Agnieszka Brochocka,
Katarzyna Majchrzycka,
Krzysztof Makowski

Modified Melt-Blown Nonwovens for Respiratory Protective Devices Against Nanoparticles

Central Institute for Labour Protection
– National Research Institute
ul. Czerniakowska 16; 00-701 Warszawa, Poland
E-mail: agbro@ciop.lodz.pl;
kamaj@ciop.lodz.pl;
krmak@ciop.lodz.pl

PO IG (Innovative Economy)
Project 01.01.02-10-018/09: "**Innovative polymer and carbon materials protecting against nanoparticles, vapours and gases**".
Project Leader: Central Institute for Labour Protection - National Research Institute CIOP-PIB. Department of Personal Protective Equipment.
Project Partner: Technical University of Lodz. Faculty of Process and Environmental Engineering. Division of Molecular Engineering.

Abstract
Epidemiological studies of the effect of harmful nanoparticles on the human body prove that efficient protective measures need to be developed. This applies, in particular, to respiratory protection equipment in which filtration nonwovens are the essential structural material. This paper discusses a method for improving the efficiency of electret filtration nonwovens for nanoparticles by using polypropylene (PP) admixed with additives with varying electrostatic potentials. The investigation was carried out using amber (negative charge) and perlite beads (positive charge) incorporated into the polymer stream using melt-blown technology. Filtration efficiency was evaluated using standard methods with paraffin oil mist and sodium chloride aerosol and non-standard methods with nanoparticles. The studies proved that strengthened electrostatic interaction effects owing to the modifiers provide a promising method for improving the efficiency of electret nonwovens against nanoparticles.

Key words: *filtration, efficiency, polypropylene nonwoven, melt-blown, modification, corona treatment, nanoparticles.*

Introduction

Scientific investigations related to exposure to nanoparticle inhalation prove that nanoparticles may be harmful for the human body due to their quantity and surface area [1, 2]. Therefore it is vitally important for the development of nanotechnology to be accompanied by thorough research into how to ensure safety and, in particular, by research that makes new solutions available for collective and personal protection measures. So far, a number of studies have been performed on the development of filtration materials aimed at ensuring efficient nanoparticle filtration [3 - 5] using mechanical microfibre filters. However, the use of nanofibres leads to a sudden increase in air resistance which translates in filters used for individual respiratory protection into higher breathing resistance and difficulties for workers in their professional activities. Filtration nonwoven systems provide one of the methods to counteract this, but they are not satisfactory when the equipment is used in a hot and humid microclimate. An alternative solution is to develop a method for improving the filtration efficiency of nonwovens widely used for respiratory protective devices by enhancing nanoparticle deposition mechanisms on fibres, in particular those related to electrostatic attraction forces. The development of melt-blown nonwovens commonly used in the manufacture of filters and filtering half-masks is a promising avenue in this respect. They have high packing density which ensures high filtration efficiency with air resistance being relatively low (of importance with regard to gaining acceptance from users). Methods which generate or enhance electrostatic attraction forces between fibres and aerosol particles captured from the flowing air stream are commonly used to improve the filtration efficiency of such materials. Studies [6 – 11] have demonstrated that fibre electrostatic activation considerably improves filtration efficiency without any increase in air resistance. Corona discharge technology is widely used in the manufacture of melt-blown filtration materials for the manufacture of respiratory protective devices, involving a potential difference generated between an electrode and counter electrode, which is sometimes the surface of the receiving device. Due to its good processability and low cost, (PP) is the fibre-forming raw material used for the manufacture of such fibres employed in respiratory protective devices. However, considering its electrostatic properties and, in particular, the persistence of the electret effect, PP is frequently considered suboptimal when used to protect against harmful nanoparticles. This work therefore discusses technological experiments conducted to determine how PP electret melt-blown nonwovens should be modified. Our objective was to develop a method for improving the efficiency of melt-blown PP electret filtration nonwovens for nanoparticles using modifiers with varying electrostatic potentials.

Experimental materials

MOPLEN HP 456 J grade isotactic polypropylene (PP) with a melt index (MLI) of 3.4 g/10 min (manufacturer: LyondellBasell, Germany) was the raw material for the filtration nonwovens.

Modifiers

Two granulates were used in the modification process:

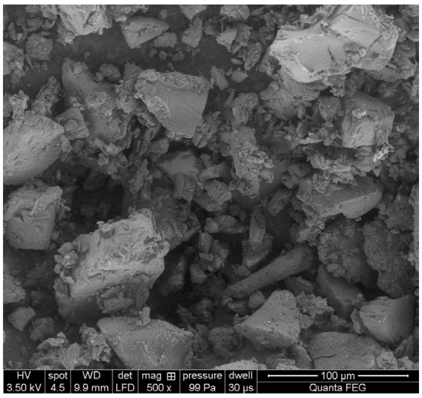

Figure 1. *SEM image of amber granulate surface.*

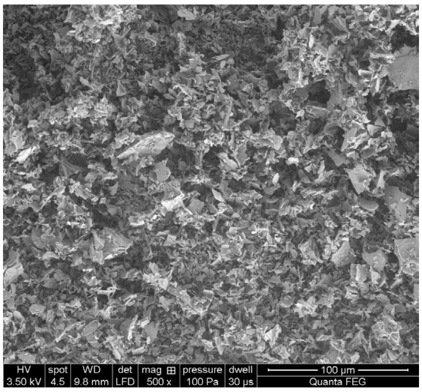

Figure 2. *SEM image of perlite granulate surface.*

- natural resin (amber) with a negative potential (supplier: EDAN, Poland),
- volcanic rock (perlite) with a positive potential (manufacturer: TERMO-FOR-BEŁCHATÓW, Poland).

To obtain the desired electrostatic effect, the modifiers were selected to occupy different positions in the triboelectric series, gathering a positive or negative electrostatic charge. They are also good insulators to prevent charge release.

A Quanta F 200 scanning electron microscope (500 x magnification) was used to determine the shape and bead size of the modifiers. In the case of amber the size of particles was in the range of 2-80 μm and for perlit the size range was from 0.2 to 10 μm. The differences are illustrated in ***Figures 1*** and ***2***. The shape and size of the NaCl aerosol nanoparticle are illustrated in ***Figure 4***.

Processing equipment

The technological research was performed at the experimental site of the Central Institute for Labour Protection – National Research Institute (CIOP-PIB), which is discussed in detail in [12].

The PP polymer (beads) was fed from the charging hopper into a heated extruder cylinder. Before extrusion from the fibre-forming head, it was brought to appropriate viscosity. Compressed air was pumped from the regulator to a heater, in which it was dried and heated to the appropriate temperature. Subsequently it was sent to the fibre-forming head, and at the outlet it blew polymer streams forced through nozzles into elementary fibres. They were deposited on the receiver and formed a compact porous fleece (nonwoven). The nonwoven production unit has adjustment points to change manufacturing parameters. The parameters listed in ***Table 1*** were used when moulding PP nonwovens with and without a modifier. ***Table 2*** shows characteristics of the structural parameters of the resulting PP nonwovens with and without a modifier.

Modifiers in the form of beads were added at the fibre formation stage (5% by weight of PP) according to the patent [13]. There is a detailed description in [12]. ***Figures 6 and 7*** show the distribution of the modifiers in the filtration nonwoven. For comparison, ***Figure 5*** shows the PP nonwoven without a modifier.

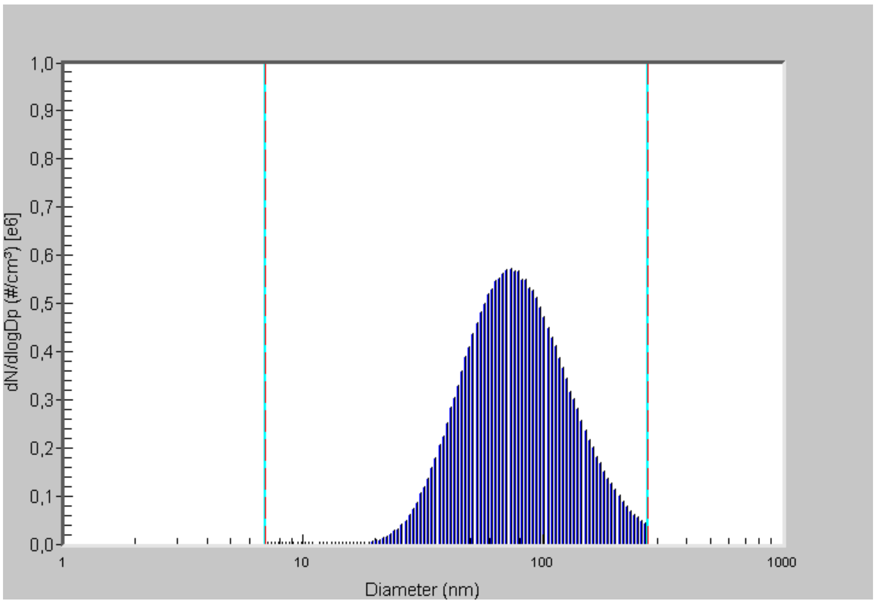

Figure 3. *Size distribution of NaCl nanoaerosol.*

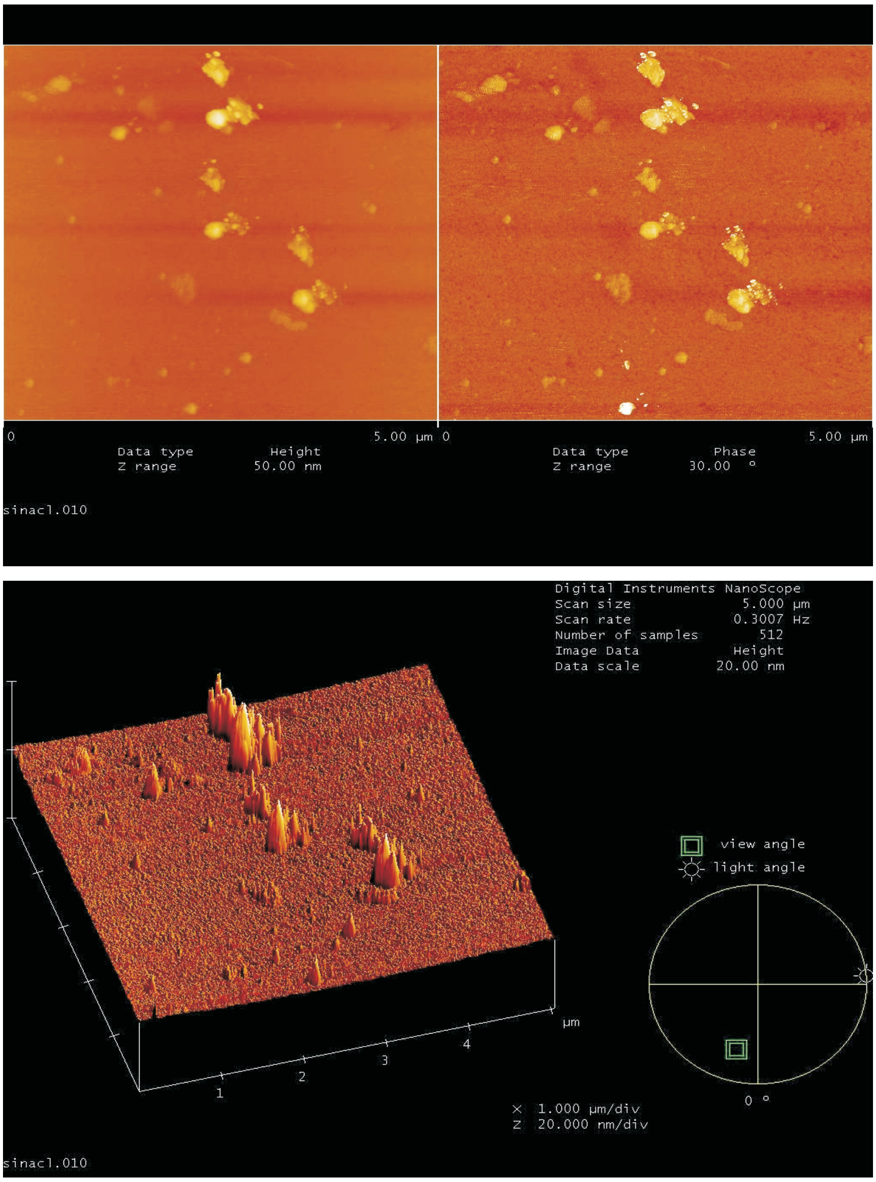

Figure 4. *NaCl aerosol nanoparticles: A) 2D view, B) 3D view.*

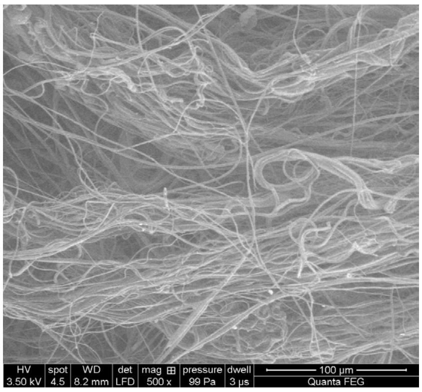

Figure 5. SEM image of (PP) nonwoven without a modifier.

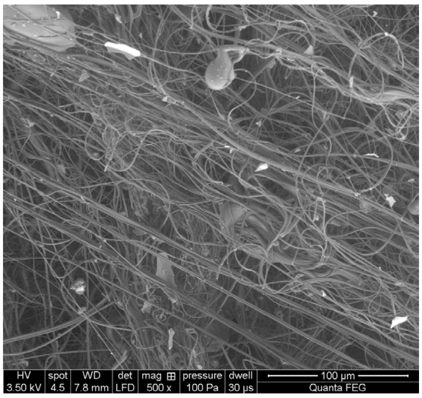

Figure 6. SEM image of amber-modified (PP) nonwoven.

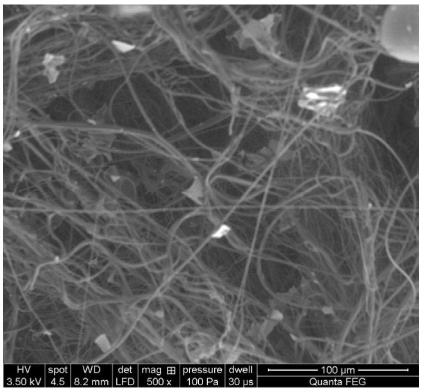

Figure 7. SEM image of perlite-modified (PP) nonwoven.

The nonwoven structural parameters with and without a modifier are shown as a pore fractional distribution (***Table 3***) due to the major impact of the parameter on filtration efficiency for aerosol particles [14].

A device for discharge emission was used to confer electret properties to the nonwoven with and without a modifier. It has a tip electrode at the receiving device, to which positive voltage is connected, and a counter electrode under the grid which collects nonwoven fleece, to which negative voltage is connected. The total charging voltage is 30 kV, which generates current in the range of 300 ± 50 μA. The system ensures control of the flow of non-dissipated charges.

Testing methods

The efficiency of the filtration materials was established by measuring the number of particles that were not blocked by these materials, described as particle penetration. Particle-penetration and air-resistance (respiratory resistance) tests were carried out using standard methods for the evaluation of respiratory protection equipment specified in the standards [15, 16] and using a non-standard method discussed below. Two model aerosols were used in the standard tests: sodium chloride and paraffin oil mist.

Sodium chloride (NaCl) in suspension, generated from a 0.1% aqueous solution using a collision nebulizer, was used for nanoparticle penetration testing. Nanoaerosol was fed through a drier and ionisation neutralizer into a chamber with a nonwoven sample tested. ***Figure 3*** shows the size distribution of the nanoaerosol used. The graf was obtained with the use of a TSI condensation particle counter connected to an electrostatic classifier.

The NaCl nanoparticles used in the testing were cubic, with the fractal dimension being similar (3). They were neutralised by an ionisation neutraliser, with a dielectric constant of 5.9. Tests of nanoparticle penetration through the filtration nonwovens were performed using a TSI 3080 electrostatic classifier and a TSI 3775 condensation particle counter. The measurement range of the system ensures a testing range of between 7 nm and 270 nm, divided into 90 measurement grades. The duration of the tests was set at 7 minutes to enable calculation of the average penetration value for three cycles of 126 s each, including 15 s breaks between measurement cycles to calculate the average value of penetration for the three cycles of 126 s each (including a 15 s break between the measured cycles to reset the electrostatic particle classifier). The tests were carried out at a volume value of aerosol flow intensity of 5400 l/h. The surface of the sample tested was constant for all measurements and was set at 0.01 m^2. The environmental conditions during the tests were as follows: surrounding temperature 20 ± 5 °C and relative air humidity 50 ± 20%.

Table 1. *Technological parameters of melt-blown production.*

Process technological parameters	PP
Temperature, extruder zone 1, °C	280
Temperature, extruder zone 2, °C	270
Air temperature, °C	300
Nozzle temperature, °C	294
Air flow rate, m^3/h	8
Polymer flow rate, g/min	24
Nozzles to collector distance, cm	16
Collector speed, m/s	0.00317
Supply voltage for fibre-forming head-heating elements, V	162

Table 2. *Structural parameters of PP nonwovens without a modifier.*

Basis weight, g/m^2	90 ± 5
Thickness of non-woven, mm	2.12
Min fibre diameter, μm	0.27
Max fibre diameter, μm	2.08
Mean fibre diameter, μm	0.74
Standard deviation, μm	0.323

A diagram of the measuring site is shown in ***Figure 8***.

The measurement results were evaluated statistically. This included:

- determination of mean values, variance and standard deviations for NaCl nanoparticle penetration, size: 50 – 275 nm,
- normal distribution tests for the results: Shapiro-Wilk test,
- variance tests (Fisher-Snedecor test) and mean tests (Student t test for equal variance values or Cochran-Cox test for different variance values depending on the results of the Fisher-Snedecor test) between paired samples.

Table 3. *Pore fractional distribution in melt-blown nonwovens without electrostatic charge.*

Nonwoven type	Equivalent diameter of the largest pores, μm	Main pore fraction, μm	Mean value for the main pore fraction, μm
Polypropylene nonwoven without-modifier	47.36	11.90 – 14.70	12.9
Perlite - modified polypropylene nonwoven	39.26	10.95 – 13.43	11.7
Amber - modified polypropylene nonwoven	37.83	9.23 – 11.63	9.7

Results and analysis

Table 4 shows the results of penetration tests for standard aerosol particles: sodium chloride (mean particle diameter: 0.5 µm) and paraffin oil mist (mean particle diameter: 0.3 µm) determined using commonly used methods for the evaluation and classification of the efficiency of respiratory protection equipment against harmful aerosols (dust, fumes, mist) according to European Standard EN 13274-7:2008 [15].

The plots (***Figure 9*** see page 110) show the results of NaCl nanoparticle penetration through nonwovens with and without modifiers, divided into nanoparticle size grades, and ***Table 5*** shows mean values for the particles in the range of 50 nm to 275 nm.

The results shown in ***Table 4*** confirm that corona discharge used when moulding fibres using melt-blown technology leads to the improved efficiency of pollutant-particle capture from the air stream. The reduced number of particles penetrating through electret filtration nonwovens compared to non-electret varieties is similar (statistically insignificant difference) in all of the varieties tested before and after modification. Because two particle types were used in standard tests: solid, represented by NaCl, and liquid, represented by paraffin oil mist, differences occurred between aerosol penetration values for the same nonwoven varieties. This results from particle size differences for both aerosol types and electrostatic properties, which lead to the prevalence of distinct liquid (mist) and solid (dust) particle deposition mechanisms on fibres. It was noted that adding modifiers (perlite and amber) with different electric potentials did not lead to an increase in non-electret nonwoven efficiency compared to non-modified nonwovens. This is primarily due to the fact that filtration efficiency in the aerosol particle size range of 0.3 µm to 0.5 µm is strongly dependent on nonwoven porosity, which is similar for all of the nonwovens tested (***Table 3***).

Distinct results were seen for NaCl nanoparticle penetration. ***Figure 9*** show the relationship between penetration and nanoparticle size for varieties modified by amber and perlite beads. For non-electret nonwovens, the modifiers did not lead to any significant changes in the efficiency of nanoparticle deposition on PP fibres. Mechanical attraction forces, whose efficiency is largely determined by pore size, were the prevalent mechanism of nanoparticle deposition. However, when modifiers were incorporated in the electret nonwovens, the expected efficiency improvement was seen as compared to unmodified non-electret nonwovens. This effect depends on nanoparticle size, and is strongest between 50 and 200 nm.

As the filtration respiratory protection equipment was evaluated using standard

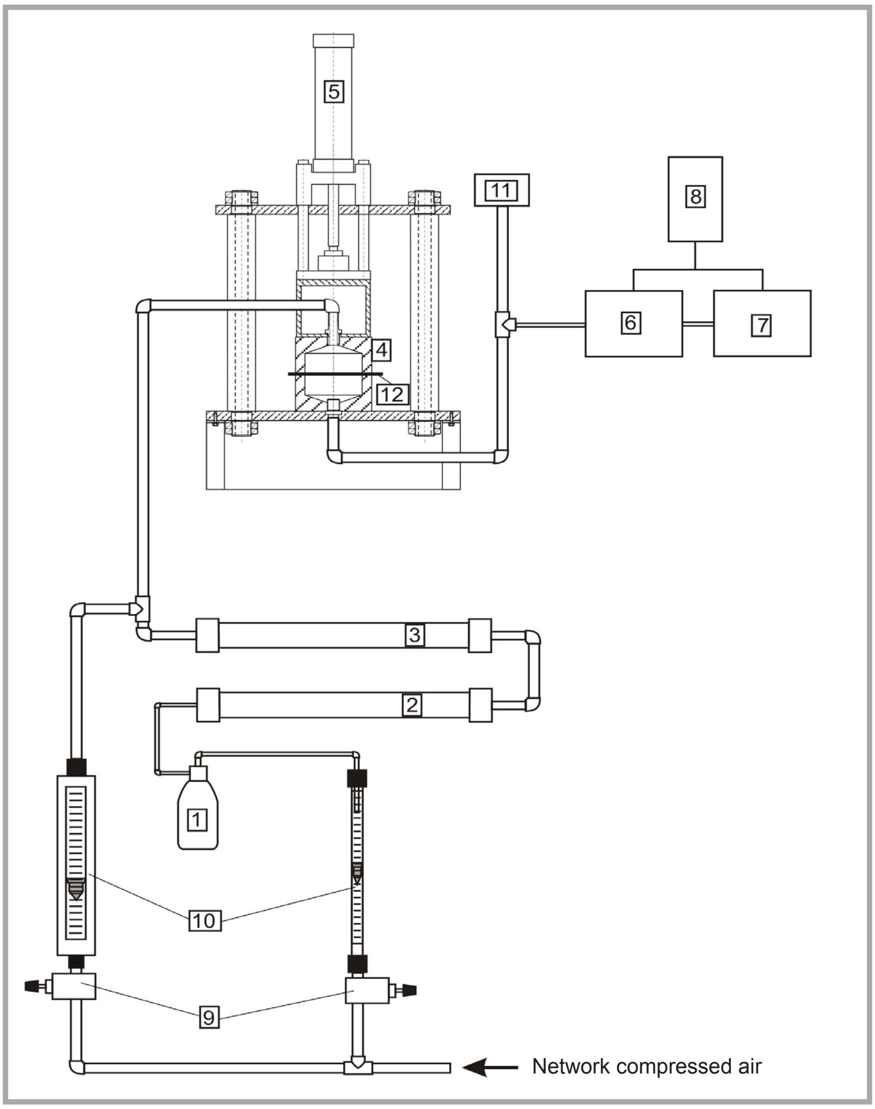

Figure 8. *Schematic diagram of the experimental set up; 1 – Nanoaerosol generator, 2 – Desiccant, 3 – Electrostatic charge neutraliser, 4 – Testing chamber, 5 – Sample holder, 6 – Electrostatic particle classifier, 7 – Condensation nanoparticle counter, 8 – Personal computer, 9 – Compressed air valve, 10 – Flowmeter, 11 – High efficiency filter, 12 – Test sample.*

Table 4. *Nonwoven filtration parameters determined by standard methods [15, 16].*

Nonwoven type	Mean sodium chloride aerosol penetration, %	Mean paraffin oil mist aerosol penetration, %	Mean air resistance, Pa
Polypropylene nonwoven, **charged**	0.78	2.89	270
Polypropylene nonwoven, **uncharged**	5.46	5.75	260
Perlite-modified polypropylene nonwoven, **charged**	0.44	1.35	290
Perlite-modified polypropylene nonwoven, **uncharged**	3.35	3.86	275
Amber-modified polypropylene nonwoven, **charged**	0.51	1.82	255
Amber-modified polypropylene nonwoven, **uncharged**	3.75	5.14	250

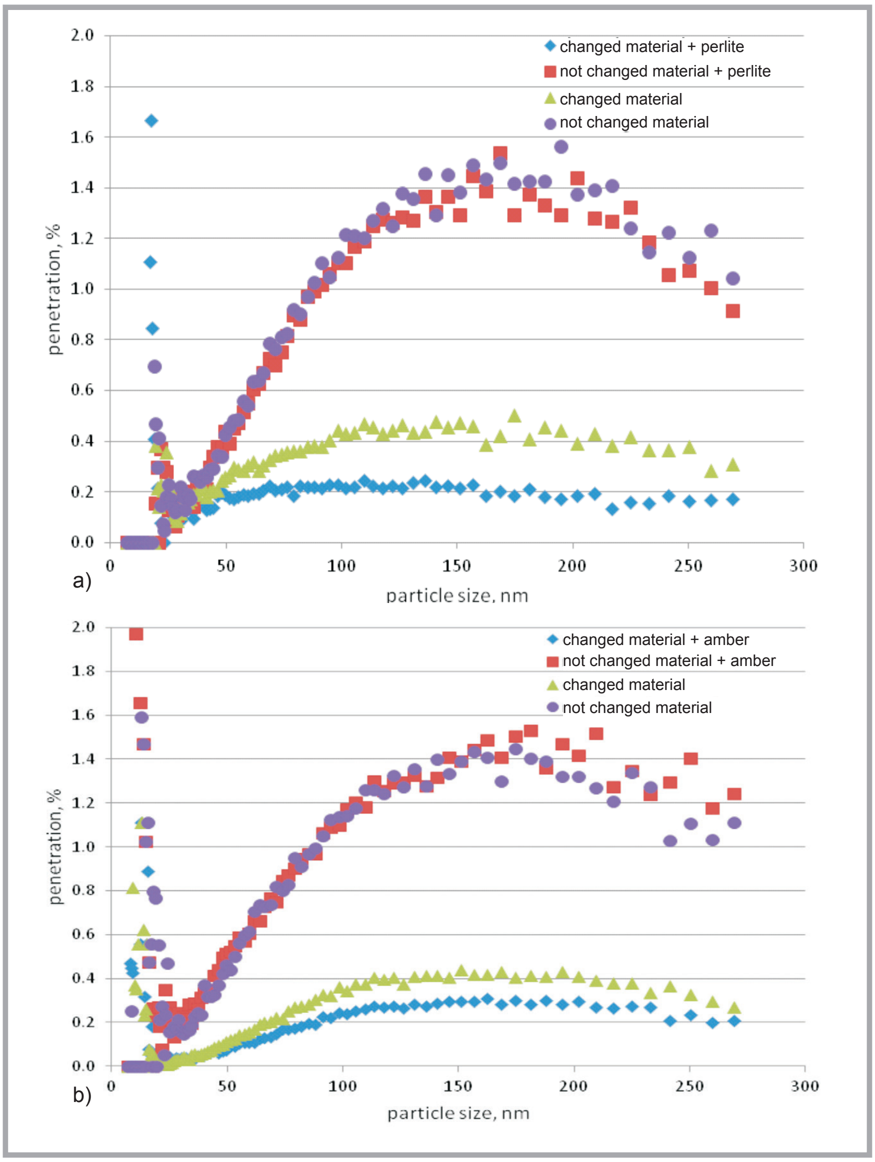

Figure 9. *Results of NaCl nanoparticle penetration through electret nonwovens with and without a modifier in the form of amber (a) and perlite (b) beads.*

methods with reference to the defined mean particle size typical of an aerosol type, the mean penetration index for nanoparticles was also determined (***Table 5***). It follows from these values that the perlite-modified electret nonwoven (positive charge) is the most favourable, having the lowest nanoparticle penetration index. This is also confirmed in the plot of the relationship between penetration values and nanoparticle sizes (***Figure 9.b***).

A statistical evaluation was performed to determine the significance of differences in the nanoparticle penetration index for the nonwoven varieties prepared. The results are shown in amatrix (***Table 6***). The statistical tests were performed at the significance level α = 0.05.

The results of the statistical analysis confirmed our earlier assumptions related to improving the efficiency of electret filtration nonwovens for nanoparticles by means of modifiers added to PP. Irrespective of the type of modifier used, all of the varieties of the melt–blown nonwovens had air resistance (breathing resistance) at a level of 250 Pa to 290 Pa (***Table 4***). This confirms that the modification method used for melt-blown nonwovens improved particle retention efficiency in the filtration material without significantly increasing breathing difficulties for equipment users. Furthermore it was noted that the values are similar to those commonly achieved by respiratory protective devices.

Conclusions

We have proved that it is possible to modify PP electret melt-blown nonwovens to improve their filtration efficiency (lower number of particles penetrating through filtration nonwovens) by adding modifiers with various electrostatic potentials to the polymer material. A greater improvement in electret filtration efficiency was seen for nonwoven modification with perlite beads (positive) and positive corona discharge than for amber beads (negative) and positive corona discharge. When the modifiers used in PP nonwovens had the same sign as the corona discharge, their electrostatic potential increased.

Acknowledgements

The project is implemented under the Operational Programme Innovative Economy (POIG) 2007–2013, Priority 1: "Research and development of modern technologies"; Measure 1.1: "Support for scientific research aimed at creation of economy based on scientific knowledge"; Submeasure 1.1.2: "Strategic programmes of scientific research and development".

References

1. Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR), The appropriateness of existing methodologies to assess the potential risks associated with engineered and adventitious products of nanotech-

Table 5. *Mean NaCl nanoparticle penetration through the nonwovens with and without a modifier.*

	Amber-modified polypropylene nonwoven		Perlite-modified polypropylene nonwoven		Polypropylene nonwoven	
	with electrostatic charges	**without electrostatic charges**	**with electrostatic charges**	**without electrostatic charges**	**with electrostatic charges**	**without electrostatic charges**
mean	2.396	12.293	1.934	11.271	3.664	11.768
standard deviation	0.253	3.059	0.679	3.025	0.774	2.971
variance	0.064	9.355	0.461	9.153	0.600	8.826

Table 6. *List of statistical test results; + Statistically significant differences (mean A $\neq$ mean B), - No statistically significant differences (mean A = mean B).*

B \ A		Amber-modified polypropylene nonwoven		Perlite-modified polypropylene nonwoven		Polypropylene nonwoven	
		with electrostatic charges	without electrostatic charges	with electrostatic charges	without electrostatic charges	with electrostatic charges	without electrostatic charges
Amber-modified polypropylene nonwoven	**with electrostatic charges**		+	+	+	+	+
	without electrostatic charges	+		+	-	+	-
Perlite-modified polypropylene nonwoven	**with electrostatic charges**	+	+		+	+	+
	without electrostatic charges	+	-	+		+	-
Polypropylene nonwoven	**with electrostatic charges**	+	+	+	+		+
	without electrostatic charges	+	-	+	-	+	

nologies, SCENIHR/002/05, September 2005.

2. Yang W, Peters JI, Williams III RO. Inhaled nanoparticles – A current review. *International Journal of Pharmaceutics* 2008; 356: 239–247.
3. Gradoń L, Podgórski A, Balazy A. Filtration of Nanoparticles in the Nanofibrous filters. In: *FILTECH EUROPA 2005 Conference*, Wiesbaden, Germany, 2005; II: 178–185.
4. Podgórski A, Balazy A, Gradoń L. Application of Nanofibers to Improve the Filtration Efficiency of the Most Penetrating Aerosol Particles In Fibrous Filters. *Chem. Eng. Sci.* 61: 6804–6815.
5. Kim SCh, Harrington MS, Pui DYH. Experimental study of nanoparticles penetration through commercial filter media. *Journal of Nanoparticle Research* 2007; 9: 117–125.
6. Fjeld RA, Ownes TM. The Effect of Particle Charge on Penetration in an Electret Filter. *IEEE Transactions on Industry Applications* 1988; 24; 4.
7. Tsai PP, Wadsworth Larry C. Electrostatic Charging of Melt Blown Webs for High-Efficiency Air Filters. *Advances in Filtration and Separation Technology, American Filtration and Separation Society* 1995; 9: 473.
8. Tsai PP, Wadsworth Larry C. Effect of Polymer Properties on the Electrostatic Charging of Different Media Structures for Air Filters. In: *SPE, ANTEC 96*, Indianapolis, s. 3642.
9. Brochocka A. Characteristics of melt-blown filter materials produced by simultaneous blowing of polymer melt from two extruders. *Fibres & Textiles in Eastern Europe* 2001; 9: 66–69.
10. Tsai PP, Schreuder-Gibson H, Gibson P. Different Electrostatic Methods for Making Electret Filters. *Journal of Electrostatics* 2002; 54: 333-341.
11. Brochocka A, Majchrzycka K, Domaradzka S. Wpływ warunków aktywacji elektrostatycznej włóknin pneumotermicznych na ich właściwości filtracyjne. *Bezpieczeństwo Pracy* 2002: 26-28.
12. Brochocka A, Majchrzycka K. Technology for the Production of Bioactive Melt-Blown Filtration Materials Applied to Respiratory Protective Devices. *Fibres & Textiles in Eastern Europe* 2009; 17(5): 92-98.
13. Patent. Poland, 388 071 (2009).
14. Jankowski T. Badania wpływu porowatości materiałów filtracyjnych na proces filtracji aerozoli cieczy. *Bezpieczeństwo Pracy* 2007; 6: 20-23.
15. Standard EN 13274-7: 2008 Respiratory protective devices. Methods of test. Part 7: Determination of particle filter penetration.
16. Standard EN 13274-3:2001 Respiratory protective devices. Methods of test. Part 3: Determination of breathing resistance.

Received 04.04.2012 Reviewed 12.11.2012

INNOVATIVE ECONOMY
NATIONAL COHESION STRATEGY

Nano Protect

EUROPEAN UNION
EUROPEAN REGIONAL DEVELOPMENT FUND