MODIFICATION OF NON-WOVEN CELLULOSE FOR MEDICAL APPLICATIONS USING NON-EQULIBRIUM GASSIOUS PLASMA

MODIFIKACIJA CELULOZNIH KOPREN, UPORABNIH V MEDICINSKE NAMENE, Z NERAVNOVESNO PLINSKO PLAZMO

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This paper presents the use of a non-equilibrium gaseous plasma technique for the activation of regenerated non-woven cellulose, as used in the preparation of wound-dressing materials. Plasma technology provides surface modification according to the required quality in terms of speed, homogeneity, process stability, and efficiency.

In this study the non-woven cellulose was exposed to oxygen plasma (O_2) in order to acquire the natural polymer's super-hydrophilicity which, among others, defines the materials' usability for wound-dressing. The influence of the plasma parameters on the material's hydrophilicity was studied; and the optimal plasma conditions defined. Combinations of different experimental techniques (contact angle, water retention value, and moisture content) were studied and correlated with the mechanical properties, as a function of plasma modification.

The specific adsorption capacity of the non-woven cellulose using oxygen plasma treatment was achieved. In the next step, this material with increased hydrophilicity and improved mechanical properties will be used in the preparation of multilayered wound-dressing materials for specific functionalities (incorporation of drugs, specific functional properties).

Keywords: plasma, oxygen, regenerated non-woven cellulose, super-hydrophilicity, mechanical properties

V prispevku je predstavljena uporaba neravnovesne plinske plazemske tehnike za obdelavo regeneriranih celuloznih vlaken v obliki netkanih kopren, ki se uporabljajo v materialih za oskrbo površinskih ran. Le-ta omogoča modifikacijo/funkcionalizacijo površine polimerov oz. vlaken in poleg ekološke neoporečnosti zagotavlja še želeno kakovost tako glede hitrosti, homogenosti, stabilnosti kot tudi učinkovitosti obdelave.

Za doseganja visoke stopnje hidrofilnosti, ki med drugim določa uporabnost materialov za oskrbo ran, smo celulozne koprene obdelovali s kisikovo (O_2) plazmo ter določili njene optimalne pogoje obdelave.

Hidrofilnost oz. interakcijsko sposobnost plazemsko modificiranih kopren smo analizirali z različnimi eksperimentalnimi metodami, kot so: določanje stičnih kotov, študij navzemanja vlage ter zadrževanja vode. Analizirane so bile spremembe mehanskih lastnosti plazemsko obdelanih kopren.

Kisikova plazemska obdelava je signifikantno vplivala na povečanje hidrofilnosti oz. spremembo adsorpcijske kapacitete celuloznih kopren ob sočasnih dobrih oz. izboljšanih mehanskih lastnostih. Tako modificirani celulozni materiali se bodo v naslednji stopnji uporabili za izdelavo večslojnih visoko funkcionalnih materialov za oskrbo ran (inkorporacija učinkovin, specifičnih funkcionalnih lastnosti).

Ključne besede: plazma, kisik, regenerirana celulozna koprena, superhidrofilnost, mehanske lastnosti

1 INTRODUCTION

Several different materials are used for medicinal products in wound-treatment and healing. By considering their composition and purpose, we can divide them roughly into three groups. The first comprises materials and products for the prevention of secondary infections[1–4], materials assuring restoration and regulation of suitable micro- and macro- environments for wound-healing are considered to be in the second group,[5–7] whilst all materials used for the mitigation of patient trauma due to the acquired surface wounds or their healing, belong the third group.[8–13]

Cellulose and its derivatives are very often used as a functional part of different wound-dressing materials (in different forms i.e. fibres, non-woven materials, hydro-gels ...). Cellulose fibres' crystalline/amorphous microfibrillar structure (two-phase model) control the accessibility of the surface, as well as those bulk polar groups responsible for fibres' hydrophilicity, an important material characteristic which, amongst others, influences the wound-healing process.

Wound-healing is a physiologic process involving a series of stages: hemostasis, inflammation, proliferation with repair and remodelling. The warm, moist microenvironment created within the wound is essential for further stages of healing.[14] In the stage of re-epithelisation, new keratinocytes must migrate onto the repair site. Migration requires a fluid environment and this is why the hydrophilicity of the material, as used in the wound-dressing, is one of the more important agents.[15]

Characteristically different chemical approaches, i.e. bleaching, treatment with alkali, are used for achieving this.[16] Thermodynamically non-equilibrium physical processes, such as the use of gaseous plasma, promise the most,[7–21] as alternative to the usual chemical reactions. The advantages of gaseous plasma such as its ecological integrity and homogenous surface treatment far outweigh the minor negative influences on the materials' mechanical properties. It has a vast variety of possibly acquired final applications,[22–23] the more often used being cleaning or etching,[24–26] sterilization,[27–28] functionalization,[29–38] and polymerization.[39–40]

This paper studies the effects of non-equilibrium oxygen plasma for the modification of regenerated non-woven cellulose. The desired final characteristics are super-hydrophilicity, specific interaction along with non-altered mechanical properties.

2 EXPERIMENTAL PART

2.1 Materials

Regenerated cellulose fibre was studied in its non-woven form, *i.e.* viscose (CV), as produced by KEMEX, The Netherlands. The surface mass of the fabrics was 175 g/m^2. Some construction parameters, important for the sorption capacity, were studied, and are presented in **Table 1**.

Table 1: Construction parameters of the non-woven cellulose sample
Tabela 1: Konstrukcijski parametri celuloznih netkanih kopren

Sample	air permeability* (L/m^{2}s)	thickness ** (mm)
Viscose	650	1.7

*DIN53 887 **SIST ISO 5084

2.2 Treatment procedures

The samples were vacuum dried (vacuum oven type VS-50SC Kambič; $T = 20$ °C, $P = 100$ mbar, $t = 24$ h) before plasma treatment. Then the samples were exposed to gaseous plasma within a discharge chamber. The discharge chamber was a spherical cylinder with an inner diameter of 36 cm, and positioned as an integral part of a vacuum system pumped using two-stage oil rotary pump. The plasma was excited with a radiofrequency generator operating at 27.12 MHz, and a power of about 1 kW. The plasma created by such a generator is a source of excited particles including neutral oxygen atoms in the ground state, excited oxygen atoms and molecules, as well as positively and negatively-charged ions. Such particles are determined by various techniques including electrical and catalytic probes, titration, laser absorption fluorescence, and mass spectrometry.[41–51]

In order to find the best/optimal conditions for the plasma modification process, several discharge parameters were varied: sample shape and dimension (fibres, fabric; spherical, square), generator power of the plasma system (between 100 W and 1000 W), frequency of the plasma system (12.56 or 27.12 MHz, DC), gas flow and pressure, and the activation time (1 s to15 min).

The optimal conditions used for the regenerated cellulose samples' treatment using plasma modification, are summarised in **Table 2**.

2.3 Methods

Hydrophilic/hydrophobic properties determination

a) Water contact angle

The hydrophilic/hydrophobic character was studied by contact angle measurements between polymer material samples and water. The powder contact angle method was used as developed for determining the wetting properties of porous materials. The samples were cut into (2×5) cm rectangular pieces and suspended in a special sample holder of a Krüss K12 processor Tensiometer. Immediately before measurement, the container with the liquid (n-heptane; water) was raised until the sample edge touched the liquid surface.

The samples' mass *(m)* changes, as a function of time *(t)* during the water adsorption phase, was monitored. The initial slope of the function $m^2 = f(t)$ is known as the capillary velocity, from which the contact angle between the solid (polymer sample) and the water was calculated using a modified Washburn equation:[52]

$$\cos\theta = \frac{m^2}{t}\frac{\eta}{\rho^2 \cdot \gamma \cdot c} \qquad (1)$$

where θ is the contact angle between the solid and liquid phases, m^2/t is the capillary velocity, η is the liquid

Table 2: Optimal oxygen plasma conditions used for the modification of non-woven cellulose. ν – frequency of RF plasma generator; p – oxygen pressure; n_i – density of ions; n_a – density of neutral atoms; T_e – electron temperature, t – activation time
Tabela 2: Optimalni parametri plazemske obdelave celuloznih netkanih kopren. ν – frekvenca RF plazemskega generatorja; p – tlak dovedenega kisika; n_i – gostota ionov; n_a – gostota nevtralnih atomov; T_e – temperature elektronov; t – čas obdelave

Sample		Plasma treatment Oxygen gas			
Shape	Dimension	Power	Frequency	Plasma parameters	Activation time
non-woven	(22×22) cm	500 W	N = 27.12 MHz	$p = 75$ Pa $n_i = 10^{15}$ m^{-3} $n_a = 10^{21}$ m^{-3} $T_e = 3$ eV	$t = 10$ min

viscosity, ρ is the liquid density, γ is the surface tension of the liquid, and c is a material constant.

The constant c was determined for each sample from contact angle measurements using n-heptane, for which the contact angle on the non-woven was zero and $\eta = 0.4$ mPa s, $\rho = 0.6836$ g/cm^3, $\gamma = 20.4$ mN/m. The results were statistically processed (a set of parallel measurements until the standard deviation was less then 2°) and represent the average value of ten measurements of the water contact angle.

For more detailed description of this experimental procedure, see Persin et al.[53] and Fras Zemljic et al.[54–55]

b) Water retention value

The water retention value of the porous polymer material was determined according to standard DIN 53 814. This method is based on determining the quantity of water that the sample can absorb and retain, under strictly controlled conditions. This property is expressed as a ratio between the mass of water retained in the sample after soaking (2 h) and centrifuging (20 min), and the mass of an absolute dry sample ($T = 105$ °C, $t = 4$ h).

c) Moisture content

The moisture content of the porous polymer material was analysed using a Halogen Moisture Analyser. This was done using the thermo gravimetric principle: the samples' weight was measured before and after heating.

Mechanical properties' determination

The tensile properties of fabrics were determined according to standard SIST ISO 13934-1.

The maximum force and elongation at maximum force i.e. at the moment of the samples' tear, was determined, using the strip method.

3 RESULTS

Hydrophilic/hydrophobic properties

Figure 1 presents the square of the adsorbed mass versus time for non-treated and oxygen plasma treated
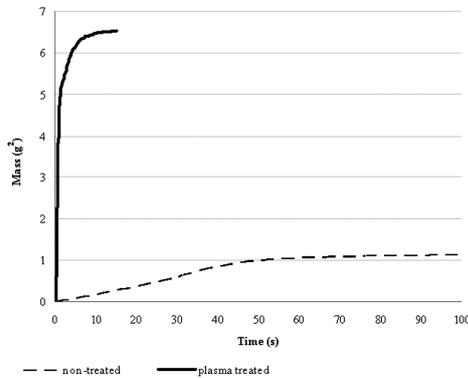
Figure 1: Capillary velocities of non-treated and oxygen plasma treated regenerated non-woven cellulose sample
Slika 1: Kapilarne hitrosti neobdelanih in s kisikovo plazmo obdelanih celuloznih netkanih kopren
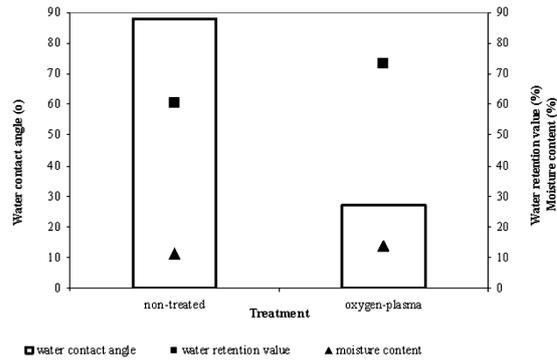
Figure 2: Hydrophilic/hydrophobic properties of a non-treated and oxygen plasma treated regenerated non-woven cellulose sample
Slika 2: Hidrofilno/hidrofobne lastnosti neobdelanih in s kisikovo plazmo obdelanih celuloznih netkanih kopren

samples. The slopes of these capillary velocities curves characterise the rate of water sorption.

The non-treated material adsorbed the water very slow. The slope even in 100 s did not reach the plateau, respectively the non-treated material was not completely wetted by the water. Within 100 s, the non-treated sample was able to absorb 1.1 g of water. The capillary velocity by the plasma treated samples was faster. After 15 s the sample was complete wetted and was able to adsorb 2.6 g of water.

Water contact angles were calculated using equation (1). The average results for the water contact angles, water retention values, and moisture content on the non-treated and oxygen plasma treated regenerated cellulose sample, are given in **Figure 2**.

The significant effect of oxygen plasma modification resulted in enhanced non-woven wettability. The water contact angle decrease by 69 % followed by simultaneous increase in water retention value (21 % improvement) and an increase in moisture content (22 %).

Mechanical properties

The tensile properties determined as breaking force and elongations, are given in **Table 3**.

Table 3: Breaking force and elongation of non-treated and oxygen plasma treated non-woven cellulose
Tabela 3: Pretržna sila in raztezek neobdelanih in s kisikovo plazmo obdelanih celuloznih netkanih kopren

Sample treatment	Mechanical properties			
	Breaking force (N)		Elongation (%)	
	horizontal	longitudinal	horizontal	longitudinal
non-treated	54.8 ±6.5	117.6 ±4.7	41 ±2.5	62.2 ±1.2
plasma treated	87.4 ±11.4	204.9 ±25.0	22.2 ±1.1	48.1 ±0.6

Plasma treatment also affects the samples' tensile properties. The breaking force, as measured in both directions, significantly increased (by 50 % horizontally and by 74 % longitudinally). Elongation in both direc-

tions decreased but the effect was smaller (i.e. by 46 % horizontally and 23 % longitudinally).

4 DISCUSSION

Applied oxygen plasma treatment significantly improved the non-woven cellulose sorption capacity – wetability. Surface modification resulted in the removal or oxidation of contaminants on the surface,[55] and increased the amount of surface polar carboxyl groups.[56–58] Thus, the plasma treatment resulted in a significantly water contact angle decrease (see **Figure 1**). Longer activation time (i.e. 10 min; see **Table 2**) also caused some morphological changes in the bulk. Therefore, the modified samples were able to retain larger amounts of water, which remained in the porous structures even after the applied mechanical stress. These changes are also responsible for moisture content increase.

Oxygen plasma treatment also improved the tensile properties. The significant increase in the breaking force after plasma treatment was caused by the decreased elongation. Low-temperature O_2 treatment caused etching and ablation action on the surface substrate, resulting in a roughening effect on the fabric surface. The rougher surface may have imparted more contact points within the non-woven fibres, resulting in enhanced fibre friction. The increased friction produces a great cohesive force between the fibres. The used plasma treatment reduced the elongation of the material. This can be explained by the increased interaction between fibres in the non-woven, after plasma treatment. This caused a reduction in the effective gap between the fibres placed in longitudinal and horizontal directions, at their crossover points, and the lateral-compressional abilities of the fibres in the non-woven, leading to a reduction in the extensibility.

5 CONCLUSION

Used optimised oxygen plasma treatment proved to be an excellent tool for the surface, as well as for the bulk modification, of regenerated non-woven cellulose material. The wettability of the non-woven was drastically improved (decreased water contact angle by simultaneously increased water adsorption capacity). The changes in morphology were, besides the improvement in wetability, responsible for the better mechanical bonding in the used non-woven. In this way the cellulose material had been functionalised without changes in their mechanical properties.

We have shown that the oxygen plasma modification of regenerated cellulose samples in non-woven form, potentially offers a flexible and environmentally friendly activation process in order to obtain super-hydrophilic matrices. Such functionalised super – hydrophilic regenerated non-woven cellulose could be used as a functional layer in wound-dressing materials and could,

among others, contribute to a better surface wound-healing process.

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