FAST AND EFFICIENT SURFACE TREATMENT FOR NONWOVEN MATERIALS BY ATMOSPHERIC PRESSURE PLASMA

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Abstract:

Plasma treatments can be used for the nano-scale surface modification of different materials including nonwovens. Penetration of plasma into solid matter is very limited, but it can penetrate into porous structures. Therefore plasma can be used to modify not only the outer surface, but also the surfaces of fibres within and the other side of the porous structure of nonwoven material. The purpose of this study was to examine the feasibility of continuous atmospheric plasma treatment for the modification of porous nonwoven materials. Firstly, the penetration of plasma through layered, porous samples, and secondly, the effect of the plasma exposure time on the surface properties and mechanical properties of the samples were studied. We found that the plasma penetrated through three nonwoven layers. It also seemed that the plasma was retained inside the samples for a while after initial exposure, thus increasing the effective exposure time. An increase of exposure time further by controlling line speed did not have significant influence on the efficiency of the treatment. The mechanical properties of the material were not prominently affected by the treatment. Our results suggest that it is possible to conduct two-sided plasma treatment on porous nonwoven materials as a continuous process with a speed feasible to be combined with conventional textile processing.

Key words:

Atmospheric pressure plasma, penetration, nonwoven, contact angle of water, tensile strength.

Introduction

Plasma treatment is commonly used for surface activation and modification of different materials including textiles. Plasma is an outwards neutral, partially ionized gas, the composition of which depends on the gas used in the formation of plasma. Gas molecules are ionized in an electric field through electron impacts, and the ionized, highly reactive species, such as ions, electrons and radicals, modify the surface of the substrate material. The textile applications of plasma include, for example, sterilization [7, 18], wettability and hydrophobicity [2, 3, 22], dyeability enhancement [24], flame retardant finishing [1, 15, 19], and antimicrobial properties [8]. Some of these treatments can be conducted using common gas plasma, but some of them utilize specific chemicals in the formation of plasma. Cold plasma technologies, the temperatures of which are suitable for textile materials, can be divided into low-pressure and atmospheric plasmas, the first of which is more studied in the literature, but the latter have gained more and more interest in recent years. The advantage of atmospheric plasma is that it is generated at atmospheric pressure and it does not need any vacuum chambers or pumps like low-pressure plasma, and this enables continuous plasma processing. The use of chemical plasmas is easier in low-pressure plasma systems, but with proper encapsulating and ventilation systems they can also be used in continuous equipment [16, 21].

It is believed that plasma only modifies the surface properties of flat substrate without affecting the bulk properties. The penetration of plasma into solid material is very limited, typically confined to less than 100 nm [4]. Textile materials, however, can be very porous and their specific surface area is generally high. Therefore, plasma can penetrate deeper into such a porous structure of nonwovens, compared, for example, to more dense structure of coated fabric or compact cloth structure of woven fabric, see Figure 1. The penetration of plasma into porous structures may enable the treatment of surfaces of individual fibres also inside the nonwoven structure.

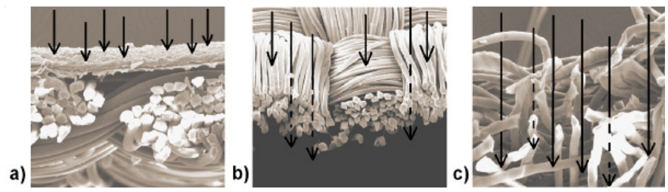


Figure 1. Different substrate structures and penetration of plasma. a) Woven fabric with membrane coating does not promote penetration. b) Compact cloth structure of woven fabric also limits the penetration. c) Open, porous structure on nonwoven fabric enables the plasma penetration.

Poll et al. [14] noticed that the effect of exposure to low pressure plasma penetrated through the whole thickness of a layered cotton fabric sample, if the treatment time was sufficient and pressure optimal. Under optimal pressure, the mean free path of gas particles remained greater than the typical pore size of the fabric structure. Similar penetration, however, was not noticed with atmospheric plasma. De Greyter et al. [5] have also studied penetration of a dielectric barrier discharge plasma into textile structures. They conducted their experiments at medium pressure. Wang and Qiu [26], on the other hand, observed that, depending on the process parameters, the effect of the atmospheric plasma treatment of one side could also be seen on the reverse side of the woven wool fabric. Furthermore, Wang et al. [25, 27] have treated polyester fabrics with atmospheric plasmas. They observed that plasma penetrated eight layers of woven polyester fabrics with pore sizes of 200 µm [27]. Their other finding was that the effect of the plasma decreased linearly with the fabric layer number [25]. Penetration of plasma into cellulose-based filter paper has been discussed by Mukhopadhyay et al. [13]. They noticed that longer exposure times led to higher penetration of plasma into layered filter paper, but they concluded that further studies are needed in order to control the penetration of plasma into such materials.

In our earlier trials [23] we have noted that atmospheric pressure plasma can penetrate and have a measurable effect on the surface properties of multilayered nonwoven samples. Plasma treatments of nonwoven materials have also been conducted by Krentsel et al. [10, 11]. They studied the penetration of plasma into layered samples of porous nonwoven media using a low-temperature cascade arc torch. The use of fluorinated gas had the highest fluorination effect on the second layer than the first layer [10]. Furthermore they noticed that the penetration mode varied depending on the penetration depth; the flow-controlled penetration (permeability) was more pronounced for the outer and diffusion-controlled within the inner layers [11].

Yu et al. [28] noticed a sharp decrease in water contact angle during the first minute of plasma treatment, while prolonged excitation did not cause further changes. From these findings one can conclude that most of the surface reactions occur during the first moments of plasma treatment. Moreover according to the studies of Kwon et al. [12], surface modification of polypropylene film by atmospheric pressure plasma is more lucrative in a relatively short plasma treatment time.

Plasma treatments are used to modify surface properties, but it is also known that plasma treatment might etch the surface of the treated material [20]. This might weaken the mechanical properties of the material. Yu et al. [28] have treated a polypropylene micro porous membrane with low-pressure air plasma. They found that both the tensile strength and the rate of elongation decreased with prolonged plasma treatment time. The weakening rate was fast in the beginning of exposure, but it became hindered with time. Ren et al. [17] did not notice any significant difference in the tensile strengths between untreated and helium/oxygen atmospheric plasma treated polyethylene single fibres. On the other hand, Hwang et al. [9] have studied the effect of helium atmospheric pressure plasma treatment on the low-stress mechanical properties of polypropylene nonwoven fabrics, and they noticed a significant increase in the tensile strength of the treated nonwovens with increased exposure time. They explain it in terms of a combination effect of increased fibre to fibre friction by etching and the cross-linking reaction between molecules.

The purpose of this study was to examine the feasibility of continuous atmospheric plasma treatment for surface modification of porous nonwoven materials. We studied the penetration of plasma into a nonwoven structure in order to determine if multiple layers of nonwovens, or at least both sides of one nonwoven sample, can be treated simultaneously. This was accomplished by conducting the treatments on single and layered nonwoven samples. The properties of different layers as well as of base material below the samples were studied. Some of the plasma treatments were also conducted using different line velocities in order to also examine the effect of the exposure time on the effectiveness of the treatment. The atmospheric plasma treatment was carried out continuously (roll to roll) at normal atmosphere (air). Helium and argon were used as the treatment gases. Corona treatment was used as a comparison to the plasma treatments. Corona treatment is a traditional surface treatment method (also plasma) for plastic films, papers, nonwovens, etc. and it is also carried out at normal atmosphere without any treatment gases. Contact angle measurements and SEM-analysing were used in order to study the effects of plasma for surface properties, but also the tensile properties of the nonwoven samples were measured in order to determine if the bulk properties, more precisely the strength, remained intact.

Experimental

Materials

The polypropylene nonwoven (Suominen Nonwovens Ltd.) was of the unfinished spunbonded type, having a basis weight of 45 g/m2 and thickness of 0.56 mm. The porosity of the nonwoven sample, calculated based on basis weight and thickness of the web and density of polypropylene (around 0.91 g/cm3), is over 90 %. The appearance of the nonwoven material sample can be seen from the SEM-image of the nonwoven in Figure 2.

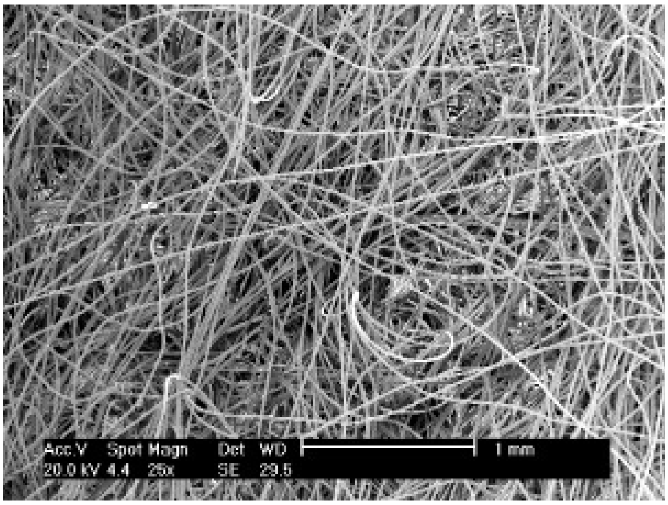


Figure 2. Appearance of the nonwoven fabric.

When studying the penetration of plasma treatment, in addition to single samples layered nonwoven samples were also used. Sheet samples (A4) were attached onto the surface of reeled base material, low density polyethylene (PE-LD) coated paperboard, before the plasma treatments. Layered samples for plasma penetration tests were stacked together before attaching to the base. The nonwoven layers were labelled as shown in Figure 3.

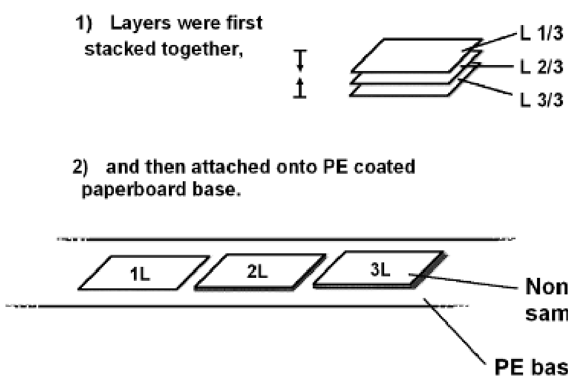
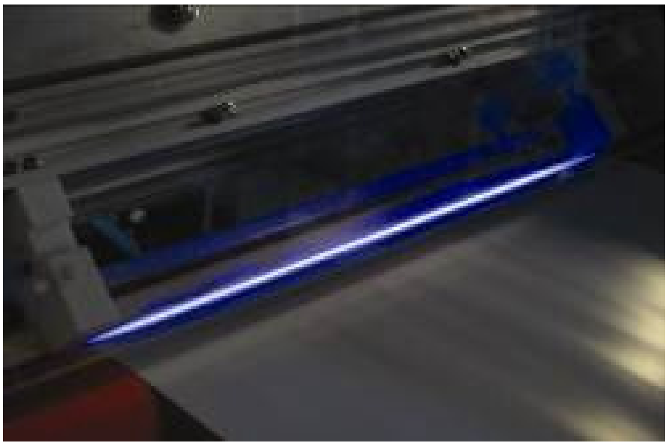


Figure 3. Sample preparation for plasma treatments in a continuous line.

Plasma Treatments

Plasma and corona treatments were performed at the pilot line of TUT/PCT. The corona treatment was performed using Vetaphone, Corona-Plus system, 4 kW power supply (AC-exited). The atmospheric plasma treatment (APT) unit utilised in this study was specially designed for surface treatment of various continuous substrates, such as plastic films, papers, laminates, nonwovens, etc., at normal atmosphere. The power supply of APT unit is provided by Vetaphone, Corona-Plus system, 2 kW power supply (AC-exited). All the treatment parameters are shown in Table 1.The penetration of plasma was studied using helium and argon atmospheric plasmas, and corona was used as a comparative method. The effect of exposure time was studied with argon plasma and corona. All the penetration studies were conducted with a line speed of 50 m/min, which was considered to be the basic treatment. When studying the effect of exposure time during treatment, different line speeds were used, keeping other parameters fixed. Besides the speed of the basic treatment (50 m/min) half speed (25 m/min) and double speed (100 m/min) were also used. For some samples double speed treatment was conducted twice (2x100 m/min) in order to obtain the same total exposure time as with basic treatment.



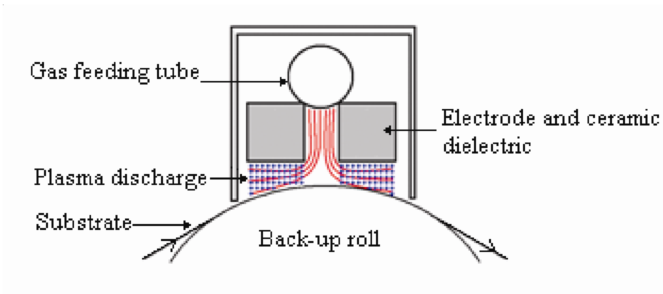


Figure 4. An atmospheric plasma treatment unit in operation (top) and a simplified sketch of an atmospheric plasma treatment unit (bottom).

De Greyter et al. [6], for example, have shown that the surface oxidation of PP proceeds faster in an argon discharge than in a helium discharge, because of the three times higher electron density of argon plasma. Because of the higher electron density of argon plasma, in this study, the gas feeding rate of helium was three times higher compared to argon plasma.

The atmospheric plasma treatment (APT) unit operates continuously (roll to roll) at normal atmosphere (air). The atmospheric plasma is generated using a dielectric barrier discharge. The discharge is generated between two dielectric electrodes and a backup roll (Figure 4). The treatment gas (in this study helium and argon) is fed between the two electrodes into the discharge where the treatment gas breaks down due to the high voltage electric field, resulting in non-equilibrium plasma rich in excited and electronic states. The treated substrate is fed through the plasma at controlled line speed. Atomic oxygen, ions, electrons and OH radicals, present in the plasma discharge, create radicals on the polymer surface, which react with oxygen species, establishing oxygen containing functional groups on the polymer surface. Unique electrode design, suitable power supply, impedance matching and controlled gas flow, help to minimise or eliminate the filamentary discharges, which are typical for a corona discharge.

The efficiency value E (Wmin/m^2) of plasma and corona treatment is evaluated with the following formula:

$$E = \frac{P}{l \cdot v} \qquad (1)$$

where P (W) is the output of power supply, l (m) is the width of the electrodes and v (m/min) is the line speed. The output of power supply of the corona and plasma treatments was measured during the trials. The efficiency values of the corona and plasma treatments were adjusted to the same range. The amount of treatment gases were set to the level where the saturation in the wetting (contact angle of water) had been observed in pre-tests. The treatment width of the corona and plasma differs, but the cross profile of the electrode is the same, 15×15 mm. In addition, the distance between the electrodes and the backup roll is 2 mm for the corona treatment and 1 mm for the plasma treatment.

Analyses

The surface morphology of the nonwoven samples was examined using a Philips XL-30 scanning electron microscope (SEM). Before the SEM observation, the nonwoven samples were coated with a vapour deposited thin layer of gold to improve the surface conductivity. The average in-plane pore size was determined from SEM images by measuring the largest dimension of 300 randomly selected pores using UTHSCSA Image Tool 3.0.

Table 1. Treatment parameters of atmospheric plasma and corona treatment.

Treatment type	Power output	Speed	Treat. width	Efficiency value	Gas feed	Frequency	Exposure time
Corona	1300 W	25 m/min	500 mm	104 Wmin/m^2	-	24.8 kHz	0.12 s
Corona	1300 W	50 m/min	500 mm	52 Wmin/m^2	-	24.8 kHz	0.06 s
Corona	1300 W	100 m/min	500 mm	26 Wmin/m^2	-	24.8 kHz	0.03 s
Helium plasma	615 W	50 m/min	380 mm	32.4 Wmin/m^2	90 l/min	27.5 kHz	0.06 s
Argon plasma	525 W	25 m/min	380 mm	55.3 Wmin/m^2	30 l/min	28.2 kHz	0.12 s
Argon plasma	525 W	50 m/min	380 mm	27.6 Wmin/m^2	30 l/min	28.2 kHz	0.06 s
Argon plasma	525 W	100 m/min	380 mm	13.8 Wmin/m^2	30 l/min	28.2 kHz	0.03 s

The effect of plasma on the nonwoven and base material was studied by determining the contact angles. The contact angles of the distilled water were measured with a Pocket-Goniometer PG2-3. The volume of the drop placed with a micro syringe on the surface was 4 µl. The average value was obtained from ten measurements tested for each sample. The purpose of contact angle measurements conducted on the nonwoven layers was to compare changes in surface properties (indicated by contact angles of water) after different treatments, not to quantify real contact angles. The penetration of the plasma through the layered samples was also studied by measuring the contact angles of the base material, since the measurement of the smooth surface is easier than that of a porous nonwoven web. If the properties of the PE surface are changed below the nonwoven sheets, it can be assumed that the plasma has penetrated through the nonwoven layers on the top of it.

Changes in mechanical strength were evaluated by the tensile strength test. Tensile strength tests of nonwovens were conducted according to ISO 9073-3 "Textiles - Test methods for nonwovens - Part 3: Determination of tensile strength and elongation". The maximum breaking strength and elongation of the test piece at the maximum breaking strength were measured for machine- and cross-machine directions of untreated and argon plasma treated nonwoven samples by using a Testometric with a 250 kg load cell at a constant rate of 100 mm/min. Instead of the standard 200 mm distance between jaws in the tensile testing machine, we used 100 mm. From untreated and argon plasma treated nonwoven samples 6-10 samples were tested for each condition.

Results and Discussion

Pore Size of Nonwoven Fabric

The diameter of the individual fibres in the nonwoven is (15 ± 0,5) µm and mean pore size about 60 µm. The distribution of pore size of the nonwoven (maximum diameter distribution) can be seen in Figure 5.

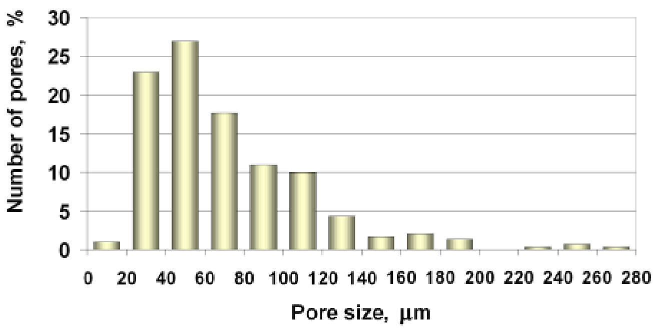


Figure 5. Pore size distribution of the nonwoven.

Penetration of Plasma

The penetration of the plasma through the layered samples was studied by measuring the contact angles of the different sample layers as well as the base material, the smooth polyethylene (PE-LD) surface, below the layered nonwoven sheets.

The effect of helium and argon plasma treatments on the different layers of nonwoven can be seen from contact angle measurement results, which are shown in Figures 6 and 7, respectively. The effect of plasma treatments extended to all layers, being strongest in the uppermost layers, and was seen to decrease with the number of layers. This is consistent with earlier findings [25]. The choice of plasma gas did not have any major effect, but some differences, however, could be seen. Argon did not seem to be as strongly penetrating to the lower layers compared with helium, since the contact angle of the second and third layers were at the same level. The greater effective penetration of helium can be explained, for example, by the smaller molecule size. If chemical plasmas with larger molecular sizes are to be used, the plasma penetration may not extend as deeply into the sample structure as for monatomic species.

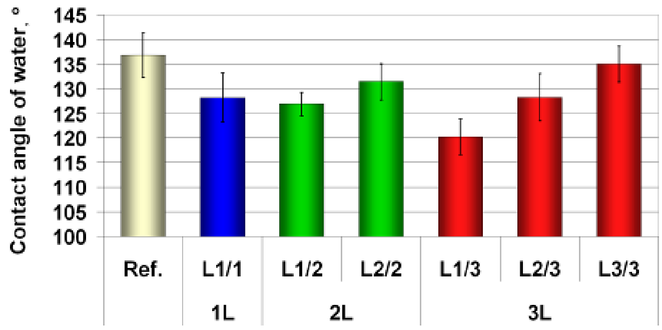


Figure 6. Contact angles of helium plasma treated nonwoven layers (L), measured two weeks after the treatments.

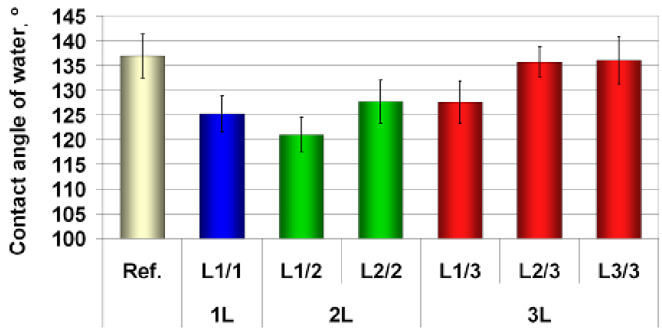


Figure 7. Contact angles of argon plasma treated nonwoven layers (L), measured two weeks after the treatments.

The contact angles on the corona treated samples are shown in Figure 8 for comparison. The effect of the corona is smaller than that of the plasmas, even though the energy per area was higher in the corona treatments. The differences between different layers were not as clear as in the case of the plasma treatments. It can still be seen, however, that the effect of the treatment has also penetrated to the innermost layers.

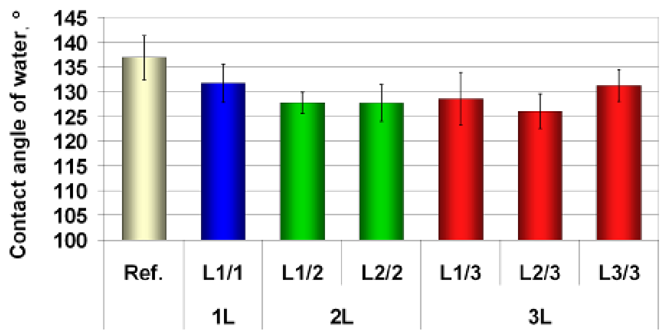


Figure 8. Contact angles of corona treated nonwoven layers (L), measured two weeks after the treatments.

The penetration of the plasma through the layered samples can also be clearly seen from measurements carried out on the base material (Figure 9). The contact angles on the base

(PE-LD) after all treatment conditions (78.3° - 84.4°) were clearly lower compared to those of the untreated base surface (99.3°). In many cases the presence of nonwoven even increased the effect of the plasma on the base compared to an uncovered treated base. The reason for this is assumed to be that the nonwoven may retain plasma gas longer in the vicinity of the base surface, and thus increase the effective plasma exposure time. This hypothesis is supported by the finding of Krentsel et al. [10], who showed that the effect of plasma was higher in the second layer relative to the first layer. Again, we could see the difference between the plasma gases. When the base surface was covered with three layers of nonwoven the effect of helium plasma was stronger than the effect of argon. This suggests once again that argon cannot extend as deeply as helium.

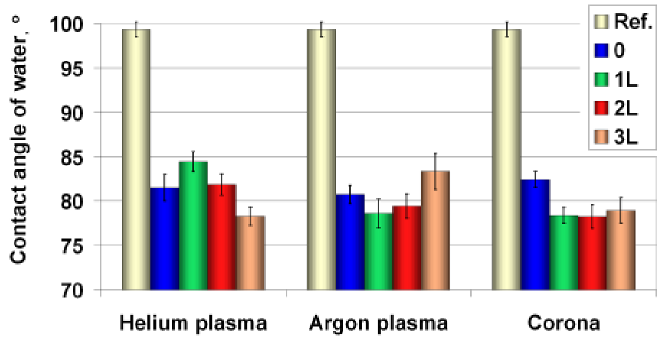


Figure 9. Contact angles of the base material surface (PE-LD) after the plasma and corona treatments measured from below different numbers of nonwoven layers (0-3 L), measured one day after the treatments.

Effect of Exposure Time of Plasma

Different treatment speeds were used to evaluate the effect of the exposure time of the plasma. The contact angles of the samples treated with different speeds are presented in Figure 10. Variation in exposure time did not have any large effect on the surface energy of the used nonwoven. The average contact angles of water for nonwovens treated with different speeds with argon plasma varied between 126° and 130°, while the contact angle of the untreated sample was 137°. When half speed (25 m/min) was used, argon plasma had on average, a slightly greater effect (contact angle decreased more) and double speed (100 m/min and 2 x 100 m/min) slightly smaller effect on the surface compared to the results of basic treatment speed (50 m/min). With corona treatments all the variations to the basic treatment yielded an increased effect on the contact angle, so the trend seen in the case of argon was not seen with corona. The effect of the change in exposure time resulting from different line speeds seemed to be negligible.

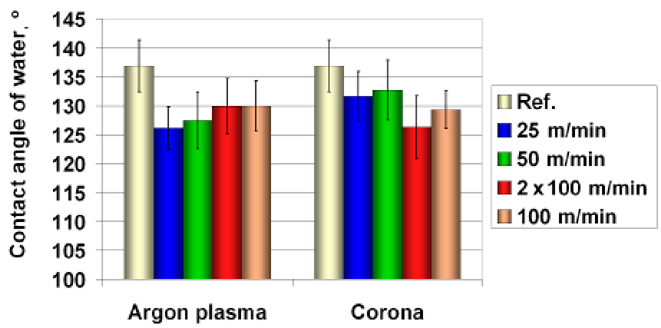


Figure 10. Contact angles of nonwoven samples treated with different speeds / exposure times, measured one week after treatments.

The effect of longer treatment time can, however, have some effect on fibre structure. The SEM observation of untreated and treated samples (Figure 11) showed that longer exposure might cause small scale erosion and fragmentation of the surface, which can be seen as the presence of small particles. Shin et al. [20] obtained similar results. They noticed that the control sample had a smooth surface, whereas the plasma treated sample showed some redeposited particles etched away during plasma treatment. This suggests that needlessly prolonged exposure time can damage the fibres.

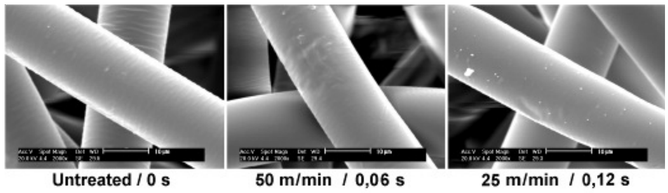


Figure 11. Appearance of argon plasma treated nonwoven treated with different speeds / exposure times.

Mechanical Strength of Treated Samples

In tensile strength test (Figure 12) no significant changes were observed after argon plasma treatment. Nonwoven treated with slower speed (25 m/min), and thus higher energy per area, had only a slight decrease in tensile strength. Also changes in elongation at break were not considered significant. In general, the plasma treatment seemed not to weaken nor change much the mechanical properties of nonwoven.

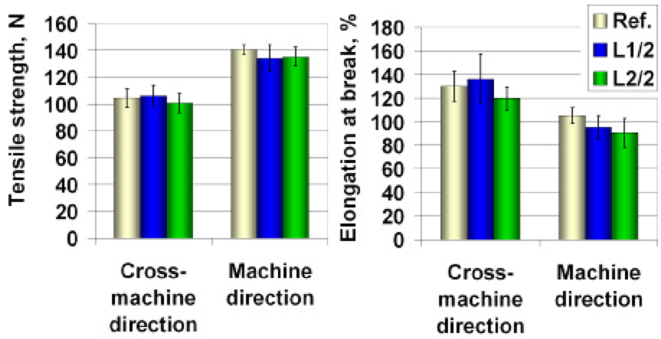


Figure 12. Maximum breaking strength and elongation of the test piece at the maximum breaking strength: argon plasma treated nonwoven layers (two-layered sample).

Conclusions

Penetration of plasma into the structure of a nonwoven sample substrate was studied using porous nonwoven polypropylene fabric, having a porosity of over 90 % and average in-plane determined pore size of 60 µm. The effect of plasma and corona treatment on the various layers in a multi-layered sample was studied using contact angle measurements applied on each layer. The effect of plasma was the strongest in the uppermost layers and decreased progressively with the amount of layers. The ease of the plasma penetration seemed to be slightly dependent on the plasma gas: the smaller the gas ion diameter, the greater the penetration. The corona treatment was also seen to penetrate into the structure, but not as efficiently as gas plasmas, regardless of the higher energy per area of the corona treatment.

The measurements of base material covered with different numbers of sample layers during plasma treatment clearly indicated that the effect of plasma penetrated through the porous structure of the nonwoven. Changes in surface properties of the base layer, such as the contact angle of the water after plasma treatments, can be seen even below several layers of nonwoven. The effect of plasma on a nonwoven-covered base surface could be more pronounced compared to an uncovered base. This suggests that the porous structure of the nonwoven material may act to retain plasma longer and so prolong the effective exposure time. Therefore, depending, of course, on the porosity and permeability of the sample, it seems possible to treat both sides of one single layer sample as well as multiple layers simultaneously. This is clearly beneficial when considering industrial production.

Experiments carried out using different line speeds (25-100 m/min) and thus different exposure times showed that reactions in surfaces also happen relatively quickly. Variation in treatment speed, at least in the studied speed range, does not have a big influence on the efficiency of treatment, evaluated by contact angle measurements. The exposure time of plasma on porous substrate may be inherently prolonged by plasma gases becoming retained within the porous structure, and, therefore, the treatment can be carried out at high line speeds. This is another advantage from the production point of view. When studying morphological properties, a prolonged exposure time slightly increased the scale erosion and fragmentation of the surface, which suggest that prolonged exposure time can damage the fibres, but with our line speeds the changes in mechanical properties of nonwoven samples were negligible.

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