Generation of nano roughness on fibrous materials by atmospheric plasma

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Abstract. Atmospheric plasma technology finds novel applications in textile industry. It eliminates the usage of water and of hazard liquid chemicals, making production much more eco-friendly and economically convenient. Due to chemical effects of atmospheric plasma, it permits to optimize dyeing and laminating affinity of fabrics, as well as anti-microbial treatments. Other important applications such as increase of mechanical resistance of fiber sleeves and of yarns, anti-pilling properties of fabrics and anti-shrinking property of wool fabrics were studied in this work. These results could be attributed to the generation of nano roughness on fibers surface by atmospheric plasma. Nano roughness generation is extensively studied at different conditions. Alternative explanations for the important practical results on textile materials and discussed.

1. Introduction
Applications of atmospheric plasma for light industry are going to substitute, in many areas, conventional liquid chemical treatments as well as low pressure plasma technology [1]. In particular, atmospheric plasma finds many important applications in textile industry. There could be noted the possibilities for improvement of fibers cohesion, of fiber sleeves and yarns breaking force, the anti-pilling property of fabrics and the anti-shrinking property of wool fabrics. Probably the most interesting application of atmospheric plasma in textile field is producing of anti-shrinking property of wool. Wool shrinking during washings occurs due the presence of scales on the fibers (of ca. 20 μm in diameter) surface. The scales are positioned on fiber similarly to roof tiles, oriented all in the same direction along the fiber. This structure creates different friction coefficients between two fibers in the cases when they are parallel or anti-parallel to each other. When anti-parallel fibers slide one over another during washing, differential friction brings to the irreversible shrinking of wool fabric. Conventional chemical anti-shrinking treatments (Basolan, Hercosett) are based on smoothing or elimination of scales from fibers surface. In the result of such strong modification (levelling) of fibers at μm level, they could slide one over the other with much less (differential) friction, thus producing minor shrinking of fabric. Plasma treatment, instead, does not eliminate the scales on the fibers. Actually, anti-shrinking effect generated by plasma on wool fabrics is not clearly attributed.

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Application of plasma produces different effects on fibers [1, 2]:
- partial elimination of adhered and covalently bounded lipids and other adhered substances (cleaning effect);
- generation of active sites on fibers, such as carbonyl CO, carboxyl COOH, amino groups and sulphonated SO3 groups in particular case of wool fibers (activation effect);
- generation of nano roughness on fibers (morphologic effect [1]).

Presented work is dedicated to the study of morphologic effect produced by atmospheric plasma on fibers. Obtained results prove that nano structuring of wool fibers is responsible for the modified mechanical properties of wool, such as anti-shrinking, anti-pilling and sleeves strength.

2. Instruments and methods
2.1. Apparatus for Dielectric Barrier Discharge treatments of fibrous materials

![Figure 1. Scheme and layout of the apparatus for DBD treatment of textile materials.](image)

Dielectric Barrier Discharge (DBD) treatments on wool and cotton fabrics were performed with original apparatus (figure 1) produced by Tigres GmbH (Rellingen, Germany). The discharge is applied in 2.0 mm gap between moving electrodes unit (2 electrodes covered by ceramic) and the grounded stainless steel plate covered with silicone sheet (ca. 1 mm). Conditioned air (RH 5 ÷ 30%) or special gas mixture flows at max 50 slpm between the electrodes and grounded plate. Current Wave and Pulsed mode (duty cycle 10 ÷ 80%) can be applied at max power 500 W and specific power 6.7 W/cm², at frequency ca. 40 kHz. The treatment can be performed in air, in pure gases or in mixtures (O₂; N₂; He; Ar; CO₂) with O₂ traces below 10 ppm.

Treatment of wool, cotton and polypropylene fiber sleeves were performed in-line by original pre-industrial scale machine "Nanofabia". Treatments of other different fibers (TiO₂, basalt fibers) were performed with remote atmospheric plasma jet produced by Plasma Treat GmbH (Steinhagen, Germany).

2.2. Preparation and characterization of samples

Industrially scored knitted wool fabric was used. Before plasma treatments fabrics were additionally cleaned with dichloromethane for 24 hours (Soxhlet extraction) [3], washed twice with ethanol and twice with deionized water and finally dried.

Chemical extraction in alcoholic basic solution was applied in different experiments on wool for partial elimination of covalently bounded lipids by hydrolysis [4].

Washings of fabrics were performed in domestic washing machine according to internal test standard, analogous to Woolmark test method TM 31. Shrinking of wool fabrics (in area) were determined after test washing by standard ISO method.
Wicking experiment (rise of water in vertical sample of fabric) was used for the evaluation of the wettability of fabrics. The accuracy of wicking measurements is of ± 1 cm due to the variations of ambient humidity. All reported values of wicking were obtained with sampling time of 5 min. 

AFM images of fibers were obtained with Scanning Probe Microscope Veeco D-3100 in tapping mode, using silicon tips NT-MDT NSG 10. The analyzed fibers were fixed on an adhesive tape before scanning. The images were elaborated with Gwyddion software and a polynomial functions were applied to exclude the fibers curvature. 

SEM images were obtained with Tescan VEGA TS 5130 LM under 30 kV acceleration. Prior to scanning, the fibers were deposited with ca. 5 nm Au layer by means of sputtering in Cressington Sputter Coater 108 auto. 

Raman spectra of fibers were obtained by scanning near field optical microscope Witec Alpha SNOM (Ar 514.5 nm). 

FTIR-ATR spectra of fabrics samples were obtained by Perkin Elmer Spectrum One.

3. Experimental results of atmospheric plasma treatments

3.1. DBD treatments of single fibers and wool fabrics in air

The effect of nano roughness generation (‘cauliflower’ effect) by atmospheric plasma jet was reported in [5]. AFM study of DBD treatment in air applied on PVC films [6] has proved the chemical (not thermal) origin of the effect. It was observed the generation of nano roughness (RMS ca. 5 nm), superimposed on the original morphology of the polymer surface.

![Figure 2](image)

**Figure 2.** AFM images of the same zone of single wool fiber not treated (a) and treated by DBD in air with applied energy 60 J/cm² (b), 120 J/cm² (c) and 240 J/cm²(d).

Subsequently, AFM studies of nano roughness effect was performed on single wool fibers (figure 2) extracted from fabric before DBD application. Analysis performed on precisely detected zone of
single fiber (2 µm x 2 µm) have demonstrated the increasing of produced nano roughness with applied treatment energy. Not treated fiber presents characteristic “striations” structure (figure 2a). Treatment by air DBD with the energy of 60 J/cm² produces nano roughness on fibers with RMS value of 10 nm. SEM images of fibers treated at the energy of 60 J/cm², that produce requested by Woolmark anti-shrinking property on wool fabric, present no difference respect to not treated fibers. Subsequent application of higher energies (120 J/cm² and 240 J/cm²) on the same single fiber increase roughness to RMS 50 nm (figure 2c, d). SEM images of the fibers treated at 120 J/cm² shows the erosion of fibers at µm level, and at 240 J/cm² the pin holes on fibers could be observed. Weight losses were measured on wool fabric samples treated at 60 J/cm² and 240 J/cm². After post-treatment conditioning (RH 65%, 24 hours), there were observed weight losses of 0.5% and 1.1%, correspondingly. Post treatment monitoring (5 months) of treated fabric samples presents the decay of wicking (from 11 cm to 3 cm), while produced anti-shrinking property was not decayed. After additional extraction of covalently bounded lipids from wool fabric, residual amount of covalently bound lipids was detected by gas chromatography measurements (GC-FID) [7]. Chemical extraction of 90% of covalently bounded lipids has not generated nano erosion of the fibers (figure 3) and has brought to fabric shrinking of -12%. Instead, air DBD treatment, eliminating only 30% of covalently bounded lipids, has brought to fabric shrinking of -8%.

**Figure 3.** AFM images of wool fibers of industrially scoured fabric: after Soxhlet extraction (left) and after additional chemical extraction of covalently bounded lipids (right).

Anti-pilling effect of DBD treatment on different fabrics was studied. Air DBD treatment of knitted wool fabric improves anti-pilling property from 2÷3 to 3÷4 (at scale of 5). Application on woven fabric (wool 65%, polyamide 33%, elastan 2%) improves anti-pilling property from 2 to 4 (at scale of 5).

In line air DBD treatments of wool and cotton non-scoured fiber sleeves were performed by innovative pre-industrial machine “Nanofabia” [8]. Increasing of wettability and of breaking force of sleeves were observed. Subsequently produced yarns present increase of breaking force for ca. 20%. Similar values for increasing of breaking force were obtained by in line air DBD treatment of cotton yarns.

Generation of nano erosion proportional to applied energy of air DBD was observed on single cotton fibers as well (figure 4).
Figure 4. AFM images of single cotton fibers not treated (left) and treated by DBD in air with applied energy of 300 J/cm² (right).

3.2. DBD treatment of single wool fibers and fabrics in N₂
The effect of nano scale erosion of single wool fibers was studied for DBD treatment in N₂ at atmospheric pressure (figure 5), with O₂ in traces (5 ÷ 20 ppm).
Micro Raman analysis at characteristic bands of sulphonated groups reveals no oxidation effect of N₂ plasma on wool single fibers, at a difference with air DBD treatment.

Figure 5. AFM images of single wool fiber not treated (a) and treated by DBD in N₂ atmosphere with applied energy 60 J/cm² (b), 120 J/cm² (c) and 240 J/cm² (d). Images (a, b) and (d) refer to the same zone of single fiber, image (c) refers to the adjacent zone of the same fiber.

The wicking effect and produced anti-shrinking properties of wool fabrics treated in N₂ DBD are at small extent lower respect treatments in air: wicking of 8 cm in N₂ DBD instead of 10 cm for air DBD, final shrinking of −7% in the result of N₂ DBD application, instead of −4% in the result of air DBD treatment of the same energy.
4. Discussion

4.1. Modified properties of wool fabrics observed in wet conditions

Anti-shrinking property of wool fabrics measured by standard washings can be related to different effects:

- Elimination of lipids (cleaning of fibers).
  Chemical extraction of lipids doesn’t produce nano roughness on fibers (figure 3) and is not sufficient for strong anti-shrinking effect on wool fabrics. It can generate active sites on fibers that bring to medium level of anti-shrinking properties.

- Generation of active sites (activation of fibers).
  Decay of wool activation was reported for low pressure plasma treatments [9]. This phenomenon was attributed to the conversion of covalently bounded lipids on the fibers surface. Observed by us permanent anti-shrinking effect on wool fabric indicates that anti-shrinking properties are not directly related to the activation of fibers by atmospheric plasma.

- Generation of nano roughness on fibers.
  DBD treatment etches the fibers, creating the nano roughness structure on their surface. Surface nano roughness increases the friction between fibers and limits their relative movement in wet conditions, thus reducing the probability for fibers scales to make fabric shrinking.

  In particular case of DBD treatment in N₂, there was not revealed the oxidation of wool. Observed anti-shrinking effect in this case can not be attributed neither to the elimination of lipids nor to the oxidative activation of fibers. Nano roughness effect on fibers and anti-shrinking properties on fabric were found less pronounced in this case respect to the DBD treatment in air.

4.2. Modified properties of textile materials observed in dry conditions

Increase of differential friction was observed in dry conditions between plasma treated fibers [10]. Optimized properties of wool fabrics, observed in dry conditions, can be attributed to the generation of active groups and to fiber-fiber interactions. Instead, they are related to nano roughness produced on fibers by plasma treatment. Observed improvement of breaking force of fiber sleeves and of yarns, as well as improvement of anti-pilling property of fabrics are due to the nano roughness effect produced on fibers by atmospheric plasma treatment.

5. Conclusions

Atmospheric plasma technology is going to substitute environmentally harmful conventional liquid chemistry technology applied nowadays in textile industry. Besides of impressive practical results and of ecological and economical advantages of this emerging technology, applications of atmospheric plasma preserve fine structure of fibers, producing modifications at nano level.

Generation of nano roughness on fibrous materials by atmospheric plasma appears to be a basic phenomenon on this kind of materials, that makes possible such important industrial applications as increasing of breaking force of fiber sleeves and of yarns, and improving of anti-pilling property of fabrics.

With the all probability, the effect of nano roughness generation plays basic role also for the production of anti-shrinking properties of wool fabrics in the result of atmospheric plasma treatments.
6. References

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