PLASMA TREATMENT OF TEXTILES FOR PROMOTED ADHESION WITH NANOFIBROUS LAYER IN INDUSTRIAL PRODUCTION OF COMPOSITE STRUCTURES

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Abstract

Elementary nanofibrous layers show insufficient mechanical properties, especially tensile strength and abrasion resistance. In order to overcome these disadvantages, they are combined with carrier substrates and cover materials. A critical factor of the usability of nanofibrous layers in composite structures is to ensure sufficient adhesion between the carrier medium, the nanofibrous layer and the cover material. The adhesion between the layers is fundamental for the processability of the composite structures into the final products. To ensure sufficient adhesion of the individual components, additional adhesives are commonly used, which, in addition to the ecological burden, bring additional technological steps and costs to the production. One of the possibilities for achieving sufficient adhesion without the use of adhesives is the utilization of the physical component of adhesion by means of plasma activation of surfaces prior to electrospinning.

Keywords: Electrospinning, adhesion, nanofibrous layer, plasma treatment

1. INTRODUCTION

The goal of the research project was focused on the development of innovative nanohybrid structures, whereby the nanofibers were produced by electrospinning and deposited onto the carrier substrate.

The project had two main goals:

1) Ensuring the adhesion between the carrier substrate and the nanofibrous layer by the means of plasma surface modification

2) Preparation of hybrid structures based on textile components from various polymers with surface modification by the means of plasma treatment

The mechanical connection of textile laminates or multi-layer media is usually carried out by applying an adhesive solution onto the substrate before covering it with nanofibers, or by one-sided or two-sided coating with a powder adhesive. To ensure the adhesion of individual layers without the use of an adhesive component, the possibility of modifying the surface layers with plasma treatment was investigated. Research was carried out on the adhesion of contact surfaces of textiles made of different fibers, the surface of which was subjected to the effect of plasma, and the development of special hybrid textile structures. Carrier textiles in the form of woven fabric, knitted fabric and non-woven fabric were used as the carrier substrate.

The effect of plasma treatment dwells in the creation of active particles (ions, excited atoms, radicals, etc.). In our case, the active particles of the working gas created in the discharge caused specific reactions on the polymer surface, where new functional groups were induced to polymer chain (especially hydroxyl groups). This can lead to change in the behavior of surface (i.e. from non-polar to polar, from hydrophobic material to hydrophilic), or can generally improve the amount of chemical and physico-chemical interactions between interacting surfaces leading to better adhesive strength and increase in the wettability.

2. EXPERIMENTAL

2.1. Selection and production of carrier and cover layers for combined nanohybride textile structures

For the carrier substrates, two types of knitted fabrics (weft-knit and warp-knit), four types of woven fabrics (from monofilaments and multifilaments) and five types of nonwoven textiles (spunbond and melt-blown) were produced. In terms of material composition, polyamide, polyester, polypropylene and polyethylene fibers were selected. **Table 1** provides an overview of selected textiles and their material composition.

A spunbond nonwoven textile of mass per unit area weight of 20-30 $g \cdot m^{-2}$ made of 100% polypropylene was used as the covering layer for the production of final layered textile structures with nanofibers.

Table 1 List of selected textile substrates

Sample	Description	Material (wt%)
1	Knitted fabric, weft-knit, 50 $g \cdot m^{-2}$	100 % polypropylene
2	Fabric, plain weave, 65 $g \cdot m^{-2}$	100 % polypropylene
3	Nonwoven, melt-blown, 25 $g \cdot m^{-2}$	100 % polypropylene
4	Nonwoven, bicomponent, spunbond, 25 $g \cdot m^{-2}$	70 % polypropylene (core) 30 % polyethylene (shell)
5	Nonwoven, melt-blown, 35 $g \cdot m^{-2}$	100 % polypropylene
6	Fabric, plain weave, 65 $g \cdot m^{-2}$	100 % polyamide
7	Nonwoven, bicomponent, spunbond, 25 $g \cdot m^{-2}$	50 % polypropylene (core) 50 % polyethylene (shell)
8	Nonwoven, bicomponent, spunbond, 25 $g \cdot m^{-2}$	80 % polyethylene terephthalate (core) 30 % polyethylene (shell)
9	Knitted fabric, warp-knit, 70 $g \cdot m^{-2}$	100 % polyamide

2.2. Selection and production of nanofibrous layers

Selected nanofibrous layers based on polyamide 6 and polyvinylidene fluoride were deposited onto carrier substrates. The deposition of the nanofibrous layer by electrospinning was performed on a Nanospider™ NSLAB 500 machine (Elmarco, Czech Republic) in an arrangement with a short wire electrode.

Electrospinning conditions for polyamide 6: 55 kV applied high voltage, 140 mm electrode-to-collector distance, 6 rpm spinning electrode rotation speed. The nanofibers were applied from a 14 % solution of polyamide 6 prepared from the polymer ULTRAMID B24 (BASF) dissolved in a 2:1 mixture of concentrated acetic acid and formic acid in one layer at a textile feed speed of 25 $mm \cdot min^{-1}$.

Electrospinning conditions for polyvinylidene fluoride: 55 kV applied high voltage, 140 mm electrode-to-collector distance, 6 rpm spinning electrode rotation speed. The nanofibers were applied in one layer at a textile feed speed of 60 $mm \cdot min^{-1}$. Solution composition was 6.75 g of polymer in 50 ml dimethylacetamide with addition of 1 ml tetraethylammonium bromide.

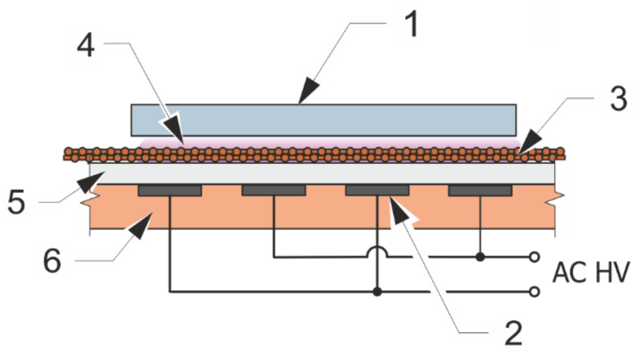
2.3. Research and development of combined textiles structures (nanofibrous layers on carrier substrates)

The aim of the work was preparation of textile composites consisting of carrier substrates made of nonwoven textiles, woven fabrics and knitted fabrics, nanofibrous layers and covering nonwoven textiles. Research into the effect of plasma pretreatment of carrier substrates on adhesion of nanofibrous layer was crucial. Adhesion between nanofibers and carrier depends on both materials and is generally low. For applications where high adhesion is required, glue is added to the product, which practically always leads to a deterioration in breathability. The goal was to achieve sufficient adhesion between the supporting substrate and the nanolayer without the use of any auxiliary adhesive (glue) while barrier functions and improved breathability are preserved.

For the intended purpose, the effect of plasma treatment of carrier substrates with different compositions was tested. The effect of Diffuse Coplanar Surface Barrier Discharge (DCSBD) and Rolling Surface Barrier Discharge (R-SBD) generated plasma in comparison with materials without treatment was investigated.

DCSBD treatment [1]

The plasma was generated under the discharge conditions of 400 W, 15 kHz, air and at atmospheric pressure. The duration of the plasma treatment ranged from 10 to 60 sec, depending on the type of material. The requirement of complete wetting was used as a measure of sufficient plasma treatment - a drop of distilled water with a volume of 5 μl placed on the surface of the treated fabric had to be absorbed into the fabric immediately. The time between the DCSBD treatment and the application of the nanofibrous layer was never longer than 60 min. **Figure 1** shows the DCSBD scheme and the discharge itself during processing. The purpose of this treatment is to create non-specific chemically active or polar groups on the surface of the textile, increasing the chemical activity and free surface energy of the material (wettability).



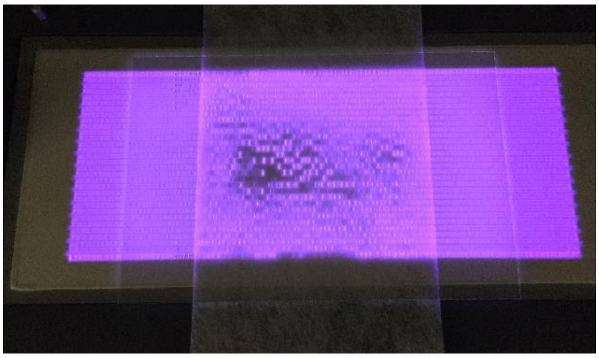
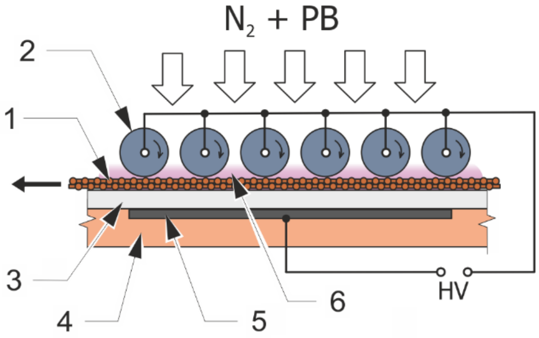


Figure 1 Plasma treatment of textiles using DCSBD. 1 – glass pressure block, 2 – coplanar electrodes, 3 – textile treated with plasma, 4 – discharge plasma, 5 – ceramic electrical barrier, 6 – cooling liquid

R-SBD treatment [2]

The plasma was generated under conditions of discharge of 130 W, 8 kHz, in a mixture of nitrogen (6 $l \cdot min^{-1}$) and propane-butane (0.6 $l \cdot min^{-1}$), at atmospheric pressure (see **Figure 2**). The textile was guided through the discharge space by a simple winding device. The duration of plasma treatment was 30 seconds. The purpose of the treatment was to create a thin layer of a non-specific plasma polymer on the surface of textile, with a significant representation of amino groups. A well-known property of this polymer is the formation of a strongly hydrophilic (water-wettable) surface, which is stable over time. A 5 μl drop of distilled water placed on the surface of the treated fabric immediately soaked into the treated fabric. The time between this plasma treatment and the application of the nanofibrous layer was 3-4 days.



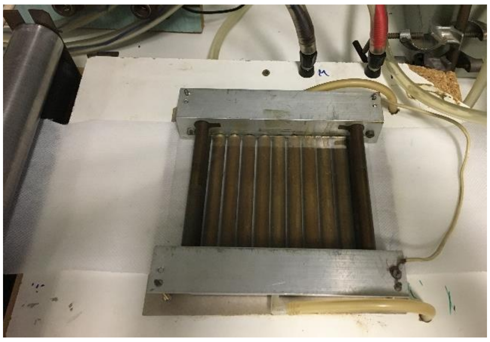


Figure 2 Plasma treatment of textiles using R-SBD. 1 – textile treated with plasma, 2 – roller electrodes, 3 – mica electrical barrier, 4 – cooling liquid, 5 – collection electrode, 6 – discharge plasma

2.4. Testing

Important part of the work was research and development of testing methodology and evaluation of nanofibrous structures. The samples were subjected to microscopic analyses (light microscopy, scanning electron microscopy – SEM) in order to determine the structure of the substrates and nanofibrous layers, to evaluate the condition of the surfaces after the separation of the nanofibrous layer. With the help of elemental analysis (using EDS - electron dispersion spectrometry) the composition of nanofibers was verified. Nanofiber mass per unit area was determined by gravimetry. The most important area of testing was adhesion tests of the nanofibrous layer before and after plasma treatment of the substrate. The evaluation of the tear-off behavior was carried out using modified method based on the adhesive tape measurements, the testing and determination of the peel force was done using a constant rate of extension (CRE) machine with 10 N force sensor.

Loop test

Tests were performed by measuring the force required to tear the deposited nanofiber layer from an area of 25 mm × 25 mm. A TA.XTplusC Texture Analyser (Stable Micro Systems, UK) with a 5 N load cell was used for the measurement. A method used for these measurements called "loop test" is a modified test based on the adhesion measurement for the adhesive tapes. The sample with cut 25 mm × 25 mm sections was glued to a plastic holder with double-sided adhesive tape on the side of the substrate, which was then fixed in the lower jaws of the measuring device. A 10 cm long test adhesive tape with sufficiently high adhesion (in accordance with ISO 2409:2003) was placed in a controlled manner into the upper movable jaws so as to form a loop (see **Figure 3**). By keeping the same length (10 cm) and the shape of the loop, a reproducible pressure force of the test adhesive tape can be achieved. The tape was not pressed to the sample in any other manner. Subsequently, the jaws were moved away, and the value of the applied force vs. jaw position was recorded. The speed of movement of the jaw head was 5 mm·s^{-1}. The trigger force was 1 g (i.e., 10 mN). As the parameter for comparison, the area under the obtained curve corresponding to the mechanical work necessary to tear off the layer W (N·mm) was calculated. A minimum of 10 measurements were carried out for each sample. Other evaluated parameters were average force (F_{avg}) and maximal force (F_{max}).

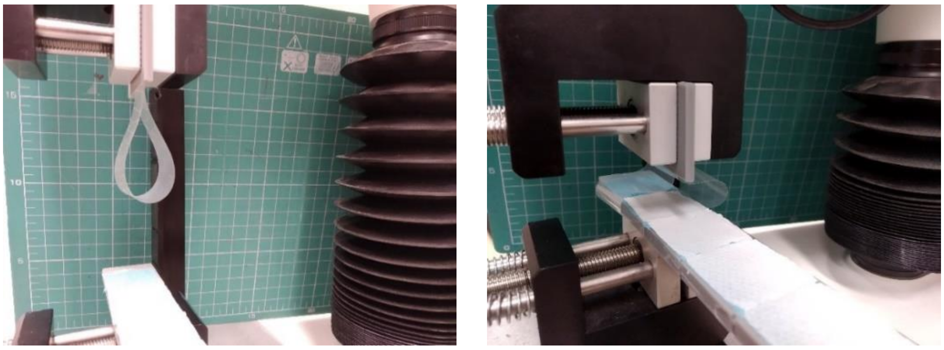


Figure 3 Illustrative photo of the adhesive force measurements by the loop test method

2.5. Verification of plasma treatment application in production conditions

The pilot test was carried out at NanoMedical s.r.o. using spinning machine Nanospider™NS 8S1600U, see **Figure 4**. Polyamide 6 based nanofibers were deposited onto a 100 % polypropylene spunbond nonwoven fabric substrate that had been plasma treated using DCSBD method at four winding speeds. **Table 2** lists the production parameters.

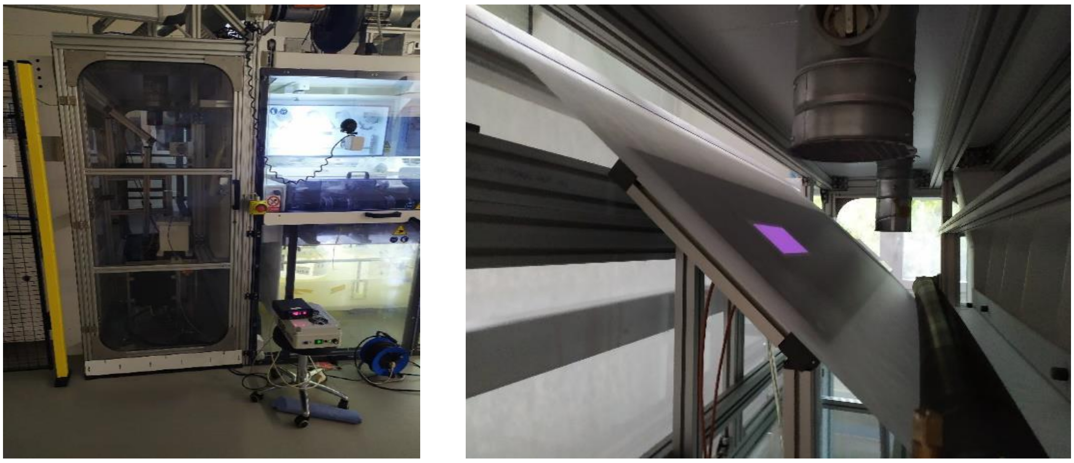


Figure 4 Integration of DCSBD plasma system into the production line

Table 2 Technical parameters of plasma treatment in production conditions

Sample	Voltage on the spinning electrode	Winding speed	Plasma exposure time
L1S7711	75 kV	2.42 $m \cdot min^{-1}$	1.98 s
L1S7712	65 kV	1.80 $m \cdot min^{-1}$	2.67 s
L1S7713	55 kV	1.23 $m \cdot min^{-1}$	3.90 s
L1S7714	45 kV	0.82 $m \cdot min^{-1}$	5.85 s

3. RESULTS

Graph below (see **Figure 5**) shows the absolute difference in the mechanical work (ΔW) necessary to tear off the layer between samples without treatment and plasma treated samples. Results of loop tests for production trials are displayed as comparison of parameter W between untreated and treated samples (see **Figure 6**).

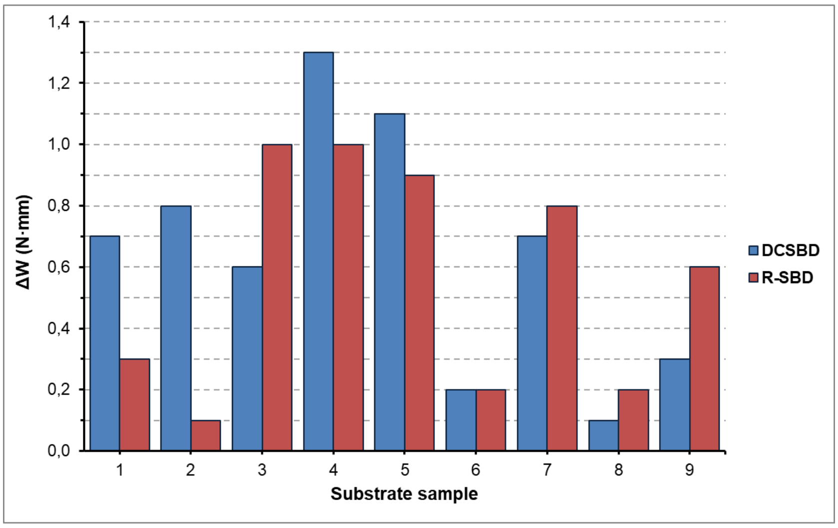


Figure 5 Absolute difference in the mechanical work necessary to tear off the polyamide 6 based nanofibrous layer between substrates without treatment and plasma treated samples

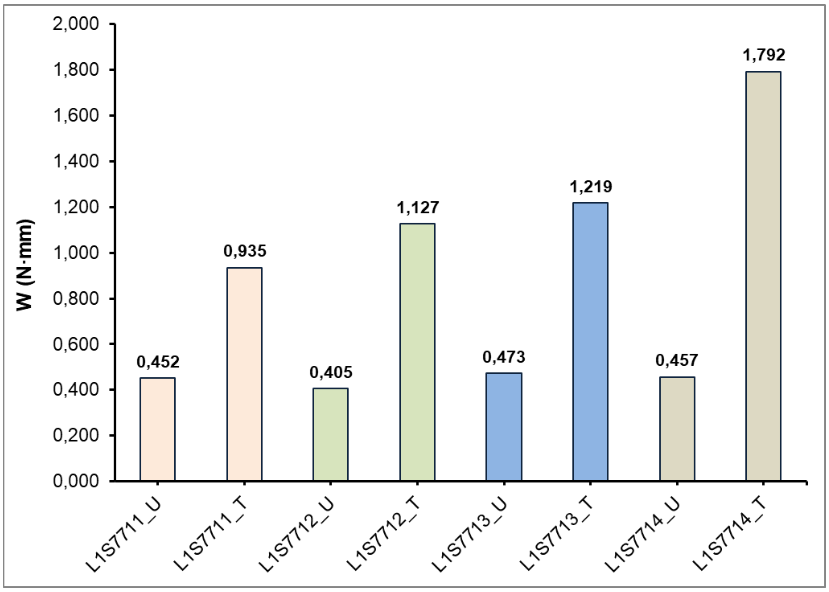


Figure 6 Comparison of work necessary to tear off the nanofibrous layer from untreated (left column) and plasma treated samples (right column of the same color) obtained in the production line trials

4. CONCLUSION

Based on the results of adhesion testing it can be said that both types of tested plasma treatments lead to an improved adhesion between tested textile substrates and nanofibrous layers. The choice of the most suitable type of plasma treatment must therefore be decided by technological aspects, such as the speed of plasma treatment, time stability of the effect, operational requirements, or energy and price requirements. The R-SBD treatment offers a slightly better energy balance (130 W vs 400 W) and temporal stability of the effect achieved (weeks vs days), but requires nitrogen gas management, which increases the operating costs of the treatment. With DCSBD, this problem disappears, because the DCSBD discharge works in a normal atmosphere (air). For both plasma generators, it is necessary to take into account the removal of gaseous products. System for DCSBD plasma treatment of carrier substrates was successfully integrated into industrial line for nanofibrous layer production. Achieved improved adhesion allowed transport and further processing of textiles with nanofibrous layer without any need for additional adhesives.

ACKNOWLEDGEMENTS

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