Andrej Buček [1, 3*], Anton Popelka [2], Anna Zahoranová [1], Dušan Kováčik [1, 3], Igor Novák [4], Mirko Černák [1, 3]

[1] Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina F2, 842 48 Bratislava, Slovakia
*e-mail: bucek@gimmel.ip.fmph.uniba.sk

[2] Center for Advanced Materials, Qatar University, P.O. Box 2713, Doha, Qatar

[3] Regional R&D Centre for Low-Cost Plasma and Nanotechnology Surface Treatments, Institute of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

[4] Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia

Acrylic Acid Plasma Treatment of Polypropylene Nonwoven Fabric

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Abstract
Nowadays hydrogel materials are being used in medical practice for wound dressing purposes. Hydrogel/textile composites can be formed to increase the mechanical strength and handling capability of hydrogel materials. Nonwoven textiles are optional for such applications, however, it is often necessary to improve their surface properties. Here plasma activation/grafting of polypropylene (PP) nonwoven fabric with an acrylate layer to improve its adhesive properties is reported. A diaphragm discharge was used for the plasma treatment of the PP fabric. The discharge was burnt in a solution of acrylic acid (AAc), which resulted in a single step process of plasma activation and plasma grafting of the fabric. Results of wettability testing and ATR-FTIR measurements showed the existence of a thin poly(acrylic acid) (PAAc) layer grafted on the fabric surface. Peel strength measurements showed a 4.7 fold increase in the peel strength when compared with untreated PP fabric.

Key words: *plasma treatment, hydrogel, diaphragm discharge, plasma grafting, biocompatibility, peel strength.*

Introduction

Nowadays hydrogel materials are being used in medical practice for wound dressing purposes [1 - 3]. Hydrogels are polymeric materials that exhibit the ability to swell in water and to retain a significant fraction of the water within their volume, yet they do not dissolve in the water. They represent an attractive material for the engineering of biocompatible interfaces [4] e.g. for tissue engineering purposes [5]. A disadvantage of these materials represents the relatively poor mechanical strength, especially in the swelled state [6 - 8]. To solve this problem a hydrogel/textile composite can be formed to increase the mechanical strength and handling capability of the hydrogel [6 - 9]. Nonwoven textiles represent an option for such reinforcing of materials due to their low price and good mechanical properties [6, 8]. Standard polymers used to manufacture such fabrics, for example polypropylene (PP), exhibit very good physico-chemical stability. However, their chemical inertness leads to a rather low surface energy, which can represent a problem when making composites. Therefore there is often a need to improve their surface properties, which can be done through grafting of the surface of the polymer with an acrylate material [6,8]. In [6] the authors prepared poly(N-vinyl-2-pyrrolidone)/poly(ethylene glycol) (PVP/PEG) hydrogel membranes reinforced by methyl methacrylate (MMA) grafted PP fibres. The resulting tensile strength of the hydrogel membranes was 800% higher than that of the ones with non-grafted fibres. In [8] authors developed a multilayer membrane wound dressing system with the first layer consisting of a porous PP nonwoven fabric, and the second of N-isopropyl acrylamide (NIPAAm) or acrylic acid (AAc) grafted material to furnish a surface for the adhesion of the third layer, the chitosan and collagen. The NIPAAm and AAc grafting of the PP nonwoven was conducted in the presence of a benzoyl peroxide initiator in a nitrogen environment. An effect of accelerated wound healing was reported for both these systems.

Plasma activation of the PP nonwoven fabric prior to making the hydrogel/textile composites can also be used to improve adhesion between the hydrogel and textile [7, 10]. Plasma activation leads to the formation of radical sites on the polymeric surface, which promote hydrogel adhesion to the polymer [7,10,11]. Considering the commercial production of such hydrogel products, however, the cost effectiveness of the process should be taken into the account. Low-pressure plasma [7,10] has certain disadvantages from an industrial point of view concerning the use of expensive vacuum apparatus, the production speed and incorporation into existing production lines. The electron beam irradiation method used for MMA layer grafting on PP fibres [6] requires a technically com-

plicated setup. Atmospheric-pressure plasma treatment, in contrast with low-pressure plasma, typically does not need any vacuum system and has an advantage of higher production speeds due to the higher concentration of active species. This allows for further energy savings and easier incorporation into existing production lines, enabling continuous in-line processing. Furthermore plasma polymerisation and plasma grafting processes allow to replace the demanding electron beam setup [11, 12], providing plasma activation of the fabric and grafting of the acrylate layer in a single step process. Plasma also allows the polymerisation reaction without the use of additional chemicals like initiators or nitrogen atmosphere [8]. In [13] the authors used underwater capillary discharge for the deposition of poly(acrylic acid) (PAAc) on thin PP foils. The discharge was burnt in a solution of AAc, and the PAAc layer was deposited in a remote process by whirling the liquid stream emerging from the discharge around the PP sample. Here the use of diaphragm discharge for the treatment and grafting of PP nonwoven fabric is reported. To the best of our knowledge, this is the first time diaphragm discharge burning in AAc has been used for direct plasma deposition of a PAAc layer on the surface of a PP nonwoven, with the fabric being in direct contact with the plasma. Diaphragm discharge has already been successfully used for the treatment of fibres [14] and PP nonwovens [15]. In our work we adopted the single step approach for the treatment and grafting of PP nonwoven in diaphragm discharge burning in a solution of AAc. The resulting grafted PAAc layer was investigated by FTIR and peel strength measurements to asses its adhesion to the surface of the PP nonwoven fabric. In light of the results published in [6,8] the grafted PAAc layer could be potentially used as an interfacial layer between a hydrogel material and reinforcing fabric. We succeeded in showing that it is possible to graft a PAAc layer onto the surface of a nonwoven fabric from a stabilized, unpurged solution of AAc directly in the plasma conditions of a diaphragm discharge.

Experimental

Materials

Industrial spun-bounded PP nonwoven fabric (50 g/m^2) supplied by PEGAS NONWOVENS s.r.o. (Czech Republic) was used for the plasma treatment. A commercial stabilized AAc supplied by Merck Schuchardt OHG (Germany) was also used during the experiments. Moreover methylene blue (MB) was utilised for the dyeing of the textiles.

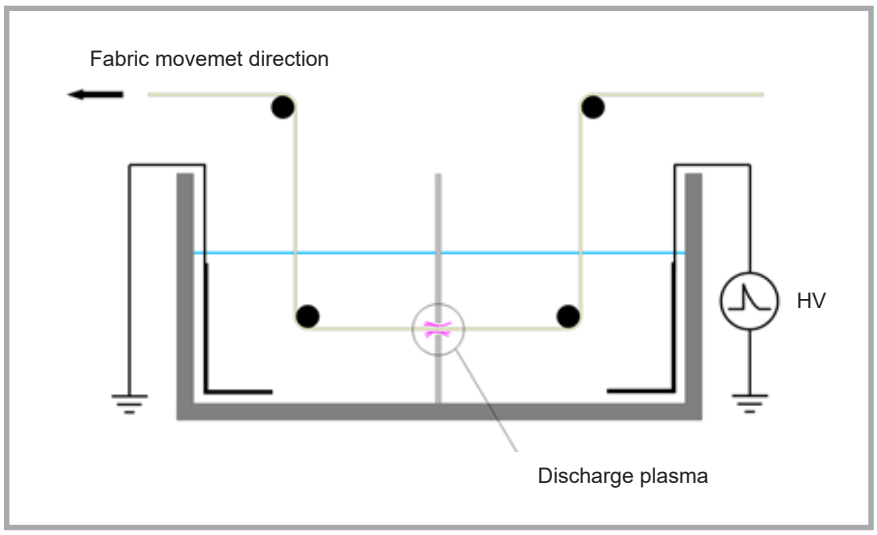

Figure 1. *Scheme of the diaphragm discharge reactor for the treatment of PP nonwovens.*

Plasma treatment

The working scheme of the reactor is depicted in ***Figure 1***. Diaphragm discharge burning in 20% v/v AAc solution was used for the treatment of the PP nonwoven. The thickness of the PMMA diaphragm was 3 mm, and the dimensions of the slit - 51 × 0.3 mm. The textile was treated in the form of 50 mm wide strips pulled through the discharge slit during the discharge operation. As the discharge power source, a thyratron source of pulsed high voltage with a pulse frequency of 100 Hz, peak voltage of 25 kV, pulse rise time of 75 ns and pulse half-width of 400 ns was used. The discharge power was approximately 20 W. The PP fabric treatment speed was set to 0.2, 0.3 and 0.6 mm/s, resulting in treatment times of 15, 10 and 5 s, respectively. In the case of the 0.2 and 0.3 mm/s treatment speeds, a piece of the textile was also treated without the operation of the discharge prior to starting it. The volume of AAc solution used in each treatment was 2 l.

Characterization

The wettability of the AAc-plasma treated PP fabric surface was examined through the dipping of the treated textile into an aqueous MB solution for ~3 s.

ATR-FTIR measurements were carried out using a Bruker Optics Vector 22 Spectrometer (USA), with additional accessories Pike MIRacle™ with Diamond/ZnSe crystal (45° incidence angle).

The adhesion between the PAAc layer and PP nonwoven substrate was characterised by the peel strength (force per unit width). A peel test was used for peel strength measurements of the adhesive joint formed of the grafted fabrics and poly(2-ethylhexyl acrylate) as an adhesive agent deposited onto polypropylene foil of 19 mm width. The measurements were performed as a 90° peel test at a rate of peel 300 mm per minute, using a 100 N universal INSTRON 4301 dynamometer (UK). Both ends of the fabric sample and PP foil with adhesive were firmly fixed into the dynamometer jaws to achieve an even tension distribution across the entire width. An average value of the peel strength and standard deviation was ob-

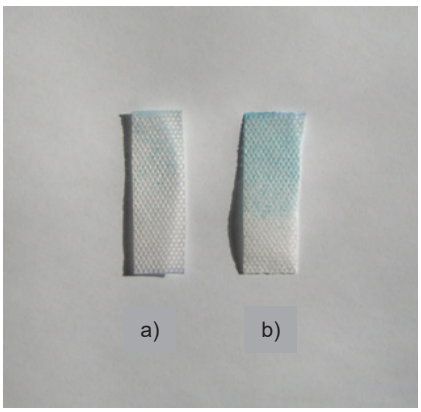

Figure 2. *Nonwoven treatment time 15 s: a) sample treated prior to starting the discharge, without plasma, b) AAc-plasma treated sample. There is no liquid spreading effect observable on the AAc solution treated fabric.*

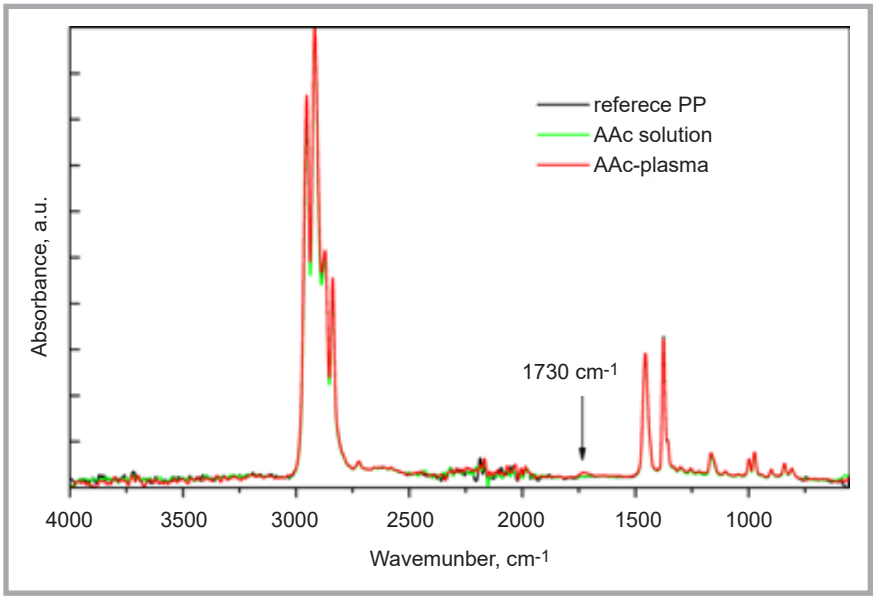

Figure 3. *ATR-FTIR survey spectra of PP nonwovens: reference PP – reference sample, AAc solution – AAc solution (prior to starting the discharge) treated sample, AAc-plasma – plasma treated (treatment time 15 s) sample.*

tained from 8 readings from different areas of each sample from 50 mm intervals of the peel extension, in which the peeling force achieved constant values. Each sample represented a strip of textile treated at a certain treatment speed, which was subsequently cut into 8 pieces and submitted to peel strength measurements.

Results and discussion

Results of the MB solution dipping of the treated textiles are shown in ***Figure 2***. From the picture it can be seen that the treatment of the PP textile by the action of the AAc-plasma led to the formation of a MB solution film (just) on the surface of the fabric, indicating its wettability. On the other hand, there is no observable liquid spreading effect on the fabric treated solely by the AAc solution, indicating the absence of any chemical modification of the PP surface solely by the activity of the AAc solution.

ATR-FTIR survey spectra of the treated fabrics are shown in ***Figure 3***. The superposed spectra show peaks between 2950 and 2800 cm^{-1}, corresponding to the various aliphatic CH stretching modes.

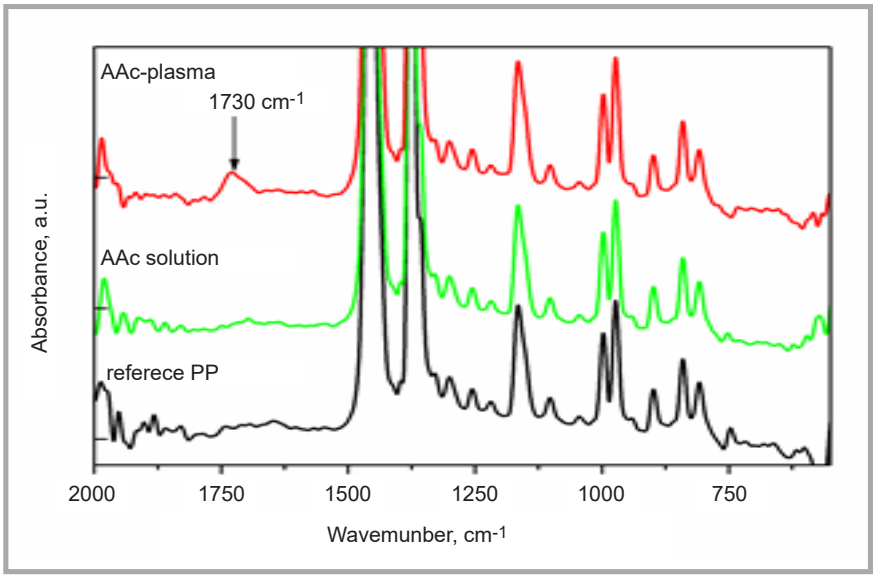

Figure 4. *Detailed ATR-FTIR spectra of PP nonwoven samples: reference PP – reference sample, AAc solution – AAc solution (prior to starting the discharge) treated sample, AAc-plasma – plasma treated (treatment time 15 s) sample. Spectra are shifted for better comprehensibility.*

The peaks near 1450 and 1380 cm^{-1} are the CH_2 and CH_3 deformation bands, respectively. The only apparent difference between the reference, AAc solution and AAc-plasma treated sample is represented by a small peak at 1730 cm^{-1}, attributed to the carbonyl C=O stretching band of the grafted PAAc layer (***Figure 4***). The ATR-FTIR spectra, together with the wettability properties of the treated fabric, indicate a thin layer of PAAc (itself a hydrogel) grafted onto the surface of the treated fabric. It is a well known fact that plasma activity on the surface of polymers produces radicals and various functional groups, and that electrical discharges in an aqueous environment produce •OH radicals [13]. The growth of the PAAc layer on the PP surface can be ascribed to the polymerization of the AAc on the radical sites, created on the PP surface, assisted by the activity of the discharge plasma (e.g. UV photons, locally increased temperature) [11].

In ***Figure 5*** are shown the results of peel strength measurements of the treated fabrics. From the picture it is apparent that the AAc-plasma treatment resulted in an increase in the peel strength measured, the improvement being more than 4.7-times better in the case of the 10 s treatment compared with the untreated reference PP fabric. It can also be seen that a certain saturation was reached at around 10 s, indicating times slightly below 10 s as sufficient for the treatment of the textiles. The slight decrease at 15 s could be considered well within the experimental error. The most probable explanation for the apparent existence of a plateau at treatment times of 10 s and 15 s is the observation of such a level of adhesive strength that exceeds the force necessary for the delamination of fibres from the surface of the fabric, as shown in ***Figure 6***. Thus the peel strength measurements showed very good adhesive properties of the AAc-plasma treated PP nonwoven fabric, making it potentially suitable for the use as a reinforcing material in hydrogel composites. The increased peel strength of the AAc-plasma treated PP nonwoven fabric can be ascribed mainly to the presence of carboxyl –COOH groups on the surface of the PAAc grafted PP.

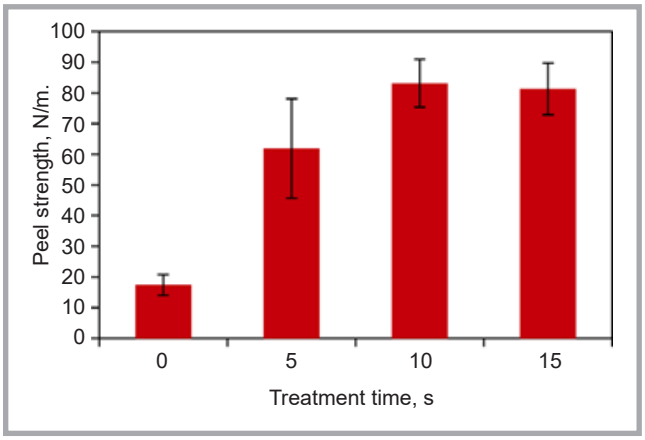

Figure 5. *Results of peel strength measurements of AAc-plasma treated PP nonwovens.*

Conclusions

PP nonwoven fabric was treated by diaphragm discharge burning in a 20% v/v solution of AAc. The treatment resulted in a more than 4.7 times increase in the peel strength in the case of the 10 s AAc-plasma treatment time when compared with the reference, untreated PP nonwoven fabric. The results indicate treatment times slightly below 10 s as sufficient for the treatment of the textiles. The apparent peel strength plateau at treatment times of 10 s and 15 s could, most probably, be ascribed to the adhesive strength exceeding the force necessary for the delamination of fibres from the fabric surface, leading to the actual delamination of fibres during the course of the measurement. The ATR-FTIR spectra and wettable properties of the treated fabric indicate a thin layer of PAAc grafted onto the surface of the PP nonwoven fabric. The results of the peel strength and ATR-FTIR measurements indicate that the treated PP nonwoven is potentially suitable for use as a reinforcing material in hydrogel composites.

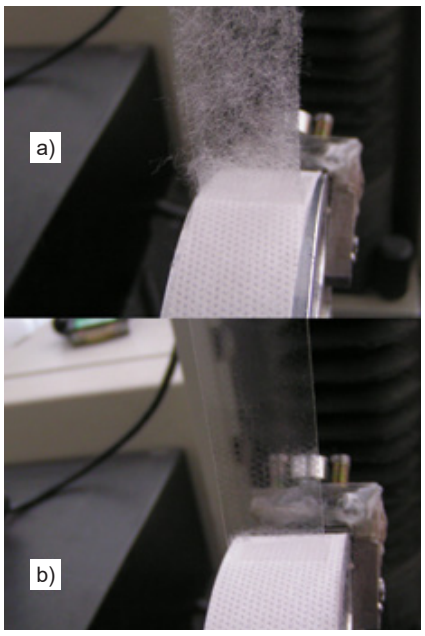

Figure 6. *Delamination of fabric fibres during the course of peel testing of AAc-plasma treated PP nonwoven fabric a) results of peel testing of untreated, reference PP nonwoven fabric b).*

Acknowledgements

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