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# Non-woven composites intensification properties for air filters by plasma pre-treatment

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**Abstract.** The nonwovens use in the automotive industry has increased significantly. Nonwovens for air filters can be changed in a desired direction to have specific properties. The use of non-woven textiles in the automotive industry has the following advantages: it reduces the weight of the vehicle, increases comfort and provides improved insulation, fire retardancy and resistance to water, fuels, extreme temperatures and abrasion. The electrospinning process is one of the nanofibres, two-layer and multilayer composites with their participation obtaining methods. The low frequency plasma surface modification of needle-punched polyethilenthertalat (PET) nonwoven fibres is good possibility to intensification the process and the rate of increase of the mass of nanolayer regarding to its' hydrophobicity. The plasma physicochemical treatment type allows adhesion change and change of electro physical properties at the expense of new active centres formation that do not exist in the native fibre. In this study, different gases (Ar, O<sub>2</sub> and air) and electrical conditions were employed. The surface changes of PET fibres were investigated by cation exchange capacity (CEC) determination and its influence on the mass nanofibres increase rate. Observation revealed the plasma treatment significantly change surface wettability of PET fibres. The effect of caused change on the electrospinning process is analysed.

## 1. Introduction

The use of nonwovens in the automotive market has increased significantly in recent years. Frequently, nonwovens can be engineered to have specific properties. By building on the essential properties that are necessary for good performance and safety, nonwovens help reduce the weight of the car, enhance comfort and aesthetics and provide advanced insulation, fire retardancy and resistance to water, fuels, extremes of temperature and abrasion.

A promising method of obtaining fibrous materials with changed porosity is the process of electrospinning (ESP-process), which provides the possibility of applying to the surface substrate – classic non-woven filter materials over a layer (mat) consisting of nanofibres. Electrospinning is a widely used technique for constructing special high-performance filters. With this technique, a wide variety of polymers can be spun. One of these is also polyvinyl alcohol (PVA), which has very good properties in this field. Its water solubility can be adjusted with crosslinking techniques – chemical or physicochemical crosslinking [1].



The principle of electrostatic spinning is based on applying a strong electromagnetic field to the polymer solution to create an electrically charged stream of polymer solution or melt. The tension created between the two electrodes then act on the polymer located on the spinning electrode. At the final stage of electrospinning, phase transformations take place, including molecular diffusion of the solvent to the filament surface, evaporation of the solvent, the formation of a solid phase of the fibre-forming polymer.

The properties of the fibres and their mats depend on the process parameters, the chosen polymer and nature of the collector on which the layer is applied. By changing these parameters it is possible to modify and to control the appearance and quality of the deposited fibres as well as the morphology of the deposited mat. The fibres are paving and oriented on the collector, and the appearance of the surface of the overlay, when the purpose is to obtain double layer or multilayer composite also is affected. To increase the mass of matte and the efficiency of the process, it is of particular importance to choose the couple – a polymer solution and a suitable surface of the collector (organic/inorganic material, smoothness / fluffiness, hydrophilicity / hydrophobicity, morphology, density, etc.). The reason for this is the interaction of the solution with the electric field, because simultaneously with the drawing of the fibres, evaporation of the solvent is carried out [2].

The collectors are used to deposit the resulting fibres. They are mostly made of metal. Changing the surface and the type of collector leads to a change in the morphology of the native nanomat. Fabric collector porosity or evenness is the result of the constructional parameters combination - aluminium foil, fabric or nonwoven material. This is because the final fibres still not completely stable because of the presence of residual solvent therein. Thus, the hydrophilicity / hydrophobicity of the pad on which the fibres are applied affects the adhesion of the mat of nanofibres and the layer formed by them to the pad [3, 4].

Surface modification via plasma treatment not only eliminates the need of wet processing, but several modifications are carried out: hydrophilicity/ hydrophobicity alterations, surface roughening, grafting, flame retardant, antimicrobial, insect repellent, stain resistant, and single or multiple surface functionalization [5]. Many novel changes using plasmas have been thoroughly analysed and well documented.

The atmospheric plasma treatment allows specific modifications of the surface properties to be carried out without causing a change in the fibre or bulk properties. Plasma provides an excellent way to study surface modifications, and is reasonable for batch processing of small product quantities. It is not, however, feasible for on-line processing in a textile mill. Thus, the hydrophobicity/hydrophilicity of the fibre-matrix adhesion, for example to perform finishing processes with synthetic fibres increased, which is important for the amount of nanofibres mat on the textile collector. The increase in adhesion strength of the boundary surface depends on the growth of roughness and the emergence of new active groups.

Most of the studies in the field of textile modification to increase adhesion relate to two-layer film materials or duplication of these materials. For inert polymers, as polyethylene terephthalate (PET), formation of the reaction centre is the only way for increased strength at the boundary between the two layers.

Polyester fibre (PET), as a very important textile fibre, has been widely used in production of nonwovens for some industrial areas in particular with different application filters due to its superiorities of high strength, mechanical stability and low cost [6, 7]. But it is known that PET fibres are characterized by a dense, fine-grained surface structure which in many cases impedes adhesion and diffusion in their volume. PET fibres has high hydrophobic behaviour and at 100 % air relative humidity absorb 1% humidity only. Therefore, it is desirable to change their surface properties because, it is very difficult for hydrophobic surface of polyester fibres to be wetted.

In that paper have been investigated the effect of pad pre-treatment in cold plasma environment. Through the electrical discharge and radicals creation, we are managed to hydrocarbons deposition on the PVA layer and increase surface hydrophobicity in a rapid way. The surface chemistry change had a

relatively small effect on the fibre structure sample and individual fibre morphology. The surface properties of PET fabrics were then characterized using ion exchange capacity determination.

In our other studies it has been found that the hydrophilicity/hydrophobicity of the material upon which the fibres are deposited in order to obtain a two-layer structure is of importance at the beginning of the process [8]. The amount of the deposited fibres depends on collector surface (hydrophobicity/hydrophilicity) properties with the same other electrospinning process parameters. The nanofibres laying process is stabilized by increased PET pad hydrophilicity and subsequent more uniform and rapid moisture diffusion in the volume of nonwoven base. When the pad has high hydrophobicity and lower thickness, the solvent evaporation in the chamber depends on the ambient humidity and as a result there is a greater unevenness of the fibre deposition process. A mat of higher density nanofibres is obtained in the case of hydrophilic pad (cotton tissue).

So, through different type of physic-chemical treatment, adhesive and electrophysical properties can be changed at the expense of formation of boundary molecular layers and thus change the nature of the polyester fibres surface that do not exist in the native fibre. It is known that after processing in cold plasma, the hydrophilic properties of the polymers change. The picture is considerably more complicated in the case of non-woven needle-punched textile materials with varying area and volume widely used in the automotive industry. As a result of the plasma treatment, the ionic groups increased on the PET fibres surface, as a result of which the interaction with the deposited PVA mat increased also. Furthermore, depending on the processing mode the amount of accelerated ions and their energy are different. At the same time there are two areas where ultraviolet radiation in the chamber has different intensity and therefore possible a photooxidative reaction occurred with variety of chemical products. This affects the amount and type of new active centres created on the polyester fibres surface.

In general, plasma treatment is associated with several effects, each of which influences on the adhesion between the two layers of the composite: the non-woven pad and the nanofibres mat.

Surface plasma activating of fibres results in:

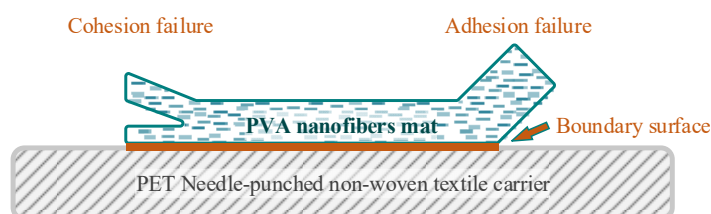
- Plasma etching, increasing the relative and active surface as a result of bombardment with accelerated ions leading to micro cracks and craters formation on the fibres surface;
- New active sites formation as a result of beat out electrons and radicals formation on the fibres surface; Other polar moieties that are formed during treatment include carbonyls ( $-CO$ ) and carboxyls ( $-COO$ ). This change in surface polarity has been widely studied for adhesion increase. Several excellent reviews are referenced here that detail the specific and mechanisms of the treatment [9-11].
- Cross-linking due to new functional groups formation with oxygen or water from the air and cross-linking with hydrogen bridges; Cross-linking is also associated with a reduction in the number of hydroxyl groups already introduced into the surface and they become inaccessible to interact with water [12].

It can be seen that plasma exposure leads to changes in the polymer composition surface. This includes free radicals formation. These radicals enable reactions such as cross-linking by activated species of inert gas surface graft polymerization, as well as the incorporation of functional groups.

The present work attempts to elucidate these complex and simultaneous changes in the materials as well as their influence on the surface properties of the non-woven fabric. It is necessary to evaluate these changes so that a suitable pretreatment regime can be selected, ensuring the desired good or poor adhesion between the two layers of the composite. Depending on the gas used in the chamber there is a difference in radical intensity for constant exposure time and duration of exposure 180 s [13]. There was is difference in radical intensity or the various substrates and gases, as specified in next order: linen > cotton > polynosic rayon > standard rayon > nylon6 > PET and  $CF_4 > CO > Ar > N_2 > O_2$ . Due to relatively low radical intensities measured for  $O_2$  in comparison to  $CF_4$ , it is concluded that the  $O_2$  plasma generated free radicals are unstable with a short lifetime. Oxygen and air plasma treatment leads to surface wetting improvement of synthetic polymers (PA, PE, PP, PET, PTFE). By oxygen or air plasma treatment, it can be controlled the hydrophilicity of the PET polymer in the desired direction.

For plasma-exposed PET nonwoven collector, the hydrophilicity/hydrophobicity of the substrate surface can be altered by the gas selection. In other words, oxygen can create  $-OH$  groups, which increase hydrophilicity.

Good adhesion property can be achieved if between the two layers, in our case needlefelt non-woven fabric and a nanofibre mat, can initiate a boundary contact area, figure 1. This happens when the contact distance is less than the cut off distance of the van der Waals attractive force [14].



**Figure 1.** Structure of double-layer gas filter media consist of PET Needle-punched non-woven textile carrier, boundary surface and PVA nanofibres mat.

For inert polymers such as PET, reactive centres formation is the only possibility to create a strong bond between the two layers [15].

Electrospun mat has a different adhesion to the collector, depending on its surface smoothness. Extraordinary adhesion properties are demonstrated by Wong and co-workers [16, 17].

The aim of the work is to define empirically the changes in nonwoven fabric designed for pad of the nanofibres layer, related to the surface modification of the fibres, their nature and their impact. Durable bilayer composites on the basis of needle punch PET non-woven fabric with a layer of nanofibres are designed for gas filters. The influence of low temperature plasma on the hydrophilic properties of a non-woven from polyester fibre was examined.

## 2. Full ion exchange capacity Determination

In the present work are presented only results related to the change of cation-exchange properties after plasma chemical modification of polyester carrier of the PVA nanofibres layer. These properties determine the adhesion strength between the two used layers due to the increase of the negatively charged group's quantity on the surface.

The nonwoven fabric used for the carrier of the layer of nanofibres is: needle felted filters produced from polyester fibres with 3.4 dtex density and 57 mm staple length, 400 g/m<sup>2</sup> surface density. They are treated by plasma. As plasma-forming gas was used argon and oxygen gases, applied plasma treatment duration is 1 min and 2 min.

The prepared samples are washed at 60°C in an ultrasonic bath for 2 min treatment time. The drying process is accomplished at 105°C.

The input parameters of the plasma unit varied within the following limits: discharge power  $W_p = 0.5-2.0$  kW, working pressure in the discharge chamber  $P = 80$  Pa; plasma gas consumption  $G = 0.04-1.2$  g/s; generator frequency  $f = 1.76$  MHz, treatment time  $t = 1$  and 2 min. The indicated times are selected because they are quite sufficient for the creation of new active centres or so called plasma-chemical modification.

Argon and oxygen are used as plasma-forming gas; arc current  $I_d = 65 \pm 5$  A, sample rotation speed 1.5-2 revolutions per minute.

Ion exchange capacity, is the measure of the number of replaceable  $H^+ / -OH$  ions per unit mass of the exchange. Determination of full cation exchange capacity is defined by titration method with 0.01N sodium hydroxide solution at room temperature. In parallel, a blank sample is also run. The complete cation/ anion exchange capacity in mgeqv/g is calculated according to well-known formula.

### 3. Results and discussion

As has already been indicated in the treatment of textile materials with plasma their properties are changed – mechanical, physical, chemical, and electrical. This happens simultaneously.

The measurement of the thickness of the plasma-treated non-woven fabric under the above conditions was performed at the follow conditions: climatic condition  $T = 20^{\circ}\text{C}$ , humidity = 62 %; work pressure  $P = 1$  kPa. The results obtained are presented in table 1.

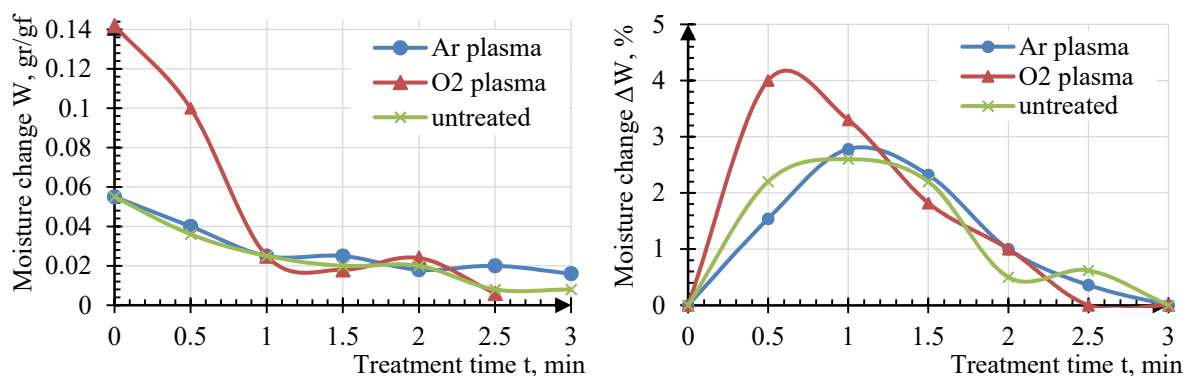
**Table 1.** Change in thickness depending on the type of gas used.

No	Untreated	Plasma treatment in oxygen ( $\text{O}_2$ ) for 1 min	Plasma treatment in oxygen ( $\text{O}_2$ ) for 2 min	Plasma treatment in argon (Ar) for 1 min	Plasma treatment in argon (Ar) for 2 min
Thickness average value $\bar{x}$ (mm)	1.948	1.929	2.043	1.853	1.910
Dispersion $s$ (mm)	0.042	0.027	0.057	0.024	0.032

The thickness change is greater when  $\text{O}_2$  is used as the plasma-forming gas at 2 min treatment time.

This is due to the introduction of bigger quantity oxygen-containing groups. This leads to an increase in surface free energy and an increase in fabric's wettability. These oxygen-containing groups may also cause additional surface modifications, which may contribute to increasing adhesion between the two layers of the filter.

Depending on the number of hydrophilic groups capable of attracting and retaining water near themselves textile fibres have more or less hydrophilicity therefore. At the same relative humidity and air temperature, studied samples have different moisture content, figure 2. That fact can be explained by the material polarization.



**Figure 2.** Summary experimental data on the change of moisture in the samples at the working pressure  $P = 80$  Pa and  $\text{O}_2$  and Ar as gas in the chamber.

To determine the plasma treatment influence on the change of the quantity of active groups on the surface and hence the change of adhesion with the applied second layer of the nanofibres composite the study of the change of moisture content is not sufficient. The electrophysical properties of the material changes as a result of the change in the amount of negatively charged active centres on the surface, the thickness of the nonwoven fabric increases and the size of the capillaries is changed at the same time. At the same time, the influence of the radius on the capillary and the amount of the negative/positive side of the active site is opposite. Therefore, it is necessary to use a parallel method by which the influence of these simultaneous changes in the material can be identified. In that study differential scanning calorimetry (DSC) analysis of treated samples is performed and the change in PET fibres shows the difference in the amount of heat required to increase the temperature, table 2.

Plasma treatment leads to additional oxygen-containing functional groups such as  $-\text{OH}$ ,  $-\text{C}=\text{O}$ ,  $-\text{COOH}$  to the samples surface that are evaluated by DSC analyses to detect possible changes in thermal stability and melting behaviour.

**Table 2.** DSC evaluation of plasma treated PET non-woven samples.

No	Type of plasma-forming gas	Plasma treatment duration $t$ , min	Enthalpy $\Delta H$ , J/g	Peak Area, mJ	Max. peak value $^{\circ}\text{C}$	Peak height, mW
1	Ar	1	60.4969	120.994	252.11	6.8683
2	Ar	2	62.2919	124.584	251.25	7.3700
3	$\text{O}_2$	2	70.3840	126.691	251.66	6.7632
4	$\text{O}_2$	1	63.0338	125.461	251.21	6.0325
5	Untreated	0	80.1161	208.302	240.31	8.7330

According to the results presented in table 2 is observed enthalpy decrease of the system after treatment in oxygen and Ar plasma compared to untreated material, which means changing the crystallinity of the surface of the PET fibres. The melting temperature of the polymer also changes. Free radicals formation on the surface due to the oxygen-containing and argon-containing gas plasma treatment leads to the formation of a chemically active surface layer and increasing the adhesion of the nonwoven fabric to the nanofibrous electrospin layer on it.

F. Rombaldoni et al. [18] used low-temperature oxygen plasma treatment to enhance the adhesion between polypropylene nonwoven and poly(ethylene oxide) and polyamide-6 nanofibrous mats deposited onto polypropylene nonwoven. Improving the adhesion between the nonwoven and the nanofibrous mat, which was attributed to the increased wettability of the supporting polypropylene fabric and polar functional groups introduced by plasma treatment, allowed a stronger interaction with the treated fabric. It should be expected that after increasing the amount of negatively charged groups on the surface it becomes negatively loaded due to the increase in weakly acidic groups as carboxylate group ( $\text{COO}^-$ ). This was attributed to the increased surface roughness of the PET fibres leading to enhanced mechanical adhesion between the two layers of non-woven PET fabric and the PVA nanofibres layer. With the IEC determination, it is observed that the amount of oxygen-associated groups increases after the plasma treatment, making the fabric surface more wettable, Figure .

After the plasma treatment the PET fibres surface are activated and the CEC increases. This is evident from the obtained results presented in table 3.

**Table 3.** CEC (cation exchange capacity) evaluation of plasma treated PET non-woven samples.

No	Type of plasma-forming gas	Treatment time $t$ , min	CEC, mEq/100g
1	Ar	1	10.9
2	Ar	2	11.2
3	$\text{O}_2$	2	19.3
4	$\text{O}_2$	1	18.6
5	Untreated	0	7.8

#### 4. Conclusion

Cold plasma activation in the  $\text{O}_2$  and Ar gas media was used as a good possibility for polyester non-woven modification used as a carrier for PVA nanofibres, designed to produce high-grade double-layer dust filters for automobile industry.

Plasma activation is an environmentally friendly (green) technology for filter functionalization which consist in improving hydrophilicity, wettability, wicking, and ion exchanging interaction.

Polyester plasma activation produce different new functional groups on the surface of the fibres as  $-\text{C}-\text{OH}$ ,  $\text{C}-\text{O}-\text{OH}$ ,  $\text{C}-\text{OH}$ ,  $\text{C}=\text{O}$ ,  $\text{O}=\text{C}-\text{O}-\text{OH}$ ,  $\text{C}-\text{O}-$ ,  $\text{O}=\text{C}-\text{O}-$ ,  $\text{C}-\text{H}^+$ ,  $\text{C}-\text{H}_2\text{O}^+$  etc.

Experimentally, as a result of pre-treatment in plasma, the adhesion between the two layers of the double layer gas filter consists of needle-punched nonwoven PET fibre and PVA nanofibres mat, has been improve.

The most significant change in the values of moisture in the samples is in O<sub>2</sub> medium. This fact can be explained by that this textile non-woven PET material is significantly thicker and characterized by a much larger surface and the greater activity of O<sub>2</sub> vs. Ar gases.

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