However more important was kept the layer's continuity than total delamination. Besides of all controversial adhesion investigation results, obtained critical forces seem to be entirely sufficient for this kind of applications.

Conclusions

As the result of the investigation following conclusions can be drawn:

1. RF PACVD/MS technology enabled manufacturing thick carbon layers onto metallic substrates. Deposited coatings are free from any surface defects like cracks and chips.
2. High hardness of a-C:H/Ti layers noticeably improved the mechanical properties of CoCr and NiCr alloys. Therefore it can be stated that gradient carbon layers provide a good protection against wear.
3. The adhesion measurement results prove that these layers are resistant to delamination. Moreover the adhesion increases with the thickness of the layer.
4. Very promising investigation results make these layers a perspective coating material possible to adapt as a protection against wear and corrosion of alloys used in prosthodontics. However for entire characteristics further investigations of metal ions release are needed.

Acknowledgements

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THE INFLUENCE OF OXYGEN PLASMA ON SURFACE FUNCTIONALITIES OF CELLULOSE FIBRES

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Abstract

Quality and quantity of groups in cellulose fiber is possible to change by chemical procedure (for example by using strong oxidizing agent). One of other possible methods to change the chemical groups in cellulose fibers is plasma treatment. In this study for plasma treatment a source of Diffuse Coplanar Surface Barrier Discharge (DCSBD) was used. Air plasma treatment of cotton at atmospheric pressure was made in a wide time scale. The chemical changes of cotton were observed and discussed.

Keywords: *cotton, plasma treatment, DCSBD*

[Engineering of Biomaterials, 85 (2009), 5-7]

Introduction

Cellulose fibers are known by their complicated chemical structure, that is not possible describe by one chemical formula. In cellulose fibers not only hydroxyl groups, but also other chemical groups in smaller concentration, e.g. carbonyl or carboxyl group are present. Oxidated groups increase the sorption of dyes and other chemicals into the fibers. High degree of oxidation is typical for some special cellulose derivates, for example oxycellulose, which has many applications in technical and medical branches.

The oxidized cellulose (oxycellulose) is used in many medical and related areas such as: absorptive material to stop bleeding, bodying agent in pharmaceutical preparations, coating material in the formulation of encapsulated hemostatic agents.

Plasma is a medium of energy transport. Molecules in plasma are of high energy level and high degree of ionization being able to modify chemistry of the polymers [1,2].

Theory of plasma interaction with cotton: All changes are in connection with the theory, that the oxygen plasma can attack polymers oxidatively. Original cotton contains almost only hydroxyl groups. The content of carbonyl and carboxylic groups is lower than 1% of hydroxyl groups quantity. Probability of reaction with these non-hydroxyl groups is smaller than 1:100. By the oxidation of hydroxyl groups in first step carbonyl groups are created and in the second step of oxidation carboxylic groups are produced.

Chemical changes in fibers were documented by the use of instrumental analytical methods FTIR and XPS, which are able to estimate chemical groups in a thin layer of fiber surface. By the help of sorption (dyeing) test quantity of carboxyl group in the fiber was determined. Quantity of carbonyl groups was estimated with the use of so-called "copper number". Possible changes of fiber surface morphology (roughness) were monitored with the use of scanning electron microscopy.

Materials and methods

Experiments in this study were made with mono-component cotton (cellulose) fabric which is recommended for fastness testing of textiles in standards (plain weave, pretreated).

Plasma treatment by DCSBD (Diffuse Coplanar Surface Barrier Discharge) A4-LIN (FIG. 1)

In this study an alternating current high-voltage about 20 kV was applied with a power of 300 W. Al_2O_3 ceramic plate was used as a dielectric barrier. Samples were attached to movable trolley by means of a vacuum sucker. Movable trolley was linked to a linear displace. After inflammation of discharge on the surface of ceramic electrode, movable trolley with fixed sample went into a contact with plasma. The plasma treatment of cotton was made in "cycles". In one cycle the cotton fabric was 10 seconds in contact with plasma. Longer time of treatment was made by repetition of treatments. For example 3 cycles is equal to 30 (3x10) seconds of plasma treatment.

The used gas was air containing oxygen – this treatment is oxygen plasma modification.

Plasma treatment was performed in atmospheric pressure, at 20°C.

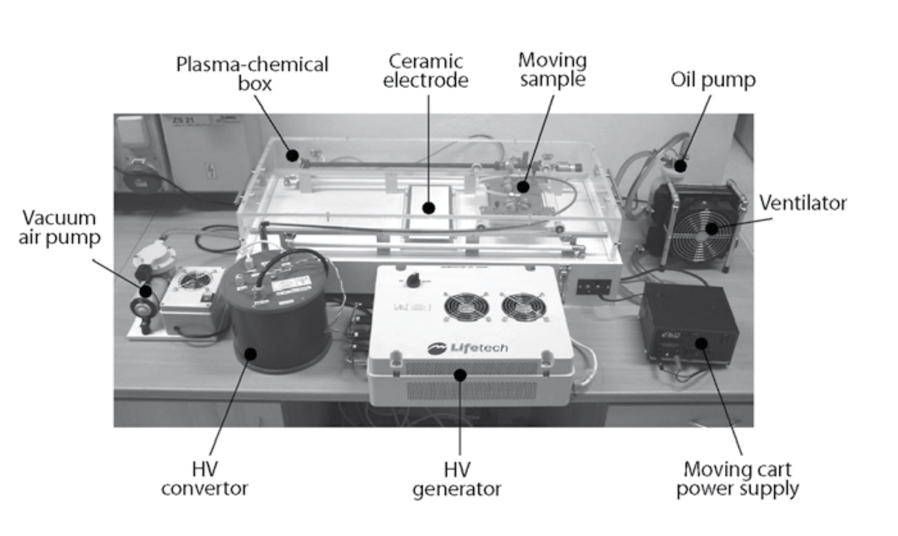

FIG. 1. DSCBD plasma reactor. DSCBD plasma-chemical box, ceramic electrode Al_2O_3 (active area 9×20 cm), HV power supply unit (500 watt, 10-20 kHz). The ceramic electrode is cooled by oil. Part of device is oil pressure pump.

FTIR Spectroscopy

FT-IR Spectrometer One (Perkin Elmer) – ATR Technique on ZnSe crystals was used to obtain the infrared spectra. Spectra were smoothed, normalized on 0.1-intensity and corrected to baseline. Conditions of measurements: used IR range 700-4000 cm^{-1}, sng velocity 0.2 cm^{-1}, step 1 cm^{-1}.

Scanning electron microscopy

The structure and the appearance of fibres surfaces before and after plasma treatment were observed by using of scanning electron microscope (SEM) on device VEGA. All the samples were coated by Platinum for two minutes before SEM testing.

Copper number of cotton

Copper number is connected with the reduction capacity of tested cotton sample, especially with the content of carbonyl groups, which quantity is estimated absolutely by this method. Copper number is used as a criterion of cotton damage, because the original cotton contains only hydroxyl groups and the quantity of other groups increases by chemical attacks.

Chemical background is reduction of Cu^{2+} to Cu^{1+} induced by the reduction potential of carbonyl groups. This reaction is stechiometric: one carbonyl group is destroyed by reduction of one Cu^{2+}. Cu^{1+} leaves this liquid in the form of water insoluble Cu_2O. Color of Cu_2O is brown – this color is possible to observe visually. Quantity of produced Cu_2O was estimated vicariously trough the soluble Fe^{2+} ions by manganometric method. The result (used volume) from titration was recalculated to Copper number.

Cationic dye sorption

In the cotton fibers carboxylic groups can be synthesized – the limit organic degree of cotton oxidation. It is possible to estimate the quantity of these groups by sorption of cationic dye. This method is based on stechiometric ratio (1:1) between carboxylic groups in cotton and quantity of absorbed cationic dye in the fiber. Direct estimation of absorbed dye quantity is difficult and as a standard test a measurement of color after dyeing test is typically used. Cotton with higher content of carboxylic groups will be colored by cationic dyes to deeper color.

Dyeing test was made with cationic dye Color Index Basic Blue 9 (Methylenblue). This dyestuff was applied for 20 minutes at 20°C, the initial dye concentration in dyeing bath was $1g \cdot l^{-1}$.

Results and Discussions

The chemical changes in the samples of untreated and plasma treated cotton were estimated by FTIR Spectroscopy. Especially the changes in quantity of hydroxyl, carbonyl and carboxylic groups were observed (FIG. 2).

FTIR experimental results show that in the spectra of plasma treated and untreated cotton samples the differences were observed at 1710, 1641 and 1620 cm^{-1}. These changes are connected with increase of carbonyl groups (1710 cm^{-1}) concentration and increase of double-bonds between carbons (1641 and 1620 cm^{-1}). Carbonyl groups are probably ketonic groups. Changes in hydroxyl groups were not observed.

The similar changes of cotton were observed by XPS method. XPS analyses thinner layer of surface (approximately 10 nm) in comparison with FTIR method (approximately 10 μm). XPS method shows more intensive changes in a thin surface layers of cotton.

The samples were observed by scanning electron microscopy, used magnification is evident from scales on each picture (FIG. 3 and FIG. 4).

Copper number increases significantly with the intensity of plasma treatment. By the plasma treatment increase of the total quantity of carbonyl groups was measured. The results of the experiment are gathered in TABLE 1.

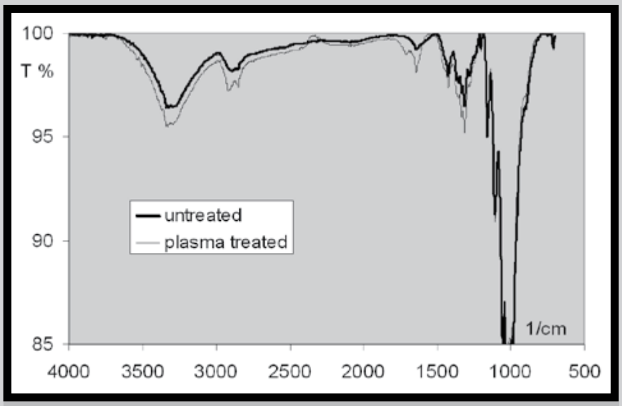

FIG. 2. FTIR results – dependence of IR light transition (T%) on wavelength in reciprocal centimeters, untreated and plasma 10x treated cotton.

TABLE 1. Copper number of cotton and Relative Color Intensity (RCI) after cationic dye sorption before and after plasma treatment.

Cotton	Copper number	RCI [%]
untreated	0.19	100
Plasma treated 1x	0.30	104
Plasma treated 3x	0.43	82
Plasma treated 10x	1.14	94

Color of cotton sample after cationic dye sorption was measured by remission spectrometer (Datacolor, Switzerland). Remission values were recalculated to K/S values according to a well-known Kubelka-Munk function. In the last step of data treatment the values were recalculated to Relative Color Intensity (RCI, %) values (TABLE 1).

The concentrations of carboxylic groups (RCI values) are practically independent on the number of used plasma treatment cycles. The quantity of carboxylic groups does not increase by plasma treatments.

Conclusion

Plasma treatment increases the concentration of carbonyl groups in cotton fibers - especially in thin surface layers. The quantity of hydroxyl and carboxyl groups does not change significantly.

Acknowledgements

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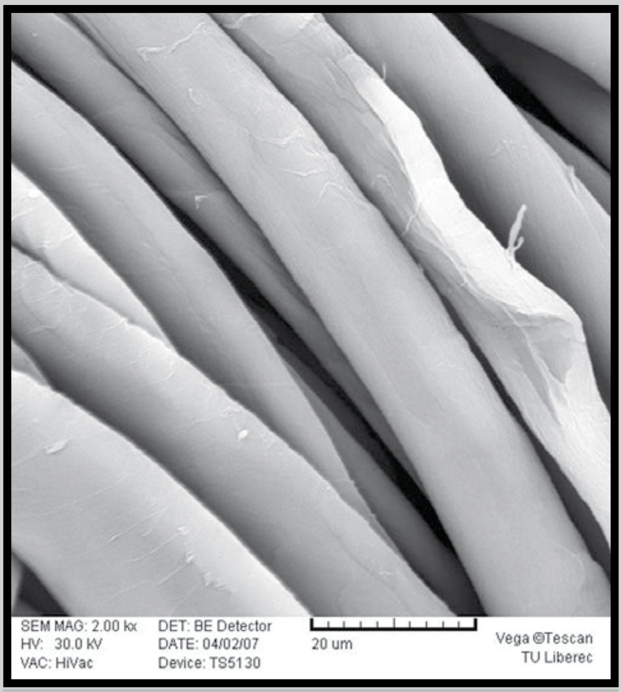

FIG. 3. Untreated cotton.

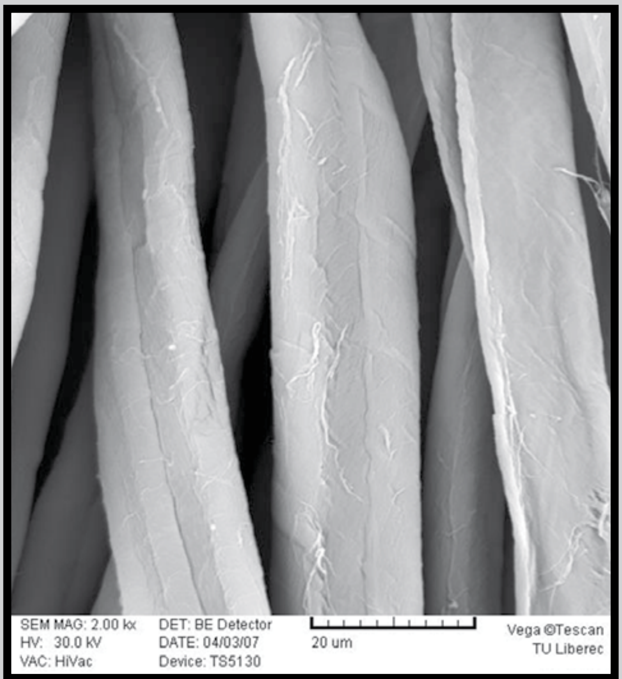

FIG. 4. Plasma treated cotton (10x treated).