Improving anti-felting characteristics of Merino wool fiber by 2.5 MHz atmosphere pressure air plasma

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Abstract. The present work investigates the effect of high frequency (2.5 MHz) Dielectric Barrier Discharge (DBD) in air on surface characteristics of Merino wool as a function of plasma exposure time (5s to 15s). The FE-SEM (Field Emission Scanning Electron Microscopy), EDS (Energy Dispersive X-ray spectrum) and Derivative ATR-FTIR (Attenuated Total Reflection- Fourier Transform Infrared) Spectroscopy are used to study physio-chemical changes induced by plasma. These physio-chemical properties of fibers can be co-related with the felting behaviour of the wool fiber, which leads to shrinkage and pilling of garments while laundering. Felting occurs mainly because of presence of outermost hydrophobic cuticle layer having sharp scales. The FE-SEM analysis of wool fiber surface reveals that cuticle scales on wool fiber become blunt after plasma processing. The ATR-FTIR analysis along with second order derivative spectroscopy demonstrates the cleavage of di-sulphide bonds of cuticle and formation of sulphur-oxygen groups such as Cystine Sulphonate (-S-SO3-), cysteic acid (-SO3-), cystine monoxide(-SO-S-), cysteine di-oxide (-SO2-S-). A possible explanation about how the combined effect of morphological and chemical changes induced by plasma results in minimizing the felting of wool fibers is discussed.

1. Introduction
Wool is one of the natural fiber, having a number of advantageous characteristics. However, one of the drawback of this fiber is having felting property. Felting is the process of the entanglement of fibers, when exposed to aqueous medium. The felting results in shrinkage and pilling of woolen products, while laundering. Wool fiber consists of multiple layers with unique properties. The outer-most layer of wool fiber called cuticle is hydrophobic and scaly in nature. When fiber is immersed in water, each layer absorbs water more or less and swells. The outer layer being hydrophobic swells less as compared to inner layer cortex which is hydrophilic. This difference in expansion leads to uprising of scales and thus entanglement of fibers [1-4]. Conventionally, chlorination process is used to impart anti-felting or shrink proof property to wool. However, worldwide research has been increasing for use of low-temperature plasmas as an eco-friendly tool for surface modification of wool. A number of previous researches have been reported for low pressure non-thermal plasmas for shrink proofing of wool [5-8]. However, industrial requirement for wool processing can be fulfilled only by atmospheric pressure plasmas, as the processing cost is much lower as compared to low pressure plasma and also inline treatment in continuous mode is possible. Atmospheric pressure non-thermal plasmas can be generated by Dielectric Barrier Discharge (DBD) technique. Few of the reported work for the use of atmospheric pressure air plasmas for shrink proofing of wool are discussed here. Jayant et.al 2011 [9] has used 50 Hz air DBD system. In their experimental results, the descaling of the wool is not
achieved even when plasma exposure time was quite more (40 to 60 minutes). The present work comprises of investigating effect of high frequency (2.5 MHz) Dielectric Barrier Discharge (DBD) air plasma on surface characteristics of Merino wool for exposure time of few seconds (0 to 15s) only. This high frequency power source has been chosen, as it generates uniform glow dielectric barrier discharge (DBD) plasma in air at atmospheric pressure with higher density (~ 2.5W/cm²) over the large surface of 70 cm² [18], which makes plasma processing significantly faster as compared to other DBD configurations.

2. Experimental Details
The DBD set-up consists of a pair of cylindrical electrodes made up of SS wire mesh (#325) and a polyester film (thickness 125 micron) separated by about 2 mm gap and high current driving power supply. A uniform glow like discharge in air at atmospheric pressure is generated in the inter-electrode gap as shown in figure 1. This power supply unit provides 2.5 MHz damped oscillations with the voltage magnitude of 5.8 KV (first cycle) and current magnitude of 50-100A (first cycle) for a duration of 0.25 μs [18]. The wool fibers are inserted manually between pair of cylindrical electrodes and discharge is generated by switching on the power supply for different exposure times from 5s to 15s, at a constant power density of 2.5 watt/cm².

3. Results & Discussion
3.1. Surface Morphology
In the present work FESEM (Field Emission Scanning Electron Microscope) Model: Merlin VP by Carl Zeiss has been used for surface analysis. The SEM images of Merino wool fiber at magnification of 10.0 KX are shown in Figure 2 (a) to (d) with plasma exposure time of 0, 5s, 10s and 15s, respectively. It can be clearly observed that the scales of untreated fiber are sharp and plasma exposure

![Figure 1](image1.png)

*Figure 1. Schematic diagram of experimental set up for dielectric barrier discharge*

![Figure 2](image2.png)

(a) 0s  
(b) 5s
results in making the cuticle scales blunt. As we increase the exposure times from 5s to 15s, the scales become more and more blunt. However, crimps and cracks are observed on the fiber surface at exposure time of 15s, which means fiber gets damaged when exposed for higher time. The FE-SEM analysis of wool fiber reveals that after plasma exposure the overlapping cuticle scales on the fiber surface become blunter. The blunting of scales results in reducing the directional friction among the fibers. This indeed lowers the chances of inter-locking of the fibers, due to uprising of scales in aqueous medium and hence the felting can be prevented [1 and 4].

3.2. FTIR Study
The IR spectra of wool fiber have been taken with the Nicolet 6700 FTIR instrument having a resolution 4 cm$^{-1}$ and multi bounce HATR accessory. The FTIR spectrum of untreated and plasma treated Merino wool fiber is shown in Figure 3. There are no significant changes between untreated and plasma treated fiber. Similar results have been previously reported by Masukuni Mori et.al [8]. However, it is known that exposure of wool fiber to air plasma leads to oxidation of fibers. In this process the protein cystine is converted to cysteic acid (-SO$_3$-) [7, 13]. This phenomenon leads to formation of intermediate products such as Cystine Mono-Oxide(-SO-S-), Cystine Di-Oxide (-SO$_2$-S-) and Cystine-Sulphonate (-S-SO$_3$-) or Bunte’s Salt. We cannot identify these individual sulphur – oxygen groups in unprocessed spectrum. Hence, we have performed second derivative analysis on IR spectra for resolving the bands and also for obtaining quantitative results by estimating concentration.
of these cystine oxides. A portion of experimentally obtained FTIR-ATR spectrum of Merino wool fiber and its second order derivative spectrum is shown in figure 4. We can easily identify peak positions of individual sulphur-oxygen group’s bunte’s salt (1020 cm⁻¹), cysteic acid (1043 cm⁻¹), cystine monoxide (1076 cm⁻¹) and cystine dioxide (1121 cm⁻¹). The concentration or absorption ratio is obtained by dividing absorbance value of these individual sulphur-oxygen groups in derivative spectrum with the absorbance value of Amide III (1232 cm⁻¹), which is the reference band. The results are shown in Figure 5, which are average of three reading. We have observed that concentration of bunte’s salt and cysteic acid is increasing with plasma exposure time, as higher exposure time leads to more oxidation of the fiber. The concentration of both Cystine Mono-oxide and Cystine – dioxide seems to slightly increase at 5s exposure time and as we increase exposure time further, we find different results and hence error obtained is relatively higher. This may have happened as

Cystine mono-oxide and Cystine di-oxides are not stable and are an intermediate product during conversion cysteine to cysteic acid. The formation of Bunte’s salt and Cysteic Acid makes wool fiber surface hydrophilic in nature, which is inherently hydrophobic. Thus the difference in wettability of inner cortex and outer cuticle layer is now minimized after plasma processing. Therefore, when plasma processed fibers are immersed in the aqueous medium, there is no non-uniform swelling of the fibers and hence the uprising of the scales can be prevented which means occurrence of felting is also minimized. Further, Gomez et.al [14] has reported shrink properties of wool fiber are improved by formation of Bunte’s Salt. Wakida et.al [17] described cysteic acid along with the bunte’s salt on polypeptide chain improves the wettability of the fabric considerably. Maclaren & Kirkpatrick [10] have explained formation of Cystine mono-oxide and cystine di-oxide generates more reactive substrate which provides suitable sites for dyes and softeners.

3.3. EDX Analysis
The EDX (Energy Dispersive X-ray spectrum) spectrum of Merino wool fiber shows mainly Carbon, Oxygen, Nitrogen and Sulphur peaks. The weight percentage of these elements is shown in figure 6 as a function of plasma exposure time. The results show the percentage of sulphur has decreased significantly after 5s plasma exposure time. As we increase the exposure time further, the decrease in sulphur percentage is relatively slow. The sulphur in the wool is present in amino acid cysteine as well as thioester linkages of lipids on the epicuticle surface [13]. The decrease in sulphur percentage can be
attributed to removal of outer most layer epicuticle [15]. It is possible that in 5s exposure time, the major portion of epicuticle is removed and hence higher reduction in sulphur percentage is observed. The nitrogen percentage has slightly increased in 5s plasma exposure time, while for 10s and 15s exposure time; there is no significant change in nitrogen percentage values. This can be explained as the outer lipid layer containing sulphur is removed; the underlying nitrogen content from proteinous part of wool in the cortex is exposed and hence shows relative increase in weight percentage. We have observed a small increase in oxygen percentage value, which may be due to oxidation of the fiber. There, is no significant change in weight percentage of carbon, as it is present in entire fiber.

3.4. Shrink Proof Test
The Aachen felt ball method has been used to examine the changes in the shrink resistance of wool fibers. This test has been carried out at Wool Research Association (WRA) with standard IWTO-20-69. The felt ball diameter for untreated fiber was found to 2.509 cm while for 10s plasma treated sample, diameter slightly increased to 2.597 cm. Hence felting density of untreated fiber is found to be approximately 0.12 gm/cc while plasma treated fiber has a value of about 0.10 gm/cc. These results as obtained in our study by using DBD are quite similar to as obtained for low pressure glow discharge system by German Wool Research Institute [16]. However to achieve a felting density value of 0.04 gm/cc as obtained by conventional chlorination treatment, additionally a resin treatment may be required.

Atmospheric Pressure Plasma consists of energetic electrons, ions, neutrals, radicals, etc. When these species interact with the wool fiber surface, the fibers are etched due to bombardment of electrons and ions and also fiber surface is oxidized. The cuticle which is the outer layer of the wool fibers mainly consists of cystine linkages having di-sulphide bonds. When high energy electrons interact with the fiber there is cleavage of di-sulphide bonds (Dissociation energy 2.6 eV) which leads to formation of highly reactive radical anion SS. These anions react in oxygen and form cystine Sulphonate (-S-SO3-) or cysteic acid (-SO3-). Cystine mono-oxide (-SO-S-) and cysteine di-oxide (-SO2-S-) are intermediate product when cystine is converted to cysteic acid. The evidence of these interactions is given by EDS (Energy Dispersive X-ray spectrum) and Derivative ATR-FTIR (Attenuated Total Reflection- Fourier Transform Infrared) Spectroscopy analysis techniques in the present work. The physio-chemical changes induced on the fiber surface can be co-related with the felting behavior of the wool fiber [2]. The SEM study indicates the plasma exposure time of 15s leads to damage of fiber and for 10s significant de-scaling is observed. The FTIR and EDS analysis also shows removal of epicuticle layer and significant oxidation of the fiber for 10s exposure time. It seems for the present experimental set-up, a plasma exposure time of 10s will do optimum surface modification of the fiber required to improve its anti-felting property. The result of shrink resistance test by Aachen Felt Ball method confirms the improvement in anti-felting property of Merino wool fiber by atmospheric pressure air plasma with the felting density value of about 0.10 gm/cc.

4. Conclusion
In the present work, we have used high frequency (2.5 MHz) atmospheric pressure dielectric barrier discharge in air to modify surface properties of Merino wool fiber and physio-chemical properties of wool fiber are studied as a function of plasma exposure time. The surface morphology is well examined by FE-SEM and results revealed how morphological changes with exposure time. The FTIR analysis with second-derivative spectroscopy explained the wool fiber oxidation by plasma and cleavage of di-sulphide bonds. The elemental study by EDS substantiates the results obtained by FTIR. The changes induced in physio-chemical properties of fibers by plasma processing are co-related with its anti-felting properties. Further, the Aachen Felt Ball method has validated the improvement in felting characteristics. The present study has revealed that exposure time of 10s resulted in optimum surface modification to achieve anti-felting properties. A higher exposure time has shown damage of the fiber and hence it may have impact on tensile strength of the fiber.
The experimental parameters reported in present study such as exposure time of 10s, use of ambient air at atmospheric pressure and simple electrode set-up makes it quite suitable for industrial use. The present work clearly demonstrates the potential of using 2.5 MHz atmospheric pressure air DBD for improving anti-felting property of wool fiber in an environmental friendly manner.

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References
[1] Liu et.al 2007 Textile research journal 77 12 957
[2] Mercer et.al 1947 Journal of Textile Institute 38 227
[3] Makinson and Sydney K R 1979 Marcel Dekker Inc. New York
[4] Udakhe J et.al 2011 Journal of the Textile Association p171-179
[5] Hesse A et.al 1995 Text.Res.Journal 65 6 p355-361
[6] P.erra et.al 1999 Text. Res. Journal 69 11 p811-815
[7] Kan et.al 2003 Autex Research Journal 3 4
[8] Mori M et.al 2006 RJTA 10 1
[9] Jayant et.al 2011 Manmade Textiles in India XXXIX No. 4 SASMIRA p137
[10] Maclaren J A et.al 1968 Journal of Society of Dyers and Colourists 84 p564
[11] Odlyha M et.al 2007 Autex Research Journal 7 1
[12] Douthwaile et.al 1994 Journ. of the society of dyers & colors 110 9 p304-307
[13] Hacke 2006 John Rylands University Library of Manchester
[14] Gomez et.al 1994 Journal of Textile Institute 85 2
[15] Restivo A et.al 2014 Microscopy and Microanalysis 07 20 p5
[16] Shishoo R 2007 (Woodhead Publishing Limited) Chapter 9 p228-244
[17] Wakida et.al 1993 Textile Research Journal 63 8 p438-442
[18] Jain V et.al 2016 IPR/RR-779/2016