**Katarzyna Majchrzycka*,
Małgorzata Okrasa**

**Central Institute for Labour Protection
– National Research Institute,
Department of Personal Protective Equipment,**
ul. Wierzbowa 48, 90-133 Łódź, Poland
*E-mail: kamaj@ciop.lodz.pl

Effect of Temperature, Simulated Breathing and Storage Conditions on the Filtration Efficiency of Biodegradable Bioactive Filters

Abstract
In the case of exposure to inhalation of pathogenic microorganisms, it is necessary to use filtering respiratory protective equipment (FRPE). When this problem concerns the sphere of non-professional use it is important to ensure the disposal of waste equipment in an environmentally safe way. The use of biodegradable nonwovens with biocidal properties in the construction of FRPE could be a good solution to this problem as their degradation time is short in comparison with traditionally used polypropylene. Bioactivity of the nonwoven would ensure the elimination of biological contaminants collected within the filtering material. However, due to the biodegradability, the properties of such materials might change during use. At the same time there are no testing procedures allowing the evaluation of protective parameter changes during the use and storage of FRPE made of biodegradable polymers. The aim of this study was to determine the effect of temperature, simulated breathing and storage conditions on the filtration efficiency of biodegradable bioactive filters prepared by melt-blowing from poly(lactic) acid polymer modified with biocidal agent. The results showed that elevated temperature greatly affects the filtration efficiency of biodegradable filters. A statistically significant decrease in the filtration efficiency after breathing simulation and storage was also observed.

Key words: *poly(lactic) acid, melt-blown nonwoven, thermal conditioning, breathing simulation, respiratory protective devices, filtration efficiency.*

Introduction

Due to the growing problem of human exposure to harmful biological factors connected with professional activities and the potential danger of occurrence of epidemics of infectious diseases or terrorist attacks, it is necessary to improve the properties of individual protective equipment [1-4]. Numerous studies have been carried out in the area of functionalization of nonwoven materials for the construction of filtering respiratory protective equipment (FRPE). One of the most interesting functionalization trends is the development of the biocidal properties of filtering nonwovens. Research in this area has been carried out in two main directions i.e. the selection of suitable biocidal agents and preparation methods of nonwovens for filtration applications. Early works in this area were related to the use of a biocidal agent (alkylammo-nium microbiocides) deposited on two mineral carriers, i.e. bentonite and perlite [5-7]. The research was focused on the application of modified nonwovens as construction materials for the production of FRPE for professional use. Powdered biocides were introduced into the stream of semi-plastic fibers during the production of nonwovens in the melt-blowing process [1]. It was shown that biocidal activity of the modified nonwovens differed depending on the type of carrier that was chosen.

More and more often, FRPE is used for protection of the respiratory tract in non-professional use. In this case, it is especially important that the equipment disposed does not pose a threat to humans and the environment. To address this issue, the use of biodegradable nonwovens with biocidal properties in the construction of FRPE was considered [8-10]. Regardless of biodegradability, such nonwovens should meet simultaneously two very important criteria. On the one hand they should have high filtration efficiency of bioaerosol particles with a relatively low value of air flow resistance, and on the other hand they should present good biocidal properties [4,11,12]. Numerous attempts to functionalise filtering nonwovens have been undertaken to obtain the ability to inhibit the development of microorganism within FRPE during its use in the workplace.

Due to the complexity of environmental conditions in which FRPE is used, special attention should be paid to such characteristics as microclimatic conditions, estimated service life and type of microbiological hazards when the equipment is designed [4,13,14]. Works related to the production of nonwovens with biocidal properties have been carried out mainly with a focus on their application in disposable FRPEs [1,8,15], but some studies indicate that their use could be even more advisable in the construction of reusable FRPE. This possibility results from the provisions included in the EU norms that are unified with the 89/686/EWG Directive [16]. In the case of reusable equipment, it is important to make sure that there will be no change in the level of protection during the many cycles of its use [4]. These properties must be verified on the basis of laboratory tests carried out under conditions that simulate the assumed application of FRPE [13,14]. This is particularly important when biodegradable polymers, such as poly(lactic) acid (PLA), are used for the production of filtering nonwovens because they are naturally prone to degradation, which may affect their efficiency.

The first works regarding the processing of biodegradable polymers by melt-blowing were conducted by Müller and Krobjilowski [17]. They showed that PLA can be processed over a wide range of

temperatures. Relatively fine webs with average fibre diameters of approximately 10 µm were produced, although the web structures were found to be vulnerable to brittle fracture. The relationships between the processing parameters, i.e. hot air temperature and die to collector distance, and the filtration performance of PLA were explored in [18]. The filtration efficiency decreased with an increase in air temperature and the width of the air gap. In normal use, PLA fibers are relatively resistant to environmental conditions. However, in specific conditions of high temperature and elevated humidity, typical for the composting of waste products, PLA fibers are completely degradable. Their disintegration takes place by hydrolysis, followed by bioconversion into H_2O and CO_2.

FRPE is usually stored at normal temperature and humidity conditions, but during use it is subjected to substantial amounts of heat and moisture from the wearer's respiratory system. Then inside the equipment a specific microclimate similar to the one within the compost occurs. These conditions should be taken into account when designing materials for the construction of FRPE. Another important aspect should also be emphasized before a new FRPE could be introduced to the market of the European Union. According to the harmonized standards of Directive 89/686/EEC [16] it is necessary to perform thermal conditioning and simulated breathing conditioning before and after evaluation of the effectiveness of filtration of such equipment.

So far, all of the nonwoven fabrics used in the construction of FRPE have been made of PP, which is resistant to the impact of high humidity and temperature. PLA as a degradable polymer may not provide the same level of stability, especially in a humid environment. The same may apply to the effects of high temperatures, especially in procedures to simulate the accelerated aging of nonwovens, in order to determine the shelf life of the FRPE. Currently there are no testing procedures allowing the evaluation of changes in protective parameters during the use and storage of biodegradable FRPE. Thus the aim of this study was to determine the effect of temperature, simulated breathing and storage conditions on the filtration efficiency and breathing resistance of biodegradable bioactive filters prepared by melt-blowing from PLA polymer modified with a biocidal agent.

Experimental

Materials

Biodegradable bioactive nonwovens were produced using a melt-blown technique from PLA 6202 D polymer (NatureWorks, LLC, USA). A powdered biocidal agent (anhydrous mixture of perlite and active substances) with grains of 50 µm in diameter was dosed centrally and symmetrically into the fibre-forming head [1,19]. It was added to the molten PLA in the amount of 10% by weight to that of the granulate. Parameters of the production of melt-blown nonwovens were as follows: temperature of extrusion zones I and II: 270°C, head temperature: 210°C, air flow velocity: 8.8 m³/h, polymer flow: 4.0 g/min, and the distance between the collector and fiber-forming head: 300 mm. In order to improve the filtration efficiency of bio-aerosol particles of the filtering material, corona discharge was used (discharge voltage 30 kV). On average, the surface weight of nonwoven fabric samples was 102 g/m² ± 10% and the thickness was 2.1 mm ± 10%.

The filtration efficiency of the bioactive biodegradable nonwovens against gram positive (*S. aureus*) and gram negative (*P. aeruginosa*) bacteria was 99%, and the survival rate of the microorganisms after 2 hours was 0% [20]. The study was conducted according to methodology developed based on the AATCC 100-2004 standard [21]. The degree of degradation was determined according to a procedure developed by the Institute of Biopolymers and Chemical Fibres (IBWCh Poland) based on the EN 14045:2003 [22], EN 14806:2005 [23] and ISO 20200:2004 [24] standards. The total degradation of the nonwovens in organic compost in an aqueous medium was observed after 8 weeks.

The biodegradable bioactive nonwovens described above were used to prepare circular filters with a diameter of 0.1 m. To test the influence of use conditions on the protective properties of filters, they were inserted into a filter holder complete with half-mask for the protection of the respiratory tract.

Methods

The influence of use conditions on the protective properties of biodegradable bioactive filters was assessed according to methodology that took into account such factors as elevated temperature, high humidity during breathing simulation in FRPE, and storage duration. Testing

procedures were developed based on European standards [16,25] relating to the performance of FRPE.

To assess changes in filtration efficiency due to elevated temperature, filters were conditioned for eight hours in a dryer (VD 53, Binder, Germany) at temperatures of 30°C, 40°C and 50°C, and then stored at normal conditions for 16 h. After that the filtration efficiency of paraffin oil mist was measured using test stana cosnisting of an aerosol generator AGW-F/BIA (Lorenz Messgerateban, Germany), an aerosol photometer AP2E (Lorenz Messgerateban, Germany). The results were related to the filtration efficiency determined for nonwovens not subjected to the conditioning. To reflect changes in the structure of the PLA fibers under the influence of elevated temperature, scanning electron microscopy images of selected samples were taken with a VEGA 5135 MM microscope (Tescan, Czech Republic).

Breathing simulation was carried out on a test stand that consisted of a breathing machine, set to 25 cycles per minute and 2.0 litres per stroke, a Sheffield dummy head, on which the FRPE was mounted, and a saturator located in the exhalation line between the breathing machine and the dummy head. The temperature of air exhaled from the mouth of the dummy head was 37±2°C. Filtration efficiency was measured after 8 h of breathing simulation and 16 h of storage in normal conditions. Breathing simulation cycles were repeated for 2, 3, 4 & 5 days for the same filter samples, which corresponded to 5 days of use of the reusable FRPE.

In order to assess the influence of storage duration on the filtering performance of biodegradable bioactive nonwovens, filtering efficiency was determined before and after storing in normal conditions for 4, 10 and 14 days since production.

The filtration efficiency of the nonwovens was determined based on measurement of the paraffin oil mist penetration index according to the EN 13274-7: 2008 standard [26], from the ***Equation (1)***:

$$FE = 100\% - P. \qquad (1)$$

The arithmetic mean and standard deviation for the filtration efficiency of paraffin oil mist were calculated. In all cases, the mean change in filtration efficiency of paraffin oil mist ΔFE_j resulting from
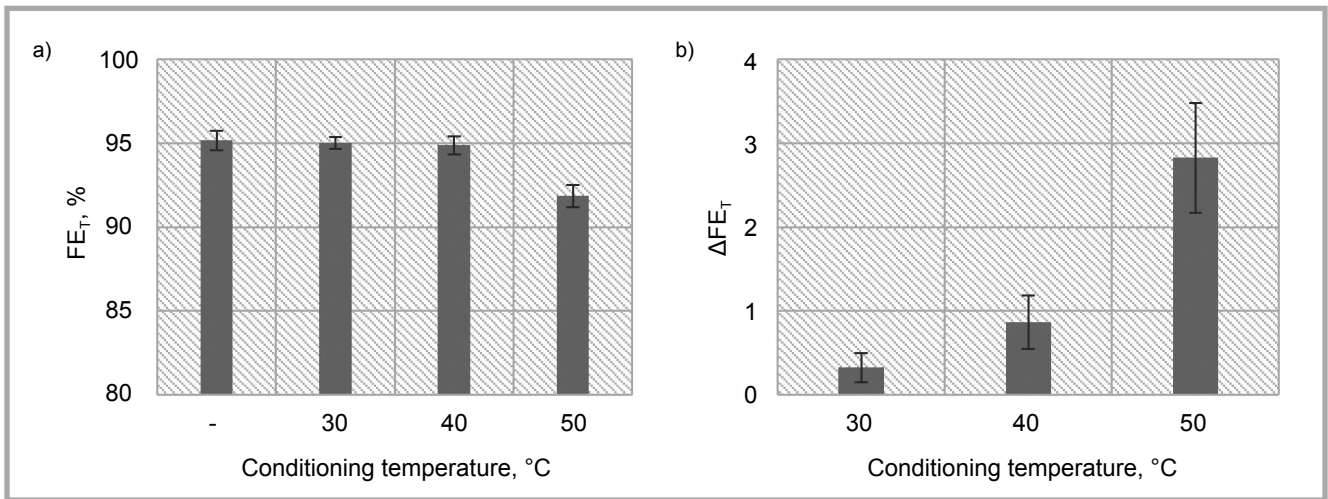
Figure 1. *Influence of thermal conditioning on protective properties of filters: a) filtration efficiency of paraffin oil mist, b) change in the relative filtration efficiency.*
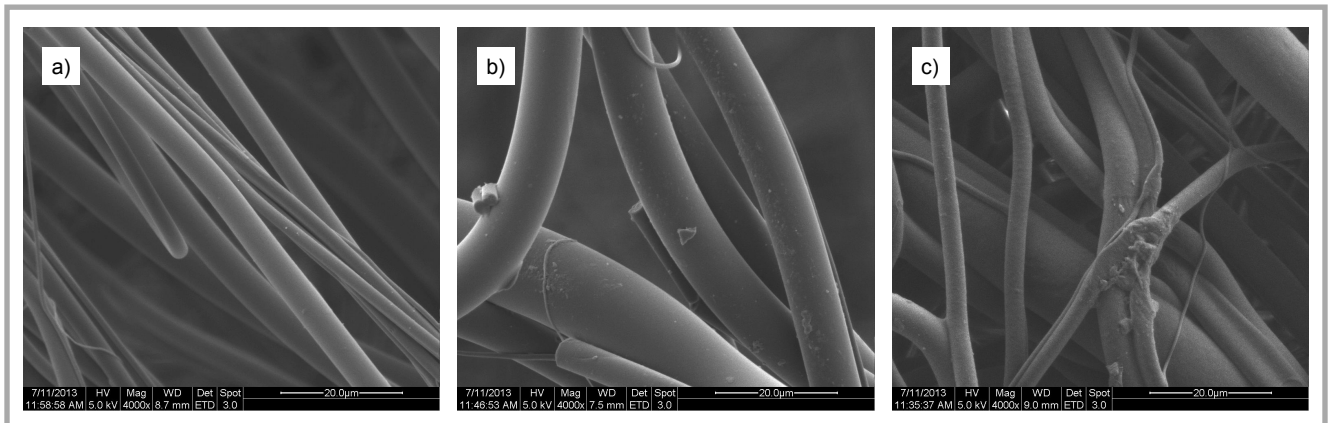

Figure 2. *SEM images of fibers: a) before thermal conditioning, b) after thermal conditioning at 40°C, c) after thermal conditioning at 50°C.*

factor were calculated from the following *Equation (2)*:

$$\Delta FE_j = \sum_n^{i=1} \frac{\frac{(FE^i - FE_j^i)}{FE^i} \cdot 100\%}{n}, \qquad (2)$$

where FE^i and FE_j^i are the filtration efficiencies of the sample before and after j has been applied (j can be equal either to T – thermal conditioning, BS – breathing simulation, or S – storing) and n denotes the number of samples tested. Differences between the initial values of filtration efficiency and those after particular treatment were analysed using one-way analysis of variance (ANOVA). Differences were considered significant at p<0.05. All data were processed using data analysis software MS Excel Microsoft, USA and Statistica 10 (StatSoft, USA).

Results and discussion

Effect of thermal conditioning

In *Figure 1* mean values and changes in filtration efficiency after thermal conditioning at 30°C, 40°C, 50°C are shown.

A small decrease in filtration efficiency due to the temperature conditioning was noticeable even at 30°C, but a rapid decrease was observed for 50°C. Statistical analysis showed changes in the filtration efficiency in relation to the reference nonwoven, due to the thermal conditioning, at a significance level of 0.05 for all of the temperatures selected. This phenomenon may have resulted from the deformation of the fibrous structure or degradation of the PLA fibers with the lowest diameter, as shown in the SEM images of fibers presented in *Figure 2*.

The results obtained are consistent with those reported by Ho et al. for PLA films subjected to conditioning in the similar temperature range [27]. Their results indicated that degradation rate of PLA film had a positive correlation with ambient temperature. The highest degradation rate was obtained at the value of glass transitional temperature (Tg) of the PLA used for the film production. In our case

the most rapid decrease in filtration efficiency was observed for 50°C while Tg was approximately 55°C, which suggests that the degradation of fibers could occur. Nevertheless, changes in the fiber structure caused by degradation of the fibers should be confirmed by thermogravimetric analysis at static conditions.

Another cause of the change in the filtration efficiency of the material could have been the deformation of the fibers during thermal conditioning resulting from the relaxation of stresses generated in the fibers during their blowing. This may be indicated by a significant shrinkage of samples conditioned at 50°C – the diameter of the sample was reduced from 0.1 m to 0.086 m. On the other hand individual fibers can adhere to one another, causing the formation of regions with higher or lower porosity within the nonwoven structure. Both of these phenomena could cause an increase in the average fiber diameter, which decreases the filtration efficiency [28].
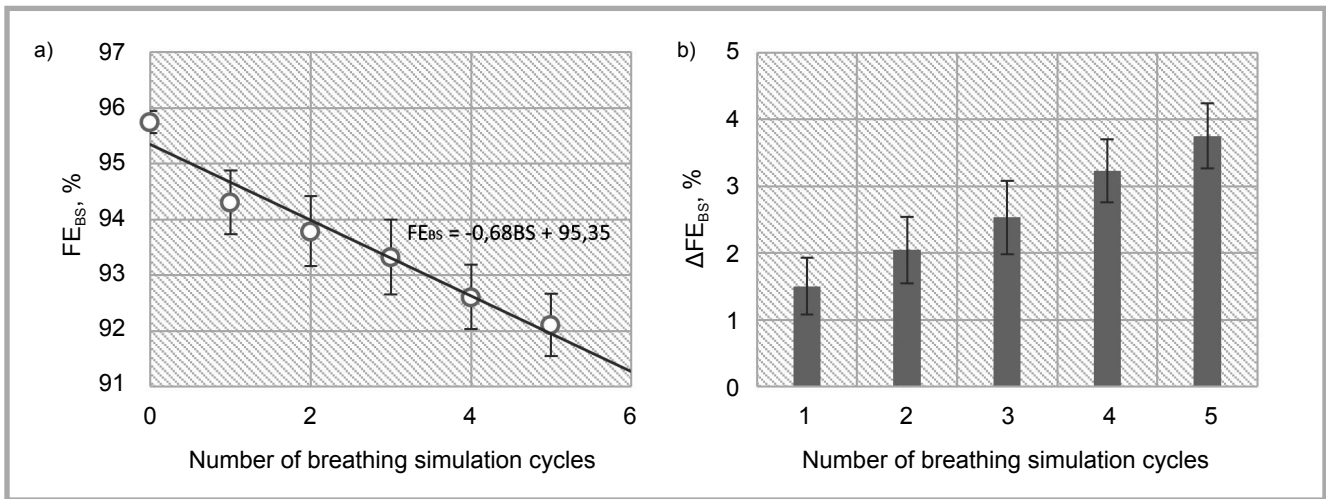
Figure 3. *Influence of breathing simulation cycles on protective properties of filters: a) filtration efficiency of paraffin oil mist, b) change in relative filtration efficiency.*
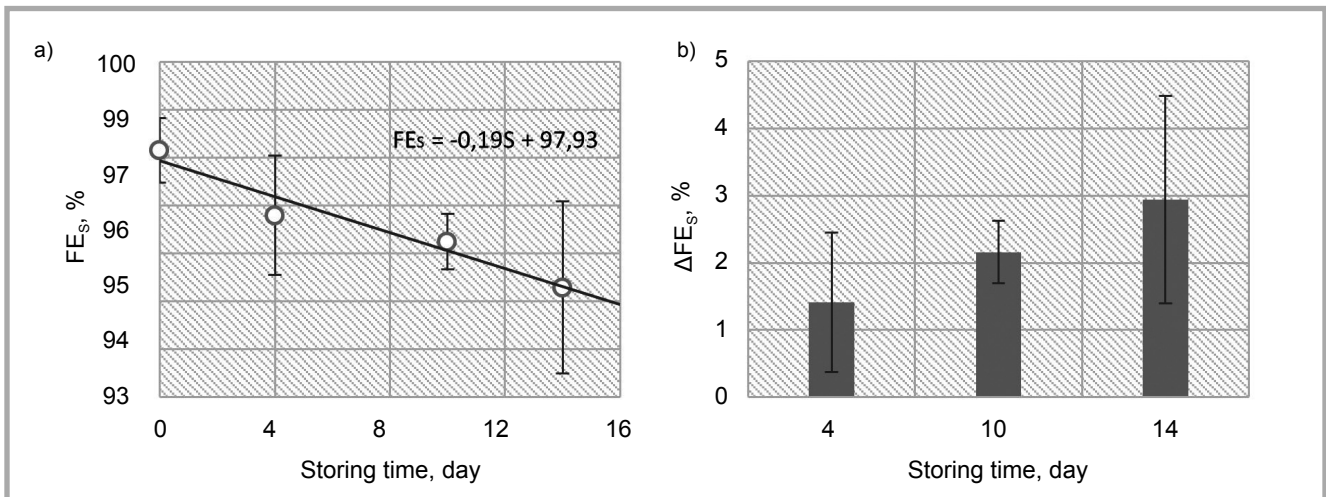

Figure 4. *Influence of storing time on protective properties of filters: a) filtration efficiency of paraffin oil mist, b) change in relative filtration efficiency.*

A decrease in filtration efficiency can also result from the electrostatic decay of corona-charged nonwovens at ambient and elevated temperatures, which was previously discussed for polypropylene by Tsai et al. [29]. The rate of charge decay was higher for elevated temperatures, which is consistent with the test results reported.

Breathing simulation cycles' influence

The impact of breathing simulation cycles (BS) on the filtration efficiency of paraffin oil mist for the samples tested are presented in ***Figure 3***.

The dependence of the filtration efficiency on the number of breathing simulation cycles can be described as a linear function. The solid line in ***Figure 3.a*** corresponds to the regression model, with the parameters resulting from the minimiza-

tion of the sum of square errors. The corresponding coefficient of determination $R^2 = 0.9577$ indicates a good quality of fit. Statistically significant differences between the filtration efficiency after subsequent breathing simulation cycles compared to the reference nonwoven were observed based on one-way analysis of variance ANOVA at the significance level 0.05.

Polymeric materials can react with water according to two mechanisms: mechanical absorption and desorption of water as well as through chemical reactions e.g. hydrolysis. In the case of the research conducted, it is likely that both phenomena occurred. This is due to test procedures that simulate the use of FRPE during its normal use in the workplace, during which alternating drying and wetting of the filter material occurs

[30]. Since the use of the equipment over a prolonged period of time leads to the accumulation of water in the filtering material, it can be assumed that the PLA fibers forming the nonwoven filter are constantly exposed to hydration. This, in turn, may lead to intense water absorption, resulting in an increase in fiber volume. Therefore it is reasonable to assume that during the breathing simulation, the swelling of fibers occurs, resulting in a decrease in filtration efficiency. Only a slight change in air flow resistance was observed after 5 cycles of simulation (less than 1%), suggesting that changes in the structure of the nonwoven due to the breathing simulation cannot be uniform because in such a case the breathing resistance would increase proportionally to the filtering efficiency. Another factor contributing to the decrease in filtering parameters of samples after

breathing simulation may be the gradual decay of electrostatic charges caused by elevated humidity and the temperature of the passing air [29,31].

Storage influence

Figure 4 presents changes in protection parameters of filters influenced by storage conditions.

The dependence of the filtration efficiency on the storage time could also be described as a linear function. The solid line in *Figure 4.a* corresponds to the linear regression model with the coefficient of determination $R^2 = 0.9447$, indicating a good quality of fit. Such data for the representative number of samples from the production series of filters chosen could be easily extrapolated in order to assess the loss rate of the protective parameters of FRPE. The research showed that the change in the filtration efficiency of biodegradable bioactive filters is substantial, which imposes serious limitations on the shelf life of that type of FRPE. This may be partially due to the gradual neutralization of electric charges of corona charged PLA nonwovens, which can be accelerated by the hydrophilic nature of the PLA fibers [32]. To assess whether it is feasible to use such materials in the construction of filtering respiratory protective equipment, further research is needed. In particular, the effect of the temperature and humidity of storage on the protective properties of the equipment over a long period of time should be evaluated.

◼ Conclusion

Elevated temperature and high humidity greatly affect the filtration efficiency of bioactive biodegradable nonwoven fabrics. Therefore when modeling FRPE, this aspect should be a primary criterion for the selection of filtering layers and their configuration. Thus the initial value of filtration efficiency should be well above the limit value for each protection class of FRPE defined in the appropriate standards.

The test results described in the paper can be useful to determine the range of use of FRPE, as well as the conditions and time of storage. The greatest impact on reducing the filtration efficiency of FRPE was observed in the case of breathing simulation cycles. This indicates that the equipment made of biodegradable bioactive nonwovens should be disposable.

In addition, in the instructions of use, the manufacturer of FRPE shall specify the exact time and conditions of storage, taking into account the degree of loss of protective properties of the filtering material. Given the influence of thermal conditioning on protective properties of the filters, it can be concluded that the equipment should not be recommended for use in a hot and humid microclimate (e.g. mining, metallurgy).

Regardless of the limitations associated with the use of biodegradable polymers, further research on their application in the production of fibrous materials is needed due to the limited availability of fossil fuels and care for the environment. Constant improvement of modification methods indicate future directions of research on new biodegradable nonwovens with a wide range of applications. At the same time, it is important to remember that any new material intended for the construction of FRPE should be assessed in terms of durability in conditions of its actual use before placing on the market to assure its full functionality in working conditions.

◻

References

1. Brochocka A, Majchrzycka K. Technology for the production of bioactive melt-blown filtration materials applied to respiratory protective devices. *Fibres and Textiles in Eastern Europe* 2009;76(5): 92-8.
2. Makison Booth C, Clayton M, Crook B, Gawn JM. Effectiveness of surgical masks against influenza bioaerosols. *J Hosp Infect. Elsevier Ltd*; 2013; 84(1): 22-6.
3. Van der Sande M, Teunis P, Sabel R. Professional and home-made face masks reduce exposure to respiratory infections among the general population. *PLoS One* 2008; 3(7): 3-8.
4. Fisher EM, Shaffer RE. Considerations for recommending extended use and limited reuse of filtering facepiece respirators in health care settings. *J Occup Environ Hyg*. 2014; 11(8): D115-28.
5. Majchrzycka K, Gutarowska B, Brochocka A, Brycki B. New filtering antimicrobial nonwovens with various carriers for biocides as respiratory protective materials against bioaerosol. *Int J Occup Saf Ergon*. 2012 Jan;18(3):375-85.
6. Gutarowska B, Brycki B, Majchrzycka K, Brochocka A. New bioactive polymer filtering material composed of nonwoven polypropylene containing alkylammonium microbiocides on a perlite carrier. *Polimery* 2010; 55(7-8): 568-74.
7. Brycki B, Gutarowska B, Majchrzycka K, Brochocka A, Orlikowski W, Krucińska I, et al. Środek biobójczy do wytwarzania włóknin filtracyjnych oraz sposób otrzymywania środka biobójczego do wytwarzania włóknin filtracyjnych. Poland; PL 211878 B1, 2012.
8. Gutarowska B, Stawski D, Skora J, Herczyńska L, Pielech-Przybylska K, Połowiński S, et al. PLA nonwovens modified with poly(dimethylaminoethyl methacrylate) as antimicrobial filter materials for workplaces. *Text Res J*. 2015;85(10):1083-94.
9. Krucińska I, Strzembosz W, Majchrzycka K, Brochocka A, Sulak K. Biodegradable Particle Filtering Half Masks for Respiratory Protection. 2012;(96):77-83.
10. Majchrzycka K, Brochocka A. Modification of biodegradable filtering nonwovens with biocidal agent, in Polish. *Przetwórstwo Tworzyw* 2013; 3(19): 217-22.
11. Brosseau LM, McCullough NV, Vesley D. Bacterial survival on respirator filters and surgical masks. *J Am Biol Saf Assoc*. 1997; 2(3): 32-43.
12. Wang Z, Reponen T, Willke K, Grinshpun SA. Survival of Bacteria on Respirator Filters. *Aerosol Sci Technol*. 1999; 30(3): 300-8.
13. Majchrzycka K, Gutarowska B, Brochocka A. Aspects of tests and assessment of filtering materials used for respiratory protection against bioaerosols. Part I:-Type of Active Substance, Contact Time, Microorganism Species. *Int J Occup Saf Ergon*. 2010; 16(2): 263-73.
14. Majchrzycka K, Gutarowska B, Brochocka A. Aspects of tests and assessment of filtering materials used for respiratory protection against bioaerosols. Part II: Sweat in the environment, microorganisms in the form of a bioaerosol. *Int J Occup Saf Ergon*. 2010; 16(2): 275-80.
15. Gutarowska B, Skóra J, Nowak E, Łysiak I. Antimicrobial Activity and Filtration Effectiveness of Nonwovens with Sanitized for Respiratory Protective Equipment. *Fibres and Textiles in Eastern Europe* 2014; 22, 3(105): 120-5.
16. 89/686/EEC. Council Directive of 21 December 1989 on the approximation of the laws of the Member States relating to personal protective equipment. Off J Eur Communities. 1989;L 399:18.
17. Müller DH, Krobjilowski A. Meltblown fabrics from biodegradable polymers. 2001; 10(1): 11-7.

18. Liu Y, Cheng B, Cheng G. Development and Filtration Performance of Polylactic Acid Meltblowns. *Text Res J.* 2010; 80(9): 771-9.

19. Brycki B, Gutarowska B, Majchrzycka K, Brochocka A, Orlikowski W, Krucińska I, Gliścińska E, Krzyżanowski J, Łysiak I. *The biocidal agent for the production of nonwoven and a method of preparing a biocide for the production of nonwoven.* Patent PL 211 878, 2011.

20. Majchrzycka K. Evaluation of a New Bioactive Nonwoven Fabric for Respiratory Protection. Fibres and Textiles in Eastern Europe 2014; 1: 81-8.

21. AATCC Test Method 100-2004. Antibacterial finishes on textile materials: Assessment of. AATCC Technical Manual/2010. 2004.

22. EN 14045:2003 Packaging. Evaluation of the disintegration of packaging materials in practical oriented tests under defined composting conditions.

23. EN 14806:2005 Packaging. Preliminary evaluation of the disintegration of packaging materials under simulated composting conditions in a laboratory scale test.

24. ISO 20200:2004 Plastics – Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test.

25. EN 143:2000/AC:2002 Respiratory protective devices. Particle filters. Requirements, testing, marking.

26. EN 13274-7:2008 Respiratory protective devices. Methods of test. Determination of particle filter penetration.

27. Ho KLG, Pometto III AL, Hinz PN. Effects of temperature and relative humidity on polylactic acid plastic degradation. *J Envrironmental Polym Degrad.* 1999;7(2):83-92.

28. Brown RC. *Air filtration: An integrated approach to the theory and applications of fibrous filters.* Oxford: Pergamon Press; 1993.

29. Tsai PP, Huang H, Wadsworth LC. Electrostatic Decay of Corona-charged Melt Blown Electret at *Ambient and Elevated Temperatures.* 1999.

30. Majchrzycka K, Okrasa M, Skóra J, Gutarowska B. Evaluation of the Survivability of Microorganisms Deposited on Filtering Respiratory Protective Devices under Varying Conditions of Humidity. *Int J Environ Res Public Health.* 2016; 13(1): 98.

31. Motyl E, Lowkis B. Effect of air humidity on charge decay and lifetime of PP electret nonwovens. *Fibres and Textiles in Eastern Europe* 2006; 14(5): 59.

32. Xiao L, Wang B, Yang G, Gauthier M. Poly (Lactic Acid) – Based Biomaterials: Synthesis, Modification and Applications. In: Ghista DN, editor. iomedical Science. *Engineering and Technology.* 2012. p. 249-83.

Institute of Biopolymers and Chemical Fibres
Laboratory of Microbiology

ul. M. Skłodowskiej-Curie 19/27, 90-570 Łódź, Poland

Tests within the range of textiles' bioactivity - accredited by the Polish Centre of Accreditation (PCA):

AB 388

- antibacterial activity of textiles **PN-EN ISO 20743:20013**
- method of estimating the action of micro-fungi **PN-EN 14119:2005 B2**
- determination of antibacterial activity of fibers and textiles **PN-EN ISO 20645:2006**.
- method for estimating the action of micro-fungi on military equipment **NO-06-A107:2005** pkt. 4.14 i 5.17

Tests not included in the accreditation:

- measurement of antibacterial activity on plastics surfaces **ISO 22196:2011**
- determination of the action of microorganisms on plastics **PN-EN ISO 846:2002**

A highly skilled staff with specialized education and long experience operates the Laboratory. We are willing to undertake cooperation within the range of R&D programmes, consultancy and expert opinions, as well as to adjust the tests to the needs of our customers and the specific properties of the materials tested. We provide assessments of the activity of bioactive textile substances, ready-made goods and half products in various forms. If needed, we are willing to extend the range of our tests.

Head of the Laboratory: Dorota Kaźmierczak Ph.D., phone 42 6380337, 42 6380300 ext. 384, mikrobiologia@ibwch.lodz.pl or ibwch@ibwch.lodz.pl