Laser Treatment of the Wool Fabric for Felting Shrinkage Control

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Abstract: Laser treatment is one of the technologies which are able to eliminate all the adverse effects on the environment caused by chemical treatment commonly used in textile finishing. In this research, we investigated the use of laser treatment for the purpose of wool felting shrinkage control, and compared its effectiveness with that of the traditional chlorination treatment method. The wool fabric was exposed to an industrial laser at two different power levels and two sweep speeds. We found that upon selecting the appropriate treatment parameters, the laser treatment is effective in reducing felting shrinkage of wool fiber by its etching effects on the scales of the wool fiber as shown by the scanning electron micrographs. Too high energy exposure of the wool fiber by laser radiation causes excessive fabric strength loss. We also found that the laser-treated wool has felting shrinkage reduction similar to that treated using the traditional chlorination procedure. The laser technology presents an alternative wool processing method to replace the tradition chlorine treatment method. If this technology can be applied to wool felting-proof finishing on a commercial scale, it will significantly benefit the environment by completely elaminating the harzardous chlorine compounds currently by the industry.

Keywords: Laser treatment, Wool, Fiber shrinkage, Dimensional stability, Surface, Fiber

Introduction

The major disadvantage of wool as a textile fiber is its severe felting shrinkage upon washing. The surface morphology of wool fiber plays an important role in felting shrinkage. Felting effects of wool are caused by the scale movement, which is induced by mechanical agitation, moisture, and heat [1]. The method commonly used by the industry for reducing the felting shrinkage of wool is chemical treatment using chlorine [2-4]. Chlorination is the most effective method for reducing the felting shrinkage of wool fibers. The treatment process is carried out by treating wool fabrics using a dilute hypochlorite solution under acidic conditions to produce a superficial attack on the fibers and to modify the scales, thus preventing scale movement on fiber surface and consequently reducing the felting shrinkage. However, the chlorination method not only releases highly reactive chlorine into the atmosphere, but also causes water pollution by generating carcinogenic chlorine-containing liquid effluent to the waste water system. Recent research on chlorination and textile waste water toxicity discovered that chlorination using hypochlorite significantly increased the toxicity of the waste water of textile mills to different organism [5]. The chlorination method may also cause wool fiber damage because of the highly oxidative nature of hypochlorite [6]. Therefore, it is imperative for the textile industry to develop alternative eco-friendly technology to replace the traditional hypochlorite in wool felt-proofing processing.

Laser technology is one of the clean industrial methods causing no pollution to the environment by gas or liquid pollutants. There have been various scientific, military, medical, and industrial applications of laser developed since the invention of the laser in the 1958. The coherency, high mono chromaticity, and ability to achieve extremely high powers make various specialized applications feasible. Laser technology has been applied in the textile industry for removal of indigo dyes from denim [7-9]. Potential applications of laser technology in the textile industry include heating threads, creating patterns on textiles, producing surface roughness, welding, cutting textile webs whilst simultaneously sealing the raw edges, and monitoring and removing surface defects [10]. Carbon dioxide lasers can emit hundreds of kilowatts radiation at 9.6 and 10.6 μm, and are often used in industry for cutting and welding. The efficiency of a CO_2 laser is over 10 %, and such laser has been used in the textile industry as an intense directional heat source [10].

Various efforts have been made in the scientific community to develop new environmental-friendly technologies, such as enzymatic and plasma treatment, to replace the traditional chlorination treatment for wool felting shrinkage control [11-15]. The objective of this research was to investigate the use of a CO_2 laser to treat wool fabric for the purpose of shrinkage control so that we can develop a new wool processing technology with high felting shrinkage control capability and low adverse impact on the environment.

Experimental

Materials

The wool fabric was a plain weave fabric (226 g/m^2, 17 warps by 15 wefts per cm). Detergent "Laventin LNB" and "Kieralon Jet B" were produced by BASF. Sodium

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hypochlorite, sodium sulfite, sodium sulfate, acetic acid, sulfuric acid, and formic acid were reagent grade chemicals supplied by Merck (Germany). Acid milling dye and acid blue HRL (C.I. acid blue 182) were produced by Sunny Chemical, China. The ethanol (95 %) was made by ROMIL (UK).

Fabric Treatment Methods

Laser Treatment Method

The woven wool fabric was machine-washed using a detergent ("Laventin LNB") for 10 min with water temperature at 40 °C, and then tumble-dried. The washed fabric was irradiated using an industrial CO_2 laser instrument (LST, Turkey) with 10.6 μm wavelength laser source. The laser system was operated using two power levels (250 and 125 W) and two sweep speed (500 and 2,000 cm/sec). The distance between the fabric and the irradiation source was 50 cm, and the size of fabric specimen was 30×30 cm.

Chlorination Treatment

The same wool fabric was treated with a solution containing sodium hypochlorite (2 % owf active chlorine) and formic acid (1 % owf) at pH 4 for 30 min at 35 °C. Then the wool fabric underwent a thorough washing procedure followed by an anti-chlorine treatment using a 0.3 % sodium sulfite solution at 40 °C for 10 min, and was finally rinsed and dried.

Fabric Performance Evaluation Method

Shrinkage

The shrinkage of the untreated, laser-treated, and chlorinated wool fabric samples were measured by IWS TM-31 Standard Test. All the samples were cut into rectangular patterns approximately 30×30 cm, marks were made on the dimensional size of 25×25 cm and at a distance of 2.5 cm from the edges. The felting shrinkage for each sample was determined after the sample was laundered using agitation (standard 5A program) in a rotary drum washing machine (model "Wascator FOM71 MP"). The load was made up to a total of 1 kg with makeweights. The non-ionic detergent ("Kieralon Jet B, BASF") 0.3 g/l was added and the water temperature was kept at 40 °C [16]. Percentage of area shrinkage was determined by the average of six measurements reported.

Scanning Electron Microscope (SEM)

The wool fabric samples were first mounted on the stubs using a double-side adhesive tape and coated with a thin layer of gold to avoid surface charging. The scanning electron microscope (model "PHILIPS XL30") was used with an acceleration voltage of 20 kV. The original micrographs were taken with magnification of 1,000.

Fourier Transform Infrared (FT-IR) Spectroscopy Analysis

FT-IR spectrometer (Bruker-Equinox 55 system) was used for detecting the removal of fragments from the wool scales.

A small piece of untreated wool and laser treated wool (0.2 g each) were placed in 2 ml ethanol for extraction, and the mixture was continuously shaken for 3 min. A drop of the extraction solution was then placed on a KBr window and let to dry for 30 min at 90 °C in an oven before the FT-IR transmission spectra was collected. We also used a ZnSe attenuated total reflection (ATR) accessory to measure the IR spectra of the untreated and treated wool fabrics. For all the FT-IR spectra, the resolution was 4 cm^{-1} and there were 32 scans for each spectrum.

Fabric pH Measurement

The pH of the wool fabric samples was measured according to ASTM Method D2165-94 after the samples were immersed in distilled water for 2 h. Results were reported by average of two readings.

Wetability Measurement

The fabric wetability was evaluated by measuring the time for a drop of distilled water to be absorbed by a fabric specimen according to Standard Method AATCC 39-1980. The time reported was the average of 10 measurements.

Fabric Dyeing and Color Measurement

The wool fabrics (treated and untreated) were dyed with the Carmoisine Red ("Milling acid dye-CI. acid Red 14") along with acetic acid and sodium sulfate at boiling temperature for 45 min. The liquor ratio was 40:1. The leveling acid dyeing was carried out using leveling acid blue HRL ("C.I. Acid Blue 182") in the present of sulfuric acid and sodium sulfate. After dyeing, the fabric samples were rinsed thoroughly in tap water and dried in open air. The color of the dyed specimens was determined using a reflectance spectrophotometer (model "Datacolor V2.3") with D_{65} at 10 visual angles.

Tensile Strength

Tensile strength test was carried out using a Testometric M500-25 CT instrument according to ASTM D5035. Dimension of the fabric specimens was 2.5×30 cm. A speed of 50 mm/min was used with an initial grip separation of 200 mm. Only the tensile strength at warp direction was measured and reported.

Results and Discussion

Shown in Figure 1 is the percent area shrinkage of the wool fabrics untreated, treated using a chlorination method, and treated with laser under different conditions. Without any treatment, the wool fabric had 7.62 % shrinkage after one home laundering cycle. The SEM micrograph of the untreated wool fiber in Figures 2(a) shows the scale structure on the surface of the untreated wool fiber. Scales are formed by the overlapping cuticle cells, similar to those found in fishes. The scales, with approximately 0.5-1.0 μm in length, all point towards the tip end of each fiber [17]. The sharp edges of the scales are also clearly visible on the surface of the untreated wool fiber (Figure 2(a)). The directional
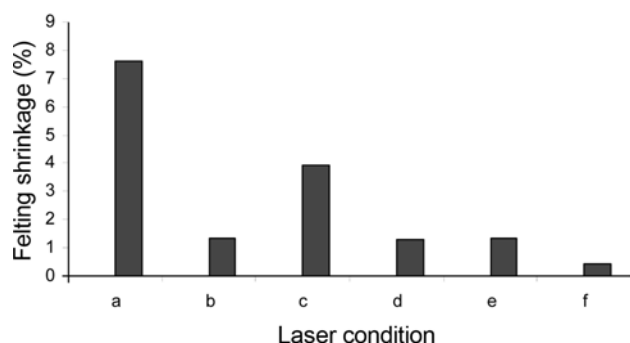
Figure 1. Felting shrinkage of the wool fabric (a) untreated, (b) chlorinated, (c) laser treated at 0.21 mJ/cm^2, (d) laser treated at 0.42 mJ/cm^2, (e) laser treated at 0.83 mJ/cm^2, and (f) laser treated at 1.67 mJ/cm^2.

friction effects of the scales on wool surface cause the fiber's preferential movement at the direction from tip to root, which is defines as felting shrinkage [18]. Moisture, mechanical agitation, and heat are needed to induce and to accelerate the felting shrinkage, as often observed during laundering of untreated fabrics of wool or other animal-hair fibers. Felting shrinkage of wool results in poor dimensional stability of wool fabrics and garments therefore must be controlled during wool fabrics' industrial processing.

The area felting shrinkage was reduced to 1.36 % after the wool fabric was treated using the chlorination method at pH 4 (Figure 1). The SEM micrograph of the wool fiber treated with chlorination is shown in Figure 2(b). Chlorination is the most commonly used chemical treatment method to achieve felting shrinkage control of wool [2,3]. The chemistry of chlorine in an aqueous media varies as pH changes. The solution of sodium hypochlorite is strongly alkaline and chlorine exists as hypochlorite (OCl$^-$). As an acid is added,

Table 1. The laser energy applied to the wool fabric surface

Laser power	Sweep speed	Energy on the wool fabric surface*
125 W	2,000 cm/sec	0.21 mJ/cm^2
250 W	2,000 cm/sec	0.42 mJ/cm^2
125 W	500 cm/sec	0.83 mJ/cm^2
250 W	500 cm/sec	1.67 mJ/cm^2

*The energy was calculated based the assumption the efficiency constant for the conversion of electric energy to laser photo energy was 10 %.

OCl$^-$ combines with the proton of the acid to form hypochlorous acid (HOCl), which is the main form of chlorine in the pH range 2-7 [19]. Both HOCl and OCl$^-$ are strongly oxidative and function to sever the cysteine disulfide bonds between the protein chains, thus degrading the scales of the wool fiber. The chlorinated wool fiber surface shows irregular scale edges, and the etching effect on the edges of scale is visible on the SEM micrograph of the treated wool fiber (Figure 2(b)). The degradation and the consequent modification of the edges on the scales were responsible for the decrease in felting shrinkage of the wool treated with the chlorination method shown in Figures 1 and 2(b).

The wool fabric was also treated with the laser irradiation at two different power levels (125 and 250 W) and two different sweeping speeds (500 and 2,000 cm/sec). The laser energy applied to the wool fabric surface was calculated and presented in Table 1, and the percent area shrinkage of the wool fabric thus treated is shown in Figure 1. When the wool fabric was treated with laser at the low power (125 W) and higher speed (2,000 cm/sec), the laser radiation had the smallest energy on the fabric surface (0. 21 mJ/cm^2). The laser treatment reduced the felting shrinkage to 3.91 %,
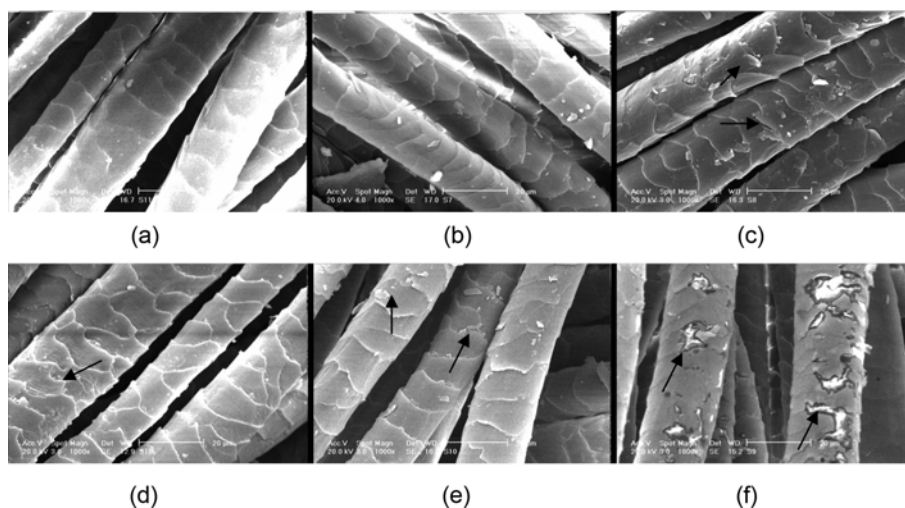

Figure 2. SEM micrographs of the wool fabric (a) untreated, (b) chlorinated, (c) laser treated at 0.21 mJ/cm^2, (d) laser treated at 0.42 mJ/cm^2, (e) laser treated at 0.83 mJ/cm^2, and (f) laser treated at 1.67 mJ/cm^2.

almost half of that of the untreated wool fabric (7.62 %). As the laser energy applied to the wool fabric surface was increased to 0.42 and 0.83 mJ/cm^2, the shrinkage of the wool fabric decreased to 1.27 and 1.32 %, respectively (Figure 1). Evidently, higher energy applied to the wool fabric caused more modification on the wool fiber surface and consequently higher felting shrinkage reduction. The wool fabric treated under such conditions achieved the felting shrinkages even slightly lower than that treated with the chlorination method (1.36 %). As the laser energy was increased further to 1.67 mJ/cm^2 when the fabric was treated at high power (250 W) and low sweep speed (500 cm/sec), the felting shrinkage was reduced further to 0.41 % (Figure 1). The data presented in Figure 1 demonstrate a clear correlation between the amount of the laser energy applied to the wool fabric and the felting shrinkage of the irradiated wool fabric. One observes that an increase in the amount of laser energy resulted in more reduction in the felting shrinkage of the treated wool fabric.

The SEM micrographs of the wool fabric treated with the laser at different energy levels are presented in Figures 2(c)-2(f). The SEM micrographs of the laser-treated wool fibers (Figures 2(c)-2(f)) and that of the untreated wool (Figure 2(a)) showed distinctive differences in their scale appearance. The edges of the scales on the untreated wool surface in Figure 2(a) were smooth whereas those of the laser-treated wool appeared to be "modified" by etching in Figures 2(c)-2(e). The scale edges on the surface of wool treated with laser at the highest energy level (1.67 mJ/cm^2) became invisible due to the damage of the fiber cuticle by its over-exposure to the laser. This was supported by the drastically reduced felting shrinkage of the wool fabric such treated (0.41 %). Therefore, we can conclude that the decrease in the felting shrinkage of the laser-treated wool fabrics was caused by the etching effects of laser radiation and the etching effects became more severe as the amount of laser energy applied to the fabric surface was increased as shown in Figure 1 and Table 1. However, it should also be pointed out that over-exposure of the wool fabric to excessively high energy laser radiation might cause severe damage of the wool fibers as shown in Figure 2(f). Therefore, optimization of the laser energy level by selecting the appropriate combination of laser power and the machine sweep speed is ultimately important to achieve the maximum wool felting shrinkage control with the minimum collateral damage to the wool fiber.

Figure 3 show the FT-IR transmission spectra of the extraction ethanol solutions of the untreated and laser treated wool fabrics. Comparison between two spectra showed some differences. In the laser-treated wool spectrum, the peaks appeared at 1531 and 1620 cm^{-1} which are associated with secondary amide (-CONH) stretching vibration modes of wool protein [20]. The intensity of these peaks are stronger than the peaks for the spectrum of untreated wool
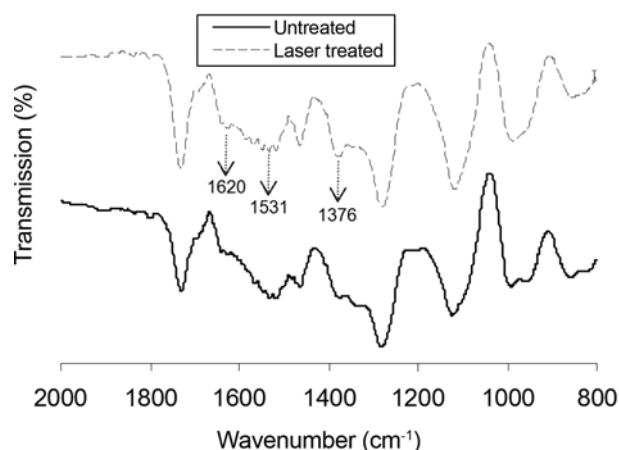

Figure 3. FT-IR transmission spectra of extraction solution of the untreated wool and the laser-treated wool.

and showed the existence of wool fragments in the extracted ethanol solution, which is related to removal of scales and moving the fragments into the ethanol solution. Wool scale surface was broken by etching effect of laser energy, as shown in SEM micrographs of laser treated wool (Figures 2(c), 2(d), 2(e)). For laser treated wool, a peak appeared at the region of 1376 cm^{-1} which is related to sulfur-oxygen bands of sulfonic acid group and it showed that S-S group of keratin changed to the S-O group. The oxidation of wool keratin led to oxidation of disulphide bonds, and therefore broke them and converted to sulfonic acid groups [19,22]. The spectrum of laser treated wool solution showed S-O groups at the region of 1376 cm^{-1} because of oxidation of S-S groups of wool scale surface to S-O groups of sulfonic acid [22]. These oxidized particles existed in extracted solution of laser treated wool, and demonstrated the evidence of wool surface fragment which removed from the surface by oxidizing and etching of high energy laser.

Figure 4(a) shows FTIR/ATR spectra of untreated, laser treated, and chlorinated wool surfaces. The spectrum of laser treated wool is related to the highest energy condition of laser radiation (1.67 mJ/cm^2). Comparison of these 3 spectra showed that laser treated wool spectrum demonstrated a peak at region of 1640 cm^{-1} which was stronger than this peak for chlorinated and untreated wool. This peak is related to increase the NH_3^+ group for laser treated wool [21]. Under laser treatment, chemical composition of wool surface changed and resulted in a change in the electro surface properties of wool [22]. ATR spectra of laser treated wool under different conditions of energy level are shown in Figure 4(b). It can be seen that there is difference between these spectra. The spectra of wool at low and medium energy level of laser (0.21 and 0.42 mJ/cm^2) are similar. As we can see in the Figure 4(b), there is not any significant change between the two spectra. The spectrum of laser treated wool at the highest level of energy (1.67 mJ/cm^2),
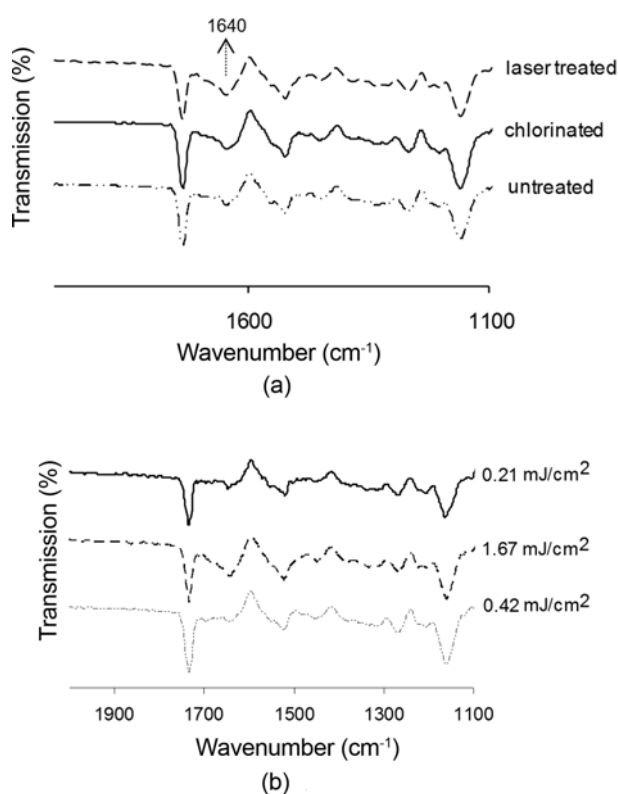
Figure 4. FT-IR/ATR spectra of (a) untreated, chlorinated, and laser treated wool at 1.67 mJ/cm^2; (b) laser treated wools at different laser energy conditions.

however, showed a peak at the region of 1640 cm^{-1} which increased its intensity as compared to the spectra of wool under low and medium level of energy. This peak belonged to the presence of NH_3^+ groups on the surface of fiber that revealed change in electro surface properties of wool fiber [21,22]. Therefore the increase in laser energy level caused changes on wool fiber surface.

We studied the change in the wettability of the wool fabric as a result of the laser treatment, and the data are presented in Table 2. The fabric wettability was measured using the time for a drop of water absorbed by a fabric sample. The wetting time of the untreated wool fabric was 83.8 s. It became 16.3 s when the wool fabric was treated with using the chlorination method. The reduction of the wetting time for the chlorinated wool was probably due to the degradation of the hydrophobic substances on fiber surface by the

oxidative hypochlorite. After the wool was treated with laser at the low energy level (0.21 mJ/cm^2), the wetting time of the wool fabric decreased to 20.8 s. The wetting time increased as the laser energy was increased, and it became to 91.3 s as the laser energy was increased to the highest level (1.67 mJ/cm^2). The data presented here indicate that the laser treatment increased the wettability of the wool fabric at a lower energy level, but the increases in the laser energy reduced the wettability. The laser treatment may remove the fragments of epicuticle from the fiber surface, thus improving the wettability of the treated wool fabric. The reduction of the wettability at higher laser energy levels was possibly due to laser-induced chemical changes which increase the hydrophobicity on the fiber surface. These results are similar to the result of plasma treatment of wool that hydrophilicity decreased due to both chemical modification and wool structure consolidation [22]. Therefore, the chemical changes on the wool fiber surface caused by the laser treatment are obviously complex and different from the chlorination process.

The tensile strength and percent breaking elongation of the untreated and treated wool fabrics were also presented in Table 2. The wool fabric had tensile strength and breaking elongation of 21.63 kgf and 32 %, respectively. Chlorination treatment of the wool fabric caused no change in fabric tensile strength where the breaking elongation decreased to 23 % (Table 2). The highly oxidative hypochlorite probably not only affected wool scales on fiber surface but also penetrated into the fiber interior, thus affecting the wool fiber's integrity and reducing the breaking elongation [23]. For the wool fabric laser-treated at a low energy level (0.42 mJ/cm^2), the tensile strength and percent breaking elongation were reduced to 18.82 kgf and 27 %, respectively. The wool fabric treated with laser at that energy level showed shrinkage similar to that treated with the chlorination method (Figure 1) whereas its tensile strength is modestly lower and breaking elongation is modestly higher than that treated with the chlorination method (Table 2). When the laser energy was increased further to 1.67 mJ/cm^2, the tensile strength and percent breaking elongation decreased drastically to 8.02 kgf and 11 %, respectively, due to the laser-induced damage in the fiber interior as shown in the SEM micrograph (Figure 2(f)). Thus, the data presented here demonstrated that exposure to too high laser energy caused excessive loss in fabric strength and elasticity.

Because laser treatment may change the colors of dyed wool fabrics, we evaluated and compared the color changes

Table 2. Wettability, tensile strength and breaking elongation of the untreated, chlorinated and laser-treated wool fabric samples

	Untreated	Chlorinated	Laser treated (energy)			
			0.21 mJ/cm^2	0.42 mJ/cm^2	0.83 mJ/cm^2	1.67 mJ/cm^2
Wettability (s)	83.8	16.3	20.8	66.3	43.6	91.3
Tensile strength (warp, kgf)	21.63	21.62	20.77	18.82	18.44	8.02
Breaking elongation (%)	32	23	27.5	27	20	11

Table 3. Color parameters and color difference of the treated, chlorinated and untreated wool fabrics

Dyes	Color parameter	Wool Untreated	Wool chlorinated	Wool, laser treated, energy (mJ/cm^2)			
				0.21	0.42	0.83	1.67
Acid leveling blue dye	L^*	25.18	23.49	25.70	25.85	23.57	25.76
	a^*	7.35	7.19	7.12	7.08	6.93	7.23
	b^*	-34.10	-34.25	-34.12	-33.71	-33.92	-29.08
	ΔE	-	1.71	0.57	0.82	1.67	5.06
Acid milling red dye	L^*	34.66	32.98	34.77	34.52	32.81	34.86
	a^*	45.14	46.53	46.31	45.71	46.20	40.1
	b^*	9.84	11.86	10.77	9.91	11.71	13.04
	ΔE	-	2.98	1.49	0.59	2.83	5.97

for the wool fabric subjected to chlorination treatment and laser treatment using CIELAB system (Table 3). The three color parameters, L, a, and b, represent lightness/darkness, redness/greenness, and yellowness/blackness of an object, respectively. The CIELAB system provides a method for quantifying overall color difference between two specimens using one single term (ΔE), which incorporates the differences of the three individual color parameters as follows [24].

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \qquad (1)$$

When wool fabric was dyed with "acid leveling blue dye", the L, a, and b values for the fabric without treatment are 25.18, 7.35, and −34.10, respectively. After chlorination they became 23.49, 7.19, and −34.25, respectively, and the ΔE was 1.71 (Table 3). The data for laser treated samples indicate that the color difference of the wool fabric after the laser treatment is significant. When the dyed fabric was subjected to the laser treatment at a low energy level (0.42 mJ/cm^2), the L, a, and b values of the laser treated fabric were closer to those of the control, and ΔE between the control and laser-treated wool fabric was 0.82. It is also evident that an increase in the laser energy increases the color change as demonstrated by higher ΔE in Table 3. A similar phenomenon for the color change was observed for the wool fabric dyed with "acid milling red dye". The ΔE of the wool fabric treated with laser at the low energy level (0.42 mJ/cm^2) was significantly lower than that treated with the chlorination method. It should also be emphasized that the amount of laser energy applied to the wool fabric is the most critical parameter for the treatment. An increase in the energy level applied to the wool fabric considerably increased the color change on the dyed wool fabric as shown in Table 3.

Conclusion

The laser treatment was effective in reducing felting shrinkage and improving dimensional stability of the wool fabric upon selecting the appropriate treatment parameters

including laser power and sweep speed. The anti-felting effects of the laser treatment increased as the laser energy applied to the wool fabric surface was increased. Increasing the laser radiation energy applied to the fabric also resulted in excessive fabric strength loss, lower breaking elongation, and more color change. Optimization of the treatment conditions is critical to achieve the highest effectiveness with the least negative effects on the treated fabrics.

The laser-treated wool had felting shrinkage reduction at a level similar to that of the wool fabric treated using a traditional chlorination procedure. The laser treatment caused slightly higher fabric strength loss than the chlorination method with modestly higher breaking elongation and lower color change.

The laser treament presents an alternative wool anti-felting processing method to replace the tradition chlorine treatment currently being used in the industry. If this technology can be applied to wool felting-proof finishing on a commercial scale, it will significantly benefit the environment by completely elaminating the use of harzardous chlorine and its derivatives.

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