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Effective removal of odors from air with polymer nonwoven structures doped by porous materials to use in respiratory protective devices

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Abstract: Filtering Respiratory Protective Devices (FRPD) is not typically evaluated for exposure to volatile compounds, even though they significantly affect their protective performance. Such compounds are released into the atmosphere by industrial processes and pose serious health risks in people inhaling them. The adsorbent materials currently used to prevent those risks include activated carbon (AC). Zeolites and mesoporous silica materials (MCM) are very popular among the sorption materials. Due to their physical and chemical properties, they are able to adsorb significant amounts of volatile compounds from air. The melt-blown technology was used to produce filtering nonwovens with modifiers. As a result, polymer nonwoven structures with modifiers in the form of AC, zeolite (NaP1 type), molecular sieves (SM, SM 4Å) and mesoporous silica materials (MCM-41) were produced. The use of ACs (AC_1 from Zgoda and AC_2 from Pleisch) and their mixtures with others modifiers allowed to obtain satisfactory sorption, protective and utility properties. The longest breakthrough time against cyclohexane (approx. 53 min) was afforded by a variant containing AC, against ammonia (approx. 12 min) for the variant with AC_2 and a mixture of AC_2 and MCM-41. In the case of acetone vapor satisfactory breakthrough times were found for the variants with AC_2 and AC_1+SM (~20–25 min.). The present work deals with scientific research to improve workers' and society's health and safety by pursuing a better working life, and creating a safe social environment.

Introduction

In recent years it has become obvious that public health is increasingly affected by all types of environmental pollution (Michalak et al. 2014, Pope III and Dockery 2016, Buteau and Goldberg 2016, Schmid et al. 2009, Buonanno et al. 2013). Air quality is now more often evaluated in terms of the presence of offensive odors. Many odoriferous substances, both organic and inorganic (Rybarczyk et al. 2019), elicit unpleasant sensations in humans even at low concentrations. Such substances may be released as a result of natural processes or human activity, such as industrial production (in the food, fuel, and chemical industries), waste management (including waste transfer stations), emissions from motor vehicles, composting facilities, etc. (Haobo et al. 2017, Kumar 2019). Malodorous compounds may lead to various adverse psychosomatic reactions (Rybarczyk et al. 2019). Long term exposure to volatile organic compounds (VOCs) results in, e.g., damage to the central nervous system and liver, and irritation of the eyes and pharynx. VOCs are organic compounds which characterize with fast evaporation at room temperature and low water solubility. These chemicals are widely used not only in various manufacture processes of, e.g., glues or pharmaceuticals and are used as industrial solvents, but they are also preset at home, because they can be found i.a. in the petroleum fuels, paints or cleaning supplies, making exposure to airborne VOCs unavoidable. In addition, most VOCs have carcinogenic properties and are precursors of photochemical smog (Das et al. 2004, Xueyang 2017, Wang et al. 2015; S.S. Anand et al. 2014). Toxic odoriferous substances also include volatile sulfur compounds and inorganic ammonia (Kumar et al. 2019). The concentration of toxic and obnoxious gases in the air may be minimized by ventilation, or alternatively by catalytic, photocatalytic, or thermal oxidation as well as adsorption and biofiltration (Wang et al. 2015, Huang et al. 2002). In recent years, numerous adsorbents have been developed to improve filtration efficiency (Tsai et al. 2008) and indeed, the most widespread and preferred method of removing offensive and toxic odors from atmospheric air is adsorption (Kumar et al. 2019). In the adsorption process, the barrier for harmful

odorous substances is the adsorbent material. It has a large specific surface (over 1000 m^2/g), which translates into its sorption capacity. Due to its porous structure, it is capable of cleaning vapors from particles of harmful and hazardous substances. There are also known methods that improve selectivity or adsorption, e.g., carbon surface impregnation with orthophosphoric acid allowed to improve the efficiency against ammonia and trimethylamine vapors (Oya and Iu 2002; Szynkowska et al. 2009). The adsorption method combines advantages such as commercial availability, possibility of recovery of adsorbed compounds, and carrying out the tests under various conditions of temperature and humidity as well as test gas concentrations. Additionally, adsorption is carried out under the dynamic flow and can be combined with other technologies (Schlegelmilch et al. 2005, Namieśnik et al. 2019). Filtering half masks, which are the most popular type of respiratory protective devices (RPD), are increasingly often made of polymeric structures containing activated carbon-based adsorbents (Deng et al. 2017). Such equipment is designated for use in workplaces in which malodorous compounds occur but do not exceed maximum allowable concentrations (MACs). Their presence may cause unpleasant sensations and trigger immediate reactions such as excessive perspiration, increased blood pressure, and an elevated heart rate, while long-time exposure may lead to allergies, headaches, nausea, diarrhea, and respiratory tract irritation (Krajewska and Kośmider 2005, Makles and Galwas-Zakrzewska 2005). The use of polymeric nonwovens containing activated carbon in respiratory protective devices results in a significant odor reduction without impeding their functional properties. However, it should be noted that due to their intended applications, filtering half masks do not have to meet the rigorous breakthrough time requirements specified in the standards harmonized with the Regulation of the European Parliament and of the Council on personal protective equipment used under conditions in which the MACs of harmful substances are exceeded (Regulation (EU) 2016/425).

The most widely used adsorbent materials include activated carbon, carbon nanotubes, biochar, molecular sieves (zeolites and mesoporous silica), activated aluminum oxide, silica gels, synthetic polymers, zirconium oxide, and metal-organic frameworks, whose properties and limitations are presented in Table 1 (Kumar et al. 2019, Amid et al. 2016, Zhang et al. 2017). Materials involving activated carbon are the most popular media used for purifying both water and air. Activated carbon may be applied in different forms, and especially powder, granules, and fibers (Yue and Vakili 2017). Indeed, the effectiveness of the removal of chemical compounds depends on the kind of activated carbon used. Activated carbons with different porous structures and specific surface areas are produced from organic precursor, such as wood, peat, lignite, hard coal, and coconut husk, as well as some waste materials (e.g., biomass and plastic) (Stelmach et al. 2006, Duad and Haushamnd 2010, Xin et al. 2019). The precursor of activated carbon (Rubahamya et al. 2019) and the activation method are of the essence as they affect the microporous structure of the resulting adsorbent and the chemical properties of its area surface, and thus influence its adsorption-desorption parameters, including kinetics and dynamics. Activated carbon is the most universal porous material due to its high thermal stability, mechanical resistance, hydrophobicity, and availability. It exhibits satisfactory chemical resistance to both acidic and basic media and good regeneration capacity. It is characterized by a high specific area and its porous structure can be readily designed to obtain very good adsorption properties (Deng et al. 2017, Chiang and Juang 2017, Balanay and Lungu 2016, Baysal 2019). Due to their large internal surface area, activated carbon pores are well-suited for the adsorption of hydrophobic organic compounds (Kraus et al. 2018). Another class of very efficient products used for adsorbing malodorous substances are activated carbon fibers, which exhibit high sorptive capacity and have attracted considerable attention for that reason (Chemg et al. 2004, Balanay et al. 2014).

Interesting alternatives to carbon media are offered by a wide range of zeolites and mesoporous silica materials characterized by greatly ranging properties (hydrophobicity and pore size and shape) determining their adsorption capacity towards VOCs (Kraus et al. 2018). These materials are widely used for filtering gases, wastewater, and soil (Czuma et al. 2016, Zendelska et al. 2018, Yin et al. 2020). Zeolites reveal numerous beneficial characteristics, including high adsorption capacity, the molecular sieve effect, and thermal stability. The adsorption parameters of these materials are related to the Si/Al ratio, cation type, pore structure, and acidity (Ki-Joong and Ho-Geun 2012). Mesoporous silica materials exhibit an ordered structure with hexagonally arranged pores, a specific surface area of more than 1000 m^2/g, and good chemical stability in VOC adsorption processes. The most popular mesoporous silica materials types are SBA-15 and MCM-41. They are used in many chemical engineering and environmental protection applications focused on adsorption, separation, and catalysis (Panek et al. 2017).

An uncomplicated, universal and environmentally friendly technology for the production of functionalized composite materials is the technique of pneumothermic formation of nonwoven structures (melt-blown). It allows to introduce in a sufficiently large amount of modifiers in the structure of polymer fibers in order to obtain different functionalities (depending on the additive) in one integrated technological process. There are known solutions characterized by the use of two extruders in the melt-blown process creating a multilayer composite consisting of two different types of polymers (Hassounah et al. 2014). Zhang et. al, used a powdered modifier (Magnesium Stearate – MgSt) which was mixed with PP granulate and added to the extruder. Due to the increased melting temperature in the extruder (282°C), MgSt particles during the process melted and did not agglomerate on the surface of the produced fibers. The role of MgSt was to sustain electrostatic charges applied in the process of producing a filtering nonwoven to improve its filtration efficiency (Zhang et al. 2018). The authors of the work (Brochocka et al. 2018) presented the method of introducing additives into nonwoven structures using the melt-blown technique, feeding a modifier in the form of a powder to the fiber-making space by a mechanical method using a screw extracting a modifying substance from a suitable vessel. At work (Cerrilo et al. 2020) research was conducted to assess the biocidal properties of the polymer

Table 1. Properties and limitations of adsorbents used for purifying waste water and air and in respiratory protective devices

Adsorbent	Main properties	Limitations	Used for purifying waste water and air	Used in respiratory protective devices
Activated carbon	– Microporosity – Large surface area – High thermal stability – Mechanical resistance – Chemical resistance – Good regeneration capacity – Hydrophobicity – High adsorption capacity – Commercial availability – Low price	– Limited applicability to certain chemicals, – Need for chemical (or thermal) treatment to remove the adsorbed compounds	+	+*
Carbon nanotubes	– Large surface area – Hydrophobicity – High adsorption capacity	– Distorted basic plane during synthesis processes	+	–
Molecular sieves: zeolites and mesoporous silica	– Microporosity – Large surface area – Thermal stability – Chemical stability – Hydrophobicity – High adsorption capacity	– High costs – Low efficiency	+	–*
Synthetic polymers	– Porosity – Large surface area – High filtration efficiency – Tight pore size and high barrier properties	– Reduction of filtration efficiency in time – charge decay	+	+*
Zirconium oxide	– Good chemical and dimensional stability – High mechanical strength and toughness – Excellent resistance to corrosion – High biocompatibility	– Reduction in adsorption capacities against basic chemicals	+	–
Metal-organic frameworks	– Microporosity – Large surface area – Modification possibility – High adsorption capacity – High thermal stability – Easy regeneration	– Low commercial availability	+	–

*** – used in described studies**

matrix containing two types of zeolites with different Si/Al ratio doped Ag. As a result the Ag-zeolite-polymer composite had a very high biocide activity against *S. aureus*. However, the incorporation of Ag-zeolites at the polymeric formulation was limited due to the darkening of the sample, probably because of the presence of reduced silver species.

In this work, a newly designed nonwoven structure was produced, into which a free-flowing modifier and modifier blends (active carbon/zeolite/mesoporous silica material) were introduced directly into the fiber-forming head in the fiber-polymers zone by the pneumatic method. While the aforementioned materials have been studied to date separately (Brochocka et al. 2019, Okrasa et al. 2019), this paper examines their innovative application in the form of mixtures of activated carbon and non-commercially used before in the respiratory protective equipment zeolites, and mesoporous silica materials, which were introduced simultaneously during the production of a filtration nonwovens. The objective of this study is to define the protective (sorption and filtering) as well as functional properties of novel melt-blown nonwoven composites incorporating not used before in this type of research adsorbents and their mixtures with reference to the textural parameters of the modifiers and the method of their introduction into the polymer structure. It is worth noting that the investigated composite materials were made with the use of melt-blown, an innovative technology of forming filter nonwovens. The multi-purpose (absorbing and filtering) character of nonwovens was given by introducing sorption materials with very good textural properties into the structure of elementary fibers in one technological process. Their basic protective and functional parameters, including their sorption capacity against various test substances, were also checked on an innovative test stand created for the purpose of testing the protective time of respiratory protective devices.

Materials and Methods

Modifiers

The modifiers included two types of activated carbon (AC_1 – S.I. Zgoda, Konstantynow Lodzki, Poland, and AC_2 – Pleisch AG, Bäretswil, Switzerland), which were ground by ball mill, and commercial molecular sieves SM 4Å and SM (Sigma-Aldrich, Poznan, Poland). Additionally, mesoporous silica (MCM-41) and zeolite Na-P1, both synthesized from fly ash by the conventional hydrothermal method, were used as modifiers. Activated carbons used as modifiers were characterized by the techniques listed below, while the other modifiers were characterized by Brochocka et. al in previous work (Brochocka et al. 2018).

Nonwovens composites and processing equipment

Filtering nonwovens were made of Borealis HL 508J isotactic polypropylene (PP) granulate (Nexeo Solutions Poland Sp. z o.o., Warsaw, Poland) with the following parameters:

- melting temperature: 156–160°C,
- melt flow index (MFI): 800 g/10 min,
- density: 50.3 g/m^3.

Nonwoven composites were made using the melt-blown technology in which polymer melt was air-blown into elementary fibers of various thicknesses and lengths, while carbon, zeolite, silica, carbon/zeolite, or carbon/silica modifiers were introduced directly into the stream of elementary polymeric fibers using the pneumatic method. The net of fibers with incorporated modifiers was electrostatically activated at 25 kV. The resulting composites were collected from the take-up device. The modifier content was 60 g/m^2; in those cases where three modifiers were used (activated carbon/zeolite, activated carbon/silica or activated carbon/molecular sieves) their ratio was 30:30 g/m^2.

Using the melt-blown technique for the development of multifunctional PP-based composites, additives with various physical and chemical properties were used, which were introduced at the polymer fiber molding stage by applying them to a plastic polymer stream, omitting zones of high extrusion temperatures. Technological parameters of the process are presented in Table 2.

Figure 1 presents the method of introducing the mixture of modifiers directly into the fiber-forming head that consists in the use of a stub supplied with compressed air. The compressed air flowing out of the injector nozzle produced a vacuum in the aerosol mixing chamber, which was used to take the modifier from the dispenser. A mixture of modifiers diluted with expanding air was administered in the form of an aerosol through a duct in the channel of the head to the fiber production space. The applied solution eliminates the administration of modifiers by means of a screw placed in the channel of the fiber-forming head and ensures convenient feeding of any modifier centrally and symmetrically to the fiber production zone, which allows its even application in the structure of the produced fleece nonwoven fabric. Moreover, this method allows for the shortening of modifier residence time in the heated head zone, thanks to which modifiers with low temperature resistance can be applied.

For the needs of the present study, 10 nonwoven polypropylene composites incorporating various adsorbents and their mixtures were produced. In order to verify the protective and functional properties of the produced filtering nonwovens with modifiers, the results were compared to the reference sample – corona charge polypropylene nonwoven (PPQ).

Methods

Textural and morphological analysis

Textural studies involved the determination of basic surface and volumetric parameters using an ASAP 2020 surface area analyzer (Micromeritics Instrument Corporation) on the basis of nitrogen vapor adsorption and desorption isotherms at liquid nitrogen temperature (77K). The specific surface area was determined by BET method. Pore size distribution and average pore volume were calculated from BJH (Barret–Joyner–Halenda) method. Micropore volume was determined from t-plot method. Additionally, micropore size distribution was calculated by DTF method. All parameters were estimated from the isotherms using ASAP 2020 software provided by the equipment manufacturer.

Materials were characterized using an ultra-high resolution scanning electron microscope SU8010 (Hitachi, Japan). To increase conductivity, the composites were gold-coated using a Quorum Technologies Q150T ES sputter coater. Observations were conducted at an accelerating voltage of 10 kV and at magnifications of ×500, ×1000, and ×2000. All tests were carried out in triplicate at 20°C. In particular, scanning electron microscopy (SEM) was used to determine the equivalent diameter of carbon particles defined as the diameter of sphere with an area equal to that of the particle. In addition, an elemental analysis for activated carbons was also made. The elemental analysis of the activated carbons tested was performed using Perkin Elmer 2000 CHN analyzer. Furthermore, SEM was used to evaluate the homogeneity of distribution of carbon, zeolite, silica, carbon/zeolite, and carbon/silica modifiers, as well as to determine the way in

Table 2. Technological parameters of the melt-blown process

Technological parameters of the process	PP
Temperature of the first zone of the extruder, °C	280
Temperature of the second zone of the extruder, °C	270
Air temperature, °C	302
Nozzle temperature, °C	230
Air flow, m^3/h	4
Polymer flow rate, g/min	7

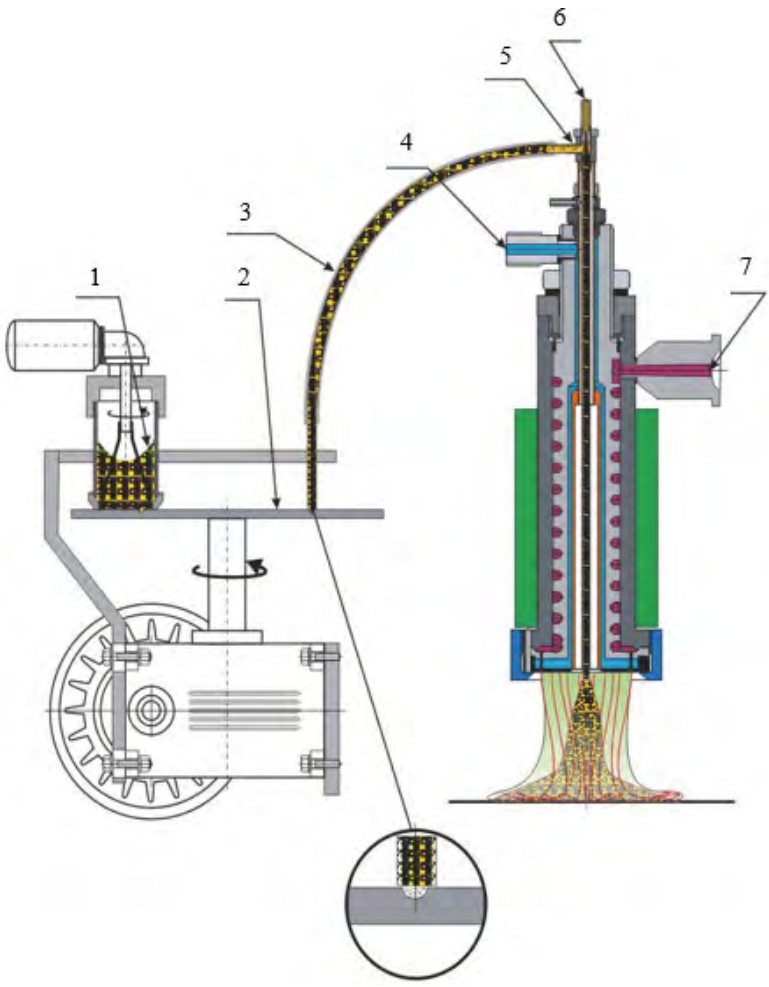


Fig. 1. Head unit and the modifier dispensing assembly: 1 – mixture of modifiers; 2 – dispenser; 3 – connecting tube, 4 – hot air; 5 – injector; 6 – compressed air; 7 – melted polymer

which modifier particles were embedded in the polymeric matrix.

In the studies of the acid-base properties of the activated carbons, the Boehm method was used. Both carbons do not have basic functional groups. Sample AC_1 has 0.20 mmol/g of acidic groups, whereas sample AC_2 has 0.43 mmol/g.

The XPS spectra for active carbons were recorded on an ESCA apparatus with a Scienta R4000 multidetection electron analyzer (VG Scienta, Sweden) in the fixed analyzer transmission mode. An unmonochromatized Al Kα source (1 253.6 eV) with a voltage of 12 kV and an emission current of 30 mA was employed. The powdered samples were placed on a molybdenum sample holder and submitted to a vacuum of 5×10^{-8} mbar. The C1s spectra were fitted, using CASA XPS software, with a Gaussian–Lorentzian peak shape after subtraction of the background with a Shirley baseline.

Sorption properties – breakthrough time

The test substances in the evaporator were subjected to compressed air to obtain gaseous aerosol (Fig. 2). Three toxic odoriferous substances: inorganic – ammonia and VOCs: cyclohexane and acetone were chosen as materials broadly used at various workplaces. Additionally, cyclohexane and acetone are organic compounds often used in this type of studies as a test substance that is safe for the operator (Okrasa et al. 2019). Moreover, cyclohexane and ammonia represent gases used to test the sorption capacity of filters and combined filters in accordance with the requirements of European standards (EN 14387:2004 + AC:2004). The concentration of those substances (ammonia – 20 ppm, cyclohexane – 86 ppm, acetone – 248 ppm) was set using a mass flow controller (*Red-y*) (no. 3, 7) and maintained at the same level for each sample. The concentrations of test substances have been selected to correspond to the values of maximum allowable concentrations established by European Union Commission Directive (Commission Directive 2000/39/EC, 2000) and to the maximum allowable concentrations (MACs) specified in the Regulation of the Minister of Labor and Social Policy of June 12, 2018 (Regulation of the Minister for Family, Labor and Social Policy on the Highest Permissible Concentrations and Intensities of Factors Harmful to Health in the Work Environment 2018) with a tolerance of ± 5 ppm.

Tests were conducted at a volumetric flow rate of 30 l/min, at a relative humidity of (70±5)% and room temperature of (20±1)°C (in accordance with European standard (EN 14387:2004+A1:2008)) (no. 13). Dräger X-am 7000 gas detectors (no. 12 and 14) were used to measure the concentration of the test gas upstream and downstream of the nonwoven sample (no. 11) mounted in a pneumatic holder (no. 10).

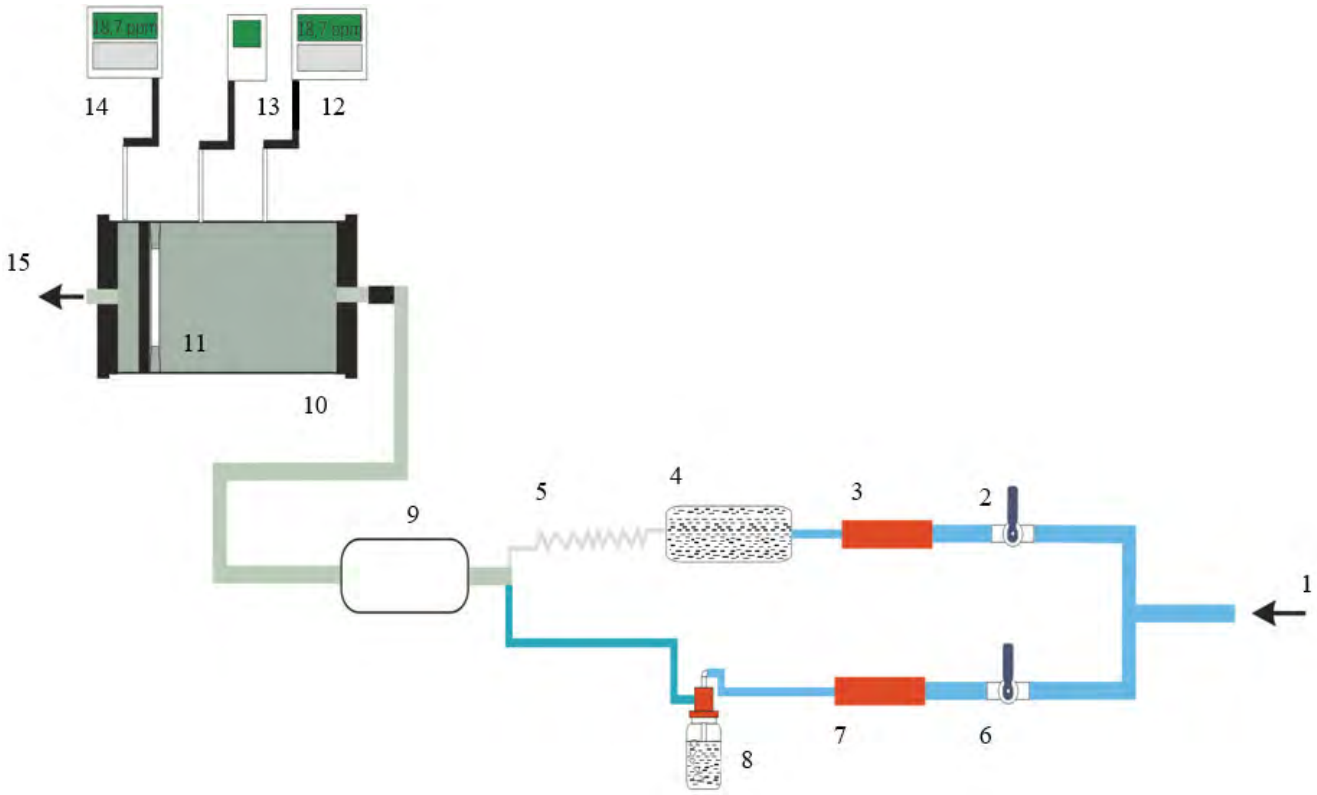


Fig. 2. Experimental stand for measuring the sorption capacity of volatile compounds for nonwovens: 1 – inlet for dried and compressed air; 2, 6 – air valves; 3, 7 – mass air flow controllers; 4 – humidifier, 5 – cooler; 8 – evaporator; 9 – test substance and air mixer; 10 – pneumatic holder; 11 – nonwoven sample; 12, 14 – gas detectors; 13 – thermohygrometer; 15 – test substance outlet to the fume cupboard

Sodium chloride aerosol penetration

Sodium chloride aerosol penetration was measured in accordance with the European standards concerning test methods and requirements for filtering facepiece respirators (EN 149:2001+A1:2009, EN 13274-7:2008). Compressed air was purified and dried by a filtering system, and then directed to an atomizer with an aqueous solution of sodium chloride to generate aerosol. The resulting polydisperse aerosol was directed to a pneumatic test chamber where the tested nonwoven sample was placed. The air passing through the sample was analyzed for the presence of the test aerosol using a flame photometer. Upstream concentration aerosol was (8±4) mg/m^3. The photometer measured the intensity of the light beam emitted by a hydrogen burner as an indicator of the aerosol concentration within the range of (0.001–100)%.

Paraffin oil mist aerosol penetration

Paraffin oil mist aerosol penetration was measured in accordance with the European standards concerning test methods and requirements for filtering facepiece respirators (EN 149:2001+A1:2009, EN 13274-7:2008). The aerosol produced using a Lorenz AGW-F/BIA generator was passed at a linear flow rate of 95 l/min through a nonwoven sample placed in a FH 143/149 pneumatic holder with a diameter of 113 mm. Aerosol concentration upstream and downstream of the nonwoven sample was measured using a Lorenz AP2E laser photometer after 3 min of the experiment (in the initial phase of filtration) and expressed as a percentage. Paraffin oil mist aerosol penetration P_{POM} was calculated from the following formula:

$$P_{POM} = ((l_2 - l_0)/(l_1 - l_0)) \times 100\% \quad (1)$$

where: l_0, l_1 and l_2 are photometric readings for pure air and paraffin oil mist aerosol upstream and downstream of the nonwoven sample.

Airflow resistance

Airflow resistance was determined pursuant to the European standards concerning test methods and requirements for particle filtering RPE (EN 149:2001+A1:2009, EN 13274-3:2008). In exhalation phase tests, air was passed through nonwoven samples at a constant volumetric flow rate and the downstream pressure differential was measured with respect to the atmospheric pressure. The airflow rate was 95 l/min, which corresponds to respiratory minute volume during strenuous work (EN 149:2001+A1:2009). Pressure was read from a *CMR-10 A* digital differential micromanometer.

Statistical Analysis

Statistical analyses were performed using STATISTICA 13.1 software (Statsoft, Tulsa, OK, USA). Descriptive statistics for all variables of interest were calculated. One-way analysis of variance (ANOVA) at the significance level 0.05 was performed to identify statistical differences between breakthrough times

determined for each of the test conditions. When statistical differences were detected ($p < 0.05$), mean values were compared using Tukey's post hoc procedure at the significance level 0.05.

Results

Modifiers – characteristics

The textural parameters of all modifiers are given in Table 3.

In terms of textural parameters, the largest BET surface area was found for the activated carbons AC_1 and AC_2 and the mesoporous silica MCM-41. In addition, while the BET surface area of the silica material SM was almost four times smaller than that of AC_1, its BJH pore diameter was similar to that of the widely used sorbents. The highest micropore volume was noted for both activated carbons and was much higher than that determined for other sorbents. On the other hand, the MCM-41 had the highest value of BJH average pore volume (even 4 to 7 times higher than AC_1 or AC_2) which is the result of a well-ordered mesoporous structure.

The distributions of equivalent particle diameters for the two activated carbon adsorbents (AC_1 and AC_2) after grinding in ball mill, were found to be markedly different (Fig. 3).

In the case of AC_1, the 300 µm fraction accounted for the highest percentage of the total (approx. 30%), followed by 250 µm (27%) and 350 µm (15%). Moreover, there was a small percentage of particles in the 600 µm fraction. In contrast, 55% of AC_2 particles had an equivalent diameter of 5 µm, and 15% of the particles were in the 10 µm fraction. None of the other diameter fractions (ranging from 15 to 50 µm) exceeded 10% of the total. The diversity in the particle size between two different activated carbons results from differences in the hardness and fragility of the materials, which effect on their susceptible to grinding. The shares of particular elements are different and depend on the type of the analyzed sample and its degree of coalification. Based on the obtained results (Table 4), it was found that the carbon content in various carbon adsorbents ranges from 70.7% to 87.7%, oxygen from about 11.4% to 26.8%, while the hydrogen content is in the narrower range 0.5–0.8%. The content of carbon, hydrogen and oxygen depends on the advancement of the degree of metamorphism. As is apparent, the increase in the content of element 'C' increases due to the increase in the degree of metamorphism. On the other hand, the oxygen content decreases and the hydrogen content decreases slightly. 'N' and 'S' shares in practice do not depend on the degree of fuel metamorphism.

The XPS spectra results showed an atomic concentration of carbon, oxygen, silicone and aluminum on the studied modifiers' surface layer. For activated carbon samples (AC_1, AC_2), the presence of carbon (approx. 90%) and oxygen (approx. 8%) in the surface layers was confirmed (Table 4), which indicates the presence of carbon atoms and carbon-oxygen connections on the surface of the tested samples.

Figure 4 summarizes the detailed spectra for the C1s band for selected modifiers from the group of active carbons. For AC_1 and AC_2 samples, the bands derived from the C1s coating, with a maximum binding energy at 284.2 eV were divided

Table 3. Characteristics of texture parameters of all modifiers

Modifier	AC1	AC2	Na-P1	SM 4Å	SM	MCM-41
BET surface area, m^2/g	1201	1003	38	3	325	953
Micropore volume (t-Plot), cm^3/g	0.410	0.400	0.010	0.001	0.020	0.003
BJH pore diameter, nm	2.10	2.08	12.07	4.51	2.23	3.12
BJH average pore volume, cm^3/g	0.19	0.12	0.16	0.01	0.13	0.85
DFT average pore diameter, nm	1.99	1.93	11.82	4.28	2.27	4.01

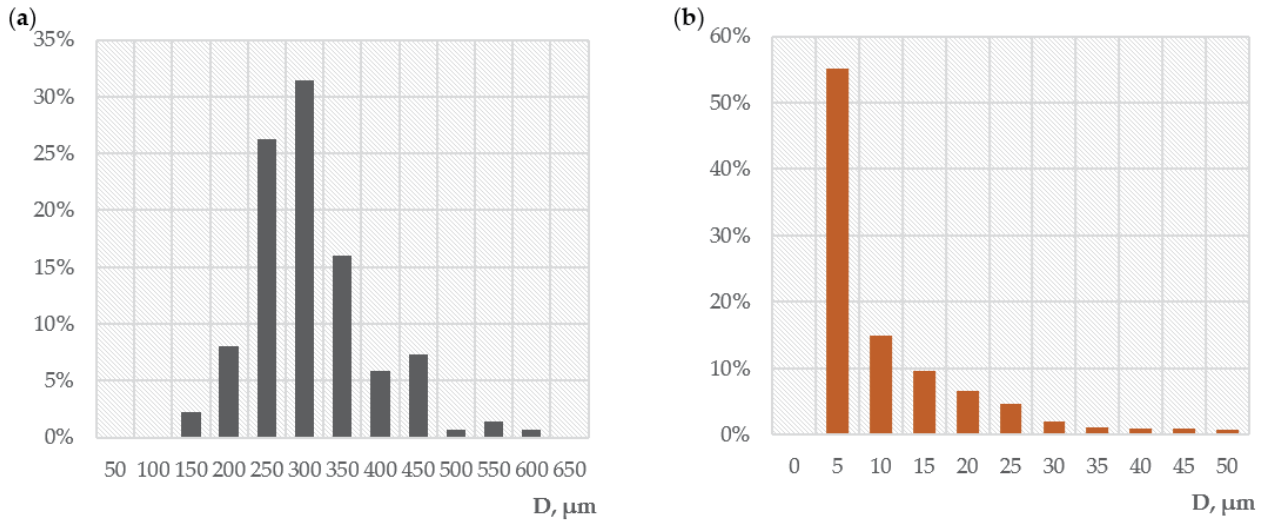


Fig. 3. Distribution of equivalent particle diameters activated carbon: (**a**) AC_1, (**b**) AC_2

into 8 components. The largest share (over 60%) in the C1s band has a component at 284.2 and 284.1 eV (respectively for AC_1 and AC_2), indicating the presence of carbon atoms from aromatic rings and the band at 285.0 and 285.7 eV (about 20% and 6–7%, respectively) for both materials, indicating CH bonds and the presence of aliphatic carbon atoms (CC, sp3 hybridization respectively). The bands with a percentage of 2.0–3.8%, for both materials, located in the range from 268 to 289 eV, indicate the presence of surface oxygen species associated with carbon atoms, i.e. COH, C-O-C, C=O and O=C-O.

Nonwoven – characteristics

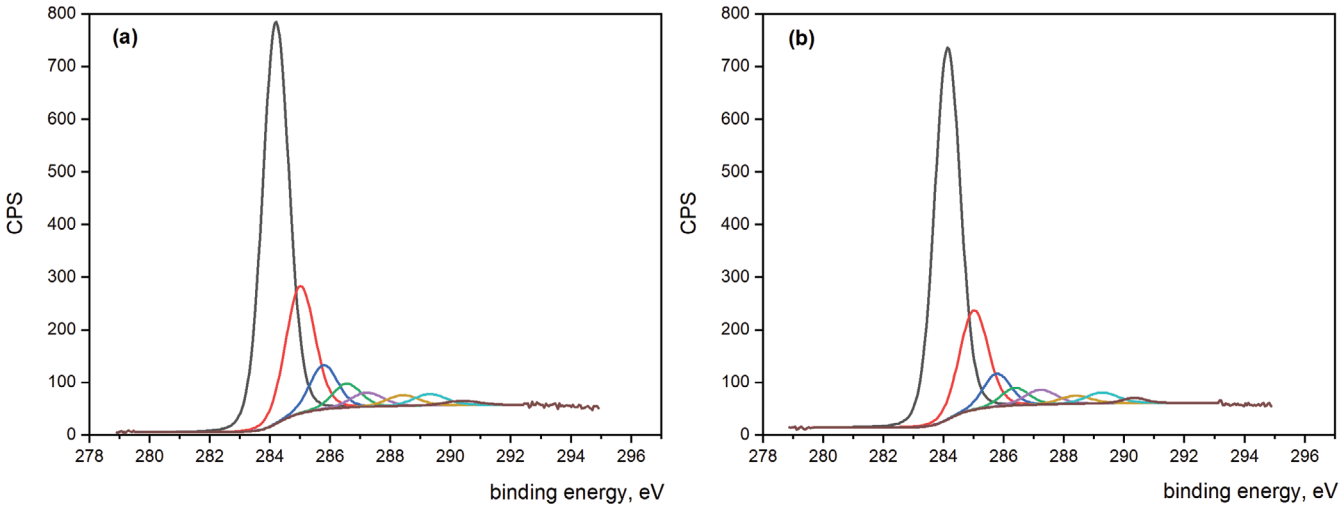
The basic characteristics of ten nonwovens composites, in terms of BET surface area, surface density and thickness, are given in Table 5 and Fig. 5.

Among the produced nonwoven composites, the variants PA with AC_1 and PB containing AC_2 were characterized by the highest BET surface areas. Significant differences of the discussed variants were observed in the case of other materials. The BET surface area for composite materials designated as PC-PJ was in the range of 478–320 m^2/g. As compared to the reference sample (PPQ), almost all variants exhibit substantially higher BET surface areas as a result of the incorporation of powdered modifiers in the nonwoven structure. It was found that the BET surface areas of the resulting composites depended on the BET surface areas of the incorporated modifiers (Table 3). It should also be noted that the addition of other sorption material to the carbon sorbent did not significantly reduce the textural properties.

The microstructure of the studied nonwoven composites incorporating carbon, mesoporous silica, molecular sieves, and zeolite modifiers is presented in Table 5. SEM images illustrate the distribution of AC_1 activated carbon particles in spaces between elementary fibers. The particles tended to form larger lumps, which indicates surface area expansion. In contrast, in the case of activated carbon AC_2, individual particles were deposited on the surface of polymeric fibers. The SEM images depict the structure of nonwoven composites incorporating modifier mixtures with the activated carbon AC_1. As can be seen, in all variants the activated carbon particles were entangled in the net of polymeric fibers, while MCM-41 (PC), Na-P1 (PD), SM 4Å (PE), and SM (PF) particles were attached to the surface of the fibers. In the case of PE, agglomeration occurred in inter-fiber spaces. Another group of nonwoven composites were structures that

Table 4. Chemical composition of studied activated carbons measured by XPS and CHNS methods

Method	Sample	C, %	O, %	Si, %	H, %	N, %	S, %
XPS	AC_1	91.7	7.5	0.5	–	–	–
	AC_2	87.3	8.0	–	–	–	–
CHNS	AC_1	87.7	11.4	–	0.5	0.3	0.1
	AC_2	70.7	26.8	–	0.8	1.0	0.7

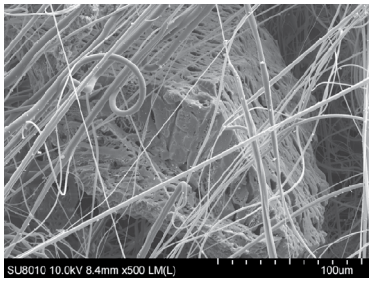
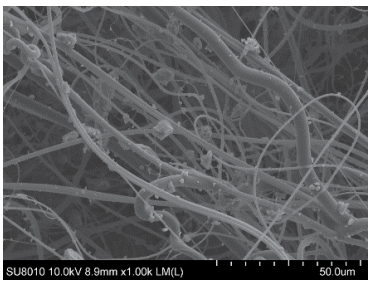
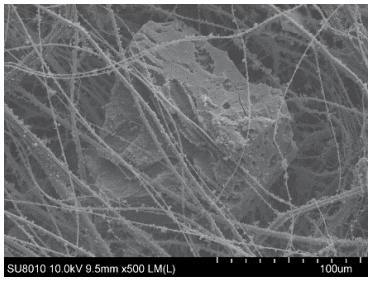
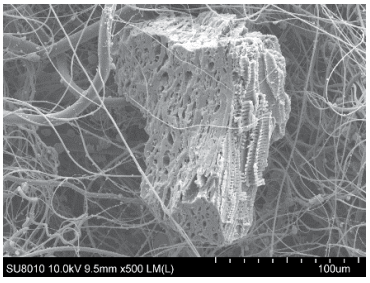
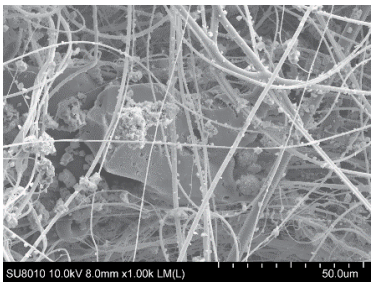
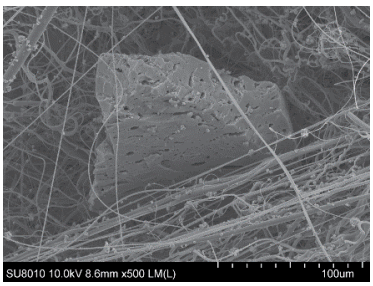


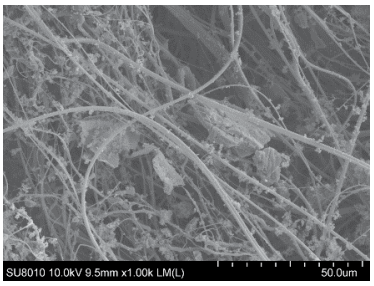
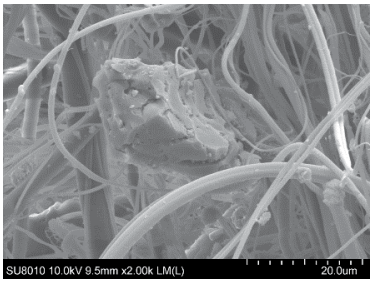
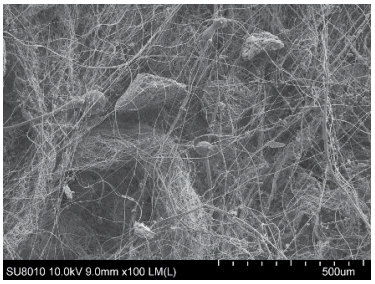
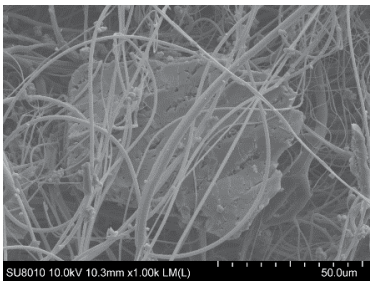
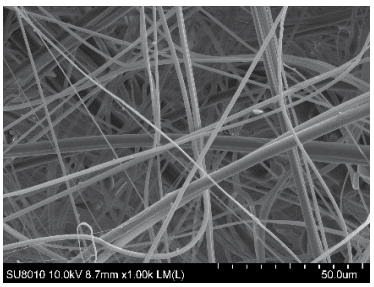
	Position	Offset	FWHM	Area	Area, %
C 1s A	284.19	0.00	1.03	868.95	60.40
C 1s B	285.00	0.81	1.14	306.50	21.30
C 1s C	285.77	1.59	1.09	101.41	7.05
C 1s D	286.54	2.35	1.10	55.18	3.84
C 1s E	287.21	3.02	1.26	37.23	2.59
C 1s F	288.41	4.22	1.23	28.11	1.95
C 1s G	289.30	5.11	1.27	30.08	2.09
C 1s H	290.40	6.21	1.29	11.24	0.78

	Position	Offset	FWHM	Area	Area, %
C 1s A	284.12	0.00	1.01	789.08	63.98
C 1s B	285.00	0.88	1.12	235.00	19.05
C 1s C	285.76	1.64	1.07	73.92	5.99
C 1s D	286.37	2.24	1.08	39.64	3.21
C 1s E	287.22	3.10	1.24	37.86	3.07
C 1s F	288.38	4.26	1.21	20.42	1.66
C 1s G	289.26	5.13	1.24	28.06	2.27
C 1s H	290.33	6.21	0.88	9.37	0.76

Fig. 4. Detailed XPS spectra for the C1s shell for: (**a**) AC_1, (**b**) AC_2

Table 5. BET surface areas of the produced nonwoven composites.

PPQ nonwoven with modifiers	Symbol of variants	BET surface area, m^2/g	SEM
PPQ-AC_1	PA	751	
PPQ-AC_2	PB	604	
PPQ-AC_1-MCM41	PC	461	
PPQ-AC_1 – NaP1	PD	469	
PPQ-AC_1-SM 4Å	PE	346	
PPQ-AC_1-SM	PF	321	

PPQ-AC$_2$-MCM41	PG	478	
PPQ-AC$_2$-NaP1	PH	359	
PPQ-AC$_2$-SM 4Å	PI	327	
PPQ-AC$_2$-SM	PJ	382	
PPQ	PK	2	

incorporated mixed modifiers containing the activated carbon AC$_2$. SEM images show activated carbon particles surrounded by MCM-41, while the mesoporous silica material was distributed quite evenly on polymeric fibers. A similar effect was observed for the other three variants (PH, PI, PJ), with non-carbon adsorbent particles predominantly deposited on the surface of elementary fibers.

As can be seen in Figure 5, most of the produced nonwoven composites were characterized by surface mass of 150–200 g/m^2. The highest value of that parameter was found for PB (212 g/m^2) at a thickness of 3.7 mm. The lowest surface density was found for the reference sample and the PC variant with AC$_1$ and MCM-41 modifier (95 g/m^2 and 150 g/m^2, respectively). Even though the same amount of modifiers by weight was added to the nonwoven structure, the resulting surface densities of the composites differed significantly due to differences in the specific densities of the modifiers. On the other hand, no statistically significant differences were found in terms of the thickness of the nonwoven composites, which ranged from 3.5 to 4.0 mm. As compared to the reference

sample, lower thickness was obtained for the variants PA, PB and PC despite their much higher surface densities.

Sorption properties – breakthrough time

Results concerning the duration of protection afforded by the obtained nonwoven composites incorporating zeolites, silica, carbon, and mixtures against acetone, ammonia, and cyclohexane are presented in figures 6–8.

In the case of acetone vapor (Fig. 6) satisfactory breakthrough times were found for the variants PB and PF. Breakthrough times for nonwoven composites containing various modifiers (AC_2) ranged from 20 to 25 min, while that for composites containing mixed modifiers (AC_1+SM) was approx. 10 min. In addition, breakthrough times for mixed modifiers containing the activated carbon AC_2 were longer than those for mixtures with AC_1.

Among the studied odoriferous substances, better protective properties were found only for cyclohexane, with breakthrough times of 10–20 min for most nonwoven composites (Fig. 7). The longest protection (approx. 53 min) was afforded by the variant PA containing activated carbon AC_1. Interestingly, PB sample, which also contained activated carbon (AC_2), but of a different type, did not exhibit such good properties. This indicates differences in the chemical composition of the tested activated carbons, translating into very different sorption parameters and breakthrough times for VOCs. In the case of the breakthrough time for cyclohexane, it was observed that the introduction of the

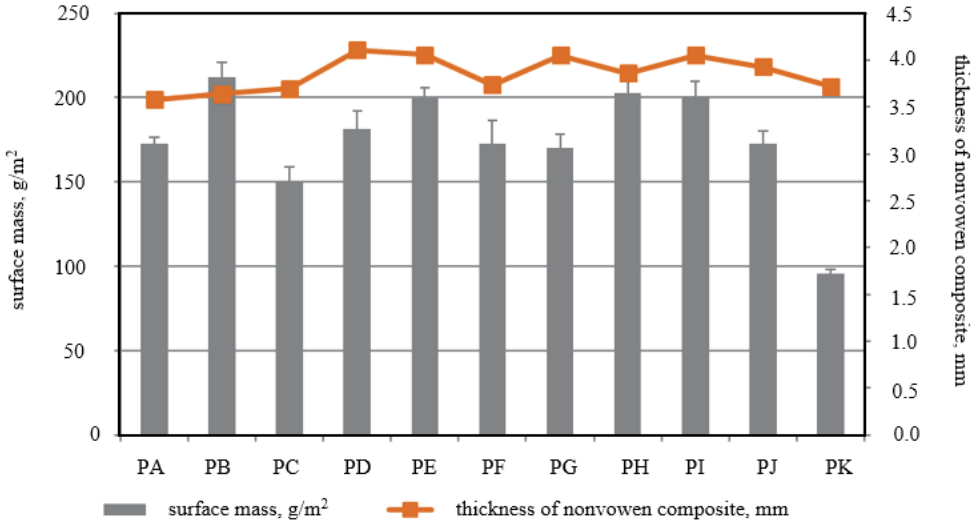


Fig. 5. Mean surface mass and thickness of the produced nonwoven composites (a–f – samples marked with different letters differ statistically significantly according to ANOVA, α=0.05 and Tukey's test, α=0.05). **PA** – PP with AC_1, **PB** – PP with AC_2, **PC** – PP with AC_1 + MCM-41, **PD** – PP with AC_1 + Na-P1, **PE** – PP with AC_1 + SM 4Å, **PF** – PP with AC_1 + SM, **PG** – PP with AC_2 + MCM-41, **PH** – PP with AC_2 + Na-P1, **PI** – PP with AC_2 + SM 4Å, **PJ** – PP with AC_2 + SM, **PK** – PPQ

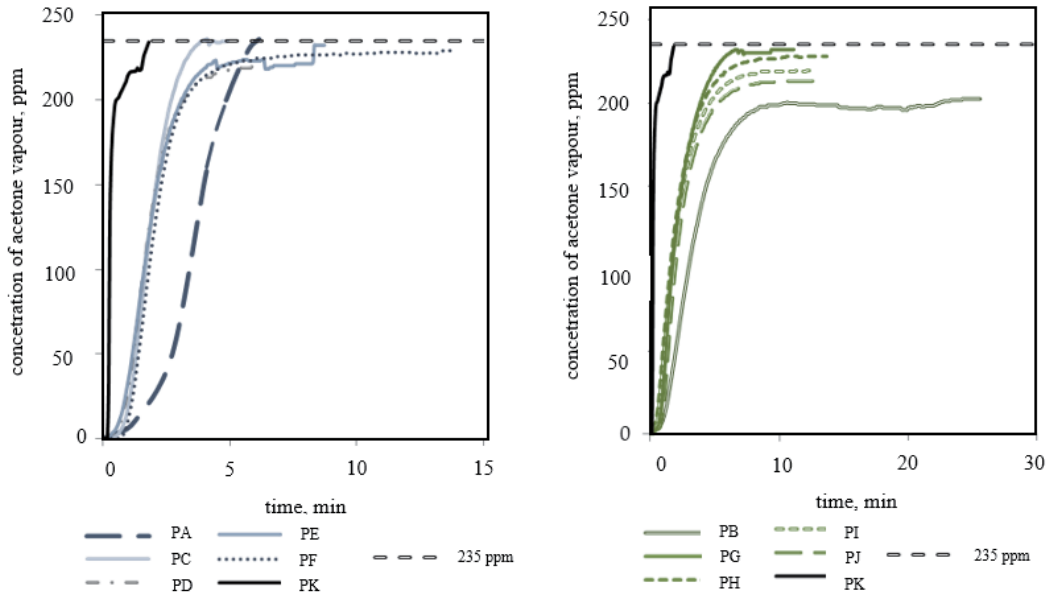


Fig. 6. Breakthrough time for nonwoven composites containing activated carbon, zeolites, and silica material against acetone vapor at MAC (235 ppm)

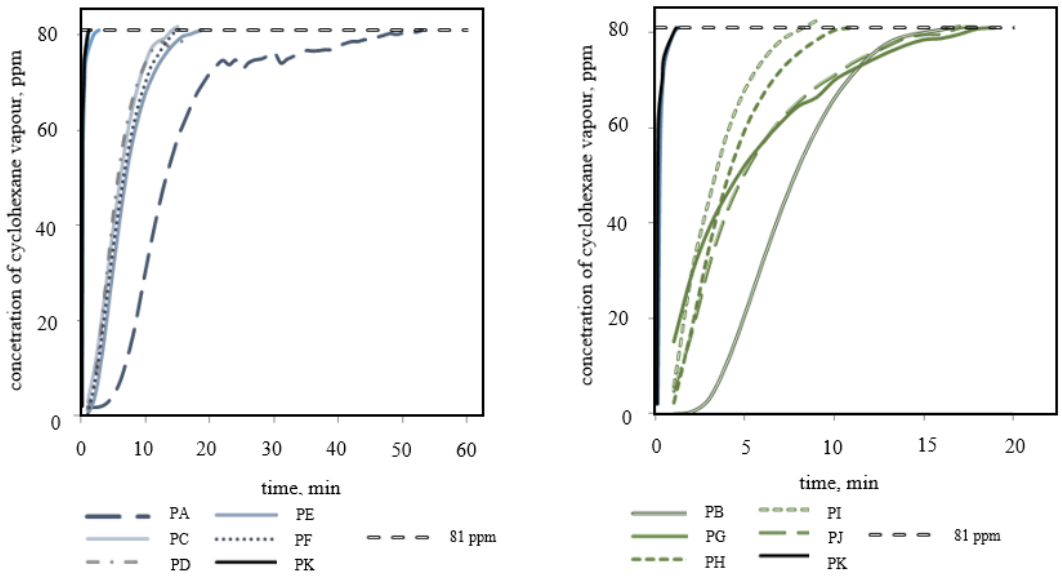


Fig. 7. Breakthrough time for nonwoven composites containing activated carbon, zeolites, and silica material against cyclohexane vapor at MAC (81 ppm)

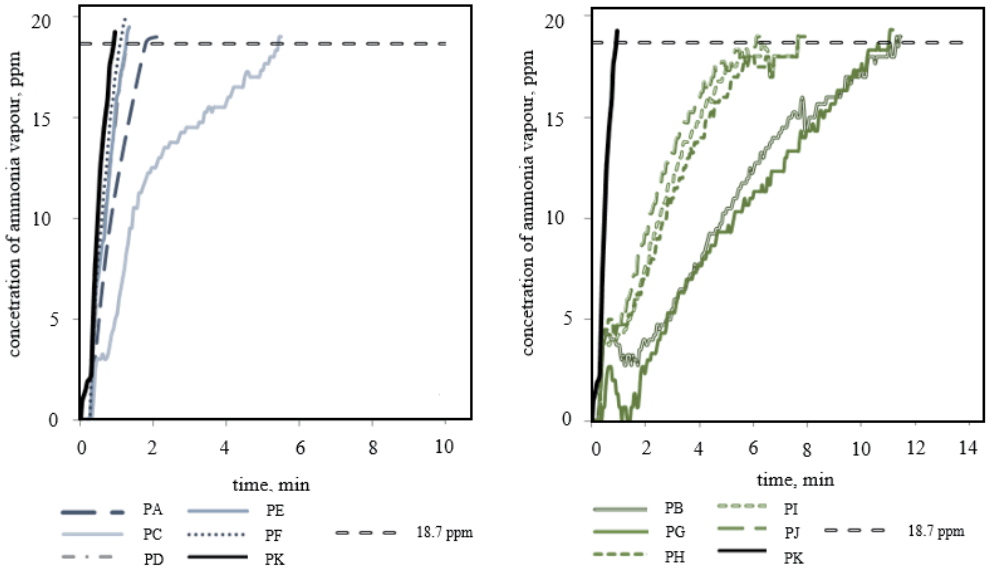


Fig. 8. Breakthrough time for nonwoven composites containing activated carbon, zeolites, and silica material against ammonia vapor at MAC (18.7 ppm)

modifier mixture into the fiber structure did not adversely affect the protective action time. This is very well visible in the PG and PJ variants, which contain activated AC_2 carbon, MCM-41 mesoporous silica material and molecular sieves SM, respectively. It is conditioned by good textural properties. Both MCM-41 and SM are characterized by high BET specific surface values (Brochocka et al. 2018) in relation to other sorption materials.

The tested nonwoven composites were challenged with the maximum allowable concentration of ammonia at 20 ppm (Fig. 8). The longest breakthrough time (approx. 12 min) was recorded for the variant containing activated carbon AC_2 (PB) and a mixture of AC_2 and MCM-41 (PG). Satisfactory results were also obtained for the PH-PJ variants incorporating mixtures of the activated carbon AC_2 and zeolites, with breakthrough times ranging from 6 to 8 min. Noteworthy is the PC variant, with a protective duration of about 6 minutes. In the case of variants based on PP and activated carbon AC_1, it is the only absorbing and filtering material that provides comfort during the presence of ammonia vapors. A similar relationship was demonstrated during studies of the absorption efficiency of these vapors for polymer materials based on activated AC_2 carbon (PG variant). Although a smaller amount of activated carbon was introduced into the fiber structure compared to the PB variant, the PG absorbent-filter material showed a similar breakthrough time to PB. It has been found that good sorption properties towards ammonia vapors are the result of the use of mesoporous silica materials (Brochocka et al. 2019).

Sorption properties – breakthrough time after regeneration of the adsorbent

The assessment of the protective action time (p. 3.1) against test substances from the group of organic and inorganic compounds allowed for the selection of variants characterized by the highest protective action times. Based on these data, the absorption efficiency and protection against the harmful effects of hazardous and toxic substances were determined.

Selected variants of filter nonwovens with the addition of porous sorbents were subjected to the regeneration process. These studies considered the best variants that had the longest breakthrough times for selected test substances. Samples of the nonwovens were placed in a Binder APT.lineTM VD, model VD53(E2.1) (BINDER GmbH, Germany) vacuum dryer and dried in a vacuum for 7 days at 90°C. After this time, the samples were sealed in sealed bags until repeated testing.

Sorption-desorption test was carried out at the stand for determining the protective action time. Properly prepared samples were treated with a gas mixture (air/test substance) until the nominal concentration (equal to NDS) – sorption was obtained, followed by tests allowing the purification and regeneration of sorbents (desorption). The study was carried out in one process. The results obtained are shown in Fig. 9a–9e.

Based on the breakthrough time of nonwoven composites' action, it was found that the sorbents regeneration used allows them to be reused to capture harmful chemical compounds found in the breathing zone. Studies have shown that the sorbent captures and provides a similar breakthrough time against acetone, cyclohexane and ammonia to the times obtained before their re-use. It should be emphasized that in the PG variant (Fig. 9e), which was treated with 20 ppm ammonia vapors, the absorption process deteriorated, which may negatively affect the protection of the respiratory system against harmful vapors and gases.

As a result of the research, it can be stated that the shape of the hysteresis formed depends on the nature of the pores present in the sorbents used. The curves representing the sorption process for each test substance were convex. From their course it can be seen that initially the adsorption value increased proportionally to time. In the case of the PA, PB and PG variants, it was found that the same number of particles adsorbs as desorption – dynamic equilibrium is established, i.e. the absorption rate equals the desorption rate.

Penetration by paraffin oil mist aerosol and NaCl

The mean penetration of the studied nonwoven composites containing activated carbon and mixture with mesoporous silica material, molecular sieves and zeolite by paraffin oil mist sodium chloride aerosol are given in Fig. 10.

The lowest penetration by paraffin oil mist aerosol was found for the composite variant PG (0.9%), followed by PE, PJ, PC, and PF (1.3% to 1.6%). The PA variant exhibited the highest penetration by paraffin oil mist aerosol at 5.5%, as compared to 4.1% for the reference sample PPQ. Thus, the incorporation of modifiers in the nonwoven structure in the melt-blown process does not have adverse effects on the protective properties of the resulting composites. The obtained materials revealed satisfactory filtering properties in relation to the reference sample.

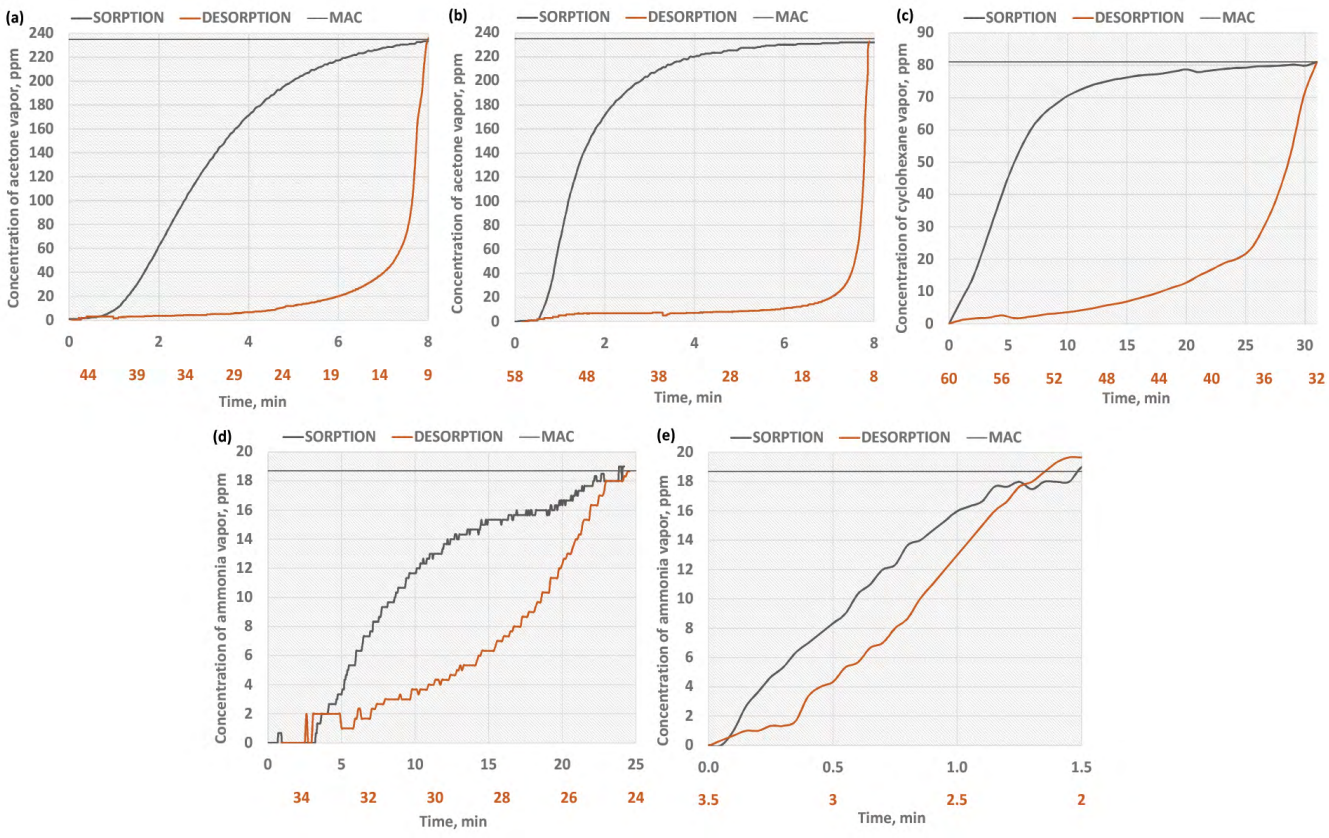


Fig. 9. Sorption-desorption of melt-blown nonwovens composites: (**a**) – **PB** (PP with AC_2); (**b**) – **PF** (PP with AC_1 + SM) against acetone vapor; (**c**) – **PA** (PP with AC_1) against cyclohexane vapor; (**d**) – **PB** (PP with AC_2); (**e**) – **PG** (PP with AC_2 + MCM-41) against ammonia vapor

The lowest penetration by sodium chloride aerosol was recorded for the following nonwoven variants: PE, PJ, PF, PD, PI (1.1%, 1.1%, 1.2%, 1.4%, and 1.5%, respectively). No significant differences with respect to the reference sample PPQ were found for the variants PB, PC, and PG at mean penetration values of 2.3%, 2.5%, and 2.5%, respectively. Finally, the variants PH and PA exhibited higher penetration by the test aerosol as compared to the reference sample, at 3.3% and 3.4% respectively. Nevertheless, it should be noted that all the tested composites revealed a satisfactory filtration performance. Statistically significant differences between mean penetration levels are marked with different letters in the diagram.

Air flow resistance

Mean airflow resistance levels for the studied nonwoven composites containing carbon, silica, and zeolite modifiers and their mixtures are given in Fig. 11.

The studied nonwoven composites incorporating a variety of adsorbents were tested for airflow resistance. No statistically significant differences were found between the variants PA, PH, and PPQ (with the lowest resistance level revealed by PA). That increase in airflow resistance was attributable to the filtering material being clogged with zeolite, silica, or carbon particles, or mixtures thereof, which filled inter-fiber spaces. However, all the obtained nonwoven composites met the limit specified by the standard EN 149:2001+A1:2009, which

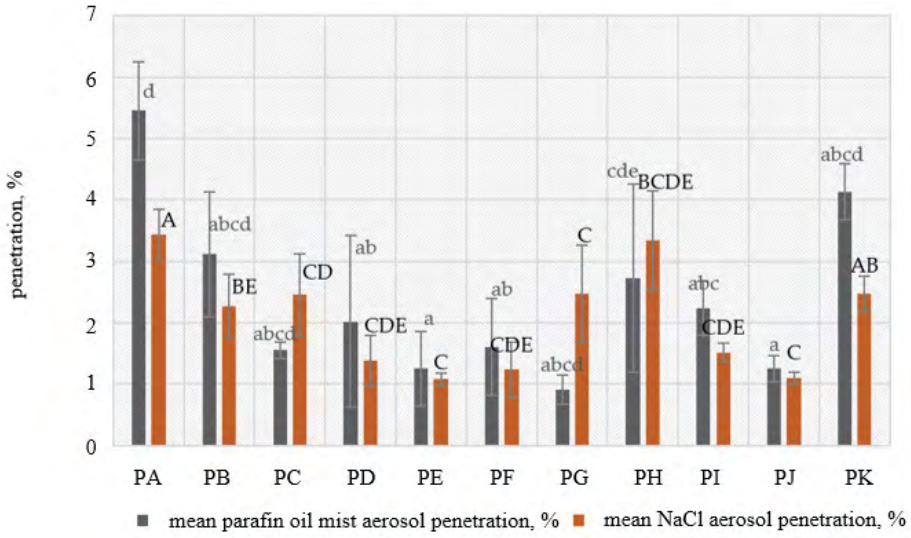


Fig. 10. Mean penetration of melt-blown nonwoven composites by paraffin oil mist and NaCl aerosol (a–e; A–E – mean penetration levels marked with different letters differ statistically significantly according to ANOVA, α=0.05 and Tukey's test, α=0.05). **PA** – PPQ with AC_1, **PB** – PPQ with AC_2, **PC** – PPQ with AC_1 + MCM-41, **PD** – PPQ with AC_1 + Na-P1, **PE** – PPQ with AC_1 + SM 4Å, **PF** – PPQ with AC_1 + SM, **PG** – PPQ with AC_2 + MCM-41, **PH** – PPQ with AC_2 + Na-P1, **PI** – PPQ with AC_2 + SM 4Å, **PJ** – PPQ with AC_2 + SM, **PK** – PPQ

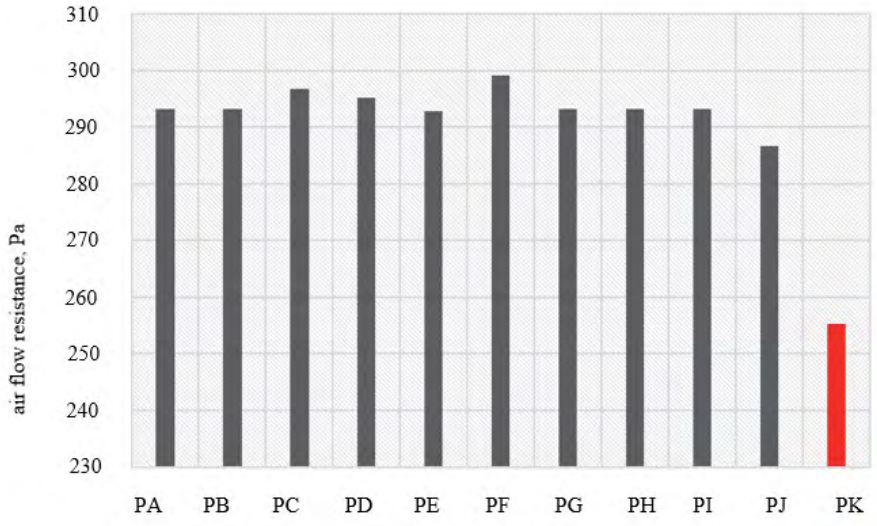


Fig. 11. Mean air flow resistance levels for melt-blown nonwoven composites containing carbon, carbon/silica, and carbon/zeolite modifiers (a–f – mean penetration levels marked with different letters differ statistically significantly according to ANOVA, α=0.05 and Tukey's test, α=0.05). **PA** – PPQ with AC_1, **PB** – PPQ with AC_2, **PC** – PPQ with AC_1 + MCM-41, **PD** – PPQ with AC_1 + Na-P1, **PE** – PPQ with AC_1 + SM 4Å, **PF** – PPQ with AC_1 + SM, **PG** – PPQ with AC_2 + MCM-41, **PH** – PPQ with AC_2 + Na-P1, **PI** – PPQ with AC_2 + SM 4Å, **PJ** – PPQ with AC_2 + SM, **PK** – PPQ

is 700 Pa at a flow rate of 95 l/min. Statistically significant differences between mean penetration levels are marked with different letters in the diagram.

Discussion

Despite considerable research efforts devoted to sorbents of chemical vapors, the developed solutions fail to meet the criteria of low production and usage costs. While the currently available products mostly contain activated carbon sorbents, new possibilities are afforded by the synthesis of zeolites from fly ashes. Being by-products of coal combustion, they are widely applied in the removal of heavy metals and other water and wastewater pollutants. The authors noted that neither synthetic nor natural zeolite sorbents have been used so far in respiratory protective equipment. In this study they were incorporated in filtering materials and subjected to a number of tests to evaluate their sorption properties with respect to harmful odoriferous substances, as well as to establish their textural, protective, and functional parameters.

The produced filtering nonwoven composites were examined to determine their breakthrough times for ammonia, acetone, and cyclohexane vapors. The composites exhibited selective effects with respect to the test gases, which is confirmed by the literature sources. Brochocka et al. (Brochocka et al. 2019) showed that the use of zeolite filtration materials with the addition of molecular sieves causes protection against the effects of acetone and cyclohexane vapors below their NDS values. However, their protective time is shorter than that of the mixtures used. The best protection against the vapors of an inorganic compound (ammonia) was afforded by the composite variant containing the activated carbon AC_2 and an inorganic mesoporous silica material (MCM-41), leading to breakthrough times of 8–12 min. In the case of cyclohexane vapor, the best results were obtained for the activated carbon AC_1 (approx. 50 min), while the activated carbon AC_2 and the mixture AC_2-SM offered the longest breakthrough times for acetone. The use of zeolite and silica materials in the polymer structure used in respiratory protective devices is an excellent alternative to materials containing activated carbon. These results were also confirmed in the work of Brochocka et.al. (Brochocka et al. 2018). Summarized results obtained for breakthrough time, mean penetration and mean air flow resistance of melt-blown nonwoven composites are listed in Table 6.

The basic adsorption properties of porous sorbents include textural parameters. It was found that greater BET surface areas led to longer breakthrough times, which is consistent with the findings of other authors (Das et al. 2004) reporting a strong correlation between breakthrough time and the surface area of the adsorbent. The protective and functional tests performed in this study indicate that sorbents do not adversely affect the basic protective indicators and exhibit good contact performance with respect to the adsorbate.

Numerous studies have shown that the adsorption of volatile chemical compounds largely depends on the surface structure and functional groups present in the sorbents (Xueyang et al. 2017, Zhang et al. 2017, Rubahamya et l. 2019, Balanay and Lungu 2016). Thus, further efforts should address the issue of expanding the specific surface area of zeolites to enhance their capacity to adsorb molecules from the gaseous phase. Another interesting research venue is the application of process solutions from zeolite synthesis for the production of mesoporous silica materials, which introduced into melt-blown technique by pneumatic method will allow for obtaining multifunctional polymer structures containing porous materials absorbing odorogenic compounds. The introduction of silica materials to the melt-blown technology made it possible to obtain a filtering-absorbing material that adsorbs both submicron aerosols as well as vapors and gases present in smog. Currently available solutions include the use of two different materials: filtering and absorbing. The proposed solution makes it possible to obtain a multifunctional material showing features that both absorb harmful and dangerous gases and vapors and filter particles in the atmospheric air. The method of producing multifunctional polymer materials

Table 6. Summary of obtained results

Nonwoven composites	Breakthrough time, min			Mean paraffin oil mist aerosol penetration, %	Mean NaCl aerosol penetration, %	Mean air flow resistance, Pa
	acetone	cyclohexane	ammonia			
PA	6.2	53.0	2.1	5.5	3.4	293
PB	NR	17.0	11.3	3.1	2.3	292
PC	4.9	15.0	5.5	1.6	2.5	297
PD	NR	NR	1.3	2.0	1.4	292
PE	8.8	19.0	1.6	1.3	1.1	291
PF	NR	16.0	1.5	1.6	1.2	299
PG	11.1	19.0	11.1	0.9	2.5	292
PH	NR	11.0	7.7	2.7	3.3	292
PI	NR	9.0	7.7	2.2	1.5	292
PJ	NR	18.0	6.1	1.3	1.1	286
PK	NR	1.2	1.0	4.1	2.5	255

*** NR – not reached**

enables the introduction of modifiers without losing their physico-chemical properties. The obtained multi-functional material can be widely used in respiratory protection devices. The present work deals with scientific research to improve workers' and society's health and safety by pursuing a better working life (e.g., for workers in the sewage treatment plant, waste sorting plant, animal farms), and creating a safe and comfortable social environment.

Conclusions

The results of the conducted research indicate that the best protection against organic compounds (cyclohexane, acetone) are activated carbons. On the other hand, for inorganic compounds (ammonia) removal, not only commercially used activated carbons, but also mesoporous silica materials (obtained from fly ash which is a by-product after coal combustion in power plants and thermal power plants) can be used in Filtering Respiratory Protective Devices. An extremely important aspect is the use of other materials obtained from waste like zeolites, because this will significantly reduce the costs of obtaining nonwovens, and on the other hand, will contribute to the increased utilization of fly ash (in this case) from the commercial power industry.

It should be remembered how important the breakthrough time is for various materials and sorbed compounds. Undoubtedly, it is necessary to conduct further research aimed at increasing the efficiency of such sorbents.

The demand for effective and efficient materials for adsorptive removal of volatile organic and inorganic compounds is driven by the need to improve air quality management. In this context, the present study provides valuable information both for scientists and manufacturers of versatile polymeric materials and respiratory protective devices who are engaged in the development and application of advanced filtering media removing toxic chemical substances from the air.

Acknowledgments

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