it is clear



**Figure 3** Relationship between dyeing time and dyeing exhaustion of wool fibers.



TABLE II  
Dyeing Kinetics Parameters of Wool Samples

Samples	$t_{1/2}$ (min)	Decrease in $t_{1/2}$ (%)	Em (%)	Increase in Em (%)	K
Untreated	21.2	–	84.18	–	5.35
IL-treated at 80°C	17.2	18.87	86.12	2.30	6.20
IL-treated at 100°C	5.5	74.06	90.27	7.23	9.28
IL-treated at 120°C	3.9	81.60	94.38	12.12	16.79

that the half-dyeing time was significantly shortened with the increase in IL treatment temperature.

Secondly, the equilibrium exhaustions (Em) of wool fibers are also improved after IL treatment. As seen in Table II, the Em of IL-treated wool fibers increases obviously with the treatment temperature. The Em of the sample treated by IL at 120°C reached 94.38% compared with 84.2% of the untreated one. To clarify the change in the equilibrium exhaustion after IL treatment, the substantivity,  $K$ , is introduced in this article.  $K$  represents the general nature of the relationship among substantivity, liquor ratio, and exhaustion percentage at equilibrium.<sup>23</sup> The  $K$  value reflects how efficiently dye has been transferred from the bath to the fiber. The greater the  $K$  value, the better dye retains in the fiber. From Table II, it is obvious that the  $K$  values of IL-treated wool fibers are increased significantly. Therefore, it could be concluded that the IL treatment is an effective method to enhance dye exhaustion on the fiber.

The changes in the dyeing behaviors including dyeing rate and dyeing equilibrium exhaustion of IL-treated wool fibers could be attributed to the following aspects. The improved dyeing rate is mainly caused by the alteration of adsorption and diffusion mode of dye molecules as a result of damages to wool scales. As a solid/liquid phase process, the dyeing process proceeds by the movement of the dye molecules from liquor to the fiber surface by terms of their affinity, and then diffusion takes place inside the fiber. A lot of dyeing experiments have shown that the wool scale functions as a barrier in the dyeing process.<sup>24</sup> The surface of the untreated wool sample is hydrophobic so it is difficult for dye molecules to access. In addition, the scale is so intact and compact that dye molecules can not diffuse vertically through the scales into wool fibers, but migrate into the fiber via the intercellular cement between the scales.<sup>25,26</sup> It is a typical intercellular diffusion mode, presenting a long diffusion route for the dye molecules to travel. In contrast, the IL-treated wool fibers scales are eroded and even dissolved, which induces the surface rough and hydrophilic. Dye molecules could be adsorbed easily at the damaged parts of the scales and directly diffuse through the scales into the wool fibers. The dye diffusion mode of the dyes is changed from the single

intercellular diffusion to the combination of intercellular diffusion and vertical diffusion after IL modification. Consequently, the dyeing rate of the IL-treated wool fibers is greatly accelerated.

The increased dyeing equilibrium exhaustion of IL-treated wool samples could be attributed to the increase of dyesite numbers. It is reported that IL has strong ability to disrupt the hydrogen bonds. Therefore, IL treatment could cause wool fibers to swell, and hence the crystallinity of wool fibers is decreased.<sup>11</sup> Some dyesites in original crystalline region are released, which allow the dye molecules to diffuse into these areas and bind with the released dyesites. Otherwise, the increase in the dyesites may also be attributed to the exposure of proteins under epicuticle. The damages to the wool scales by IL treatment make the underlying proteins more accessible. Therefore, more acid dye molecules could be adsorbed and bound to the  $-\text{NH}_2$  groups of exposed proteins, thus improving the dye exhaustion.

The dyeability of the wool fabric was studied in terms of the  $K/S$  curve. Figure 4 shows the  $K/S$  curves of IL-treated wool fabrics. The higher the  $K/S$  value, the deeper the shade depth. Therefore, from Figure 4, it is clear that the  $K/S$  value of the untreated wool fabric is lower than that of the IL-treated samples. This indicates that the shade depth of the untreated wool fabric is shallower than that of

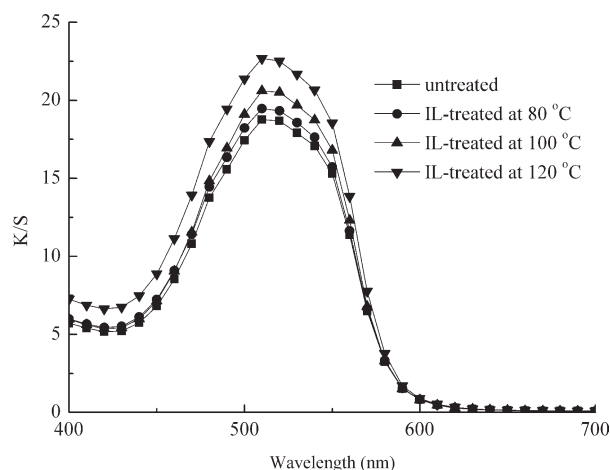


Figure 4  $K/S$  values of dyed wool fabrics.

TABLE III  
Color Fastness of Dyed Wool Fabrics (Unit: Grade)

Samples	Abrasion fastness		Washing fastness		
	Dry	Wet	Staining cotton	Staining wool	Color change
Control	4	3-4	4-5	5	4
IL-treated at 80°C	4	3-4	4-5	5	4
IL-treated at 100°C	4	3-4	4-5	5	4
IL-treated at 120°C	4	3	4	4-5	3-4

the IL-treated samples. For all the IL-treated wool fabrics, wool fabrics treated by IL at 80°C and 100°C give similar *K/S* curves, while the fabric treated by IL at 120°C shows the highest *K/S* value, indicating that this fabric presents the deepest color. It further indicates that the fabrics treated by IL could have darker apparent shades depth at the same dyeing conditions.

The color fastnesses of the untreated and IL-treated wool fabrics are shown in Table III. It can be concluded from the table that the rubbing and washing fastness of wool fabrics treated by IL at 80 and 100°C show no change compared with the untreated one. However, the wet color fastness of the wool fabric treated by IL at 120°C presents a decrease of half grade. This can be caused by the too high dyeing rate after IL treatment. In the dye exhaustion experiment, the sample treated by IL at 120°C showed the highest dyeing rate among the four samples. Therefore, some dye molecules could not diffuse into the inner part of wool fibers, but just adsorbed on the surface. Consequently, dye molecules were easily released from the fibers when the sample was wetted.

### CONCLUSIONS

This work reveals that IL treatment could produce a remarkable modification on wool and thus affects the wool dyeing behaviors. The scales of wool fibers were eroded after IL treatment and the wettability was also improved. These changes in the surface characteristics of wool fibers improved the dyeing behaviors. The dyeing rate and dyeing equilibrium exhaustion of wool fibers remarkably increased with the increase of treatment temperature. The color depth of the dyed fabrics after IL treatment was higher than that of the untreated wool. There was no considerable change in washing and rubbing fastness for IL-treated wool fabrics except a slight decrease for the fabric treated by IL at 120°C. The

mechanical test showed that tensile strength loss of IL-treated wool fibers was acceptable at a low treatment temperature.

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