Chitosan immobilization to the polypropylene nonwoven after activation in atmospheric – pressure nitrogen plasma

Abstract: Atmospheric-pressure air and nitrogen plasmas generated by surface dielectric barrier discharges have been used to incorporate new functionalities at the surface of polypropylene nonwoven fabric. The main goals were to activate the polymer surfaces for subsequent immobilization of chitosan from water solution without using any crosslinking and wetting agents. The samples were analyzed by diffuse reflectance infrared Fourier transform spectroscopy, scanning electron microscopy, and X-ray photoelectron spectroscopy. The nitrogen plasma treatment resulted in relatively high oxygen incorporation, about 9 atomic % mainly in aliphatic C=O type bonds and about 4 at.% of nitrogen incorporation in amine and other nitrogen functionalities. Chitosan was immobilized on the fabric fibers surfaces very homogeneously in amount of 2 - 5 g m⁻². The chitosan coated samples exhibited a good laundering durability and strong antimicrobial activity against *Bacillus subtilis* and *Escherichia coli*.

Keywords: chitosan, immobilization, atmospheric pressure plasma, polypropylene

1 Introduction

Textile products having a prolonged contact with the skin and in many other applications are an excellent habitat for all kinds of undesired microorganisms. As a consequence, there is a growing interest in hygienic antimicrobial finishing of textiles that prevent or retard growth of bacteria [1]. Chitosan is a derivative of chitin, a natural polysaccharide present, for example, in the exoskeleton of crustaceans. Chitosan is skin friendly, nontoxic and environmentally sound antimicrobial agent, which makes it an attractive material for hygienic antibacterial treatments of textiles [2-4].

In many applications such as in hygiene and medical materials, filter media, and packaging, polypropylene nonwoven (PPNW) fabrics need to resist microbial growth. To use chitosan as the antimicrobial agent in such applications it is necessary to attach it firmly to the PPNW fiber surface while maintaining its antimicrobial activity. Since polypropylene is well known for its poor adhesive properties, and cost efficiency is the driving force for process development in textile industry, before the chitosan immobilization it is necessary to activate PPNW fiber surfaces using a cost-effective and environmentally acceptable method.

Immobilization of chitosan onto polypropylene nonwoven fabric using antenna-coupling microwave plasma was investigated by Tyan and Liao [5]. Plasma surface activation was realized in oxygen at low pressure with the treatment time less than 10 s and then it was followed by grafting with acrylic acid (AAc), which made the plasma-treated fabric durably hydrophilic and excellent in water absorbency. With the high density of grafted chains and strong water affinity, the polyacrylic acid (pAAc)-grafted fabric greatly becomes feasible as an...
intensive absorbent and as a support to promote chitosan-immobilization through amide bonds. Experimental results demonstrated by surface analyses by ATR-FTIR showed that -CONH-, amide binding emerged between pAAc and chitosan.

Due to the capability of anticoagulation and cell adhesion, the chitosan-immobilized polypropylene fabric prepared by the mentioned way can be used as the substrate for cell culturing and then developed as a wound-dressing substitute for second-degree burns. Liao continued in his investigation of polypropylene surface grafting with chitosan and some new additional results are summarized in [6]. In this study he used the same grafting procedure as it was described in his previous paper. The similar procedure was also used for preparing the chitosan-grafted PET textiles [7]. The difference was only in the plasma source, which in this case was glow discharge burning in oxygen. The PET textiles containing chitosan on their surface showed a high inhibition of bacterial growth (S. Aureus) even after laundering. Another way to immobilize chitosan onto PPNW is to active the surface by x-ray irradiation [8], then to graft it with AAc and even after chitosan can be immobilized.

Ko-Shao Chen together with his co-workers [9] for chitosan immobilization onto PPNW used low-pressure Ar plasma activation followed by UV-light graft polymerisation of poly (N-isopropylacrylamide) gel to improve hydrophilicity of PP. Subsequently, chitosan was immobilized onto PP nonwoven composites surface using the cross-linking agent glutaraldehyde.

The majority of known low-temperature plasma activation of PPNW for subsequent grafting and surface immobilization of polymeric materials, including the immobilization of chitosan have been done at low pressures, which makes the plasma equipment expensive and continuous operation difficult. As a consequence, from a practical point of view, plasma fabric treatment techniques that need vacuum are at a disadvantage with respect to those that are applicable at 1 atm.

Low-temperature plasma activation, where polar molecular fragments and radicals are formed on the fabric fibre surfaces, is emerging as an environmentally attractive technique for surface activation of textile materials, including PPNW [10-15]. In the present work PPNW were activated using a novel type of atmospheric-pressure plasma reactor designed for low-cost, high-speed plasma treatment of web materials. The reactor is based on the so-called diffuse coplanar surface barrier discharge (DCSBD) [16-18], where a macroscopically homogenous plasma layer with a high power density on the order of 100 W cm⁻² was generated in nitrogen and air. The XPS, SEM microscopy, DRIFT spectroscopy, as well as dye uptake, bioactivity, and wash resistance tests, were made for surface characterization of the samples. DCSBD has been shown to be very efficient for activation of PPNW, which has enabled a stable and uniform chitosan immobilization.

2 Experimental procedure

2.1 Materials and methods

An industrial spun-bonded polypropylene nonwoven fabric (50 g m⁻², 272±22 µm thick, an average fibre diameter 2.6±0.2 µm, an average pore diameter 37 µm) supplied by PEGAS Company (Czech Republic) was used in the experiments. Technical purity nitrogen and ambient air were used as the plasma gas.

Chitosan from crab shells were purchased from Sigma-Aldrich. Low molecular weight chitosan (degree of deacetylation 75-85%) was diluted in 0.1 M water solution of acetic acid by stiring at room temperature.

The PPNW samples nonactivated or plasma activated were weighted and shortly dipped into the chitosan solution. Subsequently most of the chitosan solution on the surface of polypropylene was removed using a mangle to achieve an even coating, and the samples were air dried for 24 hours. All processes were performed at room temperature. Finally, the samples were several times rinsed with distilled water to remove any chitosan homopolymers adhering to the fabric. The laundering durability of chitosan layer was tested in five cycles of standard laundering at 40°C and the presence of an anionactive detergent in concentration 2 g dm⁻³.

2.2 Plasma activation

Plasma activation was carried out in the reactor illustrated by Fig. 1. The reactor’s heart is a plasma-generating 21×8 cm electrode element consisting of two systems of parallel strip like electrodes (1.2 mm wide, 50 µm thick, 210 mm long, 0.5 mm strip to strip; molybdenum). The electrodes are embedded in 96% alumina using a green tape technique. The thickness of the ceramic layer between the plasma and electrodes was 0.4 mm. A sinusoidal high frequency, high voltage (15 kHz, 400 W, up to 20 kV peak to peak) was applied between the electrodes.

Such a discharge electrode arrangement and energisation generate in the nitrogen and air working
gases visually almost uniform, diffuse, and approximately 0.5-mm-thick plasma layer [16-19] of a extremely high power density reaching the value of 100 W cm⁻³. The voltage between the discharge electrodes was measured using a Tektronix P6015A capacitive–resistive HV divider with a rise time of 10 ns. A 50 Ohm coaxial measuring resistor was used to measure the discharge current. The net power dissipated in the discharge was computed from the discharge current and voltage measurements.

As shown in Fig. 1 the electrode system was housed inside of a plastic enclosure to allow containment of the gas. The rate of nitrogen flow into the enclosure was controlled by a mass flow and set at 20 L min⁻¹. The 21-cm-wide PPNW fabric belt was fed into and out of the reactor through glands with rubber seal lips. Since the 50 g m⁻² PPNW fabric belt was treated on both sides the plasma-activation energy was computed as follows:

\[
\text{plasma activation energy (W s cm}^{-2}\text{)} = 2 \times \text{net power dissipated in the discharge (W)} / (\text{fabrics width (cm)} \times \text{fabric speed (cm s}^{-1}\text{)}).
\]

**Figure 1:** DCSBD reactor for continuous fabric treatment operating in nitrogen at atmospheric pressure.

### 2.3 Sample characterisation

The amount of chitosan immobilised on PPNW (CHi) was calculated according

\[
\text{CHi (%)} = \left( \frac{W_1 - W_0}{W_0} \right) \times 100
\]

where \(W_1\) is the weight of PPNW with chitosan, and \(W_0\) the weight of origin non-woven sample.

X-ray photoelectron spectroscopy (XPS) studies were performed by a Kratos XSAM800 spectrometer using Mg Kα 1,2 radiation, FRR mode, and a retardation ratio of 20. Data acquisition and processing were done with the Kratos Vision 2 program. Spectra were referenced to the hydrocarbon type C1s line at a binding energy (BE) of 285.0 eV.

Scanning electron microscopy (SEM) investigations were performed in the usual way using a Tesla BS 300 SEM microscope with digital microscopy imaging TESCAN on PPNW fabric specimens first sputtered-coated with a thin layer of gold.

Diffuse reflectance infrared fourier transform (DRIFT) spectra of polypropylene samples were taken using diffuse reflectance accessory of FTIR spectrometer (Excalibur FTS 3000 MX, Digilab). The remission was measured to get absorption spectra.

Since chitosan is known to have a high adsorption capacity for acid dyes, the dyeing using a standard Acid Red 87 (Sigma Aldrich) was used to investigate the homogeneity of plasma activation and chitosan immobilization. The samples were immersed in 0.1 wt.% solution of Acid Red for 1 hour at room temperature to yield an ion complex between the amino groups and the acidic dye.

The antimicrobial activity test was done by *Bacillus subtilis* (G⁺) and *Escherichia coli* (G⁻) in static test. Cultures of bacteria growing on agar plates were exposed to the untreated PP sample and the chitosan coated sample. The inhibition effect was determined qualitatively by visual assessment of the bacteria growth on the agar plates.

### 3 Results and discussion

Commonly the chitosan is immobilized at polypropylene surfaces using a two stage method. In the first step, the hydrophobic polypropylene surface is functionalized mostly by grafting with carboxylic acids, preferably acrylic acids, and in the second step the chitosan molecules are coupled with carboxylic groups by forming amide covalent bonds at their interface [5,6]. Liao [6] studied the dual properties of amino groups in chitosan for molecular immobilization and bio functional effects. They activated polypropylene nonwoven fabric by high density oxygen microwave plasma, followed by graft copolymerization with acrylic acid and then coupling with chitosan molecules. It was found that larger portion of minimum 85% amino groups in chitosan was coupled with the grafted pAAc by forming amide bond and smaller portion of them could be ionized by the acetic acid-buffered solution as polycations (NH₃⁺) likely exposed to the exterior of the immobilized chitosan. These polycations are effective in antibacterial properties. They interfere with permeability...
of the microbial membrane and therefore prevent bacteria from proliferation.

There is a limited amount of information in the literature that chitosan can be immobilized onto plasma activated polymer surfaces in a one step by exploiting either carbodiimide or glutaraldehyde chemistries [20-22]. The covalent bond between carboxylic groups of the activated surfaces and amino groups of chitosan can be formed. The mechanism with glutaraldehyde is based on the formation of imine bonds between aldehyde groups of glutaraldehyde and amino groups of chitosan and amino activate substrate [23]. In both cases carbodiimide and glutaraldehyde serves as crosslinking agent between activated polymer surface and chitosan coating.

The aim of our work was to immobilize chitosan at polypropylene fiber surface in one step, without previous chemical surface grafting, through chemical functionalities formed on the plasma treated surfaces, like amino groups, carboxyl groups or aldehyde groups. Based on our previous results on the nitrogen plasma activation of PP nonwoven [24], a plasma activation energy of 330 W corresponding to plasma exposure times of 2×5 s was selected. These are lowest activation energy and shortest times sufficient for making the samples wettable by the chitosan water solutions immediately after the plasma activation. Even when the ambient air plasma activation was found to be less efficient, for comparison and a better understanding of the plasma activation mechanism, a limited set of the plasma activations was made also using ambient air as the plasma gas.

### 3.1 XPS Analysis

XPS was used to analyze the changes of chemical composition on the polypropylene surface after activation by DCSBD at atmospheric pressure. Table 1 shows the surface composition of PPNW after plasma treatment in air and in nitrogen.

In both cases the plasma treatment significantly increased the O/C ratio from 0.02 to about 0.1 which confirmed that functional groups containing oxygen were introduced on the PPNW surface. In addition, the incorporation of nitrogen atoms was observed. In the nitrogen plasma activated samples the surface concentration of nitrogen was about 3.8 at.%, i.e., roughly two times higher than in air. Note that the oxygen content was higher than the nitrogen content both after air and nitrogen plasma treatments. To understand the effect of the plasma treatment more precisely, the C1s peak was decomposed, which is shown in Fig. 2.

| Samples            | C at.% | O at.% | N at.% | O/C | N/C |
|--------------------|--------|--------|--------|-----|-----|
| PPNW untreated     | 98.3   | 1.7    | 0.02   |     |     |
| PPNW air plasma treated | 90.1  | 8.3    | 1.7    | 0.09| 0.02|
| PPNW nitrogen plasma treated | 87.5  | 8.7    | 3.8    | 0.10| 0.04|

In the air plasma treated samples three components can be seen (Fig. 2 bottom): C1 at a binding energy (BE) of 285 eV representing hydrocarbon type C-H, C2 at 286.5 eV representing C-O type bonding, and C3 at 288 eV representing C=O and / or O-C=O type bonding. In the nitrogen plasma treated (Fig. 2 middle) sample the intensity of the shoulder of the high BE side is similar to that of the air-treated sample. The shoulder in this case is fitted by a single peak, which pertains to C=O and / or O-C=O type functionalities. Judging by the O1s peaks the built in oxygen in case of nitrogen plasma treatment is mainly in aliphatic C=O type bond (~ 532.2 eV), while in the case of air treated sample it is mainly in aliphatic C-O type bond (BE ~ 532.9 eV) as shown in Table 2.

In PPNW after air plasma activation (Table 2) the nitrogen was present in two main bonding modes: in an oxidised type one N2 (~ 407.4 eV, assigned to NO₂ and NO₃ like groups) and in a reduced type one N1 (~ 400.1 eV) which may be assigned to several functionalities like amino –C-NH₂, imine –C=N-, or nitrile –CN groups.

In samples after nitrogen plasma activation only a single N1s peak could be detected at about 400.1 eV pertaining to the reduced type nitrogen (Fig. 3).

### 3.2 Chitosan immobilization

Table 3 illustrates the amount of chitosan immobilized to the PPNW after the plasma activation in nitrogen atmosphere. About 4 wt.% to 10 wt.% of the chitosan was estimated to be coated onto PPNW using the weight difference before and after coating and washing. One major drawback of the chitosan used as an antimicrobial textile finish is its lack of strong bonding with textile fibers. The antimicrobial activity of chitosan–treated fabric decreases with repeated launderings. From that reason we tested chitosan adhesion to the plasma activated samples by washing in distilled water and by subsequent laundering at 40°C in five cycles at the presence of a detergent.
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As shown in Table 3, in the first cycle of laundering about 13 wt.% of chitosan coating was removed. During next four washing cycles the amount of chitosan remained unchanged.

### 3.3 Analysis of chitosan coated PPNW by DRIFT spectroscopy

The DRIFT spectroscopy was used for identification of the chitosan layer. In Fig. 4 the spectrum of the PPNW coated with chitosan is compared to the spectrum of untreated polypropylene sample.

The spectrum of chitosan coated PP NW (b) shows a broad absorption band between 3450 and 3100 cm\(^{-1}\) due to vibration of chitosan functional groups (-OH, -NH, and -NH\(_2\)) and absorption band between 1200 and 1100 cm\(^{-1}\) which represents C-O-C stretching vibration in glucosamine ring. Absorption bands at 1650 cm\(^{-1}\) and 1554 cm\(^{-1}\) indicate the amides I (C=O in O=C-NH) and amides II (-NH in O=C-NH), respectively. In pure chitosan amide I were determined at 1653 cm\(^{-1}\) and amide II at 1595 cm\(^{-1}\) [6]. The shifting of amide II (-NH in O=C-NH) toward right may be due to the formation of new amide bonds between amine groups of chitosan and carboxylic group on the plasma activated surfaces, which has been supported by the results of XPS analysis.

On the other hand, Tyan et al. [5] assigned the absorption peak appearing at 1550 cm\(^{-1}\) in the spectra of chitosan immobilized sample to a symmetric –NH\(_3\) deformation which confirmed the presence of NH\(_3\) in chitosan. Thus, it also can not be precluded that the chitosan immobilization occurred via ionic bonding.
The plasma activation of polypropylene leads to incorporation of radicals and also various types of reactive groups to the surface. In plasma chemistry it is very difficult to explain the exact mechanism, as both covalent, radical and ionic reaction together can participate in modification of PPNW with chitosan. We suppose that reactions between reactive groups on polypropylene surface and chitosan groups are more probable. The type of reactive groups depends on the type of gas in which the plasma activation has been done. This was the reason, why we analysed PPNW activated in air and also in nitrogen plasmas. The results of XPS showed that PPNW activated in nitrogen contained about 8 atomic % of oxygen, mainly in C=O type bond (\(-\text{COOH}, -\text{CHO}, -\text{COO}\)\) and 3.8 atomic % of nitrogen in \(-\text{NH}_2\) and other nitrogen functionalities. PPNW activated in air plasma contained in comparison with nitrogen plasma oxygen groups mainly in C-O binding.

Chitosan has both reactive amino and hydroxyl groups in his structure. It is supposed that amino groups of chitosan can be covalently bonded to the polypropylene surface both through aldehyde groups or carboxyl groups introduced to polypropylene surface after plasma activation. Aldehyde groups form covalent imine bonds and carboxy groups form amide bonds. From the point of view chitosan immobilization to the PPNW seems to be better to activate samples in nitrogen plasma, as more carboxyl and aldehyde groups are present at the surface of fibres after plasma activation. Reactions of hydroxyl groups of chitosan and secondary interaction as hydrogen bridges cannot be excluded.

### 3.4 SEM microstructure

The morphology of chitosan coated PPNW were studied using SEM. Fig. 5 shows the photo of non-modified PPNW and PPNW coated with chitosan using 1.6% chitosan solution. Here one can see in detail the chitosan layer coating the polypropylene fibre. Although chitosan has very good ability to create the films, it does not create the continuous film on the surface but covers the individual fibres. Only on some places one can see the thin film in space between the individual fibres (Fig. 6).

Figure 6 shows the cross sections of a nitrogen plasma activated sample coated with chitosan layer. As can be observed from SEM picture, because of an efficient and uniform plasma hydrophilization of PPNW, the chitosan solution penetrated into the polypropylene nonwoven fabric and covered homogeneously not only fibers at the surface, but the interior fibers as well. It is clearly seen that the chitosan layer was immobilized on the fibres surfaces.

| Chitosan solution concentration [%] | Chitosan content in PP sample [wt.%] | Chitosan content in PP sample after washing [wt.%] | Chitosan content after 1st cycle of laundering [wt.%] |
|------------------------------------|-------------------------------------|-----------------------------------------------|-----------------------------------------------|
| 1.6                               | 6.46 ± 0.17                        | 4.76 ± 0.17                                   | 3.90 ± 0.17                                   |
| 2                                 | 7.71 ± 0.16                        | 6.41 ± 0.29                                   | 5.35 ± 0.21                                   |
| 3.5                               | 17.77 ± 0.46                       | 12.10 ± 0.57                                  | 9.92 ± 0.47                                   |

Figure 4: The DRIFT spectra of a) polypropylene nonwoven, b) polypropylene nonwoven with chitosan layer.
Fig. 7 shows in detail the chitosan coated PP fibres after 5 standard laundering cycles in water about 40°C. Since the chitosan coating is of reasonable washing resistance, and is not easily washed off, it is apparent that the plasma activation resulted in a tight bond between PP fibres surface and chitosan coating. Note that after five cycles of laundering the coating was separated from the fibres only by strong mechanical forces in the gaps between the fibres and the intersections of the fabric (Fig. 7).

3.5 Homogeneity of plasma activation

The homogeneity of plasma activation and chitosan immobilization was analysed by surface dyeing of chitosan layer. Fig. 8 shows the results of the dyeing using a water solution of acid red. Untreated PP samples were not colored since hydrophobic fibre surfaces were not
wetted by the dye solution. Even when the plasma-treated PP fibres were hydrophilic, the affinity of the fiber surface for acid red dye was low, resulting in a weak dye uptake and a weak pink colour of the samples.

This contrasts with the strong red colour and uniform dye uptake of the chitosan coated PP fibres due to strong affinity of chitosan to acid red dye. The apparent high uniformity of the dyeing indicates the uniform chitosan immobilization.

### 3.6 Antimicrobial properties

In our work *Escherichia coli* (G-) and *Bacillus subtilis* (G+) were used to study the antimicrobial activity of PPNW coated with chitosan after nitrogen plasma activation. Fig. 9 illustrates the antimicrobial efficiency of the chitosan coating on PPNW fabric. The PPNW fabric was placed on an agar nutrition medium inoculated with *Bacillus subtilis*. After 24 hours the white area at the control sample surface represent colonies of bacteria which completely covered the sample. The dark zone around the chitosan coated sample represents the zone of inhibition where bacteria did not grow.

Similarly it was found that chitosan effectively inhibits the growth of *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Candida albicans* in static test. The stability of modified chitosan layer was confirmed by antimicrobial effect of samples even after five cycles of washing [24].

The inhibition effect of chitosan against *Escherichia coli* and *Staphylococcus aureus* was investigated also using cell number measurement. This method allows quantitatively compare the cell number of *Escherichia coli* (Fig. 10) and *Staphylococcus aureus* (Fig. 11) growing in the presence of polypropylene nonwoven coated with chitosan and without polypropylene sample.

Effectiveness of chitosan on antimicrobial activity depends on the strains of bacteria. Chitosan is most effective against *Escherichia coli*. Samples with PPNW coated with chitosan shows after 24 hours approximately 50% of reduction in cell number. Chitosan also shows about 30% reduction in cell number of *Staphylococcus aureus*.

It is known that the effectiveness of the antimicrobial structure of chitosan depends upon the thickness or amount of the coating, the molecular weight of chitosan and partly upon the hydrophobicity of the surface. As suggested by Dutkiewics [25] when coating a chitosan material onto the hydrophobic surface of a substrate such polypropylene, the hydrophobic surface of the polymer attracts the hydrophobic segments (-C-C-) and repels the hydrophilic segments –NH$_2$ of the chitosan. This resulted in a structure in which most of the hydrophilic segment –NH$_2$, which are effective in antimicrobial activity are
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4 Conclusions

An innovative plasma source that generates the thin diffuse plasma layer of the order of 100 W cm\(^{-1}\) power density at atmospheric-pressure in air or nitrogen has been used to generate PP surfaces with chemically reactive groups that can subsequently be used for the covalent immobilization of chitosan. It was found that chitosan forms thin homogeneous layer with reasonable washing resistance on the nitrogen plasma activated PPNW fibres surfaces. Such surface modified PPNW exhibits antimicrobial effect against both Escherichia coli and Bacillus subtilis.

XPS analysis confirmed that the nitrogen plasma treatment resulted in relatively high oxygen incorporation mainly in aliphatic C=O or O-C=O type bonds, and nitrogen incorporation mainly in amino groups. The DRIFT spectroscopy revealed the presence of amide structures O=C-NH in chitosan coated polypropylene nonwoven. Based on the results obtained it is reasonable to assume that chitosan was immobilized at the PP surface through formation of interfacial amide bond between amine groups of chitosan and surface carboxy groups at the PPNW fibres. However, the apparent presence of other functionalities on the plasma treated PP surface like aldehydes, ketones, and amine groups, allows speculation about an alternative reaction scheme in which aldehyde or amine surface groups can react with amine groups or hydroxy groups of chitosan. Consequently, further experimental investigations are necessary in order to determine which of the above mentioned mechanisms is the observed effective chitosan immobilization.

References

[1] Monticello R.A., White W.C., International Nonwovens Journal 11, 38 (2002)
[2] Shin Y., Yoo D. Il, Min K., J. of Appl. Polym. Sci. 74 (12), 2911 (1999)
[3] Takai K., Ohtsuka T., Senda Y., Nakao M., Yamamoto K., Matsuoka J., Hirai Y., Microbiol. Immunol. 46(2), 75 (2002)
[4] Huh M.W., Kang I.-K., Lee D.H., Kim W.S., Lee D.H., Park L.S., et al., J. Appl. Polym. Sci. 81, 2769 (2001)
[5] Tyan Y.-C., Liao J.-D., Lin S.-P., J. Mater. Sci.: Mater. Med. 14, 775 (2003)
[6] Liao J.-D., Lin S.-P., Wu Y.-T., Biomacromolecules 6(1), 392 (2005)
[7] Huh M.W., Kang I.-K., Lee D.H., Kim W.S., Lee D.H., Park L.S., et al., J. Appl. Polym. Sci. 81, 2769 (2001)
[8] Yang J.M., Lin H.T., Wu T.H., Chen C.-C., J. Appl. Polym. Sci. 90, 1331 (2003)
[9] Chen K.-S., Ku Y.-A., Lee C.-H., Lin H.-R., Yan T.-R., Sheu D.-C., Chen T.-M., Mater. Sci. Eng. C 25, 472 (2005)
[10] Černakova L., Kovacik D., Zahoranova A., Cernak M., Mazur M., Plasma Chem. Plasma Process. 25, 427 (2005)
[11] Akishev Y., Grushin M., Napartovich A., Trushkin N., Plasmas and Polymers 7, 261 (2002)
[12] Temmerman E., Akishev Y., Trushkin N., Leys Ch., Verschuren J., J. Phys. D: Appl. Phys. 38, 505 (2005)
[13] Hwang Y.J., An J.S., McCord M.G., Park S.W., Kang B.Ch., Fibers and Polymers 4, 145 (2003)
[14] Roth J.R., Chen Z., Sherman D.M., Karakaya F., Tsai P.P.-Y., Kelly-Wintenberg K., Montie T.C., International Nonwoven Journal 10, 34 (2001)
[15] Rahel J., Simor M., Cernak M., Stefecka M., Imahori Y., Kando M., Surf. Coat. Tech. 169, 604 (2003)
[16] Simor M., Rahel J., Vojtek P., Brablec A., Cernak M., Appl. Phys. Lett. 81, 2716 (2002)
[17] Cernak M., Rahel J., Kovacik D., Simor M., Brablec A., Slavicek P., Contrib. Plasma Phys. 44, 492 (2004)
[18] Cernak M., Černakova L., Hudec I., Kovacik D., Zahoranova A., Eur. Phys. J. Appl. Phys., 47, 22806p1 (2009)
[19] Černakova L., Stahel P., Kovacik D., Johansson K., Cernak M., In: TAPPI Press Staff (Ed.), Advanced Coating Fundamentals Symposium 2006, 8–10 Feb. 2006, Turku, Finland, TAPPI Press, Peachtree Corners, Georgia, USA, 2006, 7-14
[20] Bratskaya S., Marinin D., Nitschke M., Pleul Schwarz D., Simon F., J. Adhes. Sci. Technol. 18, 1173 (2004)
[21] Krishnan S., Gowthaman M.K., Misra M.C., Karanth N.G., J. Chem. Technol. Biotechnol. 76, 461 (2001)
[22] Vartiainen J., Rättoö M., Tapper U., Paulussen S., Hurme E., Polym. Bull. 54, 343 (2005)
[23] Yao K.D., Peng T., Goosen M.F.A., Min J.M., He Y.Y., J. Appl. Polym. Sci. 48, 343 (1993)
[24] Černakova L., Kunovská K., Klimová D., Mikulasova M., In: Dragčević Z. (Ed.), Book of Proceedings - 3rd International Textile, Clothing & Design Conference, 8-11 Oct. 2006, Dubrovnik, Croatia, Faculty of Textile Technology University, Zagreb, Croatia, 2006, 38-41
[25] Dutkiewicz J., US Patent 6197322 B1, 2001.03.06
[26] Shin Y., Yoo D.I., Jang J., J. Appl. Polym. Sci. 80, 2495 (2001)