ANTIMICROBIAL COATING OF NANOFIBROUS MEMBRANE FOR AIR FILTRATION

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Abstract

As air pollution is becoming a severe problem, especially in developing countries, it is necessary to seek the protection. It is well known that fine particle matter is the cause of some respiratory diseases, but recently, it has been found that they can also absorb aerosols with viruses and facilitate their easier spreading, thanks to their big area volume ratio. This leads to the development of antimicrobial and antiviral materials, which is the topic of this study. This contribution presents prepared nanofibers sprayed by electrospraying in an electrostatic field with chitosan, functioning as an antimicrobial agent. Chitosan is a natural, biodegradable polymer with low solubility in water. Because of this reason, diluted acetic acid was used. Polyethylene oxide was added to the solution to ensure electrospraying. Two types of polyurethane and polylactide acid were used as nanofibrous mats for spraying. These coated nanofibrous membranes were tested for their air filtration properties, such as filtration efficiency and pressure drop, porosity, antimicrobial activity and morphological structure. The filtration efficiency remained similar to pure polymer nanofiber membranes. However, the pressure drop has increased in most cases significantly. It has been achieved antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus.* These nanofibers are prepared for utilization in filtration systems.

Keywords: Nanofiber, antimicrobial, electrospraying, air filtration

1. INTRODUCTION

In recent years, air quality has become a serious environmental issue, endangering human health. Fine particular matter (PM) is making a specific issue. Air pollution is causing millions of deaths every year [1]. Particular matter smaller than 2.5 μm (PM 2.5) was proven to cause several health problems, such as cancer, fibrosis and chronic lung diseases [2]. In addition, PM can absorb aerosols with viruses and facilitate their easier spreading, thanks to their big area volume ratio [3,4].

Therefore, there arises a need for high-performance functional filter media [5]. Nanofibrous materials seem ideal for their remarkable features, such as interconnected pore structure, ample surface area to volume ratio, controllable fibre diameter and relatively high pore density with a small diameter [6].

This work focuses on electrospraying as a deposition technology of an antimicrobial agent onto nanofibrous membranes. Chitosan was chosen as an antimicrobial agent. Chitosan was chosen because of its antimicrobial, natural origin, safety and biodegradability [7].

2. EXPERIMENTAL

2.1 MATERIAL

Polyurethane Elastollan EB_95A (PUEL) at M_w= 1.1×10^5 g·mol^{-1} was bought from BASF Polyurethanes GmbH, Germany. N,N-dimethylformamide (DMF, >99.5%) was purchased from Lach-Ner, s.r.o., the Czech Republic. PLA Ingeo 4060D was purchased from Nature Works, the Netherlands. Chitosan, 4,4'-methylene bis(phenyl

isocyanate) (MDI), poly(3-methyl-1,5-pentanediol)-alt-)adipic, isophthalic acid) and 1,4-butanediol were purchased from Sigma Aldrich, Germany. Acetic acid (AA, 99%), sodium tetra-borate decahydrate (borax), citric acid and polyethene oxide (PEO) were purchased from PENTA s.r.o., the Czech Republic. Deionized water (pH 7.3, 18.2 MΩ·cm^{-1}) was created on a laboratory Milli-Q ultrapure (Type 1) water purification system, Biopak Polisher, Merck, USA, and used throughout the study.

2.2 NANOFIBERS PREPARATION

PUEL solution was prepared by dissolving PUEL at a concentration of 18 wt% in DMF/Toluen. The weight ratio of DMF/Toluen was 80/20. The solution of PLA was prepared by dissolving 16 wt% in DMF/Acetone solvent mixture. The weight ratio DMF/Acetone was 80/20. PU918 was synthesised via polyaddition in DMF. PU solution based on 4,4'-methylene bis(phenyl isocyanate) (MDI), poly(3-methyl-1,5-pentanediol)-alt-)adipic, isophthalic acid) and 1,4-butanediol was synthesized at the molar ration of 9:1:8 (PU918) at 90 °C for 6 hours. The per partes method was applied, whereby a prepolymer was synthesized from MDI and polymer diol (at a molar ratio of 2:1), the whole chain extender (1,4-butanediol) was added, followed after 1 hour by the remaining quantity of MDI of the polyaddition reaction. Electrospinning machine (SpinLine 40, SPUR, the Czech Republic) equipped with two sets of moving jets was used to prepare nanofibers. The operating parameters are shown in the **Table 1**. The electrospinning process was performed at room temperature. The borax and citric acid solution in DMF was used to enhance the conductivity of all electrospinning solutions.

Table 1 Operating parameters for electrospun nanofibers

Polymer	Viscosity (Pa·s)	Conductivity (μS·cm^{-1})	Applied voltage (kV)	Distance between electrodes (cm)	Solution flow (ml·min^{-1})	Relative humidity during the process (%)	Final fibres area weight (g·m^{-2})
PUEL	1.20	179.1	75	19	0.10	32	0.96
PU918	0.75	137.6	75	19	0.13	36	0.68
PLA	0.88	137. 3	75	20	0.13	35	0.87

2.3 SOLUTION SPRAYING

The nanofibrous membranes were sprayed-coated with a solution of chitosan with PEO (2:1 ratio) in 2 % AA. The solution was mixed for 4 h at 80 °C. An electrospinning machine SpinLine 40) was used for the spraying, with an applied voltage of 80 kV, the distance between the electrodes was 200 mm, and a solution flow of 0.14 ml·min^{-1}. Three different times of spray exposure were used for all three types of polymer membranes: 1 min, 5 min and 10 min. **Table 2** shows the samples marking.

Table 2 Naming of samples

Polymer	0 min solution exposure	1 min solution exposure	5 min solution exposure	10 min solution exposure
PU Elastolan	PUEL	PUEL 1	PUEL 5	PUEL 10
PU918	PU918	PU918 1	PU918 5	PU918 10
PLA	PLA	PLA 1	PLA 5	PLA 10

2.4 CHARACTERIZATION

The morphology of the electrospun nanofibers and subsequently sprayed nanofibrous mats were analysed from photomicrographs taken by scanning electron microscopy (SEM). Studied samples were sputtered with platinum for 1 minute under a nitrogen atmosphere. The SEM photomicrographs were obtained by Phenom

Pro microscope (Phenom-Word BV, the Netherlands) with a magnification of 10,000x. The microscope was operated in vacuum mode at an acceleration voltage of 10 kV.

Pore size characterisation was performed according to ASTM F316 – 03. Filtration efficiency and filter resistance were measured directly using Automated Filter Tester Model 3160 (TSI Inc., USA). The instrument operates with a monodisperse aerosol of charge-neutralised solid sodium chloride particles of a specified diameter (20-400 nm). The tests were performed at room temperature under a continuous airflow of 32 l·min^{-1}.

Antimicrobial activity (A) was assessed by the test method for the antimicrobial activity of textiles according to the modified standard ISO 22196:2011 using *Staphylococcus aureus* (CCM 4516) and *Escherichia coli* (CCM 4517) strains:

$$A = \log N_0 - \log N_x \quad (1)$$

where: x – incubation time with bacteria suspension (0 and 24 h)
N – number of viable bacteria (CFU·cm^{-2})
A – antibacterial activity of the sample

3. RESULTS AND DISCUSSION

The samples were tested after optimization of the chitosan/PEO ratio to achieve spraying of the solution. The SEMs in the **Figure 1** show the structure of prepared pure and sprayed fibrous materials. As can be seen, sprayed chitosan/PEO solution formed small droplets-like on the fibres after evaporating the solvent, water. The particles of chitosan are nonuniform and randomly placed.

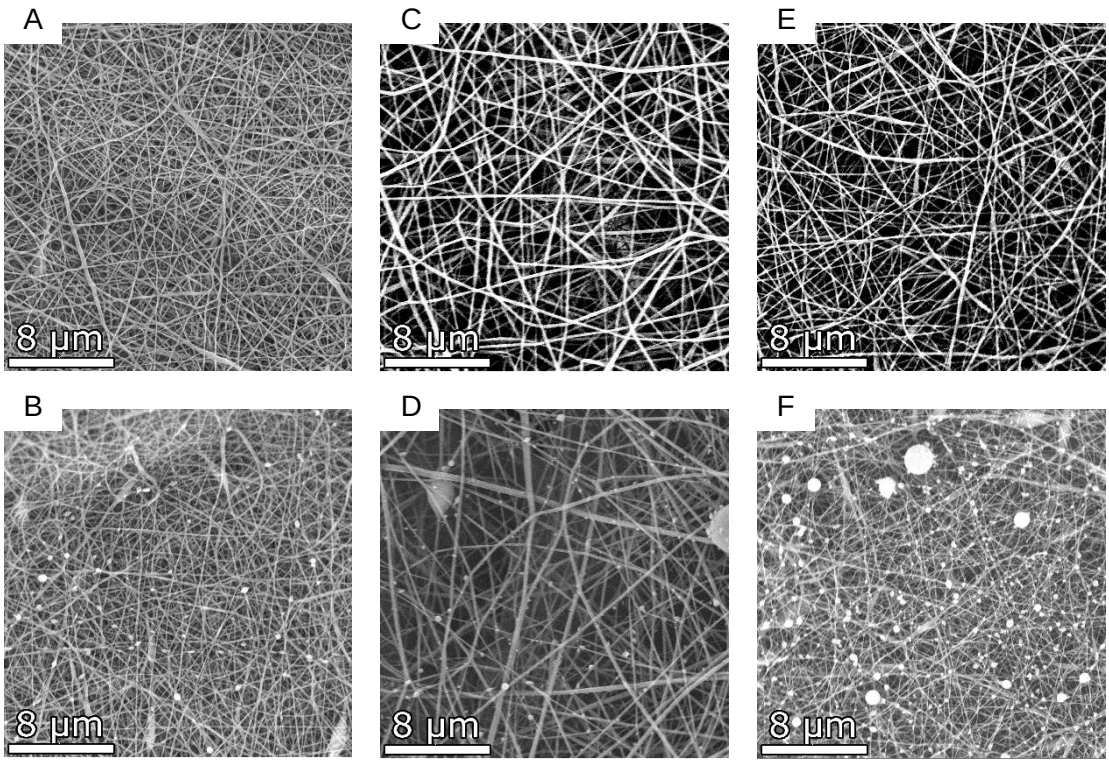

Figure 1 SEM micrographs of pure and sprayed fibres A) PUEL, B) PUEL 1, C) PU918, D) PU918 1, E) PLA and F) PLA 1

An important measurement for revealing the properties of prepared samples was porosimetry. The flow porometry technique was used as a tool for testing the changes in structures. In the **Figure 2,** can be seen the

pore size distribution of all tested samples. As SEM photographs suggest, the mean pore sizes had decreased for most of the samples after chitosan coating. The most significant decrease in the pore sizes is for PLA material. Surprisingly, the pore sizes for chitosan coated PUEL had increased, which could suggest tearing of the material, this, however, was not confirmed by SEM. For material PU918, only a sample PU918 1 had increased the pore size and widened the distribution. μ

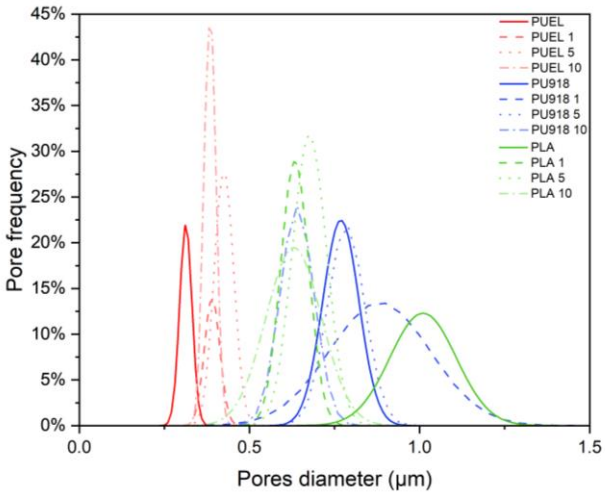

Figure 2 The pore size distribution of pure and sprayed nanofibrous membranes

Precise filtration efficiency and filter resistance measured on the Automatic Filter Tester can be seen in the graphs in the **Figure 3**. The filter efficiency increased for most coated materials, especially for PU918. The only material where the filtration efficiency decreased was the sample PU918 1. This material has also reduced filter resistance, increased porosity and had a broader pore size distribution than the pure material. A similar issue is with the sample PU918 5. This sample is distinct regarding higher filtration effectivity and lower filter resistance but has a similar pore size distribution compared to PU918. This could be linked to the destruction of the fibres.

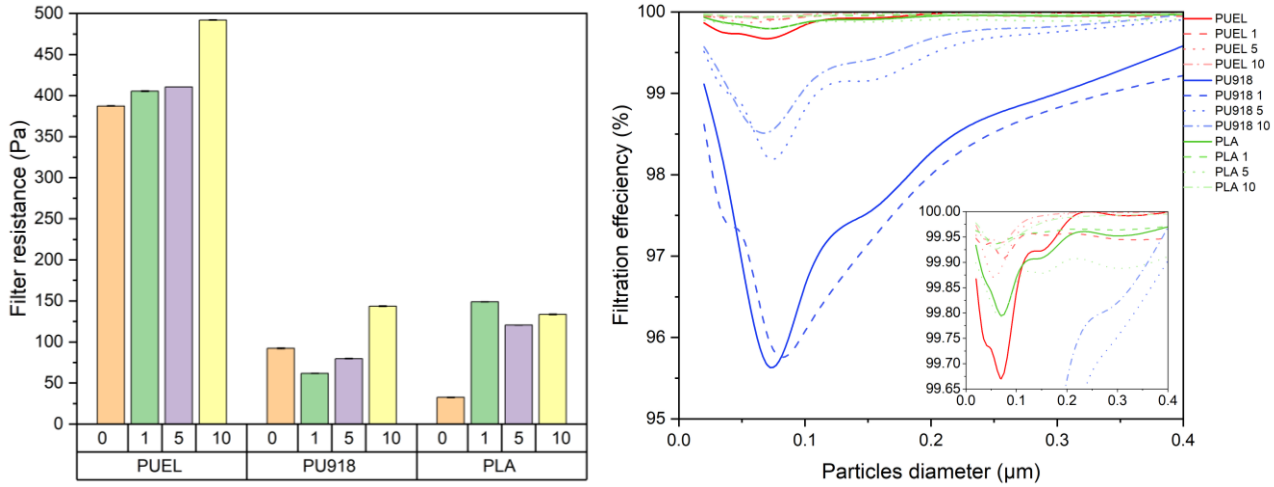

Figure 3 Graph of a) filter resistance and b) filtration efficiency of nanofibrous materials

Finally, the antimicrobial activity was tested according to the modified method EN ISO 20743:2013. *S. aureus* and *E. coli* were used as model microorganisms for the testing. After 22 hours of contact of the inoculum with the samples, the samples were processed by counting plate method and calculated by formula (1). The test was done on the samples containing the lowest concentration of the solution, thus,

samples with sprayed solution for 1 minute. All samples show a strong antimicrobial activity, shown in the **Table 3,** which shows that even low chitosan concentration is functional enough. According to the ČSN ISO 22196:2011, A ≥ 3 is considered as a strong antimicrobial activity.

Table 3 Antimicrobial activity of prepared nanofibrous materials using *S. aureus* and *E. coli* as model organisms

Sample	Contact time (h)	*S.aureus* CCM 4516		*E. coli* CCM 4517	
		N_x (cfu·cm^{-2})	A	N_x (cfu·cm^{-2})	A
PUEL	0	$1.5 \cdot 10^4$	0	$8.2 \cdot 10^3$	0
	24	$2.2 \cdot 10^4$	1.1	$9.8 \cdot 10^4$	1.1
PUEL 1	0	$3.5 \cdot 10^3$	0.6	$8.3 \cdot 10^3$	0
	24	>0	<5.5	>0	<6.1
PU918	0	$1.6 \cdot 10^4$	0	$7.6 \cdot 10^3$	0.1
	24	$2.3 \cdot 10^5$	0.1	$1.5 \cdot 10^6$	-0.1
PU918 1	0	$6.1 \cdot 10^1$	2.4	$7.7 \cdot 10^3$	0
	24	>0	<5.5	>0	<6.1
PLA	0	$1.3 \cdot 10^4$	0.1	$7.9 \cdot 10^3$	0
	24	$5.0 \cdot 10^5$	-0.2	$1.5 \cdot 10^6$	-0.1
PLA 1	0	$2.3 \cdot 10^2$	1.8	$7.6 \cdot 10^3$	0.1
	24	>0	<5.5	>0	<6.1

4. CONCLUSION

This contribution researched the effect of a sprayed solution of chitosan with PEO on filtration efficiency and antimicrobial activity. Three types of polymer nanofibrous mats were prepared, two synthetic polyurethanes and one natural-based polymer, polylactide.

The sprayed solution formed droplet-like particles on the fibres. The filtration effectivity increased, as did the filter resistance, which correlates to the decreasing pore sizes of the samples. The antimicrobial activity was demonstrated for the shortest exposure time, thus proving that a higher concentration of sprayed solution would also be antimicrobial. The antimicrobial activity has proven to be strong for all three polymer types and both types of microorganisms, Gram-negative and Gram-positive.

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