SORPTION PROPERTIES OF WOOL FIBRES AFTER PLASMA TREATMENT

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Introduction

The wool fibre exhibits a typical core – shell structure consisting of an inner protein core, cortex, and surface shell, cuticle[1] (see Fig. 1). The cuticle consists of several layers (see Fig. 2).

The upper layer, epicuticle, contains lipoproteins. Lipoid part of lipoproteins is bound by the sulfoester bond with proteinous part (see Fig. 3). Covalent bonds of branched chain fatty acids implicate hydrophobic character of wool fibres. The lipoproteins are connected with upper layer of exocuticle. Exocuticle is cross-linked by disulfide links (see Fig. 4).

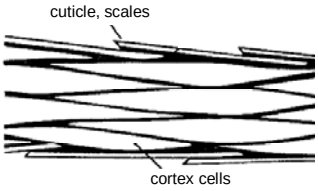

Fig. 1. **Structure of wool fibres**[3]

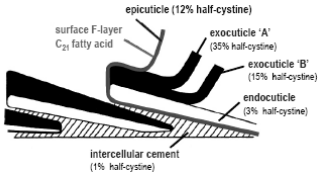

Fig. 2. **Schema of cuticle**[4]

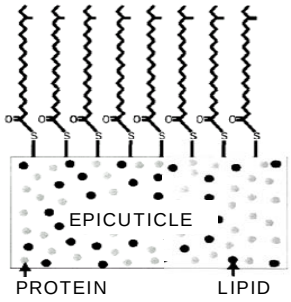

Fig. 3. **Lipoproteins in epicuticle**

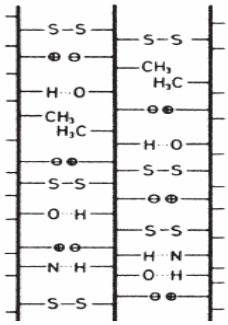

Fig. 4. **Stary`s wool fiber model**[6]

The hydrophobic nature of the cuticle and the high cross-linking density in the outermost fibre surface creates a nature diffusion barrier[2], which influences sorption properties complicates wool finishing processes, such as printing, dyeing or shrink-proofing. Surface modification plays an important role for many chemical finishing processes in textile industry.

The required surface modification is mainly accomplished by wet chemical processes using special auxiliaries which attack the cuticle by hard chemicals as for example NaClO[3,4].

Experiments

The effects of atmospheric pressure plasma treatment on wool fabric were tested in this study.

A Diffuse Coplanar Surface Barrier Discharge (DCSBD) has been used (see Fig. 5).

The operating frequency was 15 kHz, the power input 300 W. Wool fabric has been exposed by different times. Pure wool fabric has been exposed to different intensive plasma-treatment (different exposure times at constant conditions).

A conventionally-finished, plain-weave pure wool fabric (222 g m^{-2} manufactured from yarn of 2×19 tex) was used.

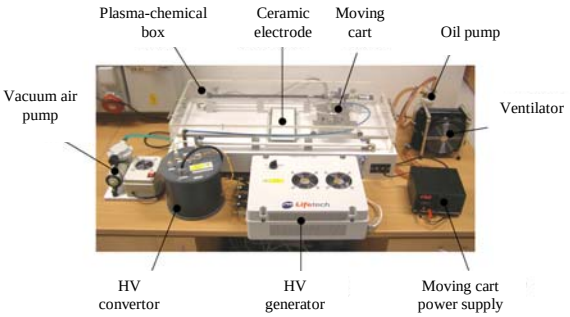

Fig. 5. **Used equipment DCSBD**

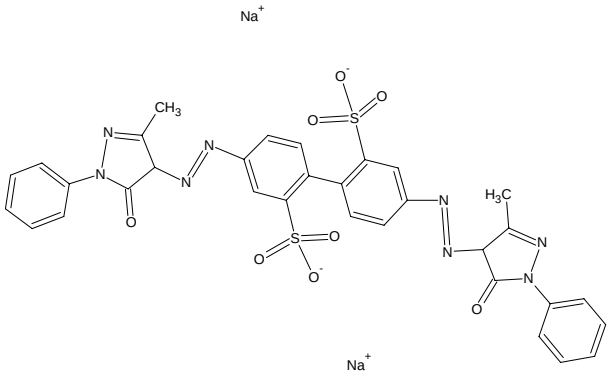

Fig. 6. **The chemical structure of acid dye with Colour Index Acid Yellow 42**

Dyeing of wool fabrics

Wool samples were pretreated by plasma for time 10, 20, 30, 50 and 100 seconds.

Untreated and plasma treated wool materials were dyed isothermal by acid dye (Colour Index Acid Yellow 42 – see Fig. 6) in weak acid solution (pH 6) at the temperature 60 °C (respectively 80 °C) for 2, 10 and similarly for 60 minutes. The dye bath contained 2 % dye of sample weight. After dyeing, the dyed fabrics were rinsed with cold water for 5 minutes.

Dry dyed materials were measured by spectrophotometer Datacolor 3890 (Datacolor, Switzerland). As results of measurement were achieved remission values. The remissions R were by the using of well known Kubelka-Munk equation recalculated to the K/S values.

Printing of wool fabrics

Wool fabrics (untreated and plasma treated for 10, 50, 100 seconds) were printed by a printing paste (pH 6) with acid dye (C. I. Acid Yellow 42). Printed wool fabrics were fixed for 1, 3, 6 and 10 minutes at 60 °C. Samples were by this fixation wet – evaporation of water was eliminated. Along the aftertreatment were realized the rinsing with cold water for 5 minutes, the soaping at 40 °C with 2 g l^{-1} Syntapon ABA for 10 minutes and the last rinsing with cold water for 5 minutes. The dyed wool materials were measured by spectrophotometer Datacolor 3890.

Visualization of surface structure

The structure and the appearance of fibres surfaces were observed with using of Scanning Electron Microscopy (SEM) on device VEGA (see Fig. 7). All the samples were coating by Gold before SEM testing.

The structure of surface was observed by the means of microscopic method Atomic Force Microscopy (AFM). AFM is the method used for characterization of prepared submicron optical elements.

The method to describe changes of chemical bonds and formation of new chemical groups after the plasma treatment was used Fourier Transform Infrared Spectroscopy (FTIR) Spectrometer One (Perkin Elmer – ATR technique on ZnSe crystals).

Next it was used method X-ray Photoelectron Spectroscopy (XPS). The XPS technique is highly surface specific due to the short range of the photoelectrons that are excited from the solid. The energy of the photoelectrons leaving the sample gives a spectrum with a series of photoelectron peaks. The binding energy of the peaks is characteristic of each element. The measurements were preceded with the using apparatus ESCA PROBE P (Omicron Nanotechnology Ltd) in ultra-high vacuum (under pressure order 10^{-10} mbar). X-rays emitter is aluminium electrode (used energy 1486.7eV). Measured spectra were analysed by way of CasaXPS programme.

Results

Results of wool dyeing

The K/S values are the observed shade-area directly proportional to dye concentration in fibres. In Fig. 8 there are marked differences in sorption properties untreated and plasma treated wool dyed at 60 °C. The dye concentration increases with dye time and plasma treatment intensity. The plasma treatment for 10 second is exactly insufficient. The best dye sorption is obtained by plasma treated wool fabric for longest time (100 second).

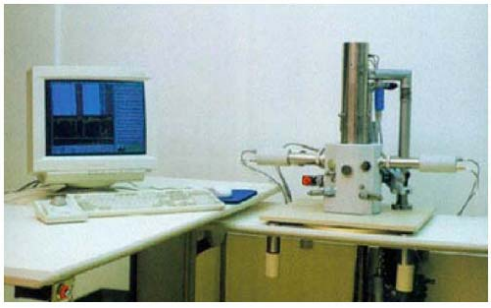

Fig. 7. **Environmental scanning electron microscope Vega TS 5130**

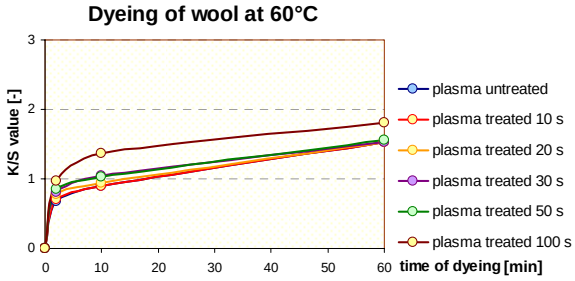

Fig. 8. **The influence of dyeing time on K/S values.** Dyed at 60 °C

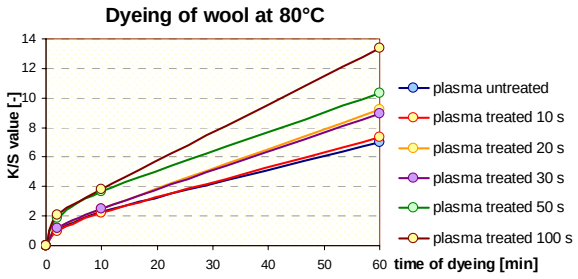

Fig. 9. **The influence of dyeing time on K/S values.** Dyed at 80 °C

Results of wool printing

Fig. 9 shows faster dye sorption and higher K/S values for dyeing of wool at 80 °C. The plasma treatment time 10 seconds doesn't return sufficient results. These K/S values are the same as K/S values of untreated wool. The plasma treated wool fabric for 100 seconds sorbs double more dye than untreated wool fabric. The similar results were stated in printing experiments.

The untreated wool fabric absorbs double under dye concentration than wool fabric which was plasma treated for

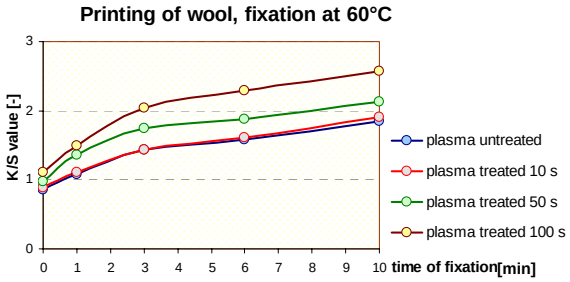

Fig. 10. **The influence of fixation time on K/S values.** Fixed at 60 °C

100 second (see Fig. 10).

Visualization of surface structure – results

SEM was used for visualization of surface structure wool fibers – epicuticle.

They were observed changes of surface wool scales. In Fig. 11–14 we can see invasion of structure of wool scales and breaking off their parts by the influence of plasma treatment.

By the using of method AFM, it visualized disturbs of epicuticle scales by plasma treatment.

In Fig. 15 and fig. 16 we can see evident differences between surfaces untreated and plasma treated wool fibres.

By means of the FTIR were proved minor changes of wool chemical structure (see Fig. 17).

From results of the XPS it is obvious that it achieved

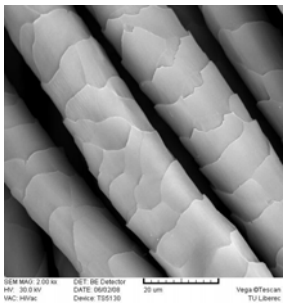

Fig. 11. **Untreated wool**

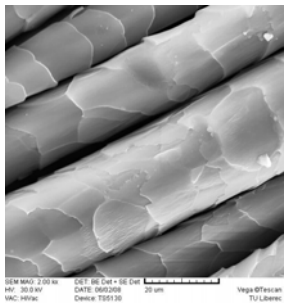

Fig. 12. **Plasma treated wool for 10 s**

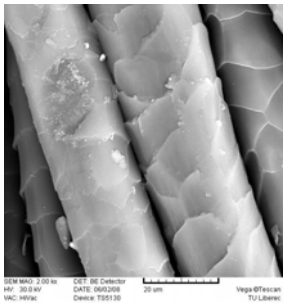

Fig. 13. **Plasma treated wool for 50 s**

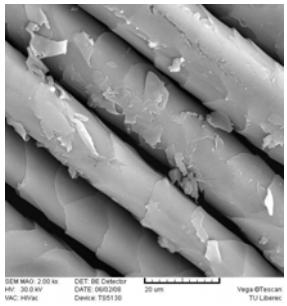

Fig. 14. **Plasma treated wool for 100 s**

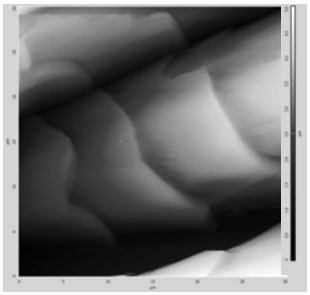

Fig. 15. **Unterated wool fibres**

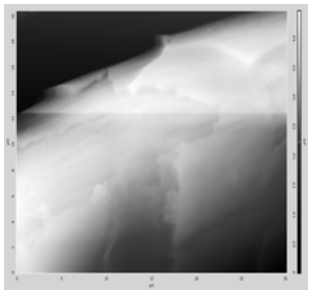

Fig. 16. **Plasma treated wool fibres for 100 s**

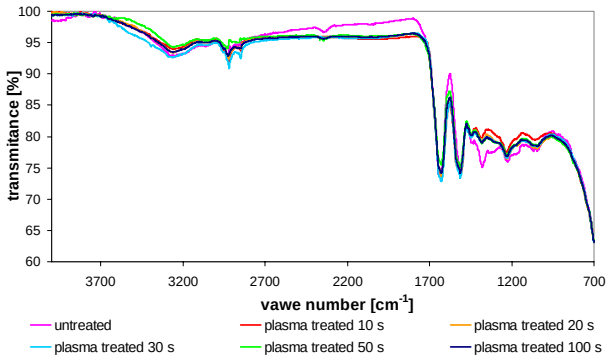

Fig. 17. **FT-IR spectrum of wool fibers**

Table I
Relative chemical composition ratios determined by XPS for wool fabric

Condition	Chemical composition [%]		
	C1s	O1s	N1s
Untreated wool	76,2	13,7	8,0
Plasma treated 10 s	67,6	19,3	9,4
Plasma treated 100 s	57,6	32,1	8,1

Table II
Relative atomic ratios determined by XPS for wool fabric

Condition	Atomic ratio [%]	
	O/C	N/C
Untreated wool	18,0	10,5
Plasma treated 10 s	28,5	14,0
Plasma treated 100 s	55,6	14,1

changes of chemical structure on surface epicuticle. The concentrations of oxygen increased after plasma treatment of wool fabric. The concentrations of nitrogen increased for 10 second plasma treatment and decreased for 100 seconds plasma treated wool fabric (see Table I).

There were stated the relative atomic ratios O/C and N/C. It was found the increasing the relative atomic ratios O/C and N/C.

Surface oxidation is possible due to the existence of reactive species from the plasma. In Fig. 16–18 are showed surveillance spectrums untreated and plasma treated wool fibres.

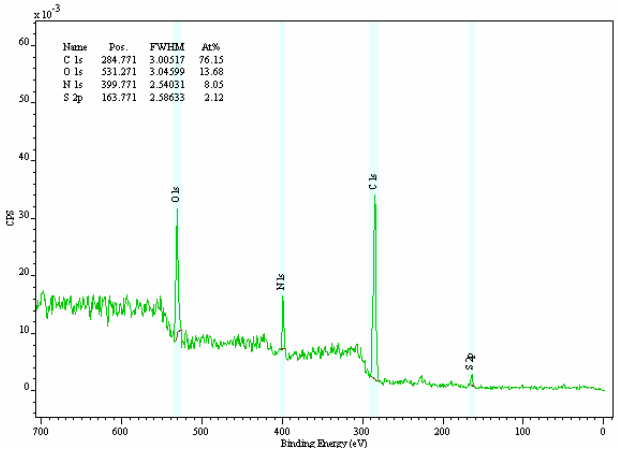

Fig. 18. **Surveillance spectrum of untreated wool**

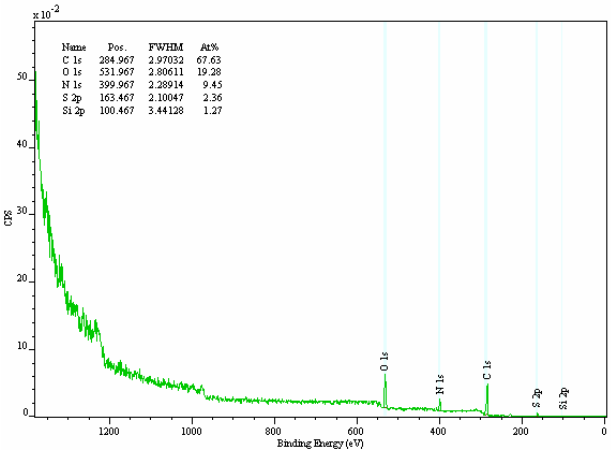

Fig. 19. **Surveillance spectrum of plasma treated wool for 10 s**

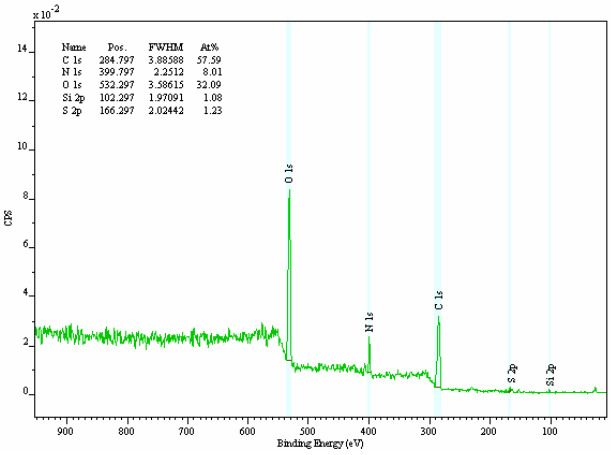

Fig. 20. Surveillance spectrum of plasma treated wool for 100 s

Conclusion

Experiments showed invasion of surface layer of cuticle by plasma. Plasma treatment wool adsorbs dye more intensive at lower temperature. Plasma treatment of wool can in future replace wet pre-treatment processes for wool dyeing and wool printing. The pre-treatment of wool with atmospheric plasma give an appropriate environmentally acceptable alternative to conventional treatments.

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R. Chvalinová and J. Wiener *(Department of Textile Chemistry, Textile Faculty, Technical University of Liberec, Liberec, Czech Republic):* **Sorption Properties of Wool Fibres after Plasma Treatment**

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Changes of fibres surface were characterized by means of XPS, FTIR spectroscopy and AFM methods. With the maximal experimental attention was observed dye sorption. Wool fabrics were dyed in dye bath by common used acid hydrophilic dyestuffs. As criterions dye sorption on wool were stated dyeing rate and dye uptake on wool fibres. Printing of wool by acid dyestuffs was carried out as well.