

Electrospun PVA Nanofibres for Gas Filtration Applications

Kaunas University of Technology,
Faculty of Design and Technologies,
Department of Textile Technology
Studentu Str. 56, LT-3031 Kaunas, Lithuania
E-mail: a.daneleviciute@yahoo.com

*Kaunas University of Technology,
Faculty of Chemical Technology,
Department of Organic Chemistry

Abstract

Nanofibres are easily produced from polymer solutions of polyvinyl alcohol using the electrospinning method. Nanofibres combined with nonwoven PP material (polypropylene) have potential uses in a wide range of filtration applications. The high surface area of a high porous structure makes nanofibres ideally suited for many filtering submicron particles from gas. The main aim of this article is to determine which organic compounds can be eliminated from gas using a nonwoven PP material filter covered by a PVA nanofibre membrane. In this study PVA solutions were prepared with 8% PVA. A nanofibre web was manufactured using the electrospinning method on a NS LAB Nanospider™ laboratory machine. Specimens of filtered gas were obtained with a device which was made especially for this research. An IR spectrum of the filtered gas and filters was written. The research showed that a nonwoven PP material filter covered by a PVA nanofibre membrane is suitable to eliminate organic polar compounds, ethers and compounds containing carbonyl groups from gas.

Key words: electrospinning, nanofibre membrane, filter, filtration.

Introduction

Electrostatic fibre spinning or 'electrospinning' is a process where nanofibres are formed using an electrostatically driven jet of polymer solution or polymer melt. More than 50 polymers have been successfully spun into fibres through this technique [1, 2].

Layers of nanofibres have a low basic weight, high permeability and small pore size that make them appropriate for a wide range of filtration applications. In addition, a nanofibre membrane offers unique properties such as a high specific surface area, good pore interconnectivity and the potential to incorporate active chemistry or functionality at a nanoscale. Nanofibre membranes are being extensively studied for air and liquid filtration [3]. Nanofibre filters could be used for water, blood, gas and oil filtration (among others).

Cigarettes contain numerous components: tobacco, paper material and additives. Therefore, after burning, a very complex mixture is generated [4]. Cigarette smoke comprises a highly complex chemical mixture of non-specific products of organic material combustion and chemicals specific to the combustion of tobacco and other components of the cigarette. For most of the compounds and substances added to tobacco, little is known of their combustion chemistry, which creates difficulties in determining the relationship between chemicals in tobacco and those actually inhaled in the smoke [5]. It has been estimated that there are over 4000 chemical constituents in tobacco smoke.

Nanofibres can be used either alone or in conjunction with other filtering media, such as larger fibres, paper, activated charcoal, etc. Filters with nanofibres need not be dense as the molecules of the smoke become attracted to the nanofibres due to quantum mechanics instead of being sieved out [6].

The main aim of this article is to explain a research project undertaken to investigate the use and effectiveness of a PVA nanofibre membrane as a cigarette smoke filter.

Materials and methods

A PVA aqueous solution was chosen to form the nanofibres. This polymer is distinguished by its chemical and thermal stability (in normal conditions it preserves excellent physical and mechanical qualities). It is produced by the polymerisation of vinyl acetate monomer after partial or complete hydrolysis of polyvinyl alcohol is obtained [7].

PVA aqueous solution was made from PVA powder dissolved in distilled water by mixing. In the making of the 8% PVA polymer solution concentrate, 0.5% phosphate (H_3PO_4) was infused, which increased the conductivity of the electric current.

Nanofibres from the PVA solution were spun into nonwoven PP material the NS LAB Nanospider™ (Elmarco, Czech Republic) laboratory machine. A working scheme of the Nanospider™ is presented in **Figure 1**.

On this device an electrostatic field was created using two electrodes with a distance of 15 cm between them. One of these electrodes was a roller *1* connected to a high voltage distributor (0 – 75 kV) *2* plough *3*. In this research the voltage was 64 kV. The roller was partially immersed or soaked in the polymer solution contained in tray *4*. Tray *4* is made from insulation material. The second electrode *5* was fixed to a grounded device carcass. Under the influence of the electrostatic field, nanofibres were formed from the polymer solution. These nanofibres were collected on base fabric *6*, which was attached to upper electrode *5*.

The nanofibre spun from the polymer solution has significant applications in the area of filtration because a nanofibre membrane has a highly porous structure of high surface area. The low basic weight and small diameter of the filaments are ideally suited for filtering submicron particles from gas or water [8]. Electrospun nanofibres have diameters three or more

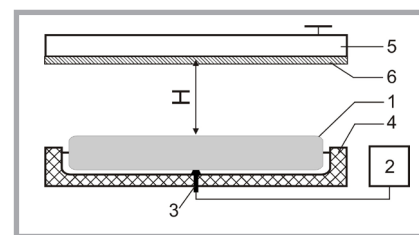


Figure 1. Working schema of the principal laboratory device - Nanospider™: 1 – roller (electrode); 2 – high voltage distributor (0 – 75kV); 3 – high voltage plough; 4 – tray with polymer solution, 5 – spinning collector, earth plate (electrode); 6 – base fabric.

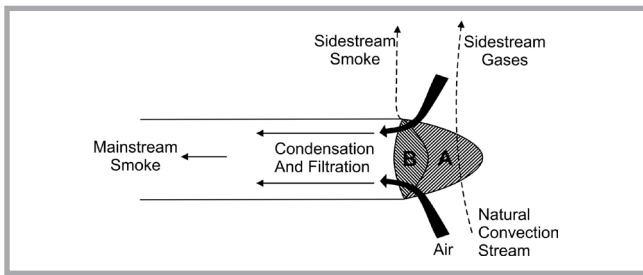


Figure 2. Schematic of cigarette combustion during puffing. Smoke is generated in two zones: (A) combustion and (B) pyrolysis.

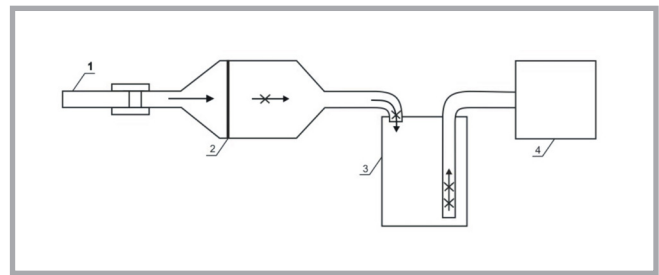


Figure 3. Device for obtaining gas specimen: 1 – specimen; 2 – filter; 3 – filtered gas container; 4 – vacuum pump.

times smaller than those of other fibres formed by other technologies [9].

Air permeability is the one of the main properties of filter materials. The air permeability of nonwoven material with the PVA nanofibres membrane was measured using an air permeability device. The method of working with this device is specified in LST EN ISO 9237 [10]. The specimen was put into the device and pressed air streams were run through it. After the pressure mounted and established a dm^3/h at 10, 20, 30, 40, 50 and 60 mm H_2O column, the rate of air through a rotameter was fixed. The arithmetical rate of the air average for each pressure was calculated, converting dm^3/h to dm^3/min . Later the air permeability at each pressure was calculated according to the formula:

$$R_n = D_n/A \times 0.167 \text{ m/s};$$

D_n – arithmetical average of the air rate in dm^3/min ; A – effective area of the specimen, which is 10 cm^2 .

The air permeability m/s of the textile material is presented for each pressure from 10 to 60 mm H_2O column.

In this research nonwoven polypropylene material with a PVA nanofibre membrane was used as a filter for cigarette smoke. Before filtering, cigarette combustion during puffing had been investigated, and the schema of it is presented in **Figure 2** [11]. This schema shows that cigarette smoke is the result of pyrolysis and combustion and that cigarette combustion from puffing is influenced by air, side streams of gases and other chemicals, any of which can influence the results of cigarette smoke filtration.

A specimen of smoke filtered through nonwoven material covered by a PVA nanofibres membrane was obtained by using a device (**Figure 3**) created particularly for this research. The main prin-

ciple of the device operation consists of imbibing the cigarette smoke through the filter with the help of a vacuum. The specimen was collected in a filtered cigarette smoke container to be used in further gas analysis. In this research smoke was filtered from one cigarette for 30 s.

Infrared spectroscopy was made for the filtered cigarette smoke and used filters

of PVA nanofibres. The spectrum was written using a Perkin Elmer FTIR Spectrum GX spectrometer (USA). A 100 mm cell with KBr was used for IR spectrum fixation.

Pictures of the filter with a nanofibre membrane before and after filtering were taken by a SEM Quanta 200 FEG electronic microscope.

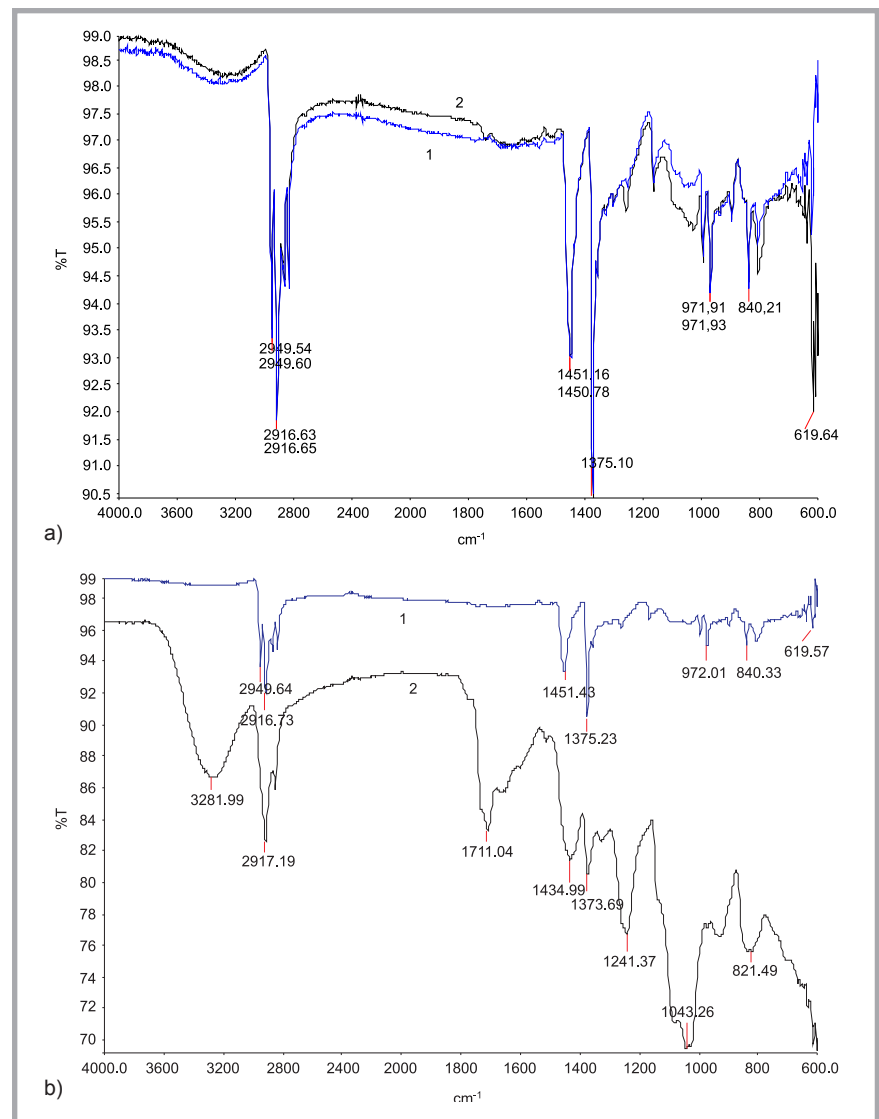


Figure 4. Infrared spectrum of nonwoven material without (a) and with (b) a PVA nanofibre membrane: 1 – before filtering; 2 – after cigarette smoke filtering.

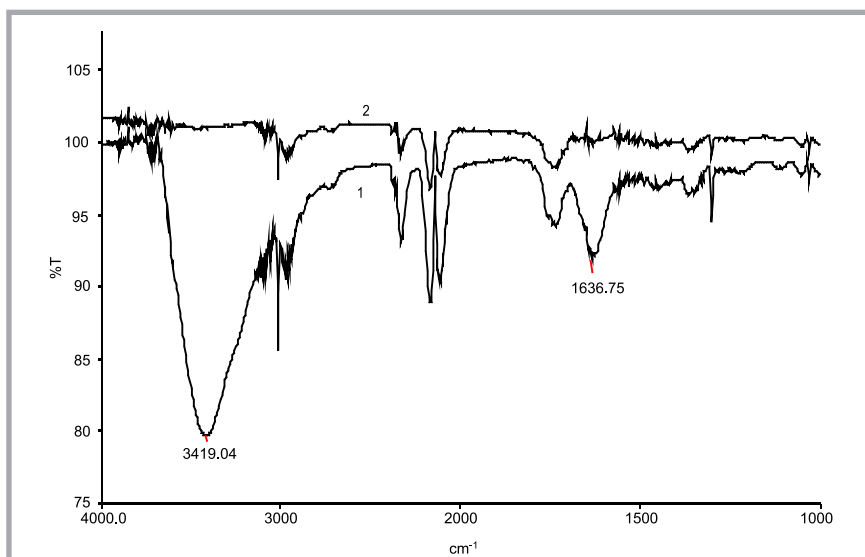


Figure 5. Infrared spectrum of cigarette smoke filtered with different thicknesses of nanofibre membrane: (1) $d = 250$ nm; (2) $d = 300$ nm.

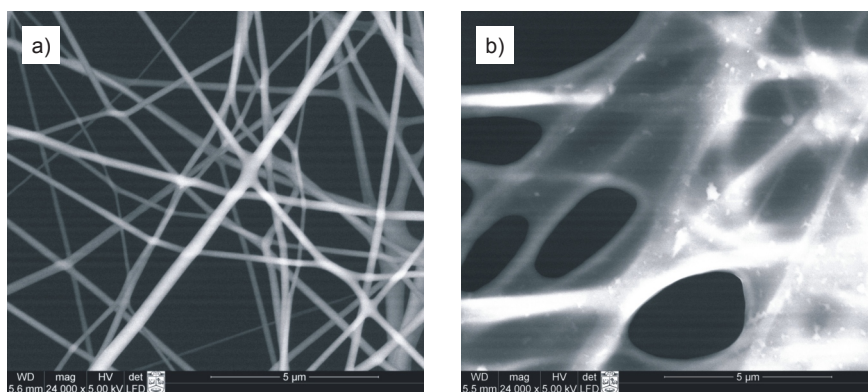


Figure 6. Nonwoven material with nanofibres membrane before (a) and after (b) filtering.

Experimental results and discussions

Three types of specimens of nonwoven PP material with a PVA nanofibre membrane were chosen for air permeability research: nonwoven material without a nanofibre membrane, nonwoven material with a nanofibre membrane $d = 250$ nm and nonwoven material with a nanofibre membrane $d = 300$ nm (d - the average thickness of nanofibres).

From the results of the test we can see that direct air permeability depends on the pressure. By increasing the pressure and fixating the rate of air (dm^3/h) at 10, 20, 30, 40, 50 and 60 mm H_2O column the air permeability of the nonwoven materials both with and without the nanofibre membrane is increased. A comparison of test results of the air permeability of nonwoven materials without a nanofibre membrane and nonwoven materials with

a nanofibre membrane show that nonwoven materials with different thicknesses of nanofibre membranes ($d = 250$ nm, $d = 300$ nm) have a lower air permeability than those without nanofibre membranes, hence nonwoven material with a membrane is more suitable for gas filtration.

In order to establish the efficiency of PVA nanofibres with respect to the gas filtering of cigarette smoke, infrared spectroscopy for nonwoven material without a nanofibre membrane was used before and after filtration and for nonwoven material with a PVA nanofibre membrane before and after filtration. In *Figure 4.a* we can see that the IR spectrum of nonwoven material without a nanofibre membrane is very similar before and after cigarette smoke filtration, which means that differences in quality and quantity did not occur. Analysis of the IR spectra in *Figure 4.b* shows that the spectra of nonwoven material with a nanofibre membrane before and after cigarette smoke filtration

are obviously different. Qualitative differences of the IR spectra are at the following wave numbers: 3282, 1711, 1241 and 1043 cm^{-1} . Peaks are in the spectrum of the specimen after filtering and not before. The peak at 3282 cm^{-1} is specific for organic compounds with polar O-H or N-H groups. The peak at 1711 cm^{-1} is specific for a carbonyl group ($>\text{C}=\text{O}$) containing compounds. The peak at 1241 cm^{-1} is specific for C-O ethers and compounds with C-N bonds. The peak at 1043 cm^{-1} is specific for ethers too. In order to analyse whether the thickness of the nanofibre membrane influences the filtering properties of nonwoven

PP material with a PVA nanofibre membrane were tested with the use of cigarette smoke. Cigarette smoke was filtered through a nanofibre membrane of varying thickness: $d = 250$ nm and $d = 300$ nm. The IR spectrum of cigarette smoke filtered through nonwoven material with nanofibre membranes of varying thickness is presented in *Figure 5*. The qualitative difference at wave numbers 3419 and 1637 cm^{-1} is observed in the IR spectrum. The spectrum of cigarette smoke filtered through the PVA nanofibre membrane of $d = 250$ nm had these peaks, as opposed to the spectrum of cigarette smoke filtered through a PVA nanofibre membrane of $d = 300$ nm. Both peaks are characteristic for secondary amines. The peak at 3419 cm^{-1} is specific for N-H bond stretching vibrations: the peak at 1637 cm^{-1} is specific for bending vibrations of secondary amines. Comparing nanofibres with membranes of 250 nm and 300 nm thickness used in filtration, we can state that a PVA nanofibre membrane with a thickness of $d = 300$ nm can hold secondary amines from cigarette smoke as opposed to one of $d = 250$ nm thickness, which cannot.

The pictures of nanofibre membranes before and after cigarette smoke filtration are shown in *Figures 6*. Comparing the IR spectra, the qualitative difference is at the following wave numbers: 3282, 1711, 1241 and 1043 cm^{-1} .

Conclusions

The results of the research have confirmed the following:

1. Comparison of the results of air permeability testing of nonwoven materials with and without nanofibre membranes show that nonwoven ma-

terials with different nanofibre membranes ($d = 250 \text{ nm}$, $d = 300 \text{ nm}$) have a lower air permeability than those without.

2. The IR spectrums of nonwoven materials without a nanofibre membrane before cigarette smoke filtering and after filtering are very similar, which shows that this kind of filter is not effective with respect to the quality and quantity of filtration. Obvious differences are shown in the infrared spectrum of nonwoven material with a PVA nanofibre membrane.
3. PVA nanofibres membranes as a filter for cigarette smoke have the advantage of average diameter nanofibre filaments, which is obvious for quality parameters. A higher diameter of nanofibre filaments makes the filter more effective. The PVA nanofibre membrane as a filter for cigarette smoke is effective for holding organic compounds with polar O-H or N-H

groups, carbonyl group ($>C=O$) containing compounds, ethers C-O and compounds with C-N bonds.



References

1. Huang Z. M., Zhang Y. Z., Kotaki M., Ramakrishna S.; *Compos Sci Technol* 2003, 63: pp. 2223-53.
2. Deitzel J. M., Kosik W., McKnight S. H., Beck Tan N. C., DeSimone J. M., Crette S.; *Polymer* 2002;
3. Barhate R. S., Ramakrishna S.; *Nanofibrous filtering media: Filtration problems and solutions from tiny materials. Journal of Membrane Science* March 2007, pp. 1-8.
4. Baker R. R., Bishop L. J.; *J. Anal. Appl. Pyrolysis* 2004, 71, p. 223.
5. Fowles J., Bates M.; *The Chemical Constituents in Cigarettes and Cigarette Smoke, A Report to the New Zealand Ministry of Health*. 2000, pp. 12.
6. Squires S.B. Gardiner M. J.; *Cigarette filter incorporating nanofibres, US Patent Application No. 2005/0139223*.
7. Tao J., Shivkumar S. *Molecular weight dependent structural regimes during the electrospinning of PVA* Department of Mechanical Engineering, Worcester Polytechnic Institute, 100 Institute Road, Worcester, MA 01609, USA *Materials Letters* 61 (2007) pp. 2325-2328.
8. Raghavendra R Hegde, Atul Dahiya, M.G. Kamath. *Nanofibre nonwovens*. 2005.
9. Kristine Graham, Heidi Schreuder-Gibson and Mark Gibson "Incorporation of Electrospun nanofibres in to Functional Structures." US Army Soldiers Systems Center, Natick, Massachusetts, http://www.inda.org/subscrip/inj04_2/p21-27-graham.pdf.
10. LST EN ISO 9237. *Textiles – Determination of the Permeability of Fabrics to Air*.
11. Thompson B.T.; *Fourier transform infrared spectroscopic measurement of carbon monoxide and nitric oxide in sedestream cigarette smoke in real time using a hollow waveguide gas cell and nonimaging optics. Dissertation, Georgia Institute of Technology, 2004*.

Received 19.01.2009 Reviewed 14.07.2009



Innovative Economy
National Coherent Strategy

European Union
European Regional
Development Fund



Scientific Donations

A Textronic System for Tissue Electrostimulation

Beneficiary: Technical University of Lodz, Department for Automation of Textile Processes

The subject of the project: Development, manufacturing and investigation of a textronic system for tissue stimulation by electric current in cases of human limb disfunction.

According to 1.1.2 PO IG subdivision activity, sponsorship comprises 100% of the project's qualified costs, from which 85% will be resources of the European Union and 15% a so - called, the national contribution.

Period of realisation: 1st January 2010 to 30th November 2012
General cost of the project: 1 176 950,00 PLN

**The project is co-financed by the European Union
from the European Regional Development Fund**