Electrostatic method for the production of polymer nanofibers blended with metal-oxide nanoparticles

A. Jaworek¹, A. Krupa¹, M. Lackowski¹, A.T. Sobczyk¹, T. Czech¹

S. Ramakrishna², S. Sundarrajan², D. Pliszka²,³

¹Institute of Fluid Flow Machinery, Polish Academy of Sciences, Gdansk, Poland
²National University of Singapore, Nanoscience & Nanotechnology Initiative, Singapore
³Institute of Physics, Pomeranian Academy, Slupsk, Poland
E-mail: jaworek@imp.gda.pl

Abstract. The paper presents investigations of a method of the production of non-woven polymer fabrics with incorporated metal oxide nanoparticles based on electrospinning and electrospraying. Two main configurations of electrospraying/electrospinning systems have been tested: two-step process of electrospinning of polymer solution followed by electrospraying of nanoparticle suspension, and simultaneous electrospinning of polymer solution and electrospraying of nanoparticle suspension. By this method TiO₂, MgO, or Al₂O₃ nanoparticles of the size from 20 to 100 nm were deposited onto electrospun PVC nanofibers.

1. Introduction

Electrostatic methods for the production of nanomaterials refer to the techniques which employ electrical processes, for example electrohydrodynamic or plasma, to the fabrication of the materials. In recent years an increasing interest in industrial or biotechnology applications of electrohydrodynamic processes, including electrospinning and electrospraying, can be observed. It is urged by looking for new more effective techniques, which can be easily automatically controlled. A brief summary of physical background and selected practical applications of electrospinning were given in the book by Ramakrishna et al. [1] and paper of Teo and Ramakrishna [2]. Applications of electrospraying in nanotechnology were reviewed by Jaworek and Sobczyk [3].

In our investigations we have used electrospinning and electrospraying methods for the fabrication of polymer nanofibers with metal-oxide nanoparticles deposited on them. Electrospinning is a process of the formation of a thin fiber from a viscous liquid, usually a polymer, by electrical shear stress on the liquid jet flowing from a capillary nozzle. Electrospraying is a technique of non-viscose liquid atomisation utilizing electrical forces by subjecting a liquid at a capillary nozzle to high voltage. The droplets obtained by this method can be of a submicron size, and this technique can be used for nanoparticle production. The reason for choosing electrospinning and electrospraying as methods of the production of such nanocomposite is that these methods can operate at atmospheric conditions, at normal temperature and pressure. They allow forming an uniform non-woven fabric with uniformly distributed nanoparticles on relatively large areas with deposition rate and film thickness easily controlled via voltage and flow rate. The electrospraying is a low-energy and low-cost material processing technology, which can deliver the products of unique properties.

In this paper, we have presented the results of morphological studies of nanocomposite material in the form of non-woven fabric from polymer material blended with metal-oxide nanoparticles. The goal of the paper was to compare the morphology of the mats produced by simultaneous electrospraying
and electrospinning with those obtained by electrospray deposition of nanoparticles as a post-spinning process. Polymer nanofibers of diameter smaller than 800 nm were blended with metal oxides nanoparticles of the size of 20 to 100 nm. In these experiments, TiO$_2$, MgO, and Al$_2$O$_3$ particles were deposited on PVC nanofibers. This type of fabric could be used for the production of masks, filters, or scaffolds in biotechnology.

2. Experimental
The electrospinning system comprised a stainless-steel capillary nozzle placed horizontally and an aluminium rotating drum of diameter of 60 mm covered with an aluminium foil (10 µm thick). The diameters of the capillary were 0.7 mm o.d. and 0.5 mm i.d. The length of the capillary was 15 mm. The distance between the nozzle tip and the drum was about 120 mm. The rotational speed of the drum was 3000 rpm. In the simultaneous electrospraying process, a second capillary nozzle of 0.45 mm o.d. and 0.25 mm i.d. was placed vertically. The distance between the nozzle tip and the drum was 50 mm. In the two-step process, the aluminium foil with deposited fabric was removed from the drum and placed onto a heated table. The table was heated in order to facilitate solvent evaporation. The substrate temperature was 30-40°C. Above this table, an electroatomizer was placed vertically. This nozzle was made of stainless steel capillary of 0.45 mm o.d. and 0.25 mm i.d. The distance between electrospray nozzle and the table was 20, 25 or 30 mm.

The electrospinning nozzle was connected to high-voltage supply SPELMANN HV SL600W/40kV/PN of positive polarity, and the drum was grounded. The electrospray nozzle was connected to high-voltage supply SPELMANN HV SL300W/30kV/P. The electrospinning process was carried out at 12 kV, and 1 ml/h flow rate of polymer solution. The particle suspension was electrosprayed for the voltage of 5.5 to 8 kV, and flow rate <1 ml/h. The voltage and the flow rate were adjusted for each suspension and configuration separately in order to obtain stable cone-jet or multijet modes. The spray plumes were recorded using the CCD camera PANASONIC NV-GS 400.

Metal oxides, such as Al$_2$O$_3$, MgO, and TiO$_2$ suspensions in methanol were used in all these experiments. Methanol was supplied from POCH Gliwice (Poland) and acetone from Chempur (Poland). MgO particles of 40.3 g/mol (99% metals basis) and size 100 nm, TiO$_2$ particles of molecular weight of 79.9 g/mol (99.9% metals basis) and mean diameter 29 nm, and Al$_2$O$_3$ particles of molecular weight 101.96 g/mol (99.6% purity) and mean diameter 30 nm were purchased from Alfa Aesar. The PVC polymer was purchased by Sigma-Aldrich. Dimethyloformamide and tetrahydrofuran were supplied from Chempur (Poland).

The electrospinning process lasted 60 min. The suspensions were electrosprayed for 10 min when deposited onto the fabric placed on the table. The morphology of nanocomposite materials produced by nanoelectrospinning and nanoelectrospraying was tested under a scanning electron microscope EVO-40 (Zeiss).

3. Results
Two main configurations of electrospraying/electrospinning systems have been tested (Fig. 1): two-step process of consecutive electrospinning of polymer solution followed by electrospraying of nanoparticle suspension (Fig. 1a), and simultaneous electrospinning of polymer solution and electrospraying of nanoparticle suspension (Fig. 1b). In the first configuration, the electrospun fibers were deposited onto a substrate (Al foil) covering a rotating drum. After the process was completed, the foil was removed from the drum and placed onto a heated table where the nanoparticle suspension was dispersed from an electrospray nozzle. In the second configuration, two separate nozzles were facing the rotating drum, one of which electrospun the fibers, and the second one electrosprayed nanoparticle suspension. In each configuration, after the particles were deposited, the fabrics were dried at elevated temperature, for example, at 50°C, before their inspection under the scanning electron microscope.

In the presented experiments, PVC was dissolved in dimethyloformamide and tetrahydrofuran mixture (1:5:5). The nanoparticle suspension in methanol with Dynasylan ® Memo surfactant was
stirred for 2 h. Next, the suspension was electrosprayed and deposited onto electrospun polymer fibers. Two examples of spray plumes for the cone-jet and multijet modes are shown in Figs. 2a and 2b, respectively. In the multijet mode, the droplets are smaller and allow a generation of smaller particles. The cone-jet mode is, however, generated by lower flow rates than the multijet mode, and longer time is required for deposition of a layer of the same thickness. Additionally, the cone-jet plume is narrower than that of the multijet mode. In the following, the presented results were obtained for the multijet mode, provided it was available for the suspension to be sprayed. Low particle concentration and ease of evaporation of the solvent enabled us to deposit a uniform tight layer on the fibers. The morphology of the layer differs depending on the structure of deposited particles and the deposition process.

![Diagram of electrospinning and electrospraying process](image)

**Fig. 1.** Methods for the production of nanocomposite non-woven fabric with incorporated nanoparticles: a. electrospinning followed by electrospraying in a separate process; b. simultaneous electrospinning and electrospraying from two separate nozzles.

![Image of TiO2 nanoparticles](image)

**Fig. 2.** Electrospray plume in cone-jet (a) and multijet (b) modes. TiO2 nanoparticles in methanol with Dynasylan® Memo surfactant.

TiO2 nanoparticle concentration 1.2 wt.%; distance to the drum 50 mm; Flow rate 0.2 ml/h; voltage 4.5 kV.

TiO2 nanoparticle concentration 0.6 wt.%; distance to the drum 50 mm; Flow rate 0.3 ml/h; voltage 8 kV.

A photograph of the electrospinning process is shown in Fig. 3a, and an example of electrospun fibers deposited onto an Al-foil substrate covering the rotating drum is shown in Fig. 3. Spinning onto a plate was also tried but fibers deposited onto rotating drum were straight, more uniform in diameter and evenly deposited onto the substrate. Sometimes beads were produced when spraying onto a plate.
Electrospinning onto rotating drum was therefore further used for the production of nanocomposite fibrous mats.

![Electrospun PVC fiber at the capillary outlet](image1)

**Fig. 3.** a. Electrospun PVC fiber at the capillary outlet, b. PVC nanofibers deposited on Al-foil substrate (solvent: dimethylformamide + tetrahydrofuran), voltage 12 kV, flow rate 1 ml/h.

![Electrospraying onto nanofiber fabric](image2)

**Fig. 4.** Post-spinning deposition of MgO (a) and TiO$_2$ (b) nanoparticles onto PVC fibers.

![Electrospraying onto nanofiber fabric](image3)

**Fig. 5.** Post-spinning deposition of Al$_2$O$_3$ nanoparticles onto PVC fibers for the substrate temperature 60°C (a) and 30°C (b).

Examples of SEM images of the fibers with deposited nanoparticles are shown in Figs. 4 and 5. In Fig. 4 there are presented PVC fibers with deposited MgO (a) and TiO$_2$ particles. The particles form a dense cover over the fibers remaining free space between them. In Fig. 5 Al$_2$O$_3$ particles were deposited onto a PVC fibers at two different substrate temperatures, 60°C and 30°C, for the same time of spraying. At lower temperatures, the number of particles is larger and the particles are more densely packed. This effect can be explained by easier solvent evaporation at higher temperatures. Smaller
amount of the solvent remaining on the deposit prevents electric charge removal from the fibers. The accumulated charge repels the on-flowing charged particles decreasing thus the deposit thickness. The optimal temperature is therefore that at which the deposit is semi-dry, allowing charge removal but at the same time preventing flooding the substrate.

Fig. 6 presents the results of simultaneous electrospraying and electrospinning production of nanocomposite fibers. The density of particles deposited onto the fiber is lower than in the post-spinning process. However, in the simultaneous process, the particles are more uniformly distributed between the fiber layers.

![Fig. 6. Simultaneous electrospraying and electrospinning deposition of MgO (a) and TiO$_2$ (b) nanoparticles onto PVC fibers.](image.png)

4. Conclusions
The paper provides experimental results of electrospray deposition of nanoparticles of metal-oxide on polymer fibers produced by electrospinning. The structures of this nanocomposite was porous at nanometer scale enabling gas to flow-through. By this technique the specific surface area of the nanoparticle material, which could be a catalyst, was increased.

Two electrospinning/electrospraying process for the production of polymer nanocomposite mat blended with nanoparticles were tested: simultaneous electrospinning and electrospraying, and two-step process, electrospinning followed by electrospraying of nanoparticles. It can be concluded that a simultaneous process produces a less dense particle coating but they are distributed more uniformly within the fiber layers. Post-spinning deposition allowed the production of a dense layer which, however, was mainly deposited on the mat surface, with only minor penetration. It was also concluded that multijet mode is more effective in the nanofiber coating giving in result denser and more uniform coverage of the fibers.

This technology can be applied for the production of filtration mats with improved efficiency via incorporated catalytic material, electrodes of high specific surface area for fuel cells, or scaffolds for tissue regeneration.

Acknowledgements
The paper was co-sponsored by the Polish Ministry of Science and Higher Education Project No. 83/SIN/2006/02 and A*STAR Project No. 062 120 0017, within the Joint Singapore-Poland Science &Technology Co-Operation programme "Fabrication of novel nanocomposite filter membranes for understanding basic principles and their advanced technology application".
References

[1] Ramakrishna S., Fujihara K., Teo W.E., Lim T.Ch., Ma Z., (2005) An introduction to electrospinning and nanofibers. World Scientific

[2] Teo W.E., Ramakrishna S., (2006) A review on electrospinning design and nanofibre assemblies. Nanotechnology 17, R89–R106

[3] Jaworek A., Sobczyk A.T., (2008) Electrospaying route to nanotechnology. An overview. J. Electrostatics. 66, No.3-4, 197-219