APPLICATION OF NANOFIBRES IN FILTRATION PROCESSES

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Abstract

Mechanisms of capture of dust particles, two- and three dimensional modelling of properties of filtration materials and effect of selected variables on electrospinning of polyurethane (PU) solutions are discussed with the aim to prepare a nanofibre structure capable of capturing ultrafine particles. The two-dimensional modelling is used to gain an idea of the effect of mass per square area, thickness of nanofibre layers and nanofibre diameter on filtration efficiency of ultrafine particles. Values of filtration efficiency calculated at the three-dimensional modelling of the filtration process are compared with experimental measurements for sets of filtered particles 100 nm in diameter or bigger. The most important characteristics affecting quality of nanofibre materials are nanofibre diameter, porosity and homogeneity of nanofibre layers. The method making possible to achieve the required diameter of the nanofibres is demonstrated on the influence of relative humidity and solvent type on the fibre-forming process taking place in an electrostatic field. The effect of homogeneity of the nanofibre deposition on the collecting substrate is assessed employing images from scanning electron microscopy (SEM) and tests of filtering abilities of the nanofibre layers. Also, some measurements obtained when nanofibres were used in filtration of air, liquids and dispersions of carbon nanotubes in a liquid are presented.

INTRODUCTION

Elimination of very small dust particles, bacteria and viruses from the ambient air and drinking water is becoming increasingly relevant in the present world and is connected with a growing number of respiratory tract diseases in industrial agglomerations and with a threat of various pandemics.

For use in filters it is necessary to consider both filtration efficiency and the admissible pressure drop (\(\Delta p\)). It can be assumed that nanofibres will find use primarily in the area of microfiltration (i.e. for removal of particles ranging from 100 nm to 15 \(\mu\)m) and ultrafiltration (for particles ranging from 5 to 100 nm).

METHODS

Material

PU solution in dimethylformamide (DMF) based on 4,4’-methylenebis(phenylisocyanate) (MDI), poly(3-methyl-1,5-pentanediol)-alt-(adipic, isophthalic acid) (PAIM) and 1,4 butanediol (BD) was synthesized
in molar ratio 9:1:8 (PU 918) at 90°C for 5 hours (per partes way of synthesis starting with preparation of prepolymer from MDI and PAIM and followed by addition of BD and remaining quantity of MDI). The prepared solutions were suitable for electrospinning and had a PU concentration of 13 wt%, viscosity of 1.5 Pa.s and conductivity of 150 µS/cm.

**Filter sample preparation by electrospinning process**

Nanofiber layers were prepared from polyurethane solutions with a commercially available NanoSpider™ machine (Elmarco s.r.o. Liberec, Czech Republic, http://www.elmarco.com/) equipped with patented rotating electrode with 4 cotton cords spinning elements (PCT/CZ2010/000042). The experimental conditions were as follows: relative humidity 25 - 36%, temperature 22°C, electric voltage applied into PU solution 75 kV, distance between electrodes 180 - 210 mm, rotational electrode speed 7 rpm and speed of supporting textile collecting nanofibers was 0.16 – 0.32 m/min. Nanofibres were collected on polyester fabric, polypropylene (PP) or viscose nonwoven textiles (NT).

**Filter sample characterization**

Nanofiber based filter, prepared through the electrospinning process, has been characterized by the Scanning Electron Microscope (Vega II, Tescan, Czech Republic). For the 2D and 3D modelling of filtration efficiency the obtained SEM pictures have consequently been used for the determination of fibre diameter, nanofibre layer thickness and fibre diameter/pore size distribution by using recently proposed digital image analysis technique [1].

For the very precisely description of the characteristics of the filtration phenomenon was used quality factor $q_F = \ln(1/P)/\Delta p$ where $P$ = permeability [2]. When nanofibre filtration materials are laid on each other the capture efficiency will increase by the multiple of the values (geometrically) and the pressure resistance by the sum of the values (arithmetically). However, the resultant quality factor will not change. Hence this fact can be used for assessing homogeneity of nanofibre layers during the electrospinning process.

**Filtration efficiency measurement**

All manufactured nanofibre based filtration materials were measured for aerosol (di-ethyl-hexyl-sebacate with geometrical average of particle diameters 0.45 µm) penetration at constant air flow rate 30 l/min. (face velocity 5.7 cm/s) by means of filter measuring system LORENZ (Germany) adjusted for EN 143.

Experimental particle penetration efficiency of fabrics in case of 3D nanofibre layer characterization was determined applying the principles of standard EN 779. Aerosol particles were produced from di-ethyl-hexyl-sebacate by a pneumatic aerosol generator. Size distribution of particles was measured before and after the fabric with the optical particle analysers – particle counters LAS X, manufactured by Particle Measuring Systems, USA, for small particles 0.1 - 0.4 µm and APS, manufactured by TSI, USA, for bigger particles 1.2 - 8.3 µm. The measurement results were reported as the collecting efficiency of fabric (%). The measured filtration efficiency curves are depicted in Figure 4 (face velocity 5.7 cm/s, pressure drop 316 Pa).

In the ultrafine particle size range, the filtration efficiency was determined as a function of particle diameter (results presented on Figure 10). The 1 g/l ammonium sulphate solution was nebulized (AGK, PALAS, Germany), a monodisperse size fraction was selected using an Electrostatic Classifier (EC 3080, TSI, USA),
and particle concentration upstream and downstream the filter (face velocity 5.7 cm/s) was recorded by a condensation particle counter (UCPC 3025 A, TSI, USA). The filtration efficiency was determined at nine mobility diameter fractions: 20, 35, 50, 70, 100, 140, 200, 280 and 400 nm.

The measurements of vehicle emission (particle sizes based on their electrical mobility 5 - 560 nm) were made by means of classifier EEPS model 3090, TSI, USA. The compression ignition (Diesel) engine Cummins ISBe4, four-cylinder system CommonRail (engine capacity 4.5 l, power 130 kW) running at mean speed 1 500 rpm and 25% load (173 Nm) was used as the particles source. Measurement was made at face velocity 4.9 cm/s over the filter surface (Figure 11).

RESULTS

1. Modelling the effect of the nanolayer structure on particle capture – 2D model

An idea of filtration capabilities of nanofibre planar structures can be obtained on the basis of relationships expressing filtration efficiencies for three most important particle capture mechanisms (interception on the fibre (Figure 2), inertial impaction and diffusion) and on the assumption of the Kuwabara flow field [3].

The resultant filtration efficiency given by the separate filtration mechanisms can be established from the relationship as follows:

\[
E = 1 - \exp(-4 \alpha E_R t/\tau d_i) \quad \text{where}
\]

\[
E_R = 1 - (1 - E_I)(1 - E_D)
\]

For calculation of separate efficiencies (\(E_R, E_I, E_D\)) corresponding to the separate filtration mechanisms relationships are used, which calculate the above efficiencies from the specific structure properties of the filtration layer, properties of the particles being captured, size of the particles and also properties and velocity of the flowing medium.

**Single fibre efficiency of the mechanism of the particle capture on the fibre (interception) \(E_R\) is given by the following relationship:**

\[
E_R = \frac{(1 + R)^2}{2 Ku (2 \ln(1 + R) - 1 + \alpha + (1/(1 + R))^2 (1 - \alpha/2) - \alpha (1 + R)^2/2)} \quad \text{where}
\]

\[
Ku = \text{Kuwabara's hydrodynamic coefficient}, \quad Ku = -\ln\alpha/2 - 3/4 + \alpha - \alpha^2/4
\]

\[
R = \text{particle size/fibre diameter ratio}, \quad R = d_p / d_i
\]

\[
\alpha = \text{SVF (Solid Volume Fraction)} \quad [4, 5].
\]

**Single fibre efficiency of mechanical inertial impaction \(E_I\) is given by the following relationship:**

\[
E_I = (Stk) J / 2 Ku^2 \quad \text{where}
\]

\[
J = (29.6 - 28 \alpha^{0.62}) R^2 - 27.5 R^{3.8}
\]

\[
Stk \quad \text{(Stokes number)}, \quad Stk = \rho_p d_p C_v V / 18 \eta d_i
\]
\( \rho_p = \) particle density
\( d_p = \) particle diameter
\( \eta = \) air viscosity
\( V = \) flow velocity

\( C_c = \) Cunningham correction slip factor, \( C_c = 1 + Kn_p (1.257 + 0.4 e^{-1.1 Kn_p}) \)

\( Kn_p = \) Knudsen number = \( 2\lambda/d_p \)

where \( \lambda = \) mean free path of molecules of air \([4, 5]\).

Single fibre efficiency of mechanical diffusion (Brownian Diffusion) \( E_D \) is given by the following relationship:

\[
E_D = 2.6((1 - \alpha)/Ku)^{1/3} Pe^{-2/3}
\]

where

\( Pe = \) Péclet number, \( Pe = Vd_p/D \)

\( D = \) diffusion coefficient \([4, 5]\).

From dependencies of filtration efficiencies on the size of the particles being captured (V curves) it is apparent that the efficiency of the particle capture is growing with decreasing nanofibre diameter (Figure 1). For a comparison, fibre diameters of 320, 160 and 80 nm capable of being prepared by a suitable combination of separate variables of the electrospinning process were chosen for calculation.
2. Modelling the effect of the nanolayer structure on the particle capture – 3D model

Penetration of the actual structure of the nanofibre layer by the particles captured

For assessment of the filtration efficiency achieved on actual nanofibre structures produced we used a 3D analysis of SEM images. The analysis was based on an examination of the change in richness of grey halftones caused by a change in the thickness of nanofibre nonwoven textiles (nNT) [1, 6]. Thus the nanostructure was divided into several layers (Figure 3) and sieved through fractions of model spheres identical with aerosol size fractions used in experimental measurements of filtration efficiency. The agreement of calculated values and measurements obtained is presented in Figure 4. So far, the model used did not consider the aerodynamic slip flow.

3. Effect of variables on electrospinning process, structure of nanolayers formed and nanofibre diameter

The most important requirement for quality of nNT with respect to their use in filtration products are homogeneity of the layer and preparation of nanofibres having the smallest possible diameter as shown by the preceding modelling of particle capture efficiency.

While optimising the structure of the nanofibre layers it is absolutely essential to monitor many variables connected with the polyurethane synthesis proper [7, 8], properties of the solutions prepared and the electrospinning process proper.

3.1 Nanofibre structure defects produced during electrospinning

The most frequent complication worsening service properties of nNT is formation of holes (Figure 5), which occurs usually in case of excessively diluted solutions due to impact of solvent drops on nNT, and an accumulation of the nanofibres around conductive microfibres of the collecting substrate (Figure 6).
3.2 Preparation of homogenous nNT comprising small-diameter nanofibres

The solvent used - dimethylformamide (DMF) or dimethylacetamide (DMAA) – and relative humidity during the electrostatic process belong to two most important variables by which a marked decrease of nanofibre diameters can be achieved (Figure 7). Combinations of almost 20 variables were used to prepare PU nanolayers with requested homogeneity (Figure 8).

![Figure 5. Holes in a nanolayer](image)

![Figure 6. Accumulation of nanofibres around conductive microfibres of a spunbond support](image)

![Figure 7. Growth of nanofibre diameter with increasing relative humidity as a function of the solvent used. Polyadduct spinned = PU 918, collecting substrate = viscose NT](image)

![Figures 8 and 9. Planar and sectional views on homogenous layer of PU nNT prepared at 25% relative humidity](image)
4. Examples of specific applications of nanofibre layers

4.1 Air filtration

The most requested properties of filtration materials is their capture efficiency for nanoparticles sizes tens of nanometers, e.g. for more dangerous sizes from the unhealthy aspects. Two various PU nanostructures and influence of their folding on filtering properties are presented in Figure 10. Comparison of PU nanostructure with filtering material from glass microfibers (Figure 11) shows that by means of PU nNT can be reached the same filtration efficiency for vehicle emission at lower pressure drop ($\Delta p = 640$ Pa in comparison with $\Delta p = 170$ Pa). More and more frequently information appears on dangerousness and health hazards of submicron particles with respect to possibility of penetration of the particles through tissues, etc. We believe that PUs, thanks to their elasticity, will be a more suitable material, for instance for manufacture of filters, than the brittle glass fibre filtration materials used at the present time.

4.2 Filtration of liquids

The PU nNT (PU 918 prepared in DMAA, mass per square area $AM = 1.6$ g/m$^2$, $d_f = 133$ nm, $\Delta p = 298$ Pa and $P = 0.0014\%$ (measured at air flow rate of 30 l/min.), which corresponds to $qF = 37$ l/kPa) on an antistatic PP NT support was used to filter $1.7 \times 10^6$ CFU/ml of Escherichia coli bacteria in 100 ml of water at a pressure of $10^5$ Pa. After 30.7 s of filtration (average flow rate = 3.3 ml/s), only 65 CFU/ml of bacteria were detected (filtration efficiency = 99,996%). Dimensions of the E. coli bacteria range between 1.1 - 1.5 x 2.0 - 6.0 µm.

4.3 Targeted filtration of nanoparticles

Besides separation of solid particles from gases the filtration of multiwall carbon nanotubes (MWCNT) aqueous dispersions via nNT can be used, for instance, for preparation of porous structures that become electrically conductive after deformation (sensors – MWCNT buckypapers) [9, 10].
CONCLUSIONS

Employing two- and three-dimensional modelling of the filtration process a clear idea of the effect of the most important variables and characteristics of non-woven textiles from nanofibres with respect to optimum filtration efficiencies and pressure drops can be obtained. Based on this knowledge the method of preparation of PU based nNT by electrospinning was optimised, which showed positively on filtering and service properties of the textiles.

Literature


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