

Production and analysis of electrospun PA 6,6 and PVA nanofibrous surfaces for filtration

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ABSTRACT – REZUMAT

Production and analysis of electrospun PA 6,6 and PVA nanofibrous surfaces for filtration

Electrospun nanofibrous surfaces were produced by using two different polymers (PA 6,6 and PVA) at three different levels of polymer feeding rate (0.2, 0.6 and 1.0 ml/h, respectively) and three different levels of production time in electrospinning (5, 10 and 15 minutes, respectively) and the effect of polymer type, polymer feeding rate and production time was determined by analyzing unit weight and thickness of the nanofibrous membranes as well as fibre fineness and pore size distributions. The results showed that much finer fibres were produced by PA 6,6 polymer compare to PVA. The minimum average fibre fineness was 150.96 nm (by PA 6,6 polymer; 0.2 ml/h; 5 min.) while maximum fibre fineness was 243.43 nm (by PVA polymer; 0.6 ml/h; 15 min.). Similarly, the pore sizes of nanofibrous surfaces produced by PA 6,6 were smaller compare to the ones produced by PVA polymer. The results also indicated that coarser fibres were produced as the polymer feed rate and electrospinning time increased. In the second part of the work, composite structures were obtained by combining nanofibrous surfaces with PP non-woven material and their air permeability and filtration efficiency by using an aerosol having 0.2–0.33 mm diameter range were analyzed. The air permeability of PA 6,6 nanofibrous surfaces were much higher compare to the ones produced by PVA and quite high filtration efficiency (99.901 %) was obtained with PA 6,6 nanofibrous surfaces. Also, potential of these nanofibrous surfaces was evaluated by analysing chemical groups eliminated following their exposure to cigarette smoke which was chosen as a specific case study.

Keywords: electrospinning, nanofibre, PA 6,6, PVA, nanofibrous surface, filtration

Producția și analiza suprafețelor nanofibroase electrofilate din PA 6,6 și PVA pentru filtrare

Suprafețele nanofibroase electrofilate au fost produse prin utilizarea a doi polimeri diferiți (PA 6,6 și PVA) la trei niveluri diferite de viteză de alimentare a polimerului (0,2, 0,6 și respectiv 1,0 ml/h), precum și trei intervale diferite de timp de producție în electrofilare (5, 10 și respectiv 15 minute), iar influența tipului de polimer, vitezei de alimentare a polimerului și timpului de producție a fost determinate prin analiza greutății unitare și a grosimii membranelor nanofibroase, precum și prin finețea fibrelor și distribuția mărimii porilor. Rezultatele au arătat că fibrele mult mai fine au fost produse din polimerul PA 6,6 comparativ cu PVA. Finețea medie minimă a fibrelor a fost de 150,96 nm (din polimerul PA 6,6; 0,2 ml/h; 5 min.), în timp ce finețea maximă a fibrelor a fost de 243,43 nm (din polimerul PVA; 0,6 ml h; 15 min.). În mod similar, dimensiunile porilor suprafețelor nanofibroase produse din PA 6,6 au fost mai mici în comparație cu cele produse din polimerul PVA. Rezultatele au indicat, de asemenea, că fibrele grosiere au fost produse pe măsură ce viteza de alimentare a polimerului și timpul de electrofilare au crescut. În cea de-a doua parte a lucrării, structurile compozite au fost obținute prin combinarea suprafețelor nanofibroase cu material nețesut PP, iar permeabilitatea acestora la aer și eficiența de filtrare au fost analizate prin utilizarea unui aerosol cu un interval al diametrului de 0,2–0,33 mm. Permeabilitatea la aer a suprafețelor nanofibroase de PA 6,6 a fost mult mai mare în comparație cu cele produse din PVA și s-a obținut o eficiență de filtrare destul de ridicată (99,901%) cu suprafețe nanofibroase de PA 6,6. De asemenea, potențialul acestor suprafețe nanofibroase a fost evaluat prin analiza grupurilor chimice eliminate în urma expunerii lor la fumul de țigară, care a fost ales ca studiu de caz specific.

Cuvinte-cheie: electrofilare, nanofibră, PA 6,6, PVA, suprafață nanofibroasă, filtrare

INTRODUCTION

A filter media is utilised to purify air that contains solid particles (virus, mine dust etc.) or liquid particles (evaporated water, chemical solvents etc.), therefore filtration is mainly a separation process. The main aim of such surfaces developed for filtration is to have pore sizes as minimum as possible while providing maximum filtration efficiency during use. As a result, including the finest possible fibres in a filtration media has been one of the important criteria for efficient removal of the particles. In conventional fibre

production methods, however, the fibre fineness usually varies between 10–50 μm while it might be reduced down to 3–8 μm by meltblown technique [1]. However, not only the fibre fineness but also the pore size in a filter media matters as indicated above, i.e. mesh pore size must be small or thick mesh is required to remove ultrafine particles so that a filtration fan can blow the air with high pressure [2]. On the other hand, small particles such as between 0.04–0.4 μm , are known as the most difficult to get caught during filtration. Therefore, developing a porous

filtration mesh surface being able to catch particles of 0.3 μm and below at high efficiency has been a challenging issue. As a result, development of filtration surfaces including very fine fibres and also being able to catch such a small particles is a need for better filtration. In this respect, electrospun nanofibre membranes, which can replace glass fibres and charcoal filters as functional nanofibre based filters or functional nanofibre combinations [3], gained an important potential and have been used in air filtration during last 20 years while a filtration market up to 700 billion USDollar in 2020 was estimated indicating the potential in this field [4,5]. In this respect, there is also a continuous search for new production perspectives for electrospun nanofibres in filtration. Production of nonwovens from short electrospun polymer nanofibre dispersion [6]; production of ultrafine (33 and 120 nm) polyamide 6 nanofibre membranes formed with needleless electrospinning [7] or fabrication of flexible and strong carbon nanofibre (CNF) membranes by electrospinning capable of efficiently rejecting NP of different sizes and materials such as Au, Ag, and TiO_2 from aqueous solution [8] can be given as examples.

Mainly PAN based nanofibre membranes produced by electrospinning is developed for ultrafiltration and nanofiltration [9, 10] while potential of other polymers have also been explored. Tsai *et al.* analyzed filtration performance of electrospun Polycarbonate, PU ve PEO nanofibre surfaces having 100–500 nm fibre fineness and tested for 300 nm NaCl aerosols by comparing with conventional meltblown fabrics [11]. They reported filtration efficiency (78%) of 3 g/m^2 electrospun PEO is equivalent to that of 100 g/m^2 of uncharged meltblown fabrics. Similarly, Ahn *et al.* studied the performance of electrospun PA6 nanofibre surfaces at different unit weights including fibres of 80–200 nm and reported surfaces of 5.75 g/m^2 and 10.75 g/m^2 exhibit HEPA level filtration efficiency [12]. Qin and Wang reported high filtration efficiency of electrospun PVA nanofibre surfaces with average fibre diameter of 200 nm and average porosity of 740 nm when tested with NaCl areosols of 0.6 μm [13]. On the other hand, Guibo *et al.*, reported high filtration efficiency of electrospun PA6 surfaces, which have average fibre fineness of 177 ± 39 nm and porosity of 147.4 ± 42.9 nm, reaching up to 99.98% efficiency levels produced at different electrospinning production times [4]. Li and Gao compared filtration efficiency of electrospun PVA nanofibre membranes produced at different concentrations and electrospinning production times [14]. The average fibre fineness was 92 ± 21 nm while they used 75 ± 20 nm NaCl particles at 32 lt/min airflow reporting 99.95% efficiency. Similarly, Hung reported higher filtration performance of PEO nanofibre surfaces with fibre fineness of 100–400 nm for aerosols of 50–500 nm compared to the microfibre surfaces [15]. Regarding PEO nanofibrous membranes, the effect of nanofibre

packing density and nanofibre layer thickness on filtration performance was studied as well by electrospinning these fibres on a microfibre substrate having mean PEO fibre diameter of 208 nm [16]. The results showed that the most penetrating particle sizes (MPPS) decreased with nanofibre packing density as the MPPS (NaCl aerosol size ranging from 50 to 480 nm) decreased from 140 to 90 nm when nanofibre packing density was increased from 3.9 to 36×10^{-3} while the effect of nanofibre layer thickness on MPPS is less prominent than that of nanofibre packing density.

On the other hand, Heikkila *et al.* studied filtration performance of different type of polyamides (PA 6, PA 6,6; PA 6,12; PA 6,14; PA 10,12 and PA 10,14) reporting that the finest fibres ($120 \pm 30\text{nm}$) can be obtained by PA 6,6 polymer [17] while effect of electrospinning parameters (such as polymer solution concentration, voltage, tip-collector distance) on filtration performance of PA nanofibrous surfaces electrospun during 15, 30, 45 and 60 min was reported by Aliabadi [18]. There was a significant increase in filtration efficiency of surfaces electrospun at 30 min. compare to the ones produced at 15 min. while the difference was not significant between the surfaces produced at 30 min. and 45 min. The effect of electrospinning parameters such as polymer solution concentration, voltage, tip-collector distance and duration of electrospinning (18, 20, 22 and 24 min.) on filtration performance was also studied by Wei *et al.* by developing so-called “needleless double rings slit electrospinning” system producing PAN nanofibrous surfaces [19]. The results showed that mean pore diameter and its distribution increased as spinning time increase and filtration efficiency was above 99.9% for surfaces produced at 18 min. while filtration resistance increased dramatically when spinning time increased from 18 to 24 min. Similarly, Ahne *et al.* studied the effect of electrospinning parameters such as polymer solution concentration, voltage, tip-collector distance and duration of electrospinning (up to 30 min.) on filtration performance as well but producing cellulose acetate (CA) based nanofibres obtaining maximum filtration efficiency of 99.8% for samples obtained with deposition time of 30 min. while maximum filter quality factor was 0.05 Pa^{-1} for a filter corresponding to a CA concentration of 20 wt.%, a tip-to-collector distance of 12.5 cm, a voltage of 8 kV and a deposition time of 5 minutes [20]. The effect of electrospinning time on filtration performance of PAN nanofibrous surfaces was also studied showing that PAN deposition time during electrospinning affected the filter quality [21]. The results showed that shorter deposition time of PAN nanofibre mats yields a better quality factor. It was also observed that thickness uniformity of nanofibre mats was getting worse as the deposition time increased and therefore diminished filter quality. In another study, nylon nanofibre filters

were fabricated with five different solution concentrations and five different electrospinning times (1, 1.5, 2, 3, and 4 h) to investigate the effect of fibre diameter, filter thickness, packing density and face velocity while a semi-empirical model was applied to predict $PM_{2.5}$ removal efficiency [22]. An air filter based on PVDF branched nanofibres having a basis weight of 1 g/m^2 with outstanding filtration efficiency (99.999%) to $0.26\text{ }\mu\text{m}$ sodium chloride particles under pressure drop of 126.17 Pa can be given as another interesting work in this field [23]. On the other hand, Daneleviciute-Vaisniene *et al.* produced electrospun PVA nanofibre membranes, but different from above works they analysed cigarette smoke filtration performance indicating that PVA surfaces were able to catch organic polar groups, ethers and carboxyl groups [24]. In this study, FT-IR analysis results of two layers (PP+PVA web) was compared with PP non-woven fabric layer itself after exposure to cigarette smoke filtration which would in fact need further confirmation including comparison of two identical structures.

Use of nanofibre webs also contributes significantly to remove small liquid drops in submicron range as well. Hajra *et al.* reported that small addition of nanofibres on the substrate of glass fibres effectively captures oil droplets of 210 nm diameter [25]. There are commercial two-layer composite nanofibre webs with supporting micron-fibre layer as dust filter bags capturing particles below 500 nm diameter size [26]. A pleated filter media prepared by nanofibres of 250 nm size wetlaid on a cellulose substrate of 10 mm fibre diameter is another example [27] while their potential for textile effluent treatment has also been studied [28]. A recent work by Shao *et al.* also show potential of composite nanofibrous membranes produced by electrospinning of polyvinyl chloride (PVC) nanofibres and polyamide-6 (PA6) nanofibres [29]. The removal efficiency was 98.75% for sodium chloride (NaCl) aerosol particles with a diameter of $0.3\text{ }\mu\text{m}$ as their performance was attributed to triboelectric effect between these two adjacent nanofibre membranes.

As cigarette smoke was chosen as a case study in this work, a brief discussion of some main findings in this field has also been included. Poisonous chemicals in cigarette smoke is known as one of the main reasons for cancer and it is combination of over 4700 chemical compounds [30] including nicotine as well as poisonous compounds like polycyclic aromatic

hydrocarbons (PAHs) and N-nitrocamins [31]. IARC, on the other hand, indicates that 9 out of 50 chemicals in cigarette smoke are in Group 2A carcinogen category [32]. Therefore, an efficient filtration of cigarette smoke is a real need and a challenging issue. Today, generally natural/synthetic fibrous materials in tow form are used in cigarette filters, by enhancing their filtration ability by additives or special chemical compounds that have been generally kept as a trade secret. The fibres used for cigarette filters are mainly cellulose diacetate or PP, however, even use of silk fibres has been reported [33]. By adding Glycine to remove aldehydes from cigarette smoke, or use of 3-aminopropylsilyl groups bonded by silica gel [34] or CGC substance obtained from *Ginkgo biloba* plant [35], or use of activated carbon within fibre tows [36] are examples for different approaches. It is also clear that maximising specific surface of fibres is advantageous for an efficient filtration, therefore fibres with specific cross-section, such as Y-cross-section, have also been used [37].

In the light of above works, electrospun nanofibre membranes were produced and their properties were analysed. During production of nanofibrous surfaces, two different polymers (PA 6,6 and PVA) were used. PA 6,6 was specifically chosen due to its high potential for finer fibre production while PVA was chosen mainly because of its common use in electrospinning for easy spinning conditions. Nanofibrous surfaces at different unit weights and thicknesses were electrospun at three different levels of polymer injection speed (0.2 , 0.6 and 1.0 ml/h , respectively) and three different electrospinning times (5 , 10 and 15 min. , respectively).

MATERIAL AND METHOD

Production of nanofibre surfaces

Single needle electrospinning set up, that includes Matsusada AU30-DC (max. 30 kV) high-power supply and Newera Ne-300 polymer injection pump, was used for production of nanofibrous surfaces [38]. The conductivity of polymers was measured by Eutech conductivity tester while Brookfield DV-F viscosimeter was used for viscosity. During production, polymer fibres were collected as membrane form onto a PP non-woven surface. Main production parameters were summarised in table 1 and table 2, respectively.

Table 1

ELECTROSPINNING PARAMETERS					
Polymer	Polymer concentration wt (%)	Solvent	Needle gauge (mm)	Distance between needle and collector (cm)	Voltage (kV)
PVA	10	Distilled water	0.7	10	20
PA 6,6	10	Formic acid			

Table 2

ELECTROSPUN NANOFIBROUS SURFACES PRODUCED IN THE WORK			
Polymer	Sample code	Production time in electrospinning (min.)	Polymer feed rate (ml/h)
PVA	PVA 5.02	5	0.2
	PVA 5.06		0.6
	PVA 5.1		1.0
	PVA 10.02	10	0.2
	PVA 10.06		0.6
	PVA 10.1		1.0
	PVA 15.02	15	0.2
	PVA 15.06		0.6
	PVA 15.1		1.0
PA 6,6	PA 5.02	5	0.2
	PA 5.06		0.6
	PA 5.1		1.0
	PA 10.02	10	0.2
	PA 10.06		0.6
	PA 10.1		1.0
	PA 15.02	15	0.2
	PA 15.06		0.6
	PA 15.1		1.0

Analysis of nanofibrous surfaces and their filtration performance

Following production of nanofibre membranes, average unit weights of surfaces were determined by testing 5 samples each. A digital micrometer (Kanon, EMS-150 model) with 0.01 mm accuracy was used for thickness measurement of the surfaces. SEM (Quanta, Feg 250) was used to analyse the fibre fineness and fineness variation within the nanofibre membranes together with Adobe Photoshop CS6. Additionally, pore sizes of nanofibre membranes were analyzed by Quanta Chrome tester according to ASTM F316-03 (2011). Following these main characterisation analyses, air permeability of the membranes were tested by Proser air permeability tester according to TS 391 EN ISO 9237:1999 at sample size of 5 cm² and pressure of 100 kPa. Certitest 8130 automatic filtration tester having liquid aerosol diameter range of 0.2–0.33 mm and 90–95 lt/min flow rate was used following EN 149:2001 to analyse filtration efficiency of the nanofibrous surfaces. Also, a basic test set up was used to simulate a simple cigarette smoke filtration (figure 1) as a specific case. In this set up, cigarette smoke was applied for each sample for 1 min. and following this, nanofibre surfaces are analyzed by FT-IR (Thermo iS10) to detect the chemical groups filtrated.

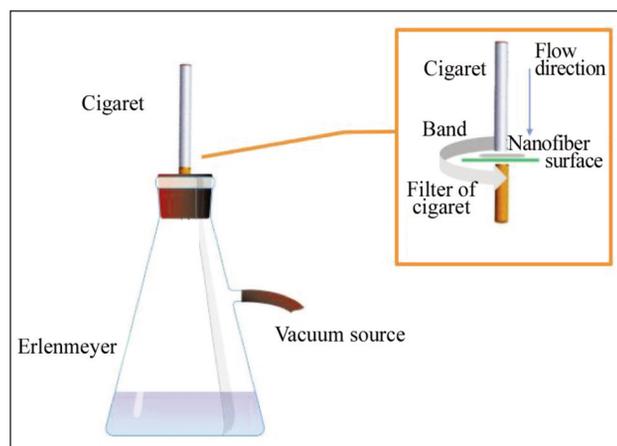


Fig. 1. The simple set-up used for cigarette smoke filtration

RESULTS AND DISCUSSIONS

Viscosity and conductivity of polymer solvents

The typical viscosity and conductivity results of the polymer solvents at 25°C were given below. The results showed that viscosity of both polymers was similar to each other while the conductivity of PA 6,6 polymer was higher (table 3).

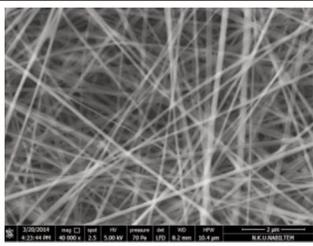
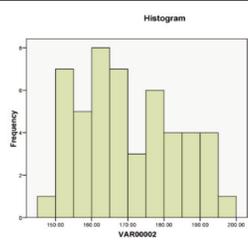
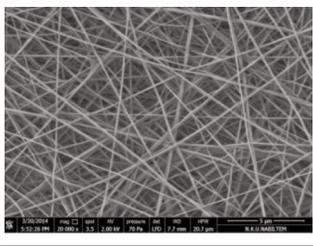
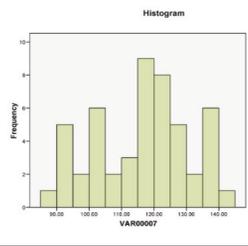
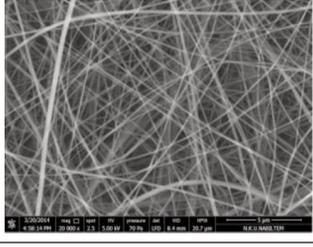
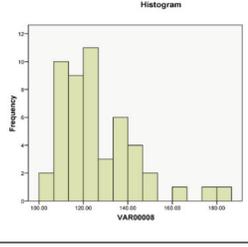
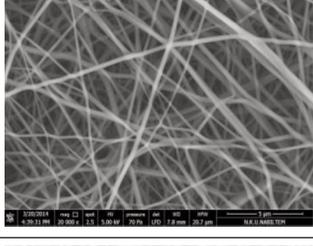
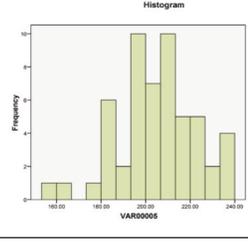
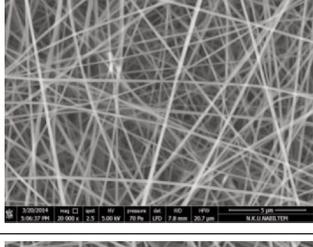
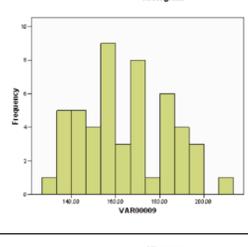
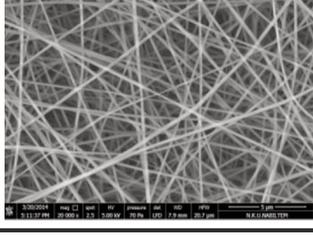
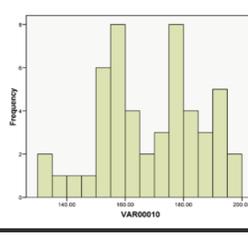
Table 3

VISCOSITY AND CONDUCTIVITY VALUES OF POLYMER SOLVENTS		
Polymer solutions	Viscosity (cP)	Conductivity (mS/cm)
PVA	810.0	575
PA 6,6	800.8	658

Characterisation of nanofibrous surfaces

The typical SEM images show that fibrous membranes were evenly produced by these two polymers (table 4). As the polymer feed rate increased during electrospinning, coarser fibres were produced as expected since the effect of polymer feed rate on fibre fineness is well-known as lower flow rates yielding fibres with smaller diameters [39, 40], although the increase in fibre fineness is more significant when PVA polymer was used (figure 2, a). The variation in fibre fineness also increased at higher polymer feeding rate. The effect of electrospinning time on fibre fineness was also analyzed as the results indicate that fibres get coarser as production time in electrospinning increases (figure 2, b). This is probably as a result of the decrease in conductivity when fibrous membrane surfaces get thicker on the collector during production in electrospinning.

Regarding the effect of electrospinning time on unit weight and thickness of fibrous mesh, the results were given by figure 3. These findings show that both unit weight and thickness values increase as the electrospinning time increases, as expected. However, there is almost 95% increase in unit weight at 10 min. compare to 5 min. electrospinning time,

TYPICAL EXAMPLES OF SEM IMAGES OF ELECTROSPUN NANOFIBROUS SURFACES AND THEIR FIBRE FINENESS DISTRIBUTIONS						
Sample code	Diameter (nm)				Sem image	Fibre fineness distribution
	N	Min. (nm)	Max. (nm)	Mean (nm)		
PA 5.06	50	134.12	202.43	165.35	17.59	 
PA 10.06	50	135.51	208.35	169.06	20.60	 
PA 15.06	50	144.90	211.00	182.98	22.67	 
PVA 5.06	50	180.34	273.87	225.39	20.53	 
PVA 10.06	50	188.50	289.09	234.96	26.60	 
PVA 15.06	50	192.08	265.56	243.43	27.57	 

while the increase at 15 min. is much lower. This result can be attributed to the decrease in conductivity on collector surface due to the increase in fibre layer thickness as production continues. Similar findings were reported by Guibo et al. earlier during electrospinning of PA 6 polymer [4]. However, with PVA

polymer, the increase in unit weight at 10 min. compare to 5 min. is % 71, i.e. much lower value compare to the results obtained by PA 6,6 polymer. That can be explained by lower conductivity of this polymer. The typical porosity values of the nanofibrous surfaces produced by this work were also analysed by

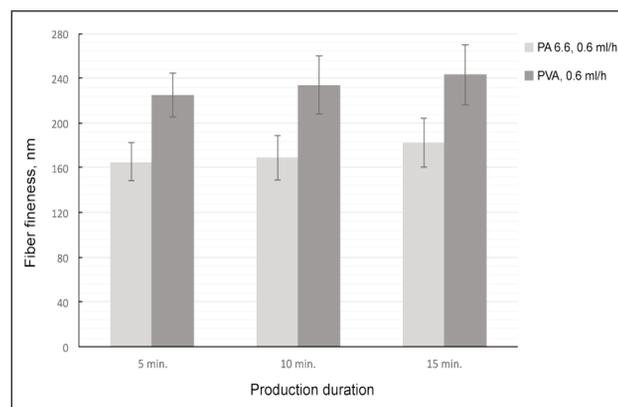
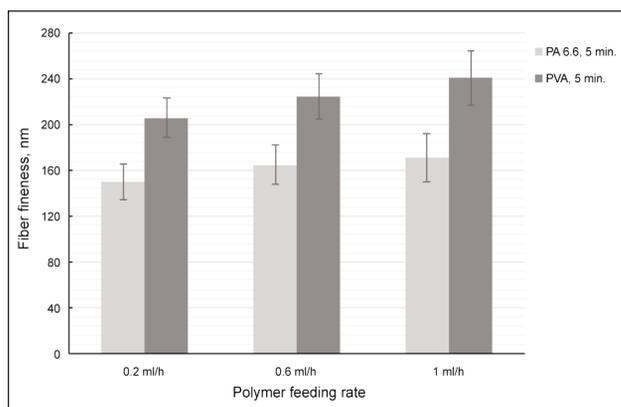


Fig. 2. The effect of: a – polymer feeding rate on fibre fineness; b – production time in electrospinning on fibre fineness

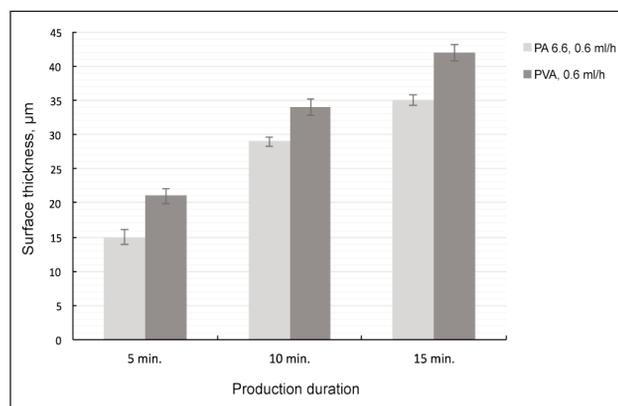
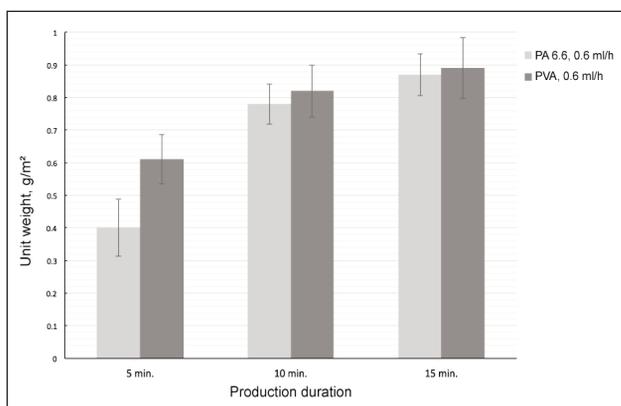


Fig. 3. The effect of production time in electrospinning on unit weight (a) and thickness (b) of nanofibrous surfaces

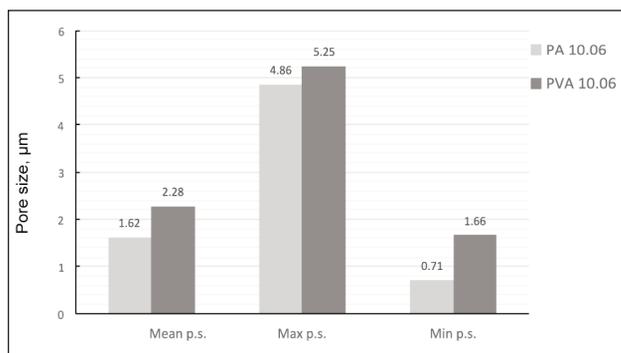


Fig. 4. Typical pore size distributions of electrospun nanofibrous surfaces

testing one sample type only to obtain a general idea (figure 4). The results show that nanofibrous surfaces produced by PA 6,6 have smaller pore size compare to PVA indicating their potential for better filtration performance. Smaller pore sizes with PA 6,6 nanofibrous surfaces is an expected result as surfaces with larger fibres would have larger holes [41].

Filtration performance

The air permeability test results of PA 6,6 and PVA nanofibrous surfaces were given by figure 5. The test results showed that fibrous meshes with PA 6,6

polymer exhibit better air permeability performance, most probably owing to much finer fibres that these filter media contain. On the other hand, the results showed that air permeability of structures decreased as electrospinning time and polymer feed rate increased due to the increase in both thickness of mesh layer and its constituent fibres. Similarly, significant effect of spinning time on the filtration property of the nanofibre membrane, especially on filtration resistance was reported earlier [19]. However, it is worth noting that effect of production time was more significant when PVA polymer was used compare to PA 6,6.

Following air permeability tests, the structures were also tested for liquid aerosol filtration efficiency. These tests were applied for PA 6,6 nanofibrous surfaces only as the filtration efficiency tests were failed during the test of PVA meshes probably due to their low tenacity and sensitivity for aerosols as well as their low air permeability as indicated by figure 5. Regarding PA 6,6 nanofibrous surfaces, the test results given by figure 6 indicate an increase in filtration efficiency as electrospinning time and feeding rate increases, as expected. It was reported earlier that longer fibre production time makes the fibrous media denser and has positive effect on filtration efficiency [42] also indicating an increase in filtration

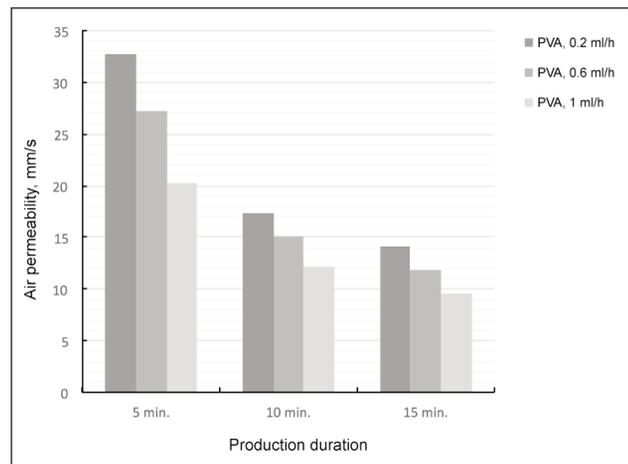
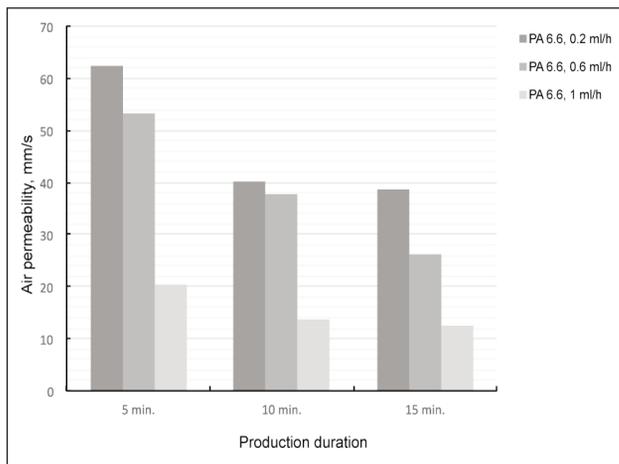


Fig. 5. Air permeability test results of nanofibrous surfaces produced by: a – PA 6,6; b – PVA

efficiency by increase in spinning time [19]. The highest performance was obtained with the structures produced at 1.0 ml/h polymer feed rate and at 10 min. electrospinning time. However, the increase in efficiency of the structures produced at 5 min. and 10 min. was greater compare to the ones produced at 10 min. and 15 min.

Finally, the nanofibrous membranes were exposed to cigarette smoke by using filtration set up shown by figure 1. Then, FT-IR spectrums of nanofibrous structures produced by PA 6,6 and PVA polymers, given by figure 7 was analyzed in comparison with unexposed structures. Following filtration, regarding PA 6,6 membranes; the peak at 1713 cm^{-1} belong to (C=O) bonds indicating filtration of aldehyd, kethon, carboxylic acids or esther functional groups while the peak at 1053 cm^{-1} indicates (C-O) bonds at primer alcohols, ethers or esters. For PVA nanofibrous membranes, however, peaks at 2917 cm^{-1} , 1707 cm^{-1} and 1600 cm^{-1} belonging to alkans, carbonyl groups and aromatic rings, respectively were observed indicating aldehyds, esthers, carboxylic acids and kethons. As indicated earlier, cigarette smoke filtra-

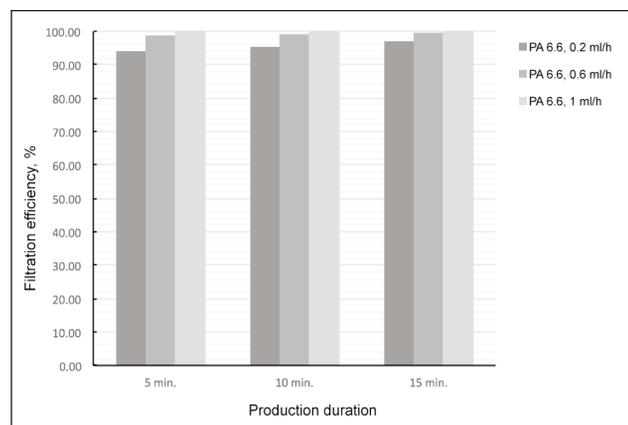


Fig. 6. Aerosol filtration efficiency of nanofibrous surfaces produced by PA 6,6

tion performance of electrospun PVA nanofibre membranes was studied earlier as well indicating that PVA surfaces were able to catch organic polar groups, ethers and carboxyl groups [24], however FT-IR analysis results of two layers (PP+PVA web) was compared with only PP non-woven fabric layer itself after

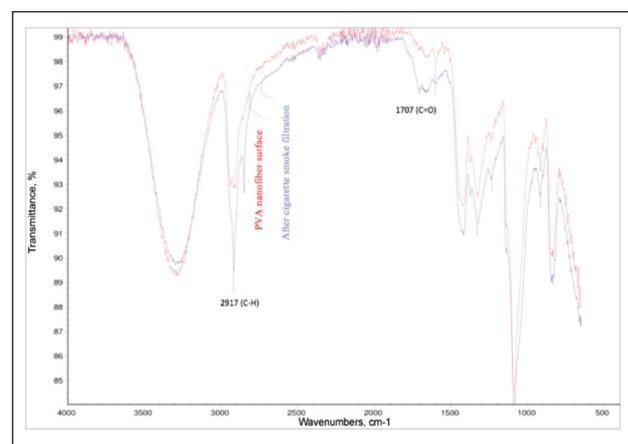
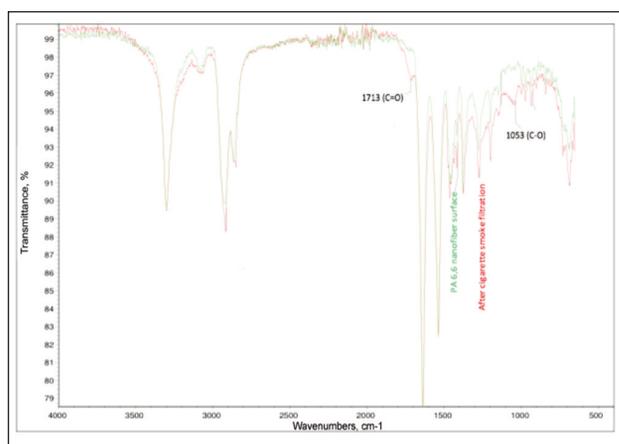


Fig. 7. FT-IR spectrum of: a – PA 6,6 nanofibrous structures; b – PVA nanofibrous structures before and after cigarette smoke filtration

exposure to cigarette smoke filtration. Therefore the results at figure 7 can be considered a further study by comparing results of two identical nanofibrous structures before and after smoke filtration.

CONCLUSIONS

In this work, 18 different nanofibrous surfaces were produced by PVA and PA 6,6 polymers by electrospinning at three different levels of polymer feeding rate (0.2; 0.6 and 1.0 ml/h, respectively) and three different levels of electrospinning time (5, 10 and 15 min., respectively). These structures were analysed in terms of fibre fineness distribution, membrane thickness and unit weight. Then, selected nanofibrous surfaces were analysed for their pore size distributions, air-permeability, aerosol filtration efficiency. In addition to that, they were tested on a simple set-up to analyse their cigarette smoke filtration potential that was chosen as a specific case.

The results show that much finer fibres were produced by PA 6,6 polymer compare to PVA polymer. The pore sizes of PA 6,6 membranes were smaller in comparison to PVA membranes as well. During electrospinning process, much coarser fibres were produced as the polymer feed rate and electrospinning time increased reducing air-permeability of these nanofibrous surfaces as expected. The minimum

average fibre fineness was 150.96 nm produced by using PA 6,6 polymer at 0.2 ml/h polymer feed rate and 5 min. production time while maximum average fibre fineness was 243.43 nm produced by using PVA polymer at 0.6 ml/h and 15 min. The air permeability of PA 6,6 nanofibrous surfaces were much higher compare to the ones produced by PVA. Aerosol filtration efficiency test results showed quite high efficiency (99.901 %) can be obtained with PA 6,6 nanofibrous surfaces (electrospun at 1ml/h and 10 min.) indicating that PA 6,6 nanofibrous surfaces have potential for such applications. The test results also showed that filtration efficiency increased as polymer feed rate and electrospinning time increased. On the other hand, the cigarette smoke tests carried out in this work showed that mainly PA 6,6 membranes can filtrate carboxylic acids and primer alcohols while PVA membranes can filtrate alkanes.

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REFERENCES

- [1] Nataraj, S.K., Yang, K.S., Aminabhavi, T.M., *Polyacrylonitrile-Based Nanofibres a State of the Art Review*, In: Progress in Polymer Science, 2012, 37, 487–513
- [2] Ramakrishna, S., Fujihara, K., *An Introduction to Electrospinning and Nanofibres*, World Scientific Publishing, USA, 2005
- [3] Sundarrajan, S., Tan, K.L., Lim, S.H., Ramakrishna, S., *Electrospun Nanofibres for Air Filtration Applications*, In: Procedia Engineering, 2014, 75, 159–163
- [4] Guibo, Y., Qing, Z., Yahong, Z., Yin, Y., Yumin, Y., *The Electrospun Polyamide 6 Nanofibre Membranes Used As High Efficiency Filter Materials*, In: J. of Applied Polymer Science, 2013, 128, 1061–1069
- [5] Ustün, A., *Nanofibre Production for Air Filtration*, MSc Thesis, Denizli Pamukkale University, Natural&Applied Science Institution, Turkey, 2011
- [6] Langner, M., Greiner, A., *Wet-Laid Meets Electrospinning: Nonwovens for Filtration Applications from Short Electrospun Polymer Nanofibre Dispersions*, In: Macromol. Rapid Commun, 2016, 37, 351–355
- [7] Yan, S., Yu, Y., Ma, R., Fang, J., *The Formation of Ultrafine Polyamide 6 Nanofibre Membranes with Needleless Electrospinning for Air Filtration*, In: Polym. Adv. Technol., 2019, 30, 1635–1643
- [8] Faccini, M., Borja, G., Boerrigter, M., Martín, D., Crespiera, S. M., Vázquez-Campos, S., Aubouy, L., Amantia, D., *Electrospun Carbon Nanofibre Membranes for Filtration of Nanoparticles from Water*, In: J. of Nanomaterials, 2015, Article ID 247471, <https://doi.org/10.1155/2015/247471>
- [9] Yoon, K., Kim, K., Wang, X., Fang, D., *High Flux Ultrafiltration Membranes Based on Electrospun Nanofibrous PAN Scaffolds and Chitosan Coating*, In: Polymer, 2006, 47, 2434–2441
- [10] Menkhaus, T.J., Varadaraju, H., Zhang, L., Schneiderman S., *Electrospun Nanofibre Membranes Surface Functionalized with 3-Dimensional Nanolayers As An Innovative Adsorption Medium with Ultra-High Capacity and Throughput*, In: Chem. Commun., 2010, 46, 3720–3722
- [11] Tsai, P.P., Schreuder-Gibson, H., Gibson, P., *Different Electrostatic Methods for Making Electret Filters*, In: Journal of Electrostatics, 2002, 54, 333–341
- [12] Ahn, Y.C., Park, S.K., Kim, G.T., Hwang, Y.J., Lee, C.G., Shin, H.S., Lee, J.K., *Development of High Efficiency Nanofilters Made of Nanofibres*, In: Current Applied Physics, 2006, 6, 6, 1030–1035
- [13] Qin, X., Wang, S., *Filtration Properties of Electrospinning Nanofibres*, In: Journal of Applied Polymer Science, 2006, 102, 1285–1290
- [14] Li, J., Gao, F., *Needleless Electrospun Nanofibres Used For Filtration of Small Particles*, In: Express Polymer Letters, 2013, 7, 8, 683–689
- [15] Hung, C., *Experimental Investigation and Theoretical Analysis on Air Filtration of Sub-micron Aerosols by Nanofibre Filter*, PhD Thesis, Hong Kong Polytechnic University, Hong-Kong, 2010
- [16] Leung, W.W., Hung, C., Yuen, P., *Effect Of Face Velocity, Nanofibre Packing Density And Thickness On Filtration Performance Of Filters With Nanofibres Coated On A Substrate*, In: Separation and Purification Technology, 2010, 71, 30–37

- [17] Heikkilä, P., Taipale, A., Lehtimäki, M., Harlin, A., *Electrospinning of Polyamides with Different Chain Compositions for Filtration Application*, In: Polymer Engineering and Science, 2008, 48, 1168–1176
- [18] Aliabadi, M., *Effect of Electrospinning Parameters on the Air Filtration Performance Using Electrospun Polyamide-6 Nanofibres*, In: Chem. Ind. Chem. Eng. Q., 2017, 23, 4, 441–446
- [19] Wei, L., Zhang, H., Qin, X., *Fabricated Narrow Diameter Distribution Nanofibre For An Air Filtration Membrane Using A Double Rings Slit Spinneret*, In: Textile Research Journal, 2019, 89, 6, 936–947
- [20] Ahne, J., Li, Q., Croiset, E., Tan, Z., *Electrospun Cellulose Acetate Nanofibres For Airborne Nanoparticle Filtration*, In: Textile Research Journal, 2019, 89, 15, 3137–3149
- [21] Zhang, Q., Welch, J., Park, H., Wu C., Sigmund, W., Marijnissen, J.C.M., *Improvement In Nanofibre Filtration By Multiple Thin Layers Of Nanofibre Mats*, In: J. of Aerosol Science, 2010, 41, 230–236
- [22] Bian, Y., Wang, S., Zhang, L., Chen, C., *Influence Of Fibre Diameter, Filter Thickness, And Packing Density On PM2.5 Removal Efficiency Of Electrospun Nanofibre Air Filters For Indoor Applications*, In: Building and Environment, 2020, 170, 106628
- [23] Zaarour, B., Tina, H., Zhu, L., Jin, X., *Branched Nanofibres With Tiny Diameters For Air Filtration Via One-Step Electrospinning*, In: J. of Industrial Textiles, 2020, 1–13
- [24] Daneleviciute-Vaisniene, A., Katunkis, J., Buika, G., *Electrospun PVA Fibres for Gas Filtration Applications*, In: J. of Fibres&Textiles in Eastern Europe, 2009, 17, 40–43
- [25] Hajra, M.G., Mehta, K., Chase, G.G., *Effects of Humidity, Temperature and Nanofibres on Drop Coalescence in Glass Fibre Media*, In: Serp. Purif. Technol., 2003, 20, 79–98
- [26] Emig, D., Klimmek, A., Raabe, E., *Dust filter bag containing nano non-woven tissue*, US Patent 6,395,046 B1, 2002
- [27] Grafe, T.H., Graham, K.M., *Polymeric Nanofibres and Nanofibre Webs: A New Class of Nonwovens*, International Non-wovens Technical Conference, Atlanta-USA, 2002
- [28] Khanmohamadi, S., Gharehaghaji, A.A., Hoseini, S.A., *Study on the Performance of Nanofibrous Filters For Colored Effluent Treatment*, International Innovative Textile Congress (Icontex2011), Istanbul-Turkey, 20–22 October 2011
- [29] Shao, Z., Jiang, J., Wang, X., Li, W., Fang, L., Zheng, G., *Self-Powered Electrospun Composite Nanofibre Membrane for Highly Efficient Air Filtration*, In: Nanomaterials, 2020, 10, 1706
- [30] Zhang, D., Tao, Y., Gao, J., Zhang, C., et. al., *Pycnogenol® in Cigarette Filters Scavenges Free Radicals and Reduces Mutagenicity and Toxicity of Tobacco Smoke in Vivo.*, In: Toxicol. and Industrial Health, 2002, 18, 215–224
- [31] Hoffmann, D., Hoffmann, I., *The Changing Cigarette: 1950–1995*, In: J. Toxicol. Environ. Health, 1997, 50, 307–364
- [32] Şeker, F.A., *Determination of Some Polycyclic Aromatic Hydrocarbons in Filter Tar of Turkish Cigarettes*, In: J. Sep. Sci., 2005, 28, 2370–2373
- [33] Tian, B.Z., Chen, P., Chen, J., Bai, L., *Blocking and Filtering Effect of Bombyx Mori Silkworm Silk Fibre Filter Tips Against Mainstream Smoke of Cigarettes*, In: Materials and Design, 2009, 30, 2289–2294
- [34] Koller, K.B., Wrenn, S.E., Houck, W.G., Paine, J.B., *Cigarette Filter*, US Patent No 6,595,218 B1, 2003
- [35] King, B., *Is the “CGC” Cigarette Filter Additive a Solution for China’s Tobacco-induced Disease Problem?*, In: Toxicological & Environmental Chemistry, 2012, 94, 3–6
- [36] Pauly, J.L., Rees, V., O’Connor, R., *Philip Morris Clinical Study of Carbon Filtered Cigarettes Challenged by Nondisclosure Issues*, In: Nicotine & Tobacco Research, 2009, 11, 1245–1246
- [37] Collazo, H., Crow, W.A., Gardner, L., Phillips, B.L., Dyer, W.M., *Aerodynamic Diameter Measurement of Cellulose Acetate Fibres from Cigarette Filters*, In: Inhalation Toxicology, 2002, 14, 247–262
- [38] Dönmez, S., *Production of Nanofibrous Webs for Air Filters By Electrospinning Process*, MSc Thesis, Tekirdağ Namık Kemal University, Natural & Applied Science Institution, Turkey, 2016
- [39] Patanaik, A., Anandjiwala, R.D., Rengasamy, R.S., Ghosh, A., *Nanotechnology in Fibrous Materials*, In: Textile Progress, 2007, 39, 2, 67–120
- [40] Andradý, A.L., *Science and Technology of Polymer Nanofibres*, Jonh Wiley&Sons, USA, 2008
- [41] Zhang, X., Chase, G.G., *Solid Aerosol Filtration by Electrospun Pyrrolidene Fibre Mats and Dependence on Pore Size*, In: J. Textile Eng. Fashion Techno., 2017, 1, 5, 180–187
- [42] Matulevicius, J., Kliucininkas, L., Martuzevicius, D., Krugly, E., Tichonovas, M., Baltrusaitis, J., *Design and Characterization of Electrospun Polyamide Nanofibre Media for Air Filtration Applications*, In: Journal of Nanomaterials, 2014, Article ID 859656

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