Andrzej Krupa,
Anatol Jaworek,
*Subramanian Sundarrajan,
*Damian Pliszka,
*Seeram Ramakrishna

The Szewalski Institute of Fluid-Flow Machinery
Polish Academy of Sciences
ul. Fiszera 14, 80-231 Gdańsk, Poland
E-mail: jaworek@imp.gda.pl

*National University of Singapore,
Singapore 117576

Mechanical Properties of an Electrospun Polymer Fibre-Metal Oxide Nanocomposite Mat

Abstract

The paper presents experimental results on the investigations of mechanical properties of nanocomposite mats produced by the method of core-shell electrospinning. By this method, the nanofibers were covered with metal-oxide nanoparticles, co-deposited from colloidal suspension during the process of electrospinning. A novel co-extrusion nozzle, with electrospun polymer solution flowing through the central nozzle and colloidal suspension of nanoparticles through the co-axial annular nozzle, was designed for the production of electrospun nanofibers. The experiments were carried out for the polyvinyl chloride (PVC), polysulphone (PSU) and polyvinylidene fluoride (PVDF) dissolved in suitable solvents. The 5 wt.% of TiO_2 particles were suspended in THF with an addition of Dynasylan R Memo (Degussa). The diameter of the produced fibers varied from 400 to 800 nm for an appropriate polymer concentration. The tensile stress at maximum load for polymer mats with TiO_2 nanoparticles was 0.64 ± 0.05 MPa, 0.25 ± 0.03 MPa, and 2.97 ± 0.30 MPa for PVC, PSU, and PVDF, respectively. The tensile modulus was 13.2 ± 1.1 MPa, 15.2 ± 1.5 MPa, and 20.6 ± 2.0 MPa, for PVC, PSU, and PVDF, respectively. The sample elongation at break point was 68.2%, 53.1%, and 149% for PVC, PSU, and PVDF, respectively.

Key words: *electrospinning, nanocomposite mat, tensile stress, filtration mat.*

Introduction

Electrospinning is a well-established electrohydrodynamic technology for micro- or nanofibre production [1, 2]. A few hundred papers are published each year on this subject, most of which are intended for the production of nanofibres for various nanotechnology applications, with an increasing number of applications in biotechnology or environmental protection, but only a few of these papers are on the fundamentals of electrospinning [3]. Recently, electrospinning has been explored for the fabrication of nanocomposite membranes for environmental engineering applications [4 - 9].

The physical background of electrospinning lies in the utilisation of electrical forces for generating shear stress on the surface of a viscous liquid, usually a polymer solution, flowing from a capillary nozzle. Under this stress the jet becomes thinner, and finally a thin fibre is formed after solvent evaporation. A similar method has been applied for the production of double-layer, core-shell nanofibres [10].

In our previous papers [5, 6], we presented two methods for the production of nanocomposite fibres covered with nanoparticles, in which two separate nozzles were used for the electrospinning of polymer solution and electrospraying of nanoparticles. In this paper, we demonstrate core-shell technology used for the production of nanofibres covered with nanoparticles, which differs from the methods previously used. In this invention, a co-extrusion nozzle is used for the electrospinning of nanofibres from a central nozzle, while from the external annular nozzle a suspension of nanoparticles in an appropriate solvent is co-deposited on this fibre. The method is applied for the production of nanocomposite mats in the form of non-woven fabric made from polymer material blended with metal-oxide nanoparticles. The goals of this paper were to determine the morphology of mats produced by the technology developed and study the mechanical properties of the product. This type of mat could be used for the production of masks and filters with catalytic material.

Experimental

The electrospinning system comprised of a co-axial stainless-steel capillary nozzle placed vertically and a rotating drum of 60 mm diameter covered with an aluminum foil (about 10 μm thick). A hypodermic needle, gauge No. 26, was used as the inner capillary, and gauge No. 17 as the outer one. The tip of the needles was cut perpendicularly to the axis. The distance between the nozzle tip and the drum was about 120 mm. The rotational speed of the drum was 330 r.p.m. A scheme of the co-extrusion nozzle for the production of nanofibre covered with nanoparticles is shown in ***Figure 1***.

The electrospinning nozzle was connected to a high-voltage supply (Glassmann) of positive polarity, and the drum was grounded. The voltage and flow rates

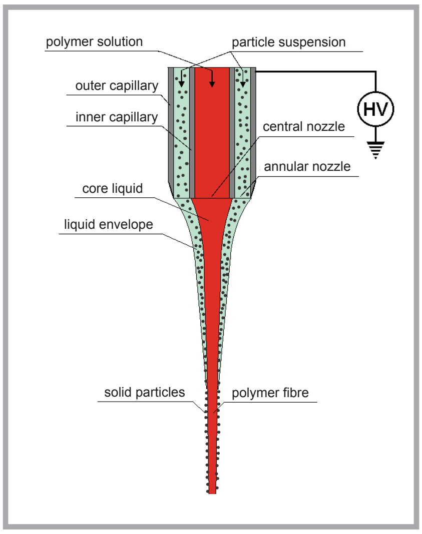


Figure 1. *Scheme of the co-extrusion nozzle for the production of nanofibre covered with nanoparticles.*

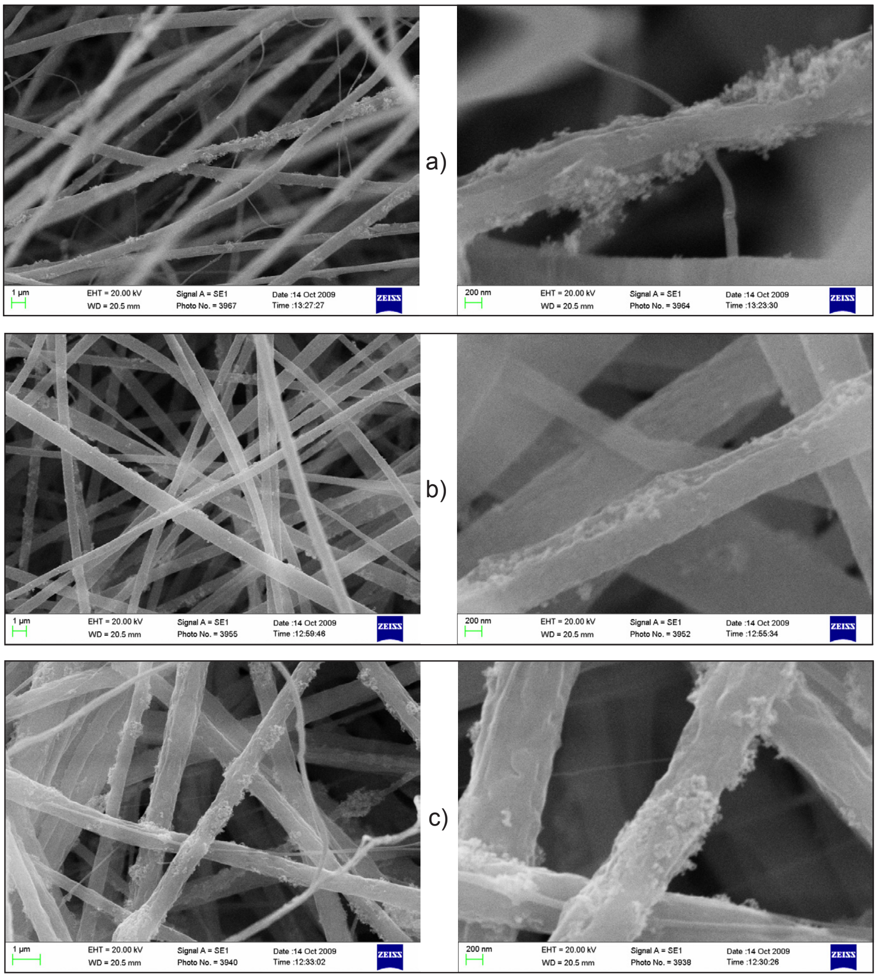


Figure 2. PVC (a), PSU (b) and PVDF (c) nanofibres covered with TiO_2 nanoparticles produced by co-extrusion electrospinning. 5 wt.% of TiO_2 nanoparticles in THF. Voltage 12 kV (a) 11.5 kV (b) and 14 kV (c) polymer flow rate 1 ml/h, and particle suspension flow rate 0.25 ml/h.

were adjusted to the magnitudes at which a stable jet was obtained. The process of electrospinning was stable for the following parameters: voltage from 11 kV to 14 kV, flow rate of polymer solution from 0.8 to 1.5 ml/h, and flow rate of particle suspension 0.1 - 0.3 ml/h.

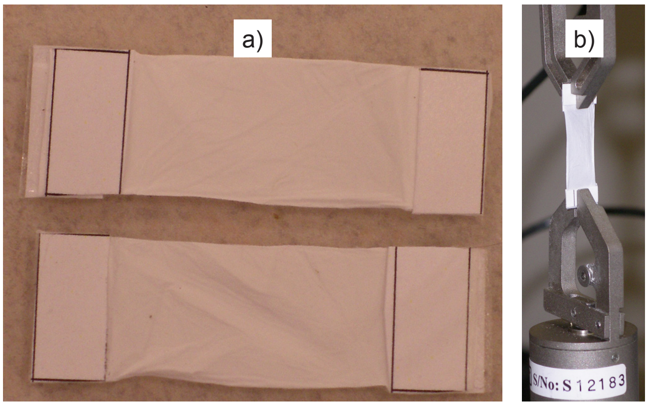
The electrospinning of nanofibres was carried out for poly(vinyl chloride) (PVC), polysulphone (PSU) and poly(vinylidene fluoride) (PVDF) polymers. The PVC was dissolved in a 1:1 dimethylformamide (DMF) and tetrahydrofuran (THF) mixture by stirring at room temperature to obtain 9% solution. 20% PSU solution was obtained by stirring PSU in DMF for 10 h at room temperature. 15% PVDF solution was obtained by dissolving 0.9 g of PVDF in 2.48 g of DMAC (N, N Dimethylacetamide) and 2.84 g of acetone. Spinning was carried out at room temperature and humidity of 45 - 50%. The flow rate of the polymer solutions was 1 ml/h, and the voltage was 12 kV for PVC, 14 kV for PVDF, and 11.5 kV for PSU. The TiO_2 particle colloidal suspension was prepared via the sonication of 5 wt.% of TiO_2 nanoparticles (<100 nm mean diameter, molecular weight 79.9 g/mol, 99.9% metal basis) in THF. The flow rate of the TiO_2 suspension was 0.25 ml/h. Dynasylan® Memo (Degussa) was added to the suspension in order to stabilise it.

The electrospinning process was carried out for 60 min. After the electrospinning process was completed, each electrospun mat was dried in a vacuum chamber. The morphology of the nanocomposite mats produced by the co-extrusion electrospinning was tested under a scanning electron microscope - EVO-40 (Zeiss). Strain-stress tests were carried out for all three nanocomposite mats using a Tensile Tester 3345 (Instron) with Bluehill Lite software (Instron). It had already been reported in literature that PSU nanofibre was found to be amorphous in nature, whereas PVDF nanofibre is crystalline [9, 11]. Hence the crystalline structure of the polymers was not investigated here.

Results

SEM micrographs of various polymer nanocomposite mats covered with TiO_2 nanoparticles, produced by the electrospinning method are shown in ***Figures 2***. PVC nanofibres covered with TiO_2 nanoparticles produced by co-extrusion electrospinning are shown in ***Figure 2.a***, PSU in ***Figure 2.b***, and PVDF in ***Figure 2.c***. The diameter of the PVC fibres was in the range of 600 to 800 nm, PSU from 400 to 800 nm, and PVDF from 400 to 600 nm. From these micrographs it can be noticed that in the case of PVC and PSU some of the fibres remain uncovered by particles, which can be a result of the uneven supply of colloidal suspensions by the syringe pump, or particles coagulation. Contrary to simultaneous electrospinning /electrospraying and post-spinning deposition (cf. [5, 6]), there remain un-covered fragments of the fibres, and on the covered fragments the particles tend to form larger agglomerates. The uneven fibre coating is a result of particle agglomeration within droplets formed on the fibre due to the force of surface tension before solvent evaporation. Higher particle concentration would be required for more uniform coating of the fibres, but this resulted in annular nozzle clogging due to the electrocoagulation process, which is difficult to control. This result indicates that further research is needed in order to improve the final product.

Strain-stress tests were carried out for all three mats produced by co-extrusion electrospinning. Samples of the nanocomposite mats were taken from the central part of the electrospun mat and cut to 20 mm length and 10 mm width. At both ends of the sample two paper stripes were glued on both sides in order to connect the sample to the jaws of the tensile tester. A photograph of the samples used for the tests are shown in ***Figure 3.a*** (see page 30). The stresses were measured in the direction of rotation of the rotating drum. The thickness of the samples was as follows: PVC - 73 μm, PSU - 31 μm, and PVDF - 120 μm. The sample was placed in the jaws of the Tensile Tester 3345 (***Figure 3.b,*** see page 30). The strain was gradually increased under the control of software, and the device measured the stress automatically after each step.



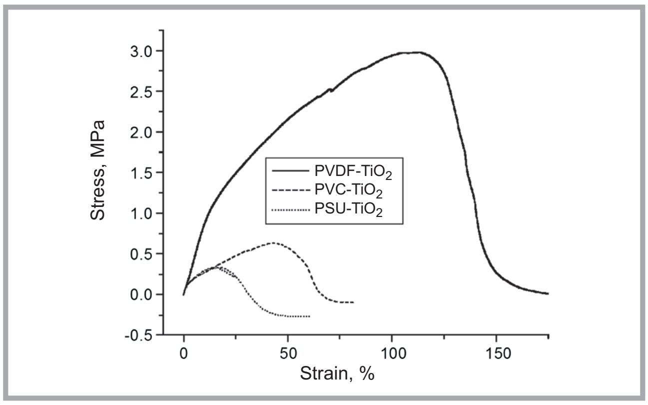


Figure 3. a. *Photograph of samples of PVC nanocomposite mat with* TiO_2 *nanoparticles.* ***b.*** *A sample placed in the jaws of a Tensile Tester 3345.*

Figure 4. *Example of stress vs. strain plots for PVC, PSU, and PVDF nanocomposite mats with* TiO_2 *particles.*

The stress-strain characteristics of PVC, PSU, and PVDF nanocomposite mats with deposited TiO_2 nanoparticles are shown in ***Figure 4.*** The tensile stress at a maximum load for PVC fabric with TiO_2 nanoparticles (3 samples) was 0.64 ± 0.05 MPa, and the tensile modulus: 13.2 ± 1.1 MPa. The tensile stress at a maximum load for PSU:TiO_2 (5 samples) was 0.25 ± 0.03 MPa, and the tensile modulus: 15.2 ± 1.5 MPa, and for PVDF:TiO_2 (5 samples) the tensile stress at a maximum load was 2.97 ± 0.30 MPa, and the tensile modulus: 20.6 ± 2.0 MPa. The sample elongation at the break point was 68.2%, 53.1%, and 149% for PVC, PSU, and PVDF, respectively.

The results obtained showed that the maximal tensile stress at a maximum load was higher for PVDF polymer with TiO_2 nanoparticles than for the other two polymers: PVC and PSU.

Conclusions

The paper presents experimental results of the mechanical property studies of nanocomposite material in the form of non-woven fabric produced by the method of co-extrusion electrospinning. By this method, polymer fibres such as PVC, PSU, and PVDF, of diameter smaller than 800 nm, were covered with TiO_2 nanoparticles (< 100 nm) to form nanocomposite mats. This type of mat can be used for the production of masks and filters with incorporated nanoparticles of catalytic material for the removal of bacteria, viruses or noxious compounds.

The advantage of co-extrusion electrospinning as a method for the production of nanocomposite non-woven fabric is that it is a single stage, low energy, and low-cost process which can be carried out at atmospheric conditions, normal temperature and pressure. The method allows for the formation of uniform non-woven fabric with nanoparticles deposited onto the fibre surface during the process of electrospinning.

Strain-stress tests were carried out for all the nanocomposite mats produced with fibres covered by nanoparticles. The best results were obtained for PVDF, for which the maximal load and tensile stress at a maximum load were higher than for the other two polymers: PVC/TiO_2 and PSU/TiO_2. Further research will be aimed at developing a method for the production of finer fibres of diameter smaller than 100 nm, with densely packed nanoparticles.

Acknowledgments

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