

# INFLUENCE OF LOW-TEMPERATURE PLASMA TREATMENT ON THE LIQUID FILTRATION EFFICIENCY OF MELT-BLOWN PP NONWOVENS IN THE CONDITIONS OF SIMULATED USE OF RESPIRATORY PROTECTIVE EQUIPMENT

Katarzyna Majchrzycka<sup>\*1</sup>, Małgorzata Okrasa<sup>1</sup>, Agnieszka Brochocka<sup>1</sup>,  
Wiesława Urbaniak-Domagala<sup>2</sup>

<sup>1</sup>Central Institute for Labour Protection – National Research Institute (CIOP-PIB), Department of Personal Protective Equipment, Wierzbowa 48, 90-133 Łódź, Poland

<sup>2</sup>Lodz University of Technology, Department of Material and Commodity Sciences and Textile Metrology, Żeromskiego 116, 90-924 Lodz, Poland

*Dedicated to Prof. Leon Gradoń on the occasion of his 70th birthday*

Filtering nonwovens produced with melt-blown technology are one of the most basic materials used in the construction of respiratory protective equipment (RPE) against harmful aerosols, including bio- and nanoaerosols. The improvement of their filtering properties can be achieved by the development of quasi-permanent electric charge on the fibres. Usually corona discharge method is utilized for this purpose. In the presented study, it was assumed that the low-temperature plasma treatment could be applied as an alternative method for the manufacturing of conventional electret nonwovens for the RPE construction.

Low temperature plasma treatment of polypropylene nonwovens was carried out with various process gases (argon, nitrogen, oxygen or air) in a wide range of process parameters (gas flow velocity, time of treatment and power supplied to the reactor electrodes). After the modification, nonwovens were evaluated in terms of filtration efficiency of paraffin oil mist. The stability of the modification results was tested after 12 months of storage and after conditioning at elevated temperature and relative humidity conditions. Moreover, scanning electron microscopy and ATR-IR spectroscopy were used to assess changes in surface topography and chemical composition of the fibres. The modification of melt-blown nonwovens with nitrogen, oxygen and air plasma did not result in a satisfactory improvement of the filtration efficiency. In case of argon plasma treatment, up to 82% increase of filtration efficiency of paraffin oil mist was observed in relation to untreated samples. This effect was stable after 12 months of storage in normal conditions and after thermal conditioning in  $(70 \pm 3)^\circ\text{C}$  for 24 h. The use of low-temperature plasma treatment was proven to be a promising improvement direction of filtering properties of nonwovens used for the protection of respiratory tract against harmful aerosols.

**Keywords:** low-temperature plasma treatment, melt-blown nonwovens, respiratory protective devices

## 1. INTRODUCTION

The basic materials used for the construction of respiratory protective equipment (RPE) against harmful aerosols are filtering nonwovens produced with melt-blown technology (Brochocka, 2001). The

\*Corresponding author, e-mail: kamaj@ciop.lodz.pl

technique of blowing molten polymer makes it possible to obtain a product of greater degree of compaction than it is in the case of traditional needle-punched nonwovens. Additionally, it ensures a possibility of spatial changes of porosity along the flow of the filtered aerosol. Fibres creating a filtering layer are arranged anisotropically in the layer plane of the nonwoven structure and often have diameters of less than 1  $\mu\text{m}$ . This guarantees high filtering efficiency but also causes greater airflow resistance. Higher filtering efficiency of melt-blown nonwovens can be also obtained without increasing airflow resistance by introducing electrostatic charges into a fibre during the process of corona discharge. During this process, a point electrode with a higher potential, emits ions of a specific character. They move in electric field towards the lower or opposite potential. The electrodes are mounted on a collector of the melt-blowing production line in the fibre forming area. Ions of greater density are trapped in the fibres and become semi-permanently bonded with the polymer material. Different arrangements of electrodes ensure obtaining electrets of different electrostatic charges per unit of fibre length.

When discussing the efficiency of electret nonwovens, it is important to realise the main mechanisms influencing the movement of a particle in the close proximity of a fibre, which translates directly into the probability of its capture by the filter (Barrett and Rousseau, 1998; Brown, 1993; Gougeon, Boulaud and Renoux, 1996; Kanaoka et al., 1987; Pich et al., 1987). In case of penetration of fine particles that are particularly harmful for respiratory system, it is precisely the Coulomb's interaction that is of particular significance (Martin and Moyer, 2000). The power of attraction between an aerosol particle and a fibre depends inter alia on the value of their electric charges. Thus, the neutralization of electric charges, which is often observed for RPE, causes a rapid decrease in filtration efficiency (Brown and Wake, 1999; Brown et al., 1988; Chen et al., 1993; Huang, 2013; Li and Jo, 2010; Yang et al., 2007).

In order to reduce the negative effects related to neutralization of electrets produced by corona discharge, works aimed at developing highly effective filtering materials with the use of other methods were carried out (Angadjivand, 1996; Carter et al., 1988; Jones et al., 2002; Nguyen 2005; Yang and Lee, 2005). Interesting results were obtained in case of low-temperature plasma treatment of polypropylene filtering nonwovens (Urbaniak-Domagala et al., 2010). This technique seemed to provide interesting results in the area of improving the efficiency of non-electret filtering materials towards solid aerosol particles. Brochocka et al. (2014) continued these works in relation to liquid aerosol particles. In their study low-pressure low-temperature plasma treatment was applied to polycarbonate nonwovens using process gases such as argon and oxygen. The effectiveness of treatment was assessed on the basis of the results of the penetration of nonwovens by paraffin oil mist and airflow resistance at linear velocity of 0.15 m/s. The effects of plasma modification on polycarbonate nonwovens, especially on their surface morphology and chemical structure, were evaluated by SEM microscopy and FTIR spectroscopy. The results indicated that argon plasma treatment is a good tool for improving the filtration properties of polycarbonate filtering materials. Majchrzycka (2013) also showed that the process of low-temperature argon plasma treatment results in a significant increase in the filtration efficiency of melt-blown nonwovens and that these materials present low tendency to losing their acquired filtering efficiency during the time they are treated with paraffin oil mist.

To-date there have been few studies devoted to the use of low-temperature plasma in the improvement of efficiency of filtering nonwovens towards liquid aerosols with use of gases that are not chemically neutral. In this case, it should be noted that while modifying a surface layer of polymers using low-temperature plasma, four basic phenomena may occur: purification of the material surface, etching (leading to removal of some material that is loosely connected with the surface), cross-linking of the particles (causing cohesion) and creation of new chemical structures (mainly under the influence of free radical, oxygen and steam). Due to synergy, interaction of these phenomena in shaping an appropriate adhesion between the surface of a solid matter and a particle of liquid aerosol is a complex process. The

influence of individual phenomena depends mainly on the type of material, type of gas filling the discharge chamber, construction of this chamber, temperature and pressure in the chamber, individual charge energy and the time of interaction of plasma with the material (Matsuo, 2008). That is why, each time when new application of low-temperature plasma modifications of polymer surface are considered, it is necessary to evaluate the influence of individual parameters of this treatment on the predicted effects.

Therefore, the aim of this paper is to analyse the influence of low-temperature plasma treatment conditions (i.e. gas type, gas flow velocity, time of treatment and electric power required for the initiation and continuation of the plasma treatment) on the improvement of efficiency of filtering nonwovens towards liquid aerosols and to evaluate the stability of the obtained effects in the conditions of simulated use of RPE.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Filtering nonwovens were produced in the Laboratory of Respiratory Protective Devices of the Central Institute for Labour Protection – National Research Institute, at the experimental line for melt-blown nonwovens production. Manufacturer's characteristics of Malen P F401 polypropylene (PP), used in the tests are presented in Table 1, while the properties of filtering nonwovens are shown in Table 2.

Table 1. Properties of PP granulate

Parameter	Values
Density, g/cm <sup>3</sup>	0.905 – 0.917
Flow speed, g/10min	2.4 – 3.2
Water content, %	max. 0.01
Softening point, °C	145 – 155
Melting point, °C	160 – 170
Intrinsic viscosity, cm <sup>3</sup> /g	190

Table 2. Properties of PP nonwovens used for modification

Parameter	Values
<sup>1)</sup> nonwoven thickness, mm	1.66
<sup>2)</sup> average diameter of fibres, µm	1.5
<sup>2)</sup> max diameter of fibres, µm	4.4
<sup>2)</sup> min diameter of fibres, µm	0.6
<sup>3)</sup> surface weight of nonwovens, g/m <sup>2</sup>	90

<sup>1)</sup> test according to ISO 9073-2 standard (ISO 9073-2:1995, 1995); <sup>2)</sup> using SEM scanning electron microscopy method based on n = 300 measurements; <sup>3)</sup> test according to EN 29073-1 standard (EN 29073-1:1992, 1992)

### 2.2. Plasma modification

The low-temperature plasma treatment process was carried out at the Department of Material and Commodity Sciences and Textile Metrology, Lodz University of Technology. The treatment was

performed with a commercial low-temperature, radio-frequency (13.56 MHz) plasma generator (CD 400 PLC Roll Cassette, Europlasma, Belgium) equipped with two parallel rectangular electrodes connected to an alternative voltage. The conditions in which the treatment was carried out (gas type, gas flow velocity, time of treatment and electric power required for the initiation and continuation of the plasma treatment) were controlled automatically and varied depending on the chosen modification variant (Table 3).

Table 3. The range of the plasma treatment conditions

Parameter	Value
Gas type	argon, atmospheric air, oxygen, nitrogen
Gas flow velocity [cssm]	50 – 700
Time of treatment [s]	30 – 600
Power supplied to the electrodes [W]	30 – 200

The neutral gas (argon) was chosen based on the assumption that the etching of the fibres' surface (physical modification) will result in the increased filtration efficiency of the filtering nonwoven, while in case of air, nitrogen and oxygen, the improvement of the filtration efficiency should be achieved due to increased free energy of fibres' surface (chemical modification) (Morent et al., 2008; Takemura et al., 2008; Verschuren et al., 2007). The selection of parameters of low-temperature plasma treatment was performed on the basis of literature data (Buyle, 2009; Gotoh and Yasukawa, 2010; Morent et al., 2008; Takemura et al., 2008; Verschuren et al., 2007) and previous experiences of the Authors.

Prior to the modification, samples of filtering nonwovens were placed between the electrodes. A three-stage treatment procedure was established:

- evacuation of the vacuum chamber for 30 minutes,
- surface modification with argon, atmospheric air, nitrogen or oxygen plasma (depending on the selected modification variant),
- conditioning of the sample after the treatment for 30 min.

In order to assess the influence of storage on the effect of plasma treatment samples of nonwovens were stored for 12 months in horizontal non-compressed state in stable climatic conditions ( $23^{\circ}\text{C} \pm 5\%$  and  $50\% \pm 10\%$ ). To assess changes in nonwoven properties due to elevated temperature, part of the plasma treated samples was placed in a dryer in horizontal non-compressed state at a temperature of  $70^{\circ}\text{C}$  and relative humidity of 20% (climatic conditions according to the EN 13274-5 standard (EN 13274-5:2001, 2001)). Samples of nonwovens to be tested for the influence of elevated humidity on the effect of plasma treatment were stored in the desiccator, under the saturation conditions (relative humidity of 100%) for 24 h (climatic conditions according to the EN 13274-5 standard (EN 13274-5:2001, 2001)).

### 2.3. Test methods

According to the requirements of European standards harmonized with Directive 89/686/EEC (89/686/EEC, 1989), the assessment of the effectiveness of filtering RPE should include, among others, testing of the penetration of solid (sodium chloride aerosol) and liquid particles (paraffin oil mist). In this case the use of paraffin oil mist as a challenge aerosol represents the worst-case scenario in terms of collection efficiency. Thus, the filtering material that meets the requirements for paraffin oil mist penetration should always meet the requirements for sodium chloride aerosol penetration. Therefore, in order to assess the effect of low-temperature plasma treatment on the efficiency of filtering nonwovens after storage as well as temperature and humidity conditioning nonwoven samples were tested in terms of penetration of a paraffin oil mist using a test stand presented in Fig. 1.

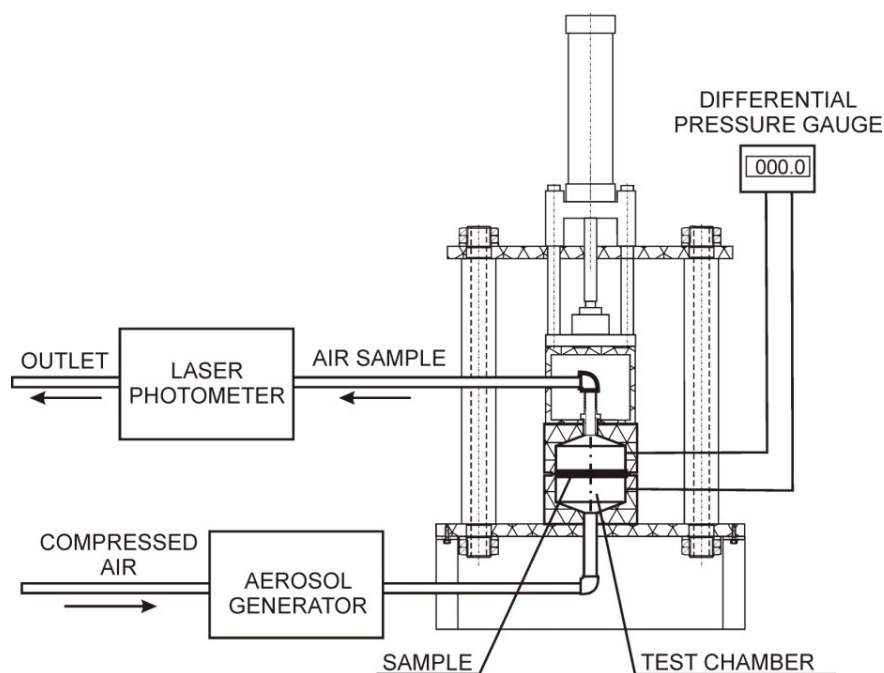


Fig. 1. The scheme of experimental set-up for testing filtration parameters of nonwoven materials

During tests the challenge aerosol was passed at a predetermined linear velocity through a nonwoven sample mounted in a sample holder of 100 mm diameter. Particle size distribution was log-normal with a median of Stokes diameter of 0.4  $\mu\text{m}$  and geometric standard deviation of 1.82. Concentration of paraffin oil mist was measured with laser photometer AP2E (Lorenz, Germany) upstream and downstream of the sample. Results were collected in the initial stage of filtration, after 3 min from the beginning of each test. Penetration was calculated from the following equation:

$$P = \frac{l_2 - l_0}{l_1 - l_0} \cdot 100\% \quad (1)$$

Additionally, airflow resistance through the filtering material was measured by establishing pressure drop on a filter according to methodology described in the EN 13274-3 standard (EN 13274-3:2001, 2001).

In order to evaluate the influence of the factor  $j$  (where  $j = T, RH, S$  for thermal conditioning, humidity influence or storage, respectively) on the properties of nonwovens, which underwent plasma modification, the relative change in penetration  $\Delta P_j$  resulting from this factor was calculated from the following equation:

$$\Delta P_j = \frac{(P_j - P)}{P} \cdot 100\% \quad (2)$$

Analogically, the relative change in airflow resistance  $\Delta O_j$  through the filtering nonwovens was established.

Scanning electron microscope (SEM) images were obtained by Nova NanoSEM 230, (FEI, USA) microscope. The images were taken in order to assess changes in the surface morphology of nonwoven fibres as a result of plasma treatment.

The chemical properties of the surface of samples exposed to different treatments were examined with use of Fourier-transformed infrared spectroscopy on a double-beam spectrophotometer FTIR–Nicolet 6700 (Thermo Fisher Scientific Inc., USA) equipped with a reflective adaptor type ITR. The obtained spectra were analyzed using OMNIC 8.0.380 software.

## 3. RESULTS AND DISCUSSION

The influence of plasma treatment on the filtration efficiency of nonwovens was established by determining changes in penetration and in airflow resistance through the filtering nonwovens after modification with various process gases and also with the use of various treatment parameters. The test results were presented in Table 4.

Table 4. Changes in the filtering parameters of nonwovens as a result of plasma treatment

Treatment variant	Gas flow velocity [cssm]	Power [W]	Time [s]	$P_R$ [%]	$P$ [%]	$O_R$ [Pa]	$O$ [Pa]	$\Delta P$ [%]*	$\Delta O$ [%]*
Nitrogen									
1	500	100	30	3.7	3.2	306	284	-14	-8
2	500	100	60	3.7	2.9	306	308	-22	1
3	500	100	120	3.7	3.6	306	365	-3	16
4	700	50	30	5.5	4.8	255	323	-13	21
5	700	50	60	5.5	5.3	255	226	-4	-13
6	700	50	120	5.5	5.0	255	278	-9	8
7	700	100	30	6.4	4.8	245	339	-25	28
8	700	100	60	6.4	5.1	245	242	-20	-1
9	700	100	120	6.4	6.3	245	215	-2	-14
Oxygen									
1	500	100	30	3.2	3.6	376	339	13	-11
2	500	100	60	3.2	4.9	376	323	53	-16
3	500	100	120	3.2	5.8	376	273	81	-38
4	700	50	30	4.6	3.6	340	401	-22	15
5	700	50	60	5.5	4.2	285	324	-24	12
6	700	50	120	5.5	3.6	285	342	-35	17
7	700	100	30	3.8	3.8	350	313	0	-12
8	700	100	60	3.8	3.9	350	273	3	-28
9	700	100	120	9.0	8.7	300	255	-3	-18
Air									
1	500	100	30	5.0	4.9	348	249	-2	-40
2	500	100	60	5.0	4.1	348	368	-18	5
3	500	100	120	4.5	3.1	340	402	-31	15
4	700	50	30	4.5	2.9	373	438	-36	15
5	700	50	60	4.5	2.6	399	480	-42	17
6	700	50	120	3.2	3.1	315	328	-3	4
7	700	100	30	3.2	3.5	343	388	9	12
8	700	100	60	3.2	4.3	307	373	34	18
9	700	100	120	3.5	5.3	337	337	51	0
Argon									
1	50	30	300	3.5	1.8	332	388	-50	14
2	50	30	600	2.8	2.4	339	237	-14	-43
3	50	100	300	2.7	0.9	345	378	-69	9
4	50	100	600	9.2	1.7	210	309	-82	32
5	50	200	300	17.0	6.6	230	209	-61	-10
6	50	200	600	16.0	6.2	228	235	-61	3
7	50	100	600	2.8	0.8	325	432	-73	25
8	50	100	600	15.0	7.2	229	224	-52	-2
9	50	100	600	12.0	6.9	196	251	-43	22

\*) color code corresponding to decreasing (green) or increasing (red) values of penetration / air flow resistance was applied

In case of argon plasma treatment, a drop in penetration of paraffin oil mist was observed, reaching up to 82% of the reference value, which was in compliance with the previously published studies (Brochocka 2014). Contradictory results were obtained for the variants of nonwovens modified in plasma with the use of gases that were chemically reactive.

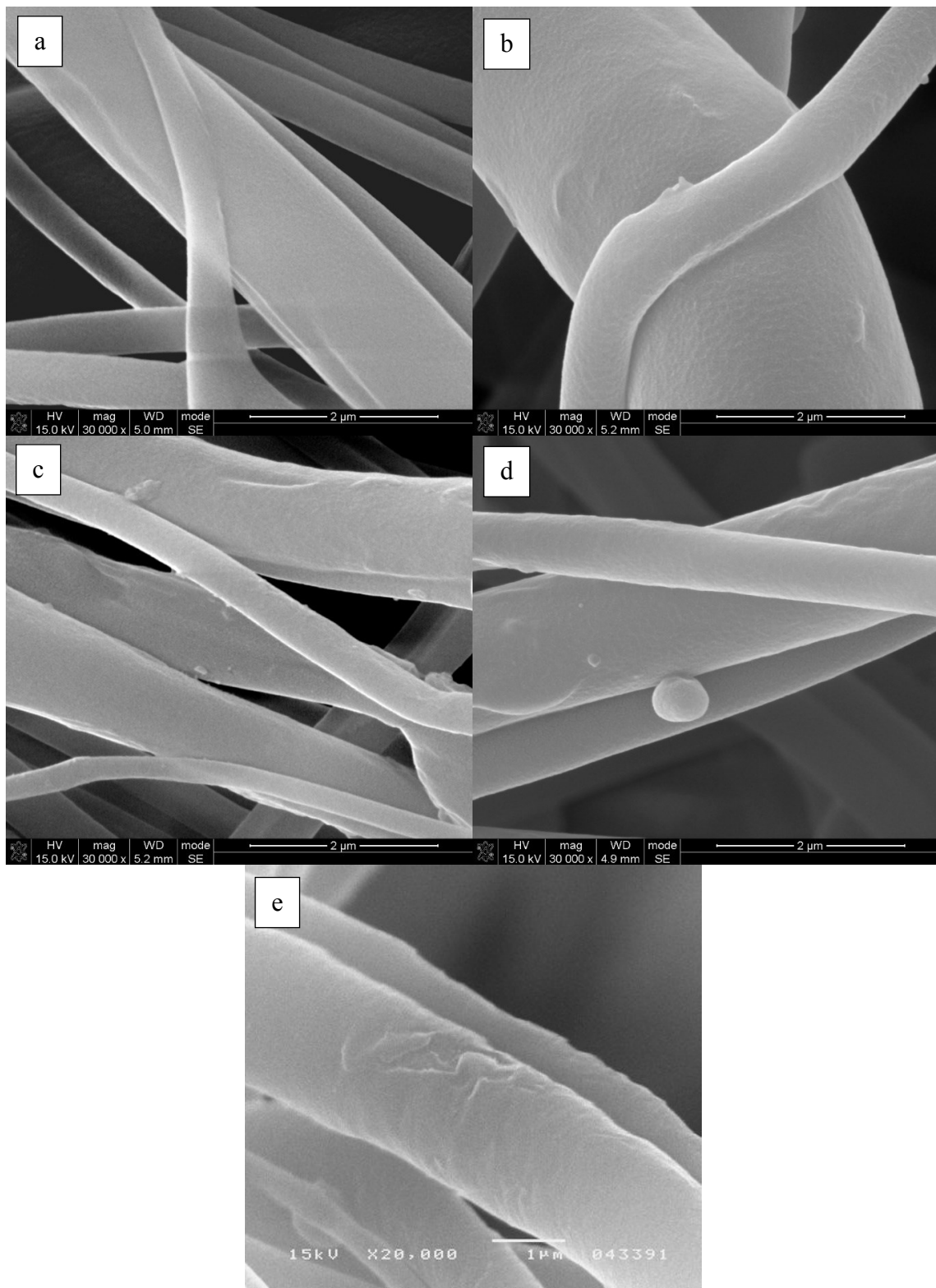


Fig. 2. SEM images of fibres of a) untreated nonwovens and nonwovens after treatment with b) nitrogen (700 cssm/100 W/60 s), c) oxygen (700 cssm/50 W/120 s), d) air (700 cssm/50 W/60 s), and e) argon (50 cssm/100 W/600 s)

The results of research on the penetration of paraffin oil mist obtained for nonwovens modified in nitrogen, oxygen and air show that in these cases interaction of low-temperature plasma influenced the efficiency of filtration in various ways. By and large, the processes of activating the surface caused both an increase in the penetration of paraffin oil mist (up to 81% for the oxygen plasma for nonwovens before modification – 500 csm, 100 W, 120 s) or its decrease (up to -42% with reference to nonwovens before modification in case of applying air plasma – 700 csm, 50 W, 60 s). However, it was not possible to establish a systematic dependence of relative change in penetration against their process parameters.

The results of tests concerning the airflow resistance (directly linked with the breathing resistance when used in the construction of RPE) in the majority of cases show an increasing tendency. However, it needs to be emphasized that these changes (on average around 30% of the initial value) are not an issue when applying them in RPE. They may be explained by the flattening of nonwovens during modification in a discharge chamber or by structural changes of nonwovens resulting from the movement of the loose fibres and creating compact and uneven filtering structures. The most beneficial relative changes in the airflow resistance were observed in case of oxygen plasma (decrease of the airflow resistance for the majority of modification variants).

SEM was employed to investigate the morphologies of the PP nonwovens treated with nitrogen, oxygen, air and argon plasma. The images obtained for selected modification variants are shown in Figure 2 (similar effects were obtained for other variants). For comparison, the SEM image of pristine PP nonwoven was also obtained under the identical conditions.

Modification of filtering nonwovens in argon plasma resulted in significant changes of fibre surface in relation to the untreated sample. With the lengthening of the treatment time and increasing power of discharge, a slight growth in the number deformations and non-uniformities on the fibre surface was observed due to the etching, which is consistent with the results described in the literature (Contal et al., 2004; Frising et al., 2005; Raynor and Leith, 2000; Walsh and Stenhouse, 1997). No significant differences in the morphology of fibre surface were observed for the nonwovens modified in nitrogen, oxygen or air plasma, regardless of the selected processing parameters. This conclusion is in compliance with the results described by Brochocka et al. (2014).

Figure 3 presents IR spectrograms for samples of nonwovens treated with nitrogen, oxygen, air, and argon plasma. The spectrograms show IR radiation absorption (Abs.) as a function of wavenumber.

Absorptive spectra of IR radiation of nonwoven samples for which the best improvement of filtration efficiency was achieved were performed in the range of 3500-700  $\text{cm}^{-1}$  for argon and 1500-1000  $\text{cm}^{-1}$  for other gases. The results show subtle changes in their chemical structure caused by interaction with the plasma environment. These changes are of varied character, depending on the type of the applied process gas.

IR spectrograms of nonwovens treated with nitrogen present absorption on a low level in a wider range of wavenumbers as opposed to the interaction with oxygen plasma: from 1300  $\text{cm}^{-1}$  to 1510  $\text{cm}^{-1}$ . A selective absorption of PP nonwovens in the ranges: 1320, 1340, 1390, 1420, 1488, 1506  $\text{cm}^{-1}$  may be observed. The majority of ranges discovered are the same as those for the PP surface treated with air plasma. IR absorption of nonwovens with lower wavenumbers may be related to the presence of nitrate ions  $\text{NO}_2$  (identified in the range of 1320  $\text{cm}^{-1}$ , group - C -N-, identified by valence vibrations in the range of 1350-1280  $\text{cm}^{-1}$ , group -  $\text{CH}_3$ , identified by deformation vibrations 1340-1360  $\text{cm}^{-1}$  in groups - CO- $\text{CH}_3$  and group C-H identified by deformation vibrations in hydrocarbons with a branched chain.



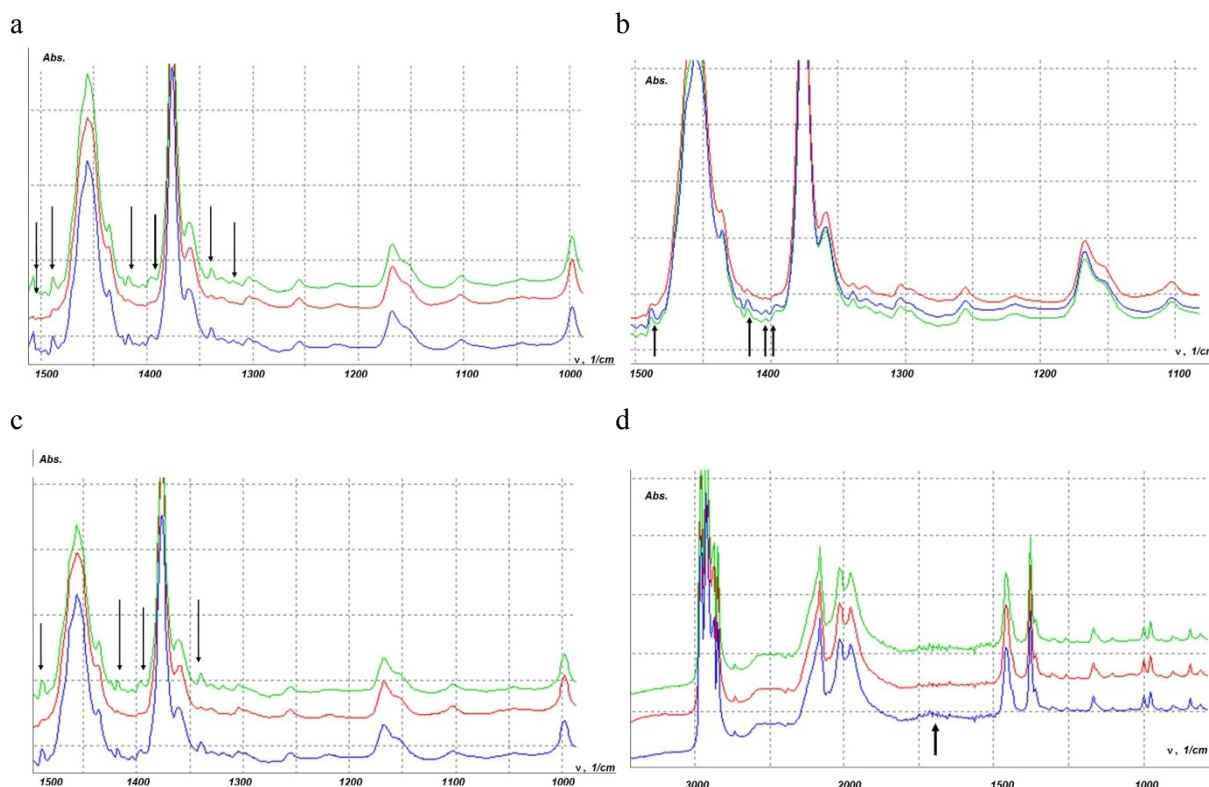


Fig. 3. IR absorption spectrum of the samples of nonwovens treated with a) nitrogen, b) oxygen, c) air and d) argon plasma; (red line – untreated sample, green and blue – plasma treated sample in two repetitions)

Nonwovens treated with oxygen plasma show absorptive ranges of low intensity, although they are well developed at the wavenumbers (1385, 1403, 1416, 1488)  $\text{cm}^{-1}$ . For nonwovens treated with air plasma selective absorption was observed at the wavenumbers (1340, 1390, 1416, 1488)  $\text{cm}^{-1}$ . Absorption may be caused by symmetric deformation vibrations of  $-\text{CH}_3$  in isopropyl and dimethyl group (1390-1370)  $\text{cm}^{-1}$ , symmetric deformation vibrations of  $-\text{CH}_3$  in t-butyl groups (1406-1393)  $\text{cm}^{-1}$  deformation vibrations of  $-\text{O}-\text{H}$  group (1400-1340)  $\text{cm}^{-1}$ , flat deformation vibration of C- (1410-1400)  $\text{cm}^{-1}$ , flat deformation vibration of C-H (1420-1400)  $\text{cm}^{-1}$  in compounds such as  $\text{RR}'\text{C}=\text{CH}_2$  and  $\text{RHC}=\text{CH}_2$  (1410-1400)  $\text{cm}^{-1}$ , scissoring vibrations of  $-\text{CH}_2$  in linear aliphatic chains 1467  $\text{cm}^{-1}$  or asymmetric valence vibrations of  $-\text{CH}_3$ .

Nonwovens treated with argon plasma demonstrate a new type of absorption for a range of wavenumbers (1660-1720)  $\text{cm}^{-1}$ . Absorption in this range may be caused by valence vibrations of  $-\text{C}=\text{C}$ ,  $-\text{C}=\text{C}-$  groups. These groups, which are not present in non-modified PP nonwovens, may occur in chemical processes between polymer and plasma particles and in the processes of polymer crosslinking under the influence of UV radiation emitted by plasma. This type of absorption did not arise in the samples of nonwovens treated with oxygen, nitrogen and air plasma.

Analysis of IR absorption spectrograms showed that the mechanism of interaction of PP nonwovens with oxygen, nitrogen and air plasma is similar. The differences result from the efficiency of the processes. No evident relation between chemical modification of the fibres surface and the improvement of filtration efficiency was observed.

Test results related to the influence of elevated temperature and relative humidity on the effect of plasma modification of PP nonwovens is presented in Table 5.

The influence of storage on the filtering and usage properties of nonwovens was evaluated for two selected types of samples that underwent modification in air and argon plasma (Table 6).

Table 5. Results of tests on the influence of elevated temperature and humidity on samples of filtering nonwovens, which underwent the plasma treatment

No.	$P$ [%]	$P_T$ [%]	$P_{RH}$ [%]	$O$ [Pa]	$O_T$ [Pa]	$O_{RH}$ [Pa]	$\Delta P_T$ [%]*	$\Delta P_{RH}$ [%]*	$\Delta O_T$ [%]*	$\Delta O_{RH}$ [%]*
Nitrogen										
1	4.0	2.8	-	367	396	-	-31	-	8	-
2	5.3	5.5	-	317	331	-	4	-	4	-
3	5.0	4.2	-	338	383	-	-16	-	13	-
4	5.0	5.4	-	312	317	-	8	-	2	-
5	1.6	-	2	474	-	447	-	25	-	-6
6	6.1	-	4.8	328	-	337	-	-21	-	3
7	4.5	-	4.0	365	-	396	-	-11	-	8
8	4.1	-	5.2	344	-	324	-	27	-	-6
Oxygen										
1	5.1	4.3	-	341	364	-	-16	-	7	-
2	3.0	2.6	-	411	434	-	-13	-	6	-
3	3.0	2.3	-	430	458	-	-23	-	7	-
4	3.3	3.6	-	405	400	-	9	-	-1	-
5	4.6	-	4.3	357	-	364	-	-7	-	2
6	9.1	-	7.9	320	-	321	-	-13	-	0
7	2.4	-	2.4	436	-	438	-	0	-	1
8	3.7	-	3.3	390	-	404	-	-11	-	4
Air										
1	6.0	5.9	-	340	346	-	-1	-	2	-
2	3.2	3.3	-	435	427	-	5	-	-2	-
3	4.0	4.1	-	375	345	-	4	-	-8	-
4	2.6	2.9	-	440	417	-	14	-	-5	-
5	7.7	-	8.1	314	-	300	-	3	-	-4
6	3.0	-	3.3	435	-	418	-	12	-	-4
7	4.2	-	4.5	358	-	338	-	7	-	-6
8	2.6	-	3.2	407	-	377	-	25	-	-7
Argon										
1	3.6	5.0	-	366	369	-	39	-	1	-
2	3.7	4.6	-	370	377	-	24	-	2	-
3	1.5	2.8	-	490	463	-	83	-	-5	-
4	9.0	5.9	-	345	348	-	-35	-	1	-
5	1.6	-	1.5	459	-	501	-	-6	-	9
6	2.7	-	3.9	382	-	404	-	44	-	6
7	5.6	-	5.0	340	-	347	-	-11	-	2
8	2.6	-	2.9	371	-	381	-	12	-	3

\* color code corresponding to decreasing (green) or increasing (red) values of penetration / air flow resistance was applied

In all the tested variants of filtering nonwovens no significant influence of the time of storage (12 months) or of elevated temperature and relative humidity on durability of the obtained results of plasma modification were observed. The modification of filtering nonwovens in argon plasma caused permanent changes on the surface of fibres, which in turn resulted in the improvement of filtration efficiency. Therefore, it may be concluded that the technique of low-temperature plasma treatment is a promising direction of further studies so as to improve the filtering properties of nonwovens used in the construction of RPE against harmful aerosols.

Table 6. Test results of paraffin oil mist penetration and airflow resistance before and after storage

No.	$P$ [%]	$P_s$ [%]	$O$ [Pa]	$O_s$ [Pa]	$\Delta P_s$ [%]	$\Delta O_s$ [%]
Air						
1	3.4	2.04	319	295	-40	-8
2	3.4	2.94	319	247	-14	-29
3	7.3	5.44	259	232	-25	-12
4	7.3	5.42	259	224	-26	-15
5	5.9	4.20	263	217	-29	-21
6	5.9	4.09	263	229	-31	-15
Argon						
1	2.4	1.55	373	345	-35	-8
2	3.5	1.75	332	388	-50	14
3	2.8	2.4	339	237	-14	-43
4	2.7	1.25	343	378	-54	9
5	2.7	0.85	345	378	-69	9
7	2.5	0.66	315	397	-74	21
8	2.8	0.76	325	432	-73	25

#### 4. CONCLUSIONS

In the paper we investigated a possibility of applying low-temperature plasma treatment to improve the filtration efficiency of melt-blown nonwovens. We also checked whether the effect of plasma modification changes after storage and conditioning in elevated temperature and increased relative humidity.

The results of the study show that in terms of an improvement of filtration efficiency low-temperature argon plasma treatment is superior to the processing with other gases. In case of argon plasma treatment up to 82% improvement of penetration of paraffin oil mist in relation to the untreated sample was achieved (for 50 csm/100 W/600 s). For other gases relative improvement of penetration caused by plasma treatment was 25% for nitrogen (700 csm/100 W/300 s), 35% for oxygen (700 csm/50 W/120 s), and 42% for air (700 csm/50 W/60 s).

The results presented in the paper indicate that argon plasma treatment could be used to improve the properties of filtering melt-blown nonwovens used in the construction of RPE along with more commonly used corona discharge.

*The publication is based on the results of Phase I of the National Programme "Safety and working conditions improvement", funded in the years 2008-2010 in the area of research and development works by the Ministry of Science and Higher Education / The National Centre for Research and Development. The Programme coordinator: Central Institute for Labour Protection – National Research Institute.*

#### SYMBOLS

- $j$  designation of a factor, which influences filtering parameters of nonwovens, it can be either thermal conditioning ( $T$ ), humidity influence ( $RH$ ) or storage ( $S$ )
- $l_1$  the photometer reading in front of the filter

$l_2$	the photometer reading behind the filter
$l_0$	the photometer reading for clean air
$O$	airflow resistance of the nonwoven before the factor $j$ has been applied, Pa
$O_j$	airflow resistance of the nonwoven after the factor $j$ has been applied, Pa
$\Delta O_j$	relative change in airflow resistance of the nonwoven resulting from the factor $j$ , Pa
$O_R$	airflow resistance of the nonwoven prior to the plasma treatment, prior to the plasma treatment, Pa
$P$	aerosol penetration through the plasma treated nonwoven before the factor $j$ has been applied, %
$P_j$	aerosol penetration through the plasma treated nonwoven after the factor $j$ has been applied, %
$\Delta P_j$	relative change in penetration of aerosol through the nonwoven resulting from the factor $j$ , %
$P_R$	aerosol penetration through the nonwoven prior to the plasma treatment, %

## REFERENCES

- Angadjivand S.A., Jones M.E., Meyer D.E., 1996. Method of charging electret filter media. Patent no. WO 1995005501 A2.
- Barrett L.W., Rousseau A.D., 1998. Aerosol loading performance of electret filter media. *Am. Ind. Hyg. Assoc. J.*, 59, 532–9. DOI: 10.1080/15428119891010703.
- Brochocka A., Mian I., Majchrzycka K., Sielski J., Tyczkowski J., 2014. Plasma modified polycarbonate nonwovens as filtering material for liquid aerosols. *Fibres Text. East. Eur.*, 22, 76–80.
- Brochocka A., 2001. Characteristics of melt-blown filter materials produced by simultaneous blowing of polymer melt from two extruders. *Fibres Text. East. Eur.*, 4, 66–9.
- Brown R., Wake D., 1999. Loading filters with monodisperse aerosols. *J. Aerosol Sci.*, 30, 227–34. DOI: 10.1016/S0021-8502(98)00042-1.
- Brown R.C., Wake D., Gray R., Blackford D.B., Bostock G.J., 1988. Effect of industrial aerosols on the performance of electrically charged filter material. *Ann. Occup. Hyg.*, 32, 271–94. DOI: 10.1093/annhyg/32.3.271.
- Brown R.C., 1993. *Air filtration: An integrated approach to the theory and applications of fibrous filters*. Pergamon Press, Oxford.
- Buyle G., 2009. Nanoscale finishing of textiles via plasma treatment. *Mater. Technol.*, 24, 46–51. DOI: 10.1179/175355509x417954.
- Carter D.H., Howells R.D., Stern R.M., Temperante J.A., 1988. Fluorochemical oxazolidinones. Patent no. EP 0260011 A2.
- Chen C.C., Lehtimäki M., Willeke K., 1993. Loading and filtration characteristics of filtering facepieces. *Am. Ind. Hyg. Assoc. J.*, 54, 51–60. DOI: 10.1080/15298669391354324.
- Contal P., Simao J., Thomas D., Frising T., Callé S., Appert-Collin J.C., Bémer D., 2004. Clogging of fibre filters by submicron droplets. Phenomena and influence of operating conditions. *J. Aerosol Sci.*, 35, 263–78. DOI: 10.1016/j.jaerosci.2003.07.003.
- Council Directive 89/686/EEC of 21 December 1989 on the approximation of the laws of the Member States relating to personal protective equipment.
- EN 13274-3:2001. Respiratory protective devices. Methods of test. Determination of breathing resistance. 2001.
- EN 13274-5:2001. Respiratory protective devices. Methods of test. Climatic conditions. 2001.
- EN 29073-1:1992. Methods of test for nonwovens. Methods of test for nonwovens. Determination of mass per unit area. 1992.
- Frising T., Thomas D., Bémer D., Contal P., 2005. Clogging of fibrous filters by liquid aerosol particles: Experimental and phenomenological modelling study. *Chem. Eng. Sci.*, 60, 2751–2762. DOI: 10.1016/j.ces.2004.12.026.

- Gotoh K., Yasukawa A., 2010. Atmospheric pressure plasma modification of polyester fabric for improvement of textile-specific properties. *Text. Res. J.*, 81, 368–78. DOI: 10.1177/0040517510387207.
- Gougeon R., Boulaud D., Renoux A., 1996. Comparison of data from model fibre filters with diffusion, interception and inertial deposition models. *Chem. Eng. Commun.*, 151, 19–39. DOI: 10.1080/00986449608936539.
- Huang S.-H., Chen C.-W., Kuo Y.-M., Lai C.-Y., McKay R., Chen C.-C., 2013. Factors Affecting filter penetration and quality factor of particulate respirators. *Aerosol Air Qual. Res.*, 13, 162–71. DOI: 10.4209/aaqr.2012.07.0179.
- ISO 9073-2:1995. Textiles. Test methods for nonwovens. Part 2: Determination of thickness. 1995.
- Jones M.E., Lyons C.S., Redmond D.B., Solomon J.L., Angadjivand S.A., 2002. Fluorinated electret. Patent no. US 2002/0152892 A1.
- Kanaoka C., Emi H., Otani Y., Iiyama T., 1987. Effect of charging state of particles on electret filtration. *Aerosol Sci. Technol.*, 7, 1–13. DOI: 10.1080/02786828708959142.
- Li K., Jo Y.M., 2010. Dust collection by a fibre bundle electret filter in an MVAC system. *Aerosol Sci. Technol.*, 44, 578–87. DOI: 10.1080/02786826.2010.481227.
- Majchrzycka K., 2013. Modification of polymeric filtration nonwovens by treatment with low-temperature plasma as a method for improvement of aerosol removal efficiency. *Przem. Chem.*, 92, 1750–4.
- Martin S.B., Moyer E.S., 2000. Electrostatic respirator filter media: filter efficiency and most penetrating particle size effects. *Appl. Occup. Environ. Hyg.*, 15, 609–17. DOI: 10.1080/10473220050075617.
- Matsuo T., 2008. Fibre materials for advanced technical textiles. *Text. Prog.*, 40, 87–121. DOI: 10.1080/00405160802133028.
- Morent R., De Geyter N., Verschuren J., De Clerck K., Kiekens P., Leys C., 2008. Non-thermal plasma treatment of textiles. *Surf. Coatings Technol.*, 202, 3427–49. DOI: 10.1016/j.surfcoat.2007.12.027.
- Nguyen L.Q., 2005. Method of making a melt-blown filter medium for use in air filters in internal combustion engines and product. Patent no. US 20040172930 A1.
- Pich J., Emi H., Kanaoka C., 1987. Coulombic deposition mechanism in electret filters. *J. Aerosol Sci.*, 18, 29–35. DOI: 10.1016/0021-8502(87)90006-1.
- Raynor P.C., Leith D., 2000. The influence of accumulated liquid on fibrous filter performance. *J. Aerosol Sci.*, 31, 19–34. DOI: 10.1016/S0021-8502(99)00029-4.
- Takemura Y., Yamaguchi N., Hara T., 2008. Study on surface modification of polymer films by using atmospheric plasma jet source. *Jpn. J. Appl. Phys.*, 5644–7. DOI: 10.1143/jjap.47.5644.
- Urbaniak-Domagala W., Henryk W., Szymanowski H., Majchrzycka K., Brochocka A., 2010. Plasma modification of filter nonwovens used for the protection of respiratory tracts. *Fibres Text. East. Eur.*, 18, 94–9.
- Verschuren J., Kiekens P., Leys C., 2007. Textile-specific properties that influence plasma treatment effect creation and effect characterization. *Text. Res. J.*, 77, 727–33. DOI: 10.1177/0040517507078820.
- Walsh D.C., Stenhouse J.I.T., 1997. The effect of particle size, charge, and composition on the loading characteristics of an electrically active fibrous filter material. *J. Aerosol Sci.*, 28, 307–21. DOI: 10.1016/S0021-8502(96)00434-x.
- Yang S., Lee G.W.M., 2005. Filtration characteristics of a fibrous filter pretreated with anionic surfactants for monodisperse solid aerosols. *J. Aerosol Sci.*, 36, 419–37. DOI: 10.1016/j.jaerosci.2004.10.002.
- Yang S., Lee W.-M.G., Huang H.-L., Huang Y.-C., Luo C.-H., Wu C.-C., Yu K.-P., 2007. Aerosol penetration properties of an electret filter with submicron aerosols with various operating factors. *J. Environ. Sci. Health A. Tox. Hazard Subst. Environ. Eng.*, 42, 51–7. DOI: 10.1080/10934520601015651.

*Received 21 June 2016*

*Received in revised form 13 March 2017*

*Accepted 20 March 2017*