Spray surface modification of electrospun nanofibers for antimicrobial air filtration

Authors:
Dominika Hanušová[a*], Lenka Lovecká[a], Miroslava Kovářová[a], Alessia Cabrini[b], Zuzana Krchňáčková[a], Hana Pištěková[a], Miroslava Dušánková[a], Marino Lavorgna[b], Vladimír Sedlařík[a]

[a]Tomas Bata University in Zlin, Centre of Polymer Systems, tr. T. Bati 5678, 760 01 Zlin, Czech Republic

[b]Institute of Polymers, Composites and Biomaterials UOS Lecco, National Research Council, Via Previati 1/C, 23900, Lecco, Italy

*corresponding author

Keywords: Chitosan, ultrasonospraying, electrospraying

Abstract:

Particulate matter is a global threat to human health. Air filtration seems like a promising method to eliminate this issue. This study utilises electrospinning to prepare the base filtration material and spaying techniques to functionalise the filtration material. Both methods were used to spray chitosan as an antimicrobial agent. Ultrasonospraying and electrospraying deposit droplets of 10 µm and <10 µm, respectively. Two types of electrospun mats, biodegradable polylactic acid and non-biodegradable polyurethane, were used as a base material for deposition. The results showed that the electrospraying is more suitable for applying chitosan onto nanofibers because the ultrasonospraying technique formed a film-like structure, affecting the porous distribution of the fibre mats. Another finding was that the electrosprayed chitosan has a better affinity to polylactic acid with a filtration effectivity 99.97 %. The antimicrobial activity test for this electrospray sample shows a strong antimicrobial effect, but the ultrasonospraying technique showed insufficient results.

1. Introduction

Air quality has declined in recent years, posing a threat to human health. The most significant risk factor is thought to be solid microparticles, especially particulate matter smaller than 2.5 µm (PM 2.5), which has been linked to several health issues. Primary issues are toxicologic consequences, leading to organ malfunction, cell toxicity and further fibrosis, cancer, or chronic lung diseases [1–3]. It was further proven that PM could adsorb aerosols with viruses and facilitate easier spreading, as a consequence, because of its large area-volume ratio [4,5]. This gets an inquiry for filtration media with increased antibacterial activity.

Nanofibrous materials seem promising for filtration applications because of their feature, including interconnected pore structure, high specific surface area, and controllable fibre diameter for efficient particulate capture and possible versatility to enhance antimicrobial activity [6,7].

To increase the antimicrobial activity of used filters, researchers are exploring various approaches. One approach is to incorporate agents such as different nanoparticles (zinc oxide [8] or silicon dioxide [9] etc.). Another promising option is the addition of chitosan (CS), a naturally antimicrobial polymer. Its antimicrobial activity acts against *gram-negative* and *gram-positive* microorganism groups because of positively charged NH_2 groups [10,11]. Production of pure chitosan nanofibers is complicated due to its high viscosity and strong hydrogen bonds in acidic aquatic solutions [12]. Chitosan was incorporated in different polymers, such as water-soluble polyethylene oxide (PEO) [13] and polyvinyl alcohol (PVA) [14], the same as water-insoluble polylactic acid (PLA) [15]. These composites offer a promising avenue for creating nanofibrous filters with enhanced antimicrobial properties.

Functional air nanofibrous filter materials can be prepared by electrospinning in an electrostatic field using several synthetic and natural polymers. The most used are polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), polyethylene terephthalate (PET) and polyurethane (PU) [16–18]. While these polymers are synthetic, non-biodegradable polymers, the focus of research in recent years has shifted towards natural and biodegradable polymers, including e.g. cellulose acetate (CA) [19], (PLA) [20] or polycaprolactone (PCL). Among synthetic non-biodegradable polymers, PU stands out for its exceptional flexibility and versatility, finding applications in various fields like medicine [21], agriculture [22], automotive [23] etc. However, as mentioned, most PUs are not biodegradable, and some researchers have begun to blend PU with other biodegradable polymers, like polyhydroxyalkanoate or PLA [24]. On the other hand, PLA is a biodegradable thermoplastic derived from natural sources. Its properties can be compared to polystyrene, mainly because of its gloss and clarity, but its disadvantage is its relatively high stiffness and brittleness [25]. PU and PLA can be dissolved in common organic solvents and processed by electrospinning for subsequent use in filtration.

However, most mentioned polymers lack antimicrobial properties on their own; therefore, it is crucial to functionalise them to enhance their antimicrobial ability by incorporating antimicrobial agents or finishing techniques, such as coatings. Some methods can be simple, e.g. suspension casting [26] or dip coating [27], while more complex coating technologies include layer-by-layer coating [28], air spraying [29], electrospray [30] or sonospraying. To the best of the authors' knowledge, no research has yet explored the use of ultrasonic spray technology on nanofibers. This technique offers precise and fast deposition with low material consumption. The principle of this technique is the implementation of high-frequency sound vibration to produce a fine mist of the sprayed mixture with a narrow distribution of fine droplets size. This allows uniform droplet size distribution on films and the preparation of homogenous and thin coating layers. Another advantage is the breakage of agglomerates in the suspension to promote a homogenous dispersion [31–33]. On the other hand, electrospray is a liquid atomisation technique employing a high-voltage electric field to distort the droplets in the range of micrometres and nanometers. The principle is based on emulating the cohesive force by the Coulomb force and releasing the surface tension with the result of nanodroplet formation. This technique can produce functional nanofibrous materials with good filtration effectivity and low-pressure resistance [30,34,35].

This study investigated the use of both types of surface modification, electrospraying and sonospraying, of the fibres to prepare antimicrobial coatings of nanofibers. Sonospraying resulted in the formation of a film-like layer over the nanofibers, while electrospraying formed droplets-like particles on the surfaces of the nanofibers. The membranes were characterised using scanning electron microscopy (SEM) and a through-pore size analyser. The antimicrobial activity of membranes was tested according to the modified standard ISO 22196:2011. Filtration performance was tested using an automated filtration tester. This study introduces techniques for using chitosan with water-insoluble polymers, paving the way for advancements in antimicrobial filtration applications.

2. Materials and method

2.1 Materials

N,N-dimethylformamide (DMF, >99.5%) was purchased from Lach-Ner, Czech Republic. PLA Ingeo 4060D was purchased from Nature Works, Netherlands. Chitosan (CS), 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 polyethylene oxide (PEO) were purchased from PENTA, Czech Republic. Deionised water (pH 7.3, 0.055µS 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

The solution of PLA was prepared by dissolving 16 wt% in a DMF/acetone solvent mixture. The weight ratio DMF/Acetone was 80/20. PU was synthesised via polyaddition in DMF. PU solution based on MDI, poly(3-methyl-1,5-pentanediol)-alt-)adipic, isophthalic acid) and 1,4-butanediol synthesized at the molar ratio of 9:1:8 at 90 °C for 6 hours. The per partes method was applied, whereby a prepolymer was synthesised 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. An electrospinning machine (SpinLine 40, SPUR, the Czech Republic) equipped with two sets of 16 moving nozzles was used to prepare nanofibers. The operating parameters are shown in Tab. 1. The electrospinning process was performed at room temperature. The borax and citric acid solution in DMF was used to enhance the conductivity of both electrospinning solutions.

Tab. 1 Operating parameters of SpinLine of electrospun nanofibers

Polymer	**Viscosity** (Pa•s)	**Conductivity** (µS•cm^{-1})	**Applied voltage** (kV)	**Distance between electrodes** (cm)	**Solution dosage** (ml•min^{-1})	**RH** (%)	**AW** (g•m^{-2})
PU	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 Electrospraying of chitosan

The nanofibrous membranes were spray-coated with a 3.5 wt % 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 dosage of 0.14 mL min^{-1}. The spray exposure time was 1 min. Samples using this technique were marked as PLA E and PU E.

2.4 Sonospraying of chitosan

Prior to coating, the PU fibres were treated using plasma surface technology in the air (Diener pico) for 1 min at 90 µA and 0.4 mbar to increase the hydrophilicity to reach homogenous deposition. Plasma surface treatment technology was not possible to use on the PLA mat, as the nanofibers were easily destroyed by plasma application. Chitosan was dissolved as a 0.5 wt % solution in 2 % AA. This solution was subsequently deposited using a SimCoat Ultrasonic Spray Coater (SONO-TEK) equipped with an Impact nozzle. This coater was linked to programmable ultrasonic vibrations within the nozzle; the pressure-controllable jet air deflector (situated above the nozzle) shapes and directs the waves, which gain enough amplitude to split the liquid stream into a fine mist of droplets. An x-y stage controls the nozzle movement. Samples using this technique were marked as PLA S and PU S.

2.5 Characterisation

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 palladium/gold alloy for 1 minute under an argon plasma. The SEM photomicrographs were obtained by Phenom Pro microscope (Phenom-Word BV, Netherlands). The microscope was operated in vacuum mode at an acceleration voltage of 10 kV.

Pore size characterisation was performed according to ASTM F316–03 using a porometry device (SPUR, the Czech Republic). The membrane was cut into a testing specimen, and a 'dry' run was obtained by subjecting the membrane to increasing pressure from a gas source. After that, the specimen was wetted with Galpor (Porometer, Belgium) wetting liquid. Once again, increasing pressure was applied to the membrane. Gas flow was measured as the gas pushed out the liquid first from the largest pores through the smallest until all the pores were emptied. Pore size could be further calculated.

2.6 Antimicrobial activity testing

Antimicrobial activity (R) 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. The samples were cut to a 20×20 mm shape, the same as covering polypropylene films. The samples were sterilised by UV light for 30 minutes. The samples were poured over with suspension with bacteria and covered with polypropylene films. Part of the samples with zero contact time was moved to a sealable vessel with a neutralising medium, and then the vessel was shaken for 30 s. The microbial solution was subsequently, with the method of gradual dilution, poured into a Petri dish, into the agar and incubated (at 35 °C for 24 h). The concentrations of viable bacteria were determined. The same method was further used for samples incubated for 24 hours.

Antimicrobial activity was calculated according to the following equation:

$$R = \log N_0 - \log N_x \tag{1}$$

where x is the incubation time with the bacterial suspension (0 and 24 h), N is the number of viable bacteria (CFU cm^{-2}), and R is the antibacterial activity of the sample.

2.7 Filtration efficiency testing

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}.

Quality factor (QF), generally used as a comprehensive parameter to evaluate the filtration performance of the filter, was calculated according to the following equation:

$$QF = \frac{-\ln(1-\eta)}{\Delta p} \tag{2}$$

where η is the filtration efficiency and Δp the pressure resistance.

3. Results and discussion

Firstly, electrospun NF membranes were prepared via electrospinning, as seen in Fig 1C. The process of preparing both PLA and PU was done based on experience. These polymers were chosen because PLA is a biodegradable polymer, whilst the chosen self-synthesised PU is not (general structure can be seen in Fig 1A). The synthesis was carried out in solution by the per partes method by polyaddition reaction. This produced PU from MDI and 1,4-butanediol has a linear structure. This reaction forms elastomers consisting of segmented structures of soft polyester polyolys segments and rigid aromatic PU segments called hard segments. These hard segments tend to agglomerate into a domain with segments of long flexible chains. This structure can be seen in Fig 1B. Our polyurethane was synthesised in the ratio to provide a maximum quantity of nitrogen atoms in its chain. Further about its character can be read in our previous work by Domincova-Bergerova et al. [36]. This PU was chosen for this study because the produced nanofibers were well-electrospinnable and flexible. The surface of the formed fibres was smooth without any beads, as can be seen in Fig 4D, which is the same as nanofibers of pristine PLA (Fig 4A). Both prepared nanofiber mats have narrow pore distribution, although the mean pore diameter of PU is lower by around 200 nm, as seen in Fig 6.

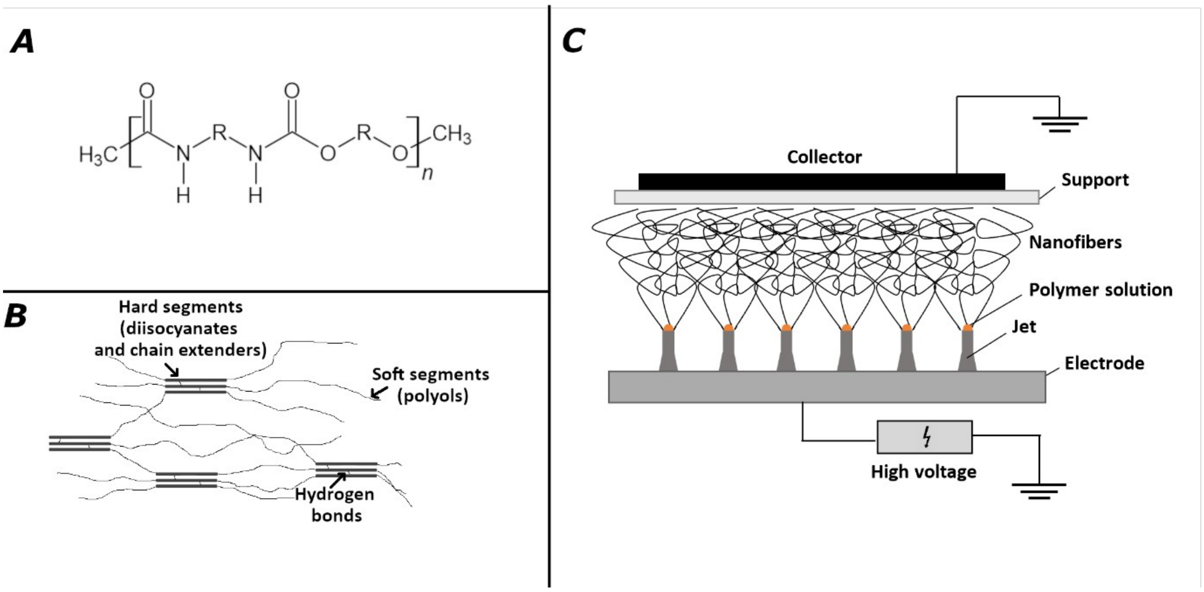

Fig 1 A) General structure of polyurethane, B) scheme of linear polyurethane chains and C) Scheme of Spin Line 40, electrospinning device

Electrospraying was used as the first coating technique; the scheme can be seen in Fig 3A. The method is based on the use of a high-voltage electric field to cause liquid atomisation and form small droplets. These droplets can be visible in Fig 4B and Fig 4E for PU E and PLA E, respectively. These droplets were formed by disturbing the cohesive force and thus surface tension by the Coulomb force [34,35]. The sprayed solution was chosen as an acidic solution of 3 wt % CS with PEO in different ratios, and the most successful ratio for electrospray proved to be 2:1. The higher amount of PEO led to electrospinning which was not the goal of this experiment. On the other hand, when the ratio was lower than 2:1, there was no effect. Another parameter of spraying is the spraying time. There were three spraying times, 1, 5 and 10 minutes, and a spraying time of 1 min was estimated as the ideal time since the amount of deposited chitosan is almost comparable between the two deposition approaches. The spraying time achieved linear regression of the sprayed CS, as seen in Fig 2. The pore size of sample PLA E decreased and narrowed compared to the pristine material. In contrast, the pore size of PU E increased, as seen in Fig 6. This could be caused by a poor affinity of CS and PEO to PU since polyurethane is insoluble in water, while CS and PEO are water-soluble. The electrospraying technique formed droplets like particles of sprayed solution on both NF mats. This was most likely due to fast water evaporation, which evaporates during the electrospraying process, thus forming nanoparticles. The tearing of electrospray samples was not confirmed by SEM analysis. While it can be seen (Fig 6) that pore sizes of sample PU S widened from 0.8 to 1.2 µm, sample PLA E, on the other hand, decreased from 1 µm to 0.6 µm, and the distribution had narrowed. This could be caused by the affinities of used polymers.

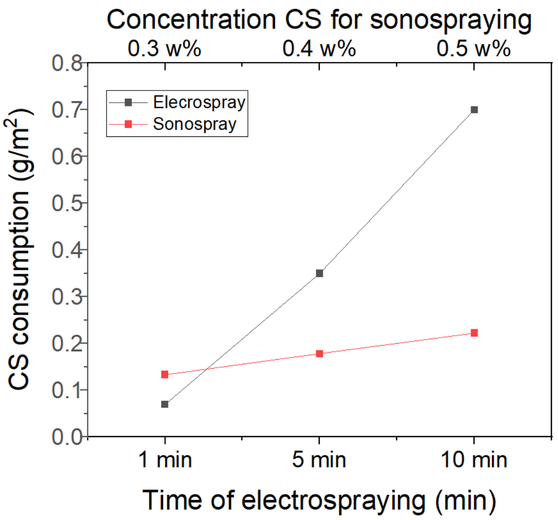

Fig 2 Graph of the amount of sprayed chitosan during electrospray (black line) and sonospray (red line)

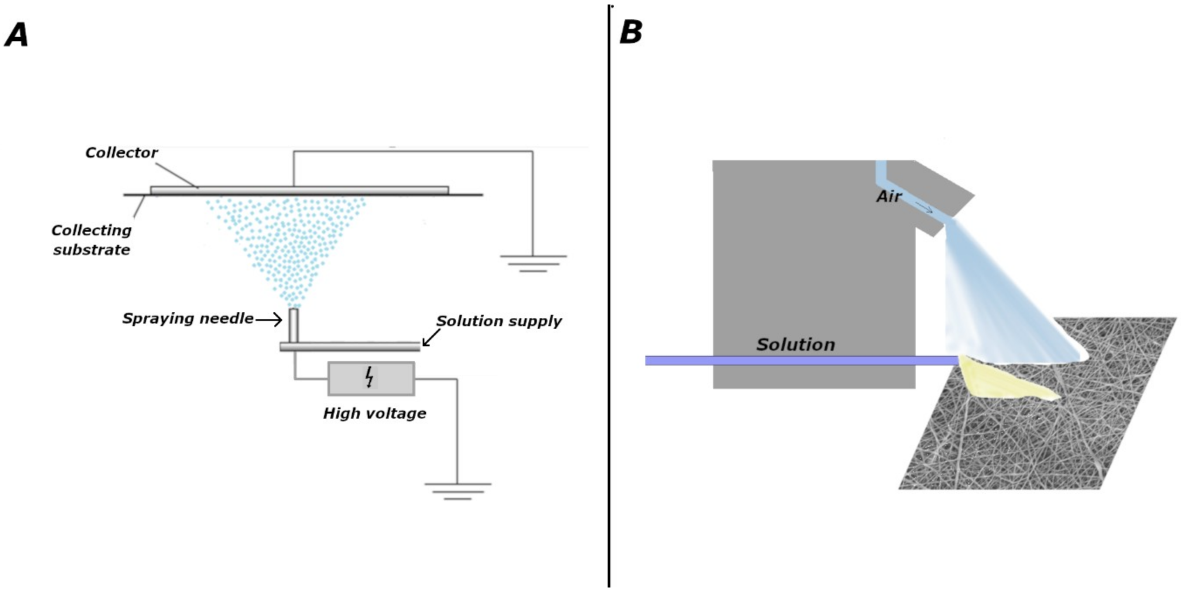

Fig 3 Scheme of A) electrospray instrument and B) sonospray instrument

Sonospraying was used as the second coating technique. This technique is unique among other coating deposition techniques, utilising high-frequency sound to create a fine mist of the sprayed solution (scheme can be seen in Fig 3B). This allows for a narrow distribution of droplets, forming a homogenous layer [31–33]. Before coating, plasma was used for PU NF to increase its hydrophilicity, a well-documented process [37]. This was not possible for PLA NF mat because, for any applied process parameter, the destruction of NF occurred. Even though plasma was avoided for the PLA sample, the NF mats were covered by CS quite well. Unlike electrospraying, sonosprayed solvent dries after the process. This causes the NF to be covered by a film-like continuous coating, as seen in Figures Fig 4C and Fig 4F. However, as shown in Fig 5, PLA is not an ideal material for the sonospraying technique because of the shrinkage of chitosan during drying, which is a well-known process [38]. According to the literature, the tensile strength of PLA is insufficient, where the tensile stress of PLA is around 0.2 MPa [39,40]. PLA fibres were very fragile and could be damaged just by handling the sample, resulting in decreased mechanical and structural properties. For this reason, no other tests were done on this sample. While PU showed better properties, the porometry showed a widening of the pore distribution, with the mean increasing from 0.8 to 1.2 µm (Fig 6).

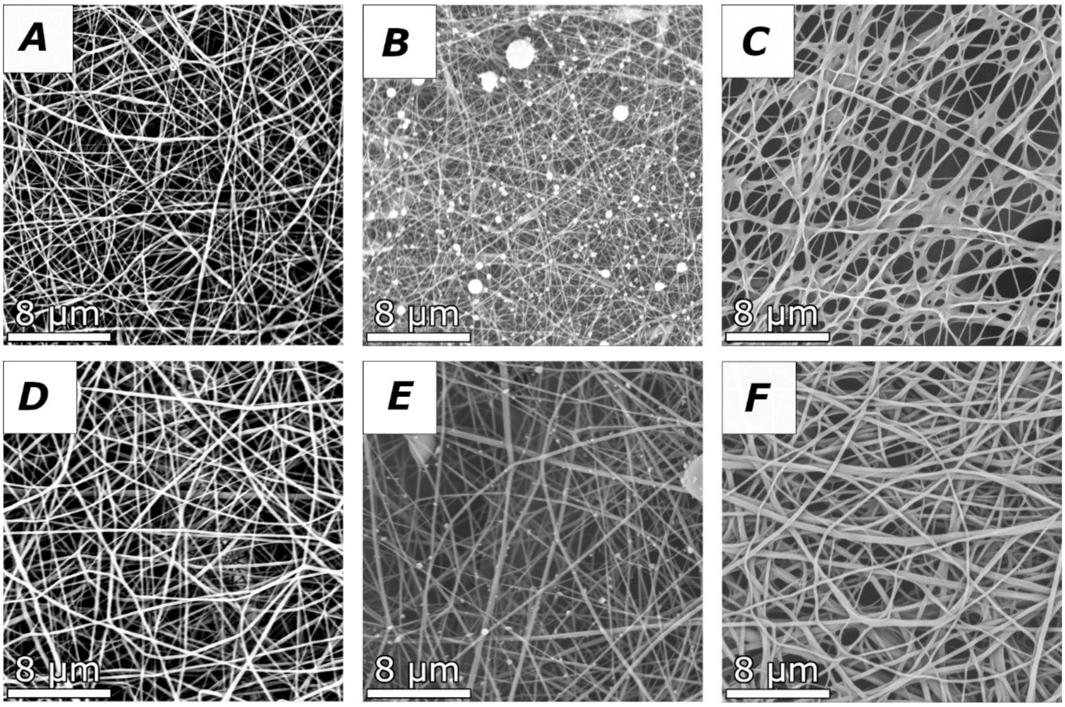

Fig 4 SEM micrographs of pure and sprayed nanofibers A) pristine PLA, B) electrosprayed PLA, C) sonosprayed PLA, D) pristine PU, E) electrosprayed PU and F) sonosprayed PU

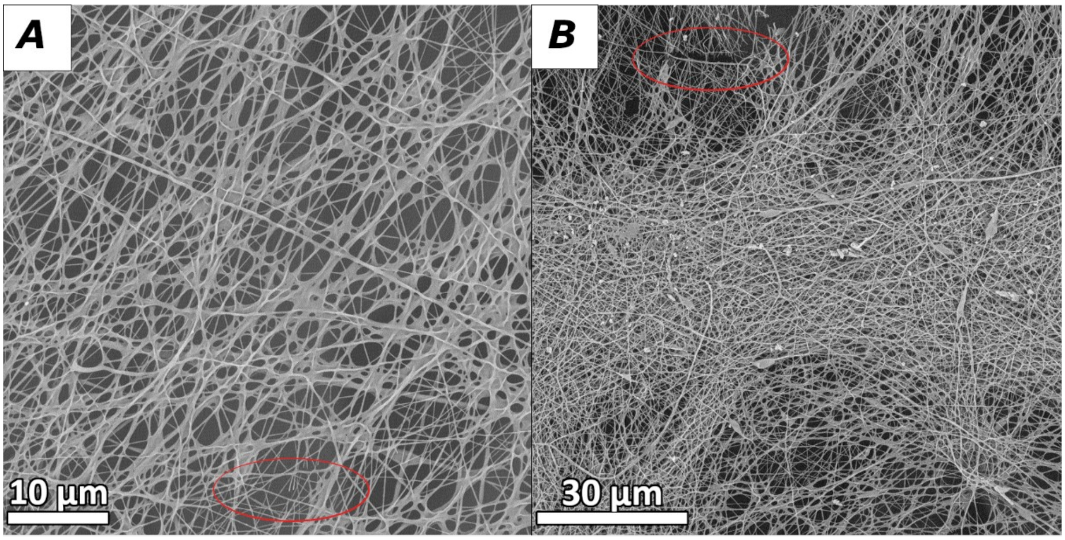

Fig 5 SEM micrographs of PLA nanofibers with sonosprayed chitosan with highlighted tearing (magnification of A) 5000x and B) 2500x)

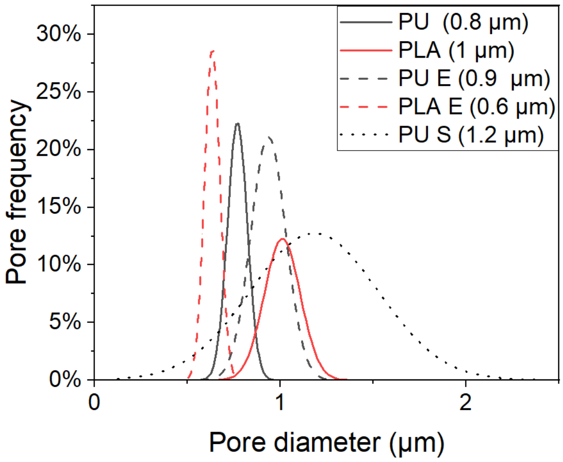

Fig 6 Pore size distribution of prepared PU (black) and PLA (red) nanofibers, elctrosprayed NFs (dashed) and sonosprayed (dots) specimens, with mean values in brackets

3.1 Antimicrobial activity of sprayed nanofibers

CS was used as an antimicrobial agent because of its natural origin. Its antimicrobial activity is caused by the positively charged NH_2 groups, which are acquired to hinder biosynthesis and energy transport through the cell wall in order to terminate bacteria [10,11].

Nanofibrous mats were tested against *Escherichia coli* (*E. coli)* as a gram-negative and *Streptococcus aureus* (*S. aureus*) as a gram-positive bacterium according to modified EN ISO 20743:2013. As seen in Tab. 2, the electrospraying technique showed strong antimicrobial activity. According to the standard, where A≥3 means strong antimicrobial activity.

The sonosprayed technique did not have outstanding results, and the test was only possible on sample PU S. This sample reported no antimicrobial activity for gram-positive bacteria but significant activity against gram-negative bacteria (*E. coli*). This could have been caused by the possible wear of the CS from the polyurethane matrix. Compared to the previous result of PU E, this could suggest that PEO not only helps with the sprayability of CS but also with better adhesion to the base layer polymer, even though plasma was used to increase hydrophobicity on sample PU S, however, it seems, it was not a sufficient method.

Tab. 2 Antimicrobial activity of nanofibers after electrospraying and sonospraying against S. aureus (CCM 4516) and E. coli (CCM 4517)

Microorganism	**Exposition Technology**	**NF material**	**Number of viable cells recovered per cm^2 of a specimen** N_x (CFU/cm^2)	**Antimicrobial activity** (log CFU)
S. aureus	Electrospraying	Ref. neat PLA	$5.0 \cdot 10^5$	(log N_0 = 5.7)
		PLA E	>0	>5.7
		Ref. neat PU	$2.3 \cdot 10^5$	(log N_0 = 5.4)
		PU E	>0	>5.4
	Sonospraying	Ref. neat PU	$1.6 \cdot 10^5$	(log N_0 = 5.2)

		PU S	$4.4 \cdot 10^5$	0
E. coli	Electrospraying	Ref. neat PLA	$1.5 \cdot 10^6$	(log N_0 = 6.2)
		PLA E	>0	>6.2
		Ref. neat PU	$1.5 \cdot 10^6$	(log N_0 = 6.2)
		PU917 E	>0	>6.2
	Sonospraying	Ref. neat PU	$2.9 \cdot 10^6$	(log N_0 = 6.5)
		PU S	$2.5.10^4$	2.1

3.2 Filtration efficiency

The filter pressure resistance and filtration efficiency are the main properties of air filtration. Fig 7 shows the filtration efficiency of surface-modified nanofibers. This picture does not include the sonospraying technique for either PU or PLA. PLA is not included because of low mechanical strength and easy destruction of fibres, as mentioned in the previous chapter (2.5 Characterisation). Although PU material did not exhibit problems while manipulating the NFs mat, the average filtration efficiency was below 50%, e.g. 24% for particles of 400 nm (as seen in Tab. 3), and thus is not included in the graph. However, the pristine material has a filtration efficiency of over 95%, which could suggest the failure of the sprayed polymer of the nanofibers because of its high fragility.

On the contrary, samples sprayed with electrospraying techniques manifested similar or even higher filtration efficiency. However, the pressure resistance of the PLA E sample increased significantly, caused by the decrease in pore size, from 32 to 148 Pa for the pristine and PLA E, respectively. This is followed by a decreased QF, which is the highest for pristine PLA. The lowest QF is for the sonosprayed sample, which is in understanding with the low filtration efficiency.

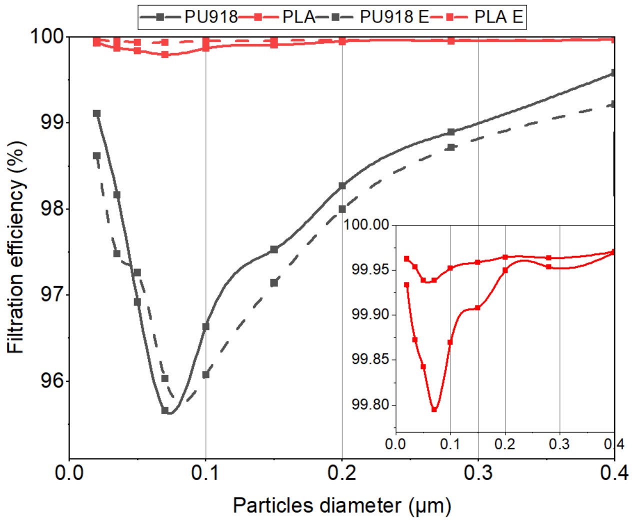

Fig 7 Graphs of filtration efficiency of neat material (solid lines), electrosprayed samples (dashed lines) of PU (black) and PLA (red) polymers

Tab. 3 Filtration efficiency, pressure resistance and quality factor at 400 nm

Polymer	**Technique**	**Filtration efficiency at**	**Pressure resistance at**	**Quality Factor (-)**

		400 nm (%)	400 nm (MPa)	
PLA	neat	99.9698	118.2	0.0507
	electrospraying	99.9708	148.6	0.0507
	sonospraying	-	-	-
PU	neat	99.5831	93.0	0.0359
	electrospraying	99.2190	63.1	0.0537
	sonospraying	24.0488	45.9	0.0044

Many other researchers have used CS as an antimicrobial agent. However, CS used with water-insoluble polymers is mainly used as an additive during electrospinning [10]. In these cases, chitosan is used as an NP because of the phase separation caused by the different solubility of these polymers. Other researchers are choosing polymers soluble in water, like PVA, PEO, etc, and further crossing them [14,41–44]. In these cases, both the carrier polymer and functional polymer (CS) are electrospun together as a blend. To our best knowledge, no publications use PU as a chitosan carrier polymer. That could be caused by their incompatibility and the nondegradable character of PU.

Some of these research papers are summarised in Tab. 4, where the filtration efficiency, pressure resistance, and quality factor were compared with prepared sprayed nanofibers. In all of these publications, tested membranes achieved antimicrobial properties. Considering the observed parameters, membranes with the electrospray modification showed good potential in fabricating antimicrobial filter membranes. The PLA membrane exceeds almost every compared membrane in filtration effectivity, and the QF is comparable to the prepared nanofibers in the other studies.

Tab. 4 Comparison between studies using chitosan agent and this study

Sample	Technology of preparation	Velocity (cm s^{-1})	Particle size	Filtration efficiency (%)	Pressure resistance (Pa)	QF (Pa^{-1})	Reference
PU/CS	Sonospraying	5	20-400 nm	40.76	46.178	0.004	This study
PU/CS/PEO	Electrospraying			97.48	61.74	0.053	
PLA/CS/PEO	Electrospraying			99.95	148.76	0.050	
PVA/CS	Electrospinning	4.8	70- 250 nm	96.58	108.1	0.031	[41]
PEO/CS + MOF-5 crystals	Electrospinning + metal incorporation	-	<2.5 µm	96.46–99.96	44–54	0.074	[42]
PVA/GA*/CS	Electrospinning	-	<2.5 µm	95	290	0.012	[14]
PVA/CS	Electrospinning	-	<2.5 µm	93.10	<45	>0.0825	[43]

PVA/CA/ AgNP/CS	Dual electrospinning	5	2.5 µm	99.78	61.15	0.090	[44]
PLA/CS	Electrospinning	14	75/260 nm	98.90	147	0.027	[10]

*GA as glutaraldehyde

Conclusion

This study utilised sonospraying and electrospraying techniques to modify the surface of nanofibrous mats with chitosan as an antimicrobial agent for filtration. Chitosan was sprayed on two types of polymer nanofiber (NF), namely synthetic polyurethane (PU) and one naturally derived (PLA). Electrospraying formed drop-like particles on the fibres, while sonospraying seemed to cover the nanofibers, for which it has been shown to be a poor surface modification technique for PLA polymer, as the shrinkage occurred as the chitosan dried, causing breaking of the polymer nanofibers due to low strength of PLA nanofibers. The electrospray technique exhibited strong antibacterial activity against both strains (*E. coli* and *S. aureus*), while the sonospray technique showed only significant activity against the gram-negative strain. The sonospraying technique further showed low filtration properties, while electrospray showed high potential. Both used polymers exhibited high filtration efficiency, up to 99.95 % and 99.2 % for PLA and PU mats, respectively. This proved that the electrospraying technique could be used as a fast and easy technique to modify nanofibers.

CRediT authorship contribution statement

Dominika Hanušová: Conceptualization, Methodology, Investigation, Writing – original draft, Data Curation. **Lenka Lovecká**: Formal analysis, Investigation, Writing - Review & Editing, Data Curation. **Miroslava Kovářová**: Formal analysis, Investigation, Writing - Review & Editing, Data Curation. **Alessia Cabrini**: Investigation, Formal analysis, Validation. **Zuzana Krchňáčková**: Investigation, Formal analysis, Validation. **Hana Pištěková**: Investigation, Formal analysis, Validation. **Miroslava Dušánková**: Investigation, Formal analysis, Validation. **Marino Lavorna**: Supervision, Funding acquisition, Validation. **Vladimír Sedlařík**: Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements:

This work was supported by the European Just Transition Fund within the Operational Programme: Just Transition under the aegis of the Ministry of the Environment of the Czech Republic, project CirkArena number CZ.10.03.01/00/22_003/0000045 and the Ministry of Education Youth and Sports of the Czech Republic, Operational Programme Johannes Amos Comenius OP JAC ""Application potential development in the field of polymer materials in the context of circular economy compliance (POCEK)"", number CZ.02.01.01/00/23_021/0009004.

Authors are further grateful for co-funding from the development process of the Centre of Polymer Systems, Tomas Bata University in Zlin, program DKRVO (RP/CPS/2024-28/002) supported by the Ministry of Education Youth and Sports of the Czech Republic and by the Internal Grant Agency of TBU in Zlin (IGA/CPS/2025/002).

Data availability

Data will be made available upon request.

References:

[1] S. DeWeerdt, Mobility: The urban downshift, Nature 531 (2016) S52–S53. https://doi.org/10.1038/531S52a.

[2] R. Givehchi, Q. Li, Z. Tan, Quality factors of PVA nanofibrous filters for airborne particles in the size range of 10–125nm, Fuel 181 (2016) 1273–1280. https://doi.org/10.1016/j.fuel.2015.12.010.

[3] W.W.-F. Leung, Q. Sun, Charged PVDF multilayer nanofiber filter in filtering simulated airborne novel coronavirus (COVID-19) using ambient nano-aerosols, Separation and Purification Technology 245 (2020) 116887. https://doi.org/10.1016/j.seppur.2020.116887.

[4] N.S.M. Nor, C.W. Yip, N. Ibrahim, M.H. Jaafar, Z.Z. Rashid, N. Mustafa, H.H.A. Hamid, K. Chandru, M.T. Latif, P.E. Saw, C.Y. Lin, K.M. Alhasa, J.H. Hashim, M.S.M. Nadzir, Particulate matter (PM2.5) as a potential SARS-CoV-2 carrier, Sci Rep 11 (2021) 2508. https://doi.org/10.1038/s41598-021-81935-9.

[5] R. Mishra, P. Krishnamoorthy, S. Gangamma, A.A. Raut, H. Kumar, Particulate matter (PM10) enhances RNA virus infection through modulation of innate immune responses, Environmental Pollution 266 (2020) 115148. https://doi.org/10.1016/j.envpol.2020.115148.

[6] S. Jiang, Y. Chen, G. Duan, C. Mei, A. Greiner, S. Agarwal, Electrospun nanofiber reinforced composites: a review, Polym. Chem. 9 (2018) 2685–2720. https://doi.org/10.1039/C8PY00378E.

[7] C. Liu, P.-C. Hsu, H.-W. Lee, M. Ye, G. Zheng, N. Liu, W. Li, Y. Cui, Transparent air filter for high-efficiency PM2.5 capture, Nat Commun 6 (2015) 6205. https://doi.org/10.1038/ncomms7205.

[8] K. Čech Barabaszová, S. Holešová, M. Hundáková, K. Hrabovská, L. Plesník, D. Kimmer, K. Joszko, B. Gzik-Zroska, M. Basiaga, Antimicrobial PVDF nanofiber composites with the ZnO - vermiculite - chlorhexidine based nanoparticles and their tensile properties, Polymer Testing 103 (2021) 107367. https://doi.org/10.1016/j.polymertesting.2021.107367.

[9] X. Ding, Y. Li, Y. Si, X. Yin, J. Yu, B. Ding, Electrospun polyvinylidene fluoride/SiO2 nanofibrous membranes with enhanced electret property for efficient air filtration, Composites Communications 13 (2019) 57–62. https://doi.org/10.1016/j.coco.2019.02.008.

[10] H. Li, Z. Wang, H. Zhang, Z. Pan, Nanoporous PLA/(Chitosan Nanoparticle) Composite Fibrous Membranes with Excellent Air Filtration and Antibacterial Performance, Polymers 10 (2018) 1085. https://doi.org/10.3390/polym10101085.

[11] S. -G. Hu, C. -H. Jou, M. -C. Yang, Surface grafting of polyester fiber with chitosan and the antibacterial activity of pathogenic bacteria, J of Applied Polymer Sci 86 (2002) 2977–2983. https://doi.org/10.1002/app.11261.

[12] H. Homayoni, S.A.H. Ravandi, M. Valizadeh, Electrospinning of chitosan nanofibers: Processing optimisation, Carbohydrate Polymers 77 (2009) 656–661. https://doi.org/10.1016/j.carbpol.2009.02.008.

[13] N. Fereydouni, M. Zangouei, M. Darroudi, M. Hosseinpour, A. Gholoobi, Antibacterial activity of chitosan-polyethylene oxide nanofibers containing silver nanoparticles against aerobic and anaerobic bacteria, Journal of Molecular Structure 1274 (2023) 134304. https://doi.org/10.1016/j.molstruc.2022.134304.

[14] B. Yang, J. Wang, L. Kang, X. Gao, K. Zhao, Antibacterial, efficient and sustainable CS/PVA/GA electrospun nanofiber membrane for air filtration, Mater. Res. Express 9 (2022) 125002. https://doi.org/10.1088/2053-1591/aca74a.

[15] R. Shen, W. Xu, Y. Xue, L. Chen, H. Ye, E. Zhong, Z. Ye, J. Gao, Y. Yan, The use of chitosan/PLA nano-fibers by emulsion eletrospinning for periodontal tissue engineering, Artificial Cells, Nanomedicine, and Biotechnology 46 (2018) 419–430. https://doi.org/10.1080/21691401.2018.1458233.

[16] F. Mokhtari, A. Samadi, A.O. Rashed, X. Li, J.M. Razal, L. Kong, R.J. Varley, S. Zhao, Recent progress in electrospun polyvinylidene fluoride (PVDF)-based nanofibers for sustainable energy and environmental applications, Progress in Materials Science 148 (2025) 101376. https://doi.org/10.1016/j.pmatsci.2024.101376.

[17] L. Yang, X. Li, J. Yu, S. Zhang, B. Ding, Transparent and antibacterial air filters based on nanofiber/nets membrane, Composites Communications 48 (2024) 101916. https://doi.org/10.1016/j.coco.2024.101916.

[18] B. Ding, ed., Electrospinning: nanofabrication and applications, Elsevier, Amsterdam, Netherlands ; Cambridge, MA, 2019.

[19] A. Ashori, S. Sepahvand, M. Jonoobi, Development of biodegradable nanofiber filters based on surface-modified cellulose nanofibers with graphene oxide for high removal of airborne particulate matter, International Journal of Biological Macromolecules 261 (2024) 129687. https://doi.org/10.1016/j.ijbiomac.2024.129687.

[20] X. Wang, J. Wang, J. Kang, Y. Zhao, H. Tian, Y. Jin, R. Kumar, J. Wang, Natural filter: Adjustable hydrophobicity from biodegradable zein nanofiber membrane for high efficiency air purification, Separation and Purification Technology 358 (2025) 130422. https://doi.org/10.1016/j.seppur.2024.130422.

[21] N.B. Shelke, R.K. Nagarale, S.G. Kumbar, Polyurethanes, in: Natural and Synthetic Biomedical Polymers, Elsevier, 2014: pp. 123–144. https://doi.org/10.1016/B978-0-12-396983-5.00007-7.

[22] R. V.R., J.S. George, S. Thomas, Polymer formulations for controlled release of fertilisers, in: Controlled Release Fertilisers for Sustainable Agriculture, Elsevier, 2021: pp. 183–194. https://doi.org/10.1016/B978-0-12-819555-0.00011-X.

[23] T.M. Schmitt, POLYMERS | Polyurethanes, in: Encyclopedia of Analytical Science, Elsevier, 2005: pp. 266–272. https://doi.org/10.1016/B0-12-369397-7/00480-5.

[24] J. Brzeska, A. Tercjak, W. Sikorska, B. Mendrek, M. Kowalczuk, M. Rutkowska, Degradability of Polyurethanes and Their Blends with Polylactide, Chitosan and Starch, Polymers 13 (2021) 1202. https://doi.org/10.3390/polym13081202.

[25] M.F. Ashby, Material profiles, in: Materials and the Environment, Elsevier, 2013: pp. 459–595. https://doi.org/10.1016/B978-0-12-385971-6.00015-4.

[26] X. Cao, M. Huang, B. Ding, J. Yu, G. Sun, Robust polyacrylonitrile nanofibrous membrane reinforced with jute cellulose nanowhiskers for water purification, Desalination 316 (2013) 120–126. https://doi.org/10.1016/j.desal.2013.01.031.

[27] M. Ranjbar Mohammadi, E. Naghashzargar, M. Kamali Moghaddam, R. Khorshidi, Production of PLA fibers with surface modifications and silver nanoparticle coating to impart antibacterial activity, Polym. Bull. 81 (2024) 6055–6072. https://doi.org/10.1007/s00289-023-04989-x.

[28] Q. Chen, C.J. Brett, A. Chumakov, M. Gensch, M. Schwartzkopf, V. Körstgens, L.D. Söderberg, A. Plech, P. Zhang, P. Müller-Buschbaum, S.V. Roth, Layer-by-Layer Spray-Coating of Cellulose Nanofibrils and Silver Nanoparticles for Hydrophilic Interfaces, ACS Appl. Nano Mater. 4 (2021) 503–513. https://doi.org/10.1021/acsanm.0c02819.

[29] M.C. Karlapudi, M. Vahdani, S.M. Bandari, S. Peng, S. Wu, A Comparative Study on the Effects of Spray Coating Methods and Substrates on Polyurethane/Carbon Nanofiber Sensors, Sensors 23 (2023) 3245. https://doi.org/10.3390/s23063245.

[30] E. Gezmis-Yavuz, C.E. Cansoy, D.Y. Koseoglu-Imer, Fabrication of mixed matrix nanofibers with electrospraying and electrospinning techniques and their application to gas toluene removal, Journal of Environmental Chemical Engineering 11 (2023) 110067. https://doi.org/10.1016/j.jece.2023.110067.

[31] A. Cabrini, A. Ghalayani Esfahani, A. Petraconi, M. Lavorgna, L. De Nardo, G.G. Buonocore, R.J.E. Andrade, P. Cerruti, Ultrasonic spray deposition of PEGDE-crosslinked chitosan/graphene oxide coatings for enhancing gas barrier properties of polybutylene succinate films, Progress in Organic Coatings 183 (2023) 107760. https://doi.org/10.1016/j.porgcoat.2023.107760.

[32] M. Dobre, L. Bolle, Practical design of ultrasonic spray devices: experimental testing of several atomiser geometries, Experimental Thermal and Fluid Science 26 (2002) 205–211. https://doi.org/10.1016/S0894-1777(02)00128-0.

[33] K. Sreeja Sadanandan, A. Bacon, D.-W. Shin, S.F.R. Alkhalifa, S. Russo, M.F. Craciun, A.I.S. Neves, Graphene coated fabrics by ultrasonic spray coating for wearable electronics and smart textiles, J. Phys. Mater. 4 (2021) 014004. https://doi.org/10.1088/2515-7639/abc632.

[34] M. Kavimughil, M. Maria Leena, J.A. Moses, C. Anandharamakrishnan, Electrospining and electrospraying technologies for nutraceutical delivery system development, in: Industrial Application of Functional Foods, Ingredients and Nutraceuticals, Elsevier, 2023: pp. 279–323. https://doi.org/10.1016/B978-0-12-824312-1.00009-1.

[35] S. Kumari, B.S. Yadav, R.B. Yadav, Synthesis and modification approaches for starch nanoparticles for their emerging food industrial applications: A review, Food Research International 128 (2020) 108765. https://doi.org/10.1016/j.foodres.2019.108765.

[36] E. Domincova Bergerova, D. Kimmer, M. Kovarova, L. Lovecka, I. Vincent, P. Drohsler, V. Adamec, K. Kobolova, V. Sedlarik, Effect of polyurethane structure on arsenic adsorption capacity in nanofibrous polymer/ferrous sulphate-based systems, Environ. Sci.: Water Res. Technol. 8 (2022) 2663–2681. https://doi.org/10.1039/D2EW00566B.

[37] B. Jaleh, P. Parvin, P. Wanichapichart, A.P. Saffar, A. Reyhani, Induced super hydrophilicity due to surface modification of polypropylene membrane treated by O2 plasma, Applied Surface Science 257 (2010) 1655–1659. https://doi.org/10.1016/j.apsusc.2010.08.117.

[38] R. Katsumata, S. Ata, K. Kuboyama, T. Ougizawa, Evaporation rate effect on starting point of shrinkage stress development during drying process in solvent cast polymer film, Journal of Applied Polymer Science 128 (2013) 60–65. https://doi.org/10.1002/app.38132.

[39] C. Liu, H. Wong, K. Yeung, S. Tjong, Novel Electrospun Polylactic Acid Nanocomposite Fiber Mats with Hybrid Graphene Oxide and Nanohydroxyapatite Reinforcements Having Enhanced Biocompatibility, Polymers 8 (2016) 287. https://doi.org/10.3390/polym8080287.

[40] Y. Dong, J. Marshall, H.J. Haroosh, S. Mohammadzadehmoghadam, D. Liu, X. Qi, K.-T. Lau, Polylactic acid (PLA)/halloysite nanotube (HNT) composite mats: Influence of HNT content and modification, Composites Part A: Applied Science and Manufacturing 76 (2015) 28–36. https://doi.org/10.1016/j.compositesa.2015.05.011.

[41] G.C. Da Mata, M.S. Morais, W.P. De Oliveira, M.L. Aguiar, Sustainable surgical masks: optimising fine/ultrafine particle filtration using PVA/chitosan electrospun nanofibers, Environ. Sci.: Nano 10 (2023) 2185–2200. https://doi.org/10.1039/D3EN00182B.

[42] W. Pan, J.-P. Wang, X.-B. Sun, X.-X. Wang, J. Jiang, Z.-G. Zhang, P. Li, C.-H. Qu, Y.-Z. Long, G.-F. Yu, Ultra uniform metal−organic framework-5 loading along electrospun chitosan/polyethylene oxide membrane fibers for efficient PM2.5 removal, Journal of Cleaner Production 291 (2021) 125270. https://doi.org/10.1016/j.jclepro.2020.125270.

[43] C.-W. Lou, M.-C. Lin, C.-H. Huang, M.-F. Lai, B.-C. Shiu, J.-H. Lin, Preparation of Needleless Electrospinning Polyvinyl Alcohol/Water-Soluble Chitosan Nanofibrous Membranes: Antibacterial Property and Filter Efficiency, Polymers 14 (2022) 1054. https://doi.org/10.3390/polym14051054.

[44] R. Chueachot, V. Promarak, S. Saengsuwan, Enhancing antibacterial activity and air filtration performance in electrospun hybrid air filters of chitosan (CS)/AgNPs/PVA/cellulose acetate: Effect of CS/AgNPs ratio, Separation and Purification Technology 338 (2024) 126515. https://doi.org/10.1016/j.seppur.2024.126515.