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Selected Properties of Wool Treated by Low-Temperature Plasma

Abstract
Low-temperature plasma treatment is one of the methods for physically modifying the functional and aesthetic properties of textiles. Selected properties of wool textiles are changed by the influence of low-temperature plasma on the fibre's surface layers, acting only on a very small thickness. The level of changes is limited by parameters of the low-temperature plasma. Lowering of the dyeing temperature and of water absorption was achieved.

Key words: *wool, woollen knitted fabrics, low-temperature plasma, dyeing temperature, morphology, capillarity, FT-IR, WAXS.*

Introduction

In order to improve certain properties of fibres and textiles, they are modified by physical treatment. Physical modifications result in specific changes in the fibre's physical microstructure and its surface properties changing the functional and aesthetic features of fibres. One such physical modification is treatment with low-temperature plasma (LTP).

Low-temperature plasma (LTP) is produced almost exclusively in glow discharges in a gaseous environment. A key property of this type of plasma is the lack of equilibrium between the temperature of the electrons and the energy of the un-ionised gas particles. This allows the creation of conditions in which the temperature of the plasma gas remains close to that of the environment, while the energy of the electrons is sufficient to break intermolecular and covalent bonds. This property of LTP makes it useful for initiating modifications in polymers which are not resistant to high temperatures, that is, of almost all fibre-forming polymers [1-3].

The LTP generated in glow discharges is the source of:
- ultraviolet radiation with a wavelength λ of 100 nm,
- electrons with energies of 1-10 eV,
- gases in an atomic state.

It has been established that applying LTP results in two kinds of effects:
- 'surface' effects (the so-called plasma pyrolysis) - occurring in the outer part of the fibre up to 5 nm, depending on the kind of the gas used;
- 'deep' effects - which includes the production of radicals, hydrogenation and changes in the polymer's network density. These effects occur from 1-5 μm, irrespective of the kind of gas used [5-10].

The process of plasma modification is characterised by an interaction between the plasma and a thin outer layer of the fibres. It causes surface changes in the fibres, and among other effects increases their wettability.

In wool, the surface character of plasma treatment is limited to a small part of the fibre, in relation both to its mass and volume. Physical properties such as the fibre friction coefficient, dye diffusion, etc. depend on the highly-networked layer known as the epicuticle. Modifying this layer, without causing changes in the wool cortex, facilitates and accelerates some technological processes, including the dyeing of fibres [11-15].

The aim of our work was to carry out by LTP the dyeing process at considerably lower temperatures than those conventionally used (from 90°C to 130°C). This could be done by LTP treatment of wool. In addition, the products obtained from the LTP-treated fibres should be characterised by better water absorption.

Object of Research, Processing and Measuring Methods

Woollen knitted fabrics with interlock weave and an area weight of 258.7 g/m^2 were the test object. The wool consisting of the knitted fabrics was treated with LTP in an air environment with the following parameters constant over time:
- air flow - 100 l/ h
- initial pressure - 4.6 mbar
- final pressure - 4.6 mbar
- distance between the electrodes - 18 cm
- wool surface treated with plasma - 324 cm^2

The energy parameters (power, time) of the plasma treatment for each sample are shown in Tables 1 and 2. The LTP treatments of the woollen knitted fabrics were carried out at the Textile Research Institute in Łódź, Poland.

For examining the samples treated with plasma, the following techniques were used:
- IR spectroscopy,
- wide-angle X-ray scattering (WAXS),
- scanning electron microscopy (SEM).

Water absorption, capillarity and dyeing with an acid dye (Alizarinbrillantreinblau) were also examined. A sample of woollen knitted fabric which was not modified with plasma was used for comparison.

The **IR spectroscopy** examination was conducted in the transmission technique, using a MAGNA IR 860 spectrophotome-

Table 1. *Parameters of plasma treatment for series 1; the processing was performed at constant power value of 150 W.*

Sample No	Time of LTP treatment, s	Energy, Ws
1	10	1500
2	20	3000
3	30	4500
4	40	6000
5	50	7500
6	60	9000
7	70	10500
8	80	12000
9	90	13500
10	100	15000
11	110	16500

Table 2. *Parameters of plasma treatment for series 2; the processing was performed at constant time, over 60 s.*

Sample No	Time of LTP treatment, s	Energy, Ws
12	60	1800
13	60	2700
14	60	6300
15	60	12600
16	60	16800

ter from Nicolet. Fibres were taken out of the samples, then cut and pressed in a KBr tablet at a pressure of about 100 MPa.

The **wide-angle X-ray scattering (WAXS)** examination was conducted in a deflection angle range of 4° to 40°, with a 0.1° step and 20-second impulse counting, using a HZG-4 diffractometer, CuK_{α} radiation, an accelerating voltage of 30 kV and an anode current intensity of 20 mA. Beam monochromatisation was achieved by using a nickel filter and an impulse height analyser. A scintillating counter was used as detector.

The morphology of wool surface was examined using a JSM 5500 LV **scanning electron microscope** from Jeol. Observations were conducted with an accelerating voltage of 10 kV and magnifications of 2000, 5000 and 10,000.

Water absorption and capillarity were determined in accordance with Polish Standards [17,18].

Dyeing was carried out in order to assess the influence of LTP treatment of wool on its ability to exhaust a dye from the dyebath. The process was conducted for selected samples in one dyebath. In addition, UV-Vis spectra of dyeing intensity were obtained by a Hitachi 2001 spectrophotometer equipped with an RSA-Hi-20 labsphere. Crucial for the process was the possibility to lower the dyeing temperature as far down as 60°C.

Results

An analysis of **IR transmission** spectra reveals that the greatest changes occur in the area of absorption by groups containing the C-H oscillator. Figure 1 shows the disappearance of the 2940 cm^{-1} and 2850 cm^{-1} peaks. The absorption areas in these ranges correspond to the $-CH_3$ and $-CH_2-$ oscillators. This means that these groups are oxidised during LTP treatment. At the same time, hardly any changes are observed in the 1800-1450 cm^{-1} absorption area characteristic of the amide I and amide II bands, which are the result of absorption by the basic link of the keratin chain, that is, by -CO-NH- (Figure 2). These phenomena are accompanied by a slight increase in absorption within the 3650-3150 cm^{-1} area, which is characteristic of the O-H and N-H groups (Figure 3).

The spectrum changes observed after LTP treatment may be explained by surface

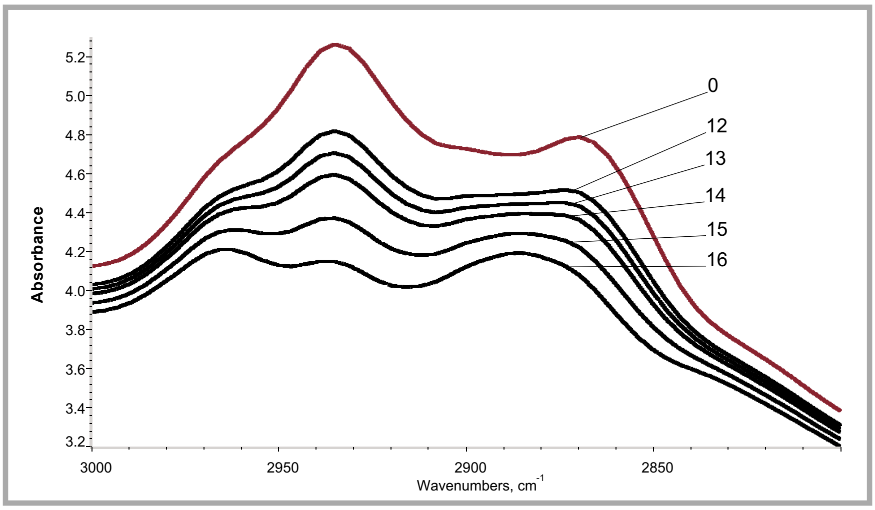

Figure 1. Fragments of transmission spectra of wool fibres in the 3000-2800 cm^{-1} range of IR absorption by groups with the C-H oscillator; 0 - spectrum for wool not modified with plasma, 12, 13, 14, 15, 16 - IR spectra for wool samples treated with LTP, with an increasing value of the electric power of the plasma and constant time (Table 2).

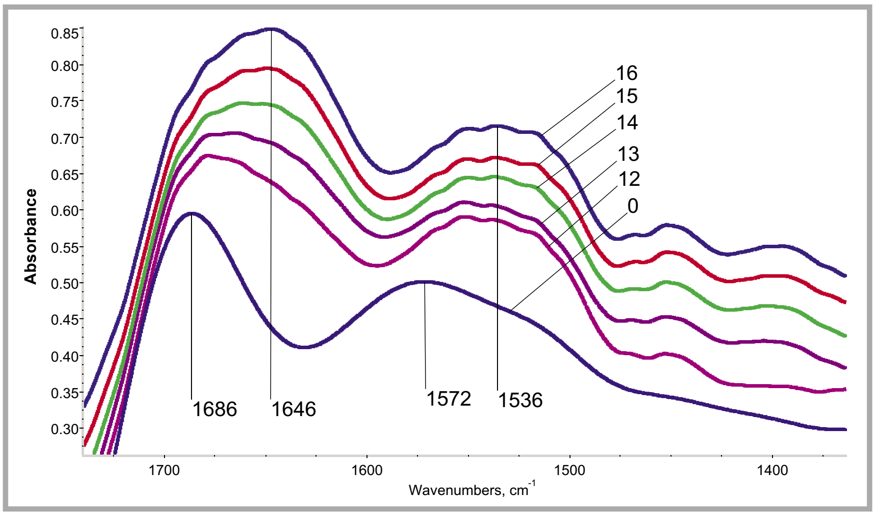

Figure 2. Fragments of transmission spectra of wool fibres in the 1800-1450 cm^{-1} range of IR absorption by groups with the CO-NH- oscillator for the samples: 0, 12, 13, 14, 15 and 16.

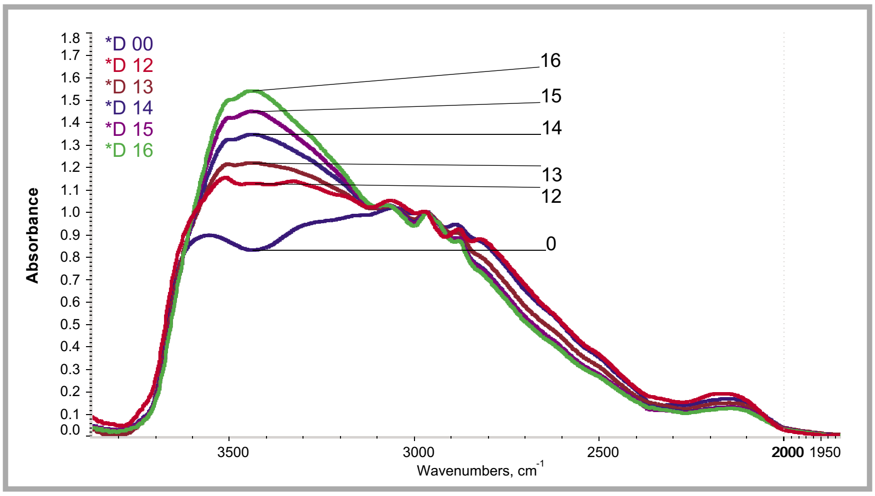

Figure 3. Fragments of transmission spectra of wool fibres in the 3650-3150 cm^{-1} range of IR absorption by groups with the O-H, N-H oscillator. Spectrum shapes change in relation to the intensity of plasma treatment (samples 0, 12, 13, 14, 15 and 16).

oxidation of the $-CH_3$ and $-CH_2-$ groups characteristic of the outside groups of α-amino acids. IR examination clearly reveals that the treatment is limited to the surface only. A dominant process is the oxidation of hydrophobic aliphatic chains which originate in the outside groups of α-amino acids and probably of the lipids connected with the fibre surface. However, it should be emphasised that the IR examination was successful, notwithstanding the fact that it is a volumetric test technique, whereas the changes occur only in the surface layers. This phenomenon proves the strength of the changes induced by LTP treatment.

The **wide-angle X-ray scattering** examination was conducted on selected samples of knitted wool, both treated with plasma and unmodified. Exemplary runs are presented in Figures 4 and 5, and the crystallinity parameters obtained in Table 3. The results of examining the crystallinity level and the size of crystal areas (Table 3) do not prove any direct influence of LTP treatment on the supermolecular structure of wool.

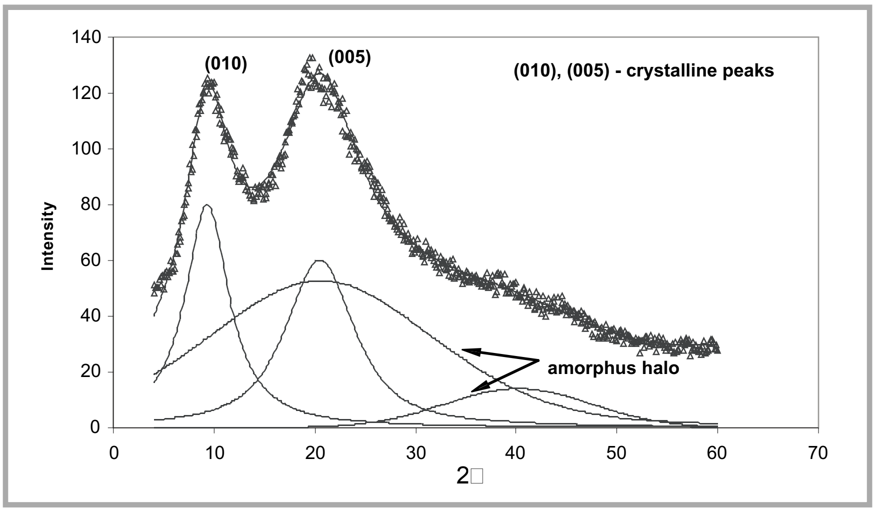

Figure 4. *Peak deconvolution of the WAXS profile in the wool not modified with plasma.*

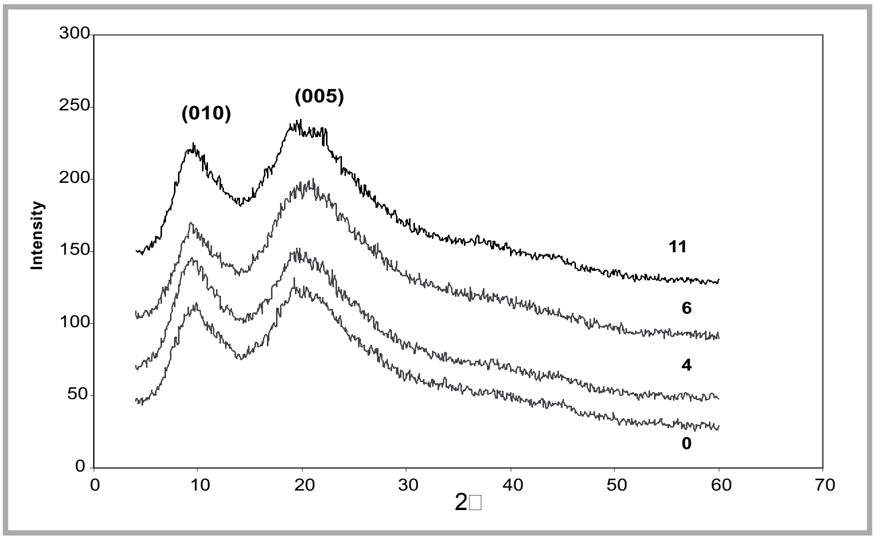

Figure 5. *Diffraction WAXS for samples of not modified with plasma (0), for wool samples treated with LTP 4,6, 11 (Table 1).*

Table 3. *Results of WAXS investigations.*

Sample	Degree of crystallinity, %	Crystallite size $D_{(010)}$, Å
0	35	38
4	37	36
6	39	43
11	36	36
12	40	41
14	34	41
16	34	40

Table 4. *Results of measuring water absorption and capillarity for series 1.*

Sample No	Water absorption, %	Capillarity, mm
0	135	0
1	692	53
2	711	92
3	727	114
4	738	117
5	753	119
6	781	124
7	783	126
8	785	135
9	797	137
10	799	141
11	801	172

Table 5. *Results of measuring water absorption and capillarity for series 2.*

Sample No	Water absorption, %	Capillarity, mm
0	135	0
12	729	102
13	746	119
14	767	124
15	780	132
16	795	167

The **SEM analysis of surface morphology** reveals slight changes which occur on the surface of wool fibres as a result of plasma modification. The rising parameters of LTP treatment (time and power, or the total energy) lead to a slight increase in these changes causing a rounding of scales, microcracks, recesses and tiny grooves, all caused by the 'etching' of the material. SEM micrographs of wool fibres after plasma modification are shown in Figures 6-9.

The most important effect of LTP treatment of wool is the change in the character of the wool fibre surface from hydrophobic to hydrophilic.

The **water absorption** measurements reveal the substantial influence of the LTP treatment on the absorption values for all samples. An increase of more than 5 times was observed between sample No. 0 (not modified) and sample No 1, for which the water absorption is 692%. The value grows gradually with intensifying the plasma treatment, as far as 801% for sample No 11 (showing the greatest influence of the plasma parameters). Similar results of measuring water absorption are obtained for samples of the second series. When comparing the energy of plasma treatment as well as the values of water absorption between both series, one can observe a relationship showing that the improvement of water absorption depends to an approximately

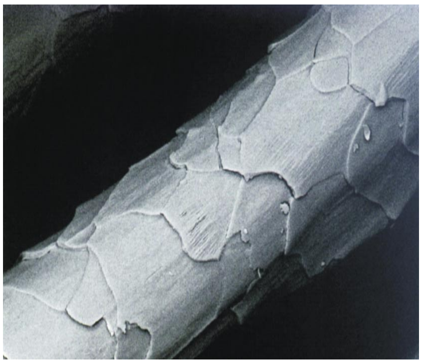

Figure 6. *SEM micrograph of the surface of a wool fibre not modified with plasma, magnification×2000.*

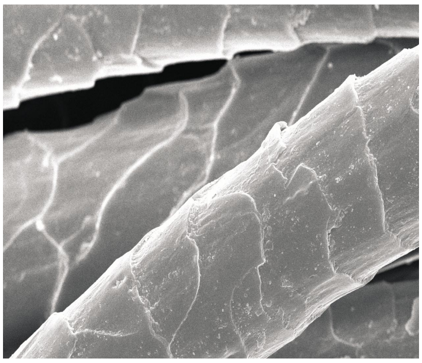

Figure 7. *SEM micrograph of the surface of wool fibres after plasma treatments, sample No 11, magnification×2000.*

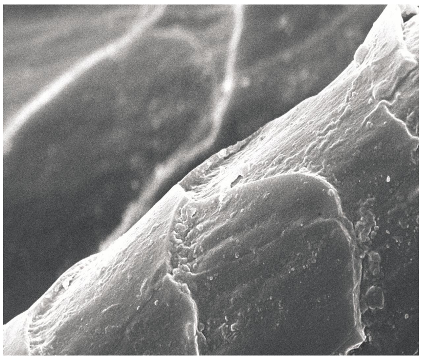

Figure 8. *SEM micrograph of the surface of wool fibres after plasma treatments, sample No 11, magnification×5000.*

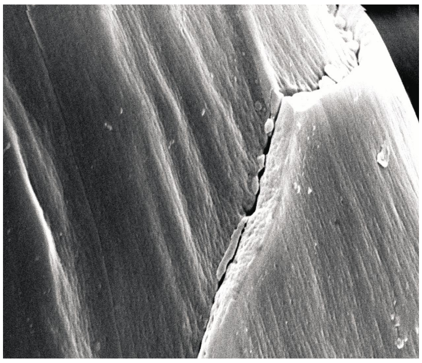

Figure 9. *SEM micrograph of the surface of a wool fibre after plasma treatments, sample No 1, magnification×5000.*

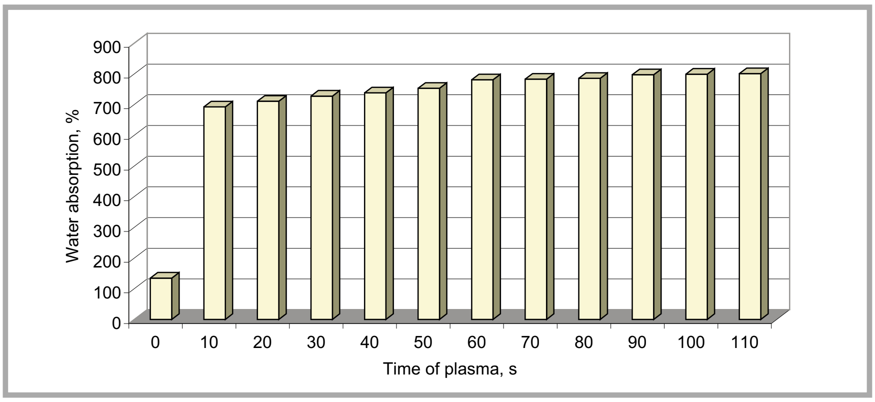

Figure 10. *Water absorption growing in relation to time of plasma treatment.*

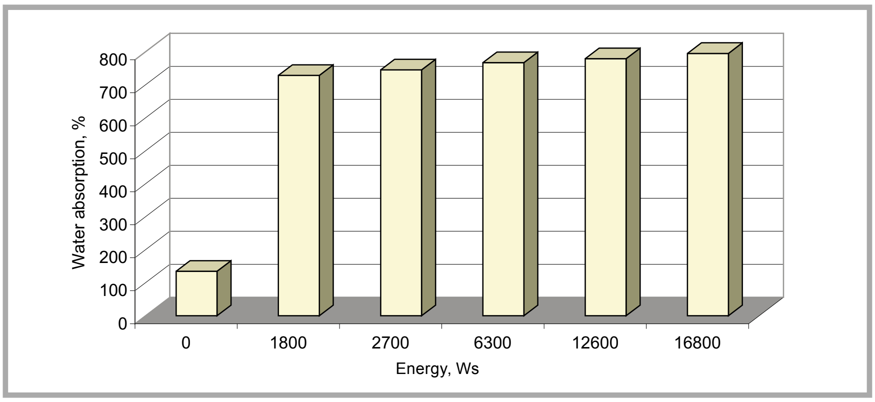

Figure 11. *Water absorption growing in relation to energy of plasma treatment.*

similar degree on the time and power of the LTP treatment.

Analysing the water absorption and capillarity of the samples tested in dependence on the plasma energy used for processing the samples, it can be noted that at small energy doses, the increase in the given property are large, whereas at higher doses the increase essentially lowers. The boundary between high and low sensitivity to plasma treatment is clearly visible, and different for water absorption and capillarity. The explanation may be that, up to a given limit of plasma energy, the majority of the possible changes occur, and further treatment is not so efficient.

The results of **measuring the capillarity** of the woollen knitted fabrics prove that this property is particularly affected by LTP treatment. Before the treatment, the hydrophobic layer on the epicuticle surface prevents any wetting of the fibre surface and thus of the knitted product. The sample not modified with plasma did not reveal any capillary action. The smallest dose of LTP decreases or destroys the hydrophobic layer. The hydrophilic groups created on the surface as a result of the treatment affect the value of surface tension and allow for the wetting of fibres and at the same of the woollen products. Increasing the plasma treatment parameters results in increasing capillarity, from 53 mm to 172 mm for samples in series 1, and from 102 mm to 167 mm for samples in series 2. The capillarity of the woollen knitted fabrics is substantially dependent on the LTP modification and its parameters. The results of measuring water absorption and capillarity are shown in Tables 4 and 5, and Figures 10-13.

It should be emphasised that both the water absorption and the capillarity depend on the plasma energy to different degrees. Beginning with zero and up to a certain energy value, the changes of both above-mentioned quantities are significant. Above this value, the influence of LTP is several times lower.

The **process of dyeing** at 60°C, conducted for selected samples of woollen knitted fabrics previously treated with LTP as well as for an unmodified sample, proves that the dye is better exhausted from dyebath by the samples modified with plasma. These latter also have a deeper colour shade and absorb dye at 60°C much better. The influence of plasma treatment on the dyeing intensity of the samples tested is clearly visible from the UV-Vis spectra presented in Figure 14. The spectra were obtained with the use of a Hitachi 2001 spectrophotometer equipped with an RSA-Hi-20 labsphere. The lowest energy parameters of plasma treatment which we used resulted in the lowering or even the destruction of the barrier layer. This allows for dyeing wool at temperatures lower than those conventionally used. When washed after dyeing, the LTP-treated samples of both series also prove to have bound the dye better than in the unmodified sample.

Conclusions

- LTP damages an ultra-thin hydrophobic layer on the protective surface of the fibre. This process occurs only on the surface, and does not damage the inner structure of keratine.
- Removing the barrier layer results in increased sorption of humidity and dye and improved wettability of the knitted woollen fabrics. These properties are advantageous for textiles, and in particular they improve the comfort of wearing clothes.

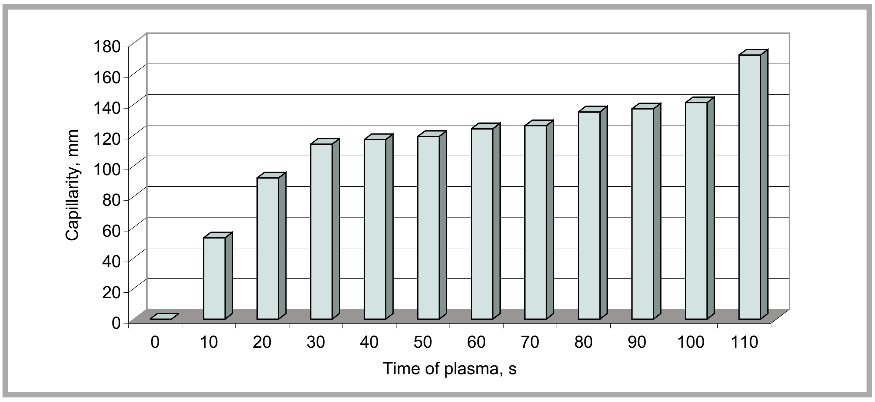

Figure 12. *Capillarity growing in relation to time of plasma treatment.*

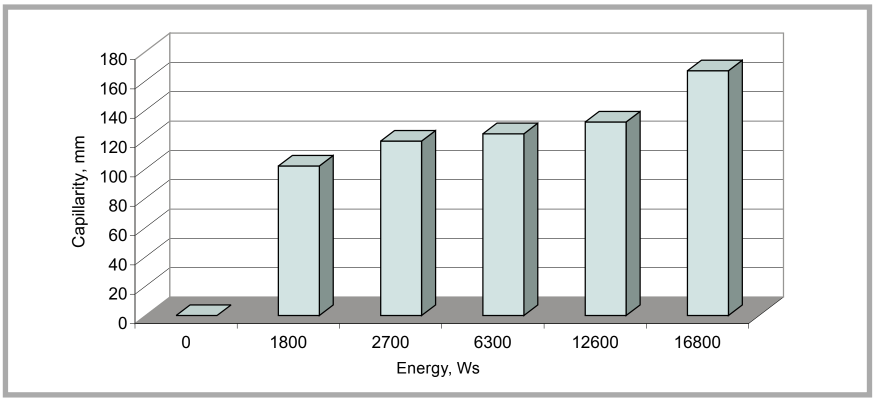

Figure 13. *Capillarity growing in relation to energy of plasma treatment.*

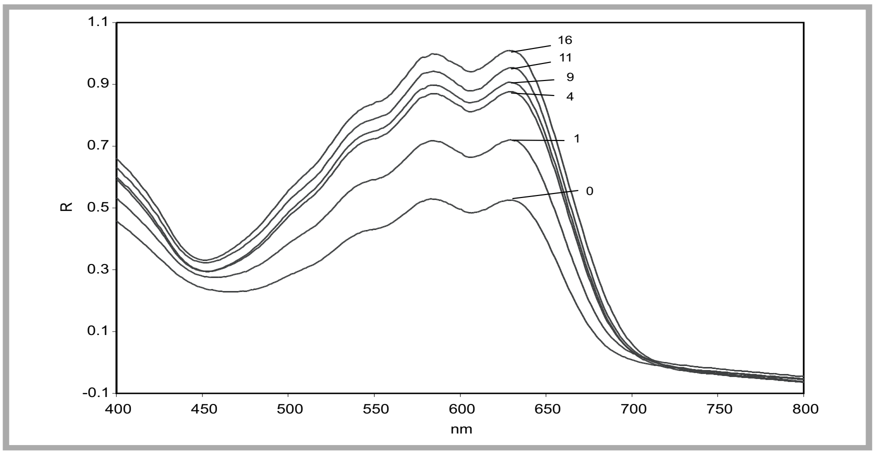

Figure 14. *Fragments of spectra of dyed samples in the 400-800 nm range of UV-Vis remission; 0 - UV-Vis spectra for wool not modified with plasma; 1, 4, 9, 11, 16 - UV-Vis spectra for wool samples treated with LTP.*

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