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Electrospinning and Electrospraying Techniques for Nanocomposite Non-Woven Fabric Production

Abstract
Electrospinning and electrospraying processes were tested as tools for the production of non-woven nanocomposite fabric from a polymer material with nanoparticles deposited on a fibre surface. The suitability of two main electrospraying/electrospinning systems was investigated: the consecutive electrospraying of nanoparticle colloidal suspension after electrospinning polymer solution, and the simultaneous electrospinning of polymer solution and electrospraying of nanoparticle colloidal suspension from two separate capillary nozzles. In our experiments the fibres were electrospun from PVC, PSU and PA6 polymers in suitable solvents. Electrosprayed fibres were the colloidal suspensions of TiO_2, ZrO_2, MgO, or Al_2O_3 nanoparticles of 20 to 100 nm in size.

Key words: *electrospinning, electrospraying, non-woven fabrics, nanofibers, nanocomposites.*

Introduction

Electrospinning is a physical process used for the formation of thin fibres in which a viscous liquid is subjected to an electrical shear stress by maintaining the nozzle at a high electric potential [1]. In the electrospinning process no additional mechanical energy other than that from the electric field is applied for the fibre elongation. Electrospinning was used for the production of thin fibres of diameter smaller than 0.5 μm from a variety of materials [1]. It is important to note that the supermolecular structure of electrospun fibres does not differ significantly from the that of fibres produced via wet spinning [2]. It has been shown (cf. [3]) that the diameter of electrospun fibres is smaller than that of fibres produced by other methods, for example, blow spraying. Interest in polymer materials has grown in recent years due to their potential application as smart or intelligent materials (cf. [4]). It should be mentioned that electrospinning from a capillary nozzle is not the only electrostatic method for nanofibre production. Fibres can also be spun from a drum covered by solution and placed in an electric field [5 - 7]. Such a device, known as a "Nanospider", was developed at the Technical University of Liberec and patented.

Electrospraying is a process similar to electrospinning but is used when the viscosity of the liquid is sufficiently low. The electric charge draws the liquid from the capillary nozzle in the form of a fine jet, which eventually disperses into droplets [8]. The droplets produced by electrospraying are highly charged, usually close to one-half of the Rayleigh limit, and can be smaller than 1 μm. The size distribution of the droplets is usually narrow, with low standard deviation. Electrospraying can be used for the production of small, nearly monodisperse particles when a colloidal suspension of solid nanoparticles or a solution of a material is sprayed [9]. In electrospraying the size of the droplets can be controlled mainly by the liquid flow rate, and the droplet charge by adjusting the voltage applied to the nozzle. The charged aerosol is self-dispersing, which prevents the droplets from coagulation.

Nanocomposites are materials produced from various nanosized components of different physical and chemical properties, for example, nanofilms produced from nanoparticles of different kinds, yarns or fabrics made from different nanofibres, or nanofibres blended with nanoparticles.

In this paper the electrospinning and electrospraying processes were tested as tools for the production of non-woven nanocomposite fabric from a polymer material blended with nanometer particles, with respect to its application for the fabrication of masks, filters, or scaffolds in biotechnology. In previous publication [10], nanoparticles were mixed with polymer and then subjected to electrospinning. However, in this method the nanoparticles were covered by polymer and therefore not accessible on the surfaces for catalytic applications. In the experiments presented in this paper, two separate nozzles were used: one for electrospinning, and the second for electrospraying particle colloidal suspension. By this method, PVC, PSU or PA6 (nylon) in suitable solvents were used as electrospun solutions, and TiO_2, ZrO_2, MgO, or Al_2O_3 nanoparticles of 20 to 100 nm in size suspended in methanol were electrosprayed from a capillary nozzle in order to deposit them onto the fibres after solvent evaporation. The diameter of the polymer nanofibres was smaller than 500 nm. The suitability of the two main configurations of electrospraying/electrospinning for these purposes was investigated: the consecutive electrospraying of nanoparticle colloidal

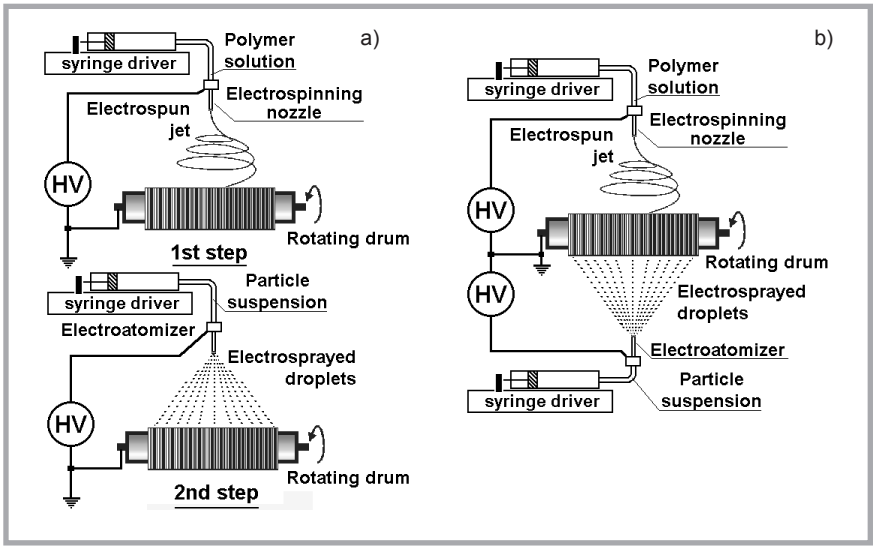

Fig.ure 1. *Schematic of the methods for the production of nanocomposite mats: a) in a two-step process: electrospray deposition after electrospinning; b) via simultaneous electrospinning and electrospraying from two separate nozzles.*

suspension after electrospinning polymer solution, and the simultaneous electrospinning of polymer solution and electrospraying of nanoparticle colloidal suspension from two separate nozzles.

Experimental

Fibres were electrospun from a stainless-steel capillary of 0.45 mm o.d. and 0.25 mm i.d. diameter, and 15 mm length, placed horizontally. The fibres were collected on an aluminium drum of 60 mm diameter, covered with aluminium foil (10 μm thick), rotating at a rotational speed of about 3000 r.p.m. The distance between the nozzle tip and the drum was about 120 mm. In the simultaneous electrospraying process, a second capillary nozzle of 0.7 mm o.d. and 0.5 mm i.d. diameter was placed vertically above the drum. This nozzle served as a source of nanoparticles which were deposited onto the fibres on the rotating drum. The distance between the nozzle tip and the drum was 50 mm.

In the two-step process: consecutive electrospraying after electrospinning, the electrospun nozzle was replaced with an electrospray nozzle. This nozzle also comprised a stainless steel capillary of 0.7 mm o.d. and 0.5 mm i.d diameter. The distance between the electrospray nozzle and the drum was 50 mm.

The electrospinning nozzle was maintained at a potential of 12 kV by its connection to a high-voltage supply (SPELMANN HV SL600W/40kV/PN) of positive polarity. The electrospray nozzle was also connected to a high-voltage supply (SPELMANN HV SL300W/30kV/P) maintained at a voltage of 8 to 10 kV. The drum was grounded. The electrospinning process was carried out at a 1 ml/h flow rate of polymer solution for a time of 30 to 60 min. The particle colloidal suspension was electrosprayed at a flow rate of 0.5 ml/h for a time of 30 - 60 min. The polymer solutions and particle suspensions were supplied to the nozzles using two syringe pumps of the AP22 type (Ascor - Poland).

In these experiments the voltage and distances were adjusted for each configuration and particle suspension separately in order to obtain a stable multijet mode. Although the viscosity of the polymer solutions was not measured due to the large volume of solution required for such measurements, the concentration of each polymer in a suitable solvent was chosen experimentally in order to obtain a stable electrospun jet that produced even, bead and pore free fibres. Before deposition, the particles were stirred for a time of 20 h in methanol with an addition of Dynasylan ® Memo surfactant in order to stabilise the suspension. Metal oxide nanoparticle (MgO, TiO_2, ZrO_2, and Al_2O_3) suspensions in methanol were used in all these experiments.

MgO particles of 40.3 g/mol (99% metals basis) molecular weight and <100 nm in size, TiO_2 particles of 79.9 g/mol (99.9% metal based) molecular weight and mean diameter of 29 nm, and Al_2O_3 particles of 101.96 g/mol (99.6% purity) molecular weight and mean diameter of 30 nm were purchased from Alfa Aesar. ZrO_2 particles of 123.22 g/mol molecular weight and mean diameter of < 100 nm were supplied from Aldrich. PVC (Mw = 233 000) and PSU (Mw = 22 000) were purchased from Sigma-Aldrich and nylon from UBE Nylon. Dimethylformamide and tetrahydrofuran, used as solvents for the polymers, were supplied by Chempur. Methanol, which was used as solvent for nanoparticles, was supplied by POCH Gliwice (Poland).

The electrospinning process was carried out under a fume hood at room temperature in air with a relative humidity of 45 - 50%. Spray plumes were recorded using a PANASONIC NV-GS 400 CCD camera. The structure of the nanocomposite materials produced by electrospinning and electrospraying was tested under a Zeiss EVO-40 or FEI Quanta 200 scanning electron microscope.

Results

Nanocomposite non-woven fabric from polymer material blended with nanoparticles was produced via simultaneous application of electrospinning and electrospraying processes. Polymer nanofibres were produced from PVC, PSU and nylon. PVC (9 wt.%) was dissolved in a mixture of DMF (dimethylformamide) and THF (tetrahydrofuran) (1 : 1), PSU was dissolved in DMF (20 wt.%), and nylon was dissolved in 1,1,1,3,3,3 Hexafluor-2-propanol (8 wt.%). Metal oxide nanoparticles such as TiO_2, ZrO_2, MgO, and Al_2O_3 of 20 to 100 nm in size were suspended in methanol with Dynasylan® Memo surfactant. The diameter of fibres produced was smaller than 500 nm.

The schematics of the experimental set-up are shown in ***Figure 1***. The two main configurations of electrospinning and electrospraying from the two separate nozzles used for nonwoven fabric production are consecutive electrospinning followed by electrospraying (***Figure 1.a***), and simultaneous electrospinning and electrospraying (***Figure 1.b***). In the first configuration the electrospun fibres were deposited onto a substrate (Al foil) covering a rotating drum, and after the process was completed, the electrospinning nozzle was replaced with an electrospray nozzle which dispersed the nanoparticle colloidal suspension. In the second configuration two separate

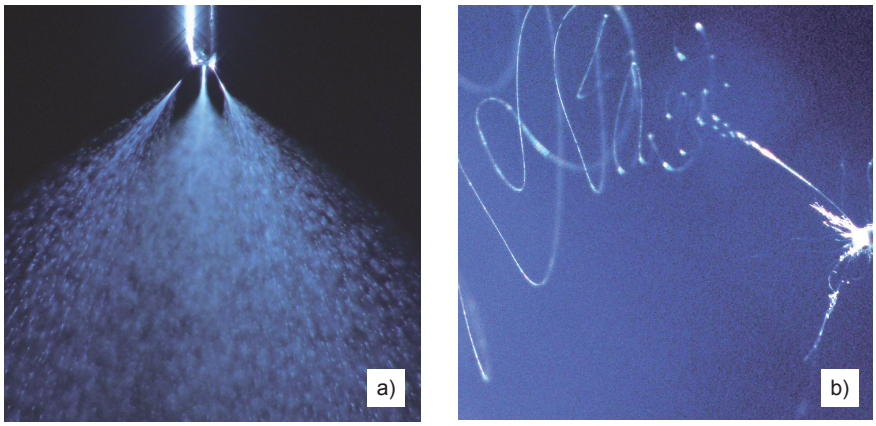

Figure 2. *Electrospray plumes taken with a stroboscopic light of 3 μs: a) multijet modes for electrosprayed MgO suspension in methanol with Dynasylan® Memo surfactant, at a flow rate of 1 ml/h; b) single electrospun fibre of PVC.*

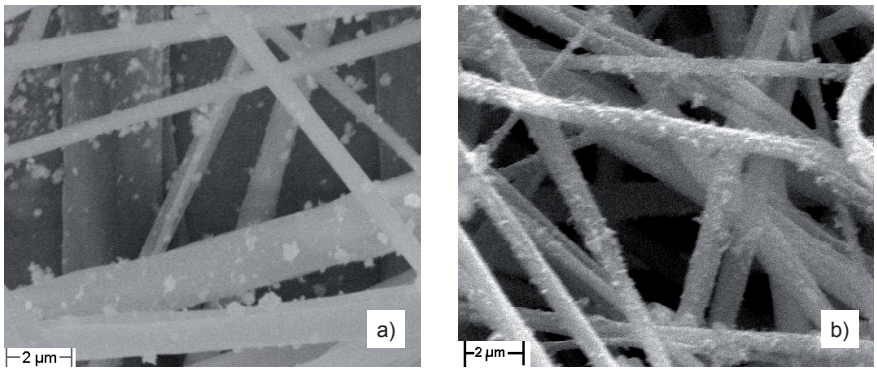

Figure 3. *SEM images of PVC electrospun fibres with deposited MgO nanoparticles (particle concentration: 0.6 wt.%): a) Simultaneous electrospinning and electrospraying process; b) Postspinning deposition.*

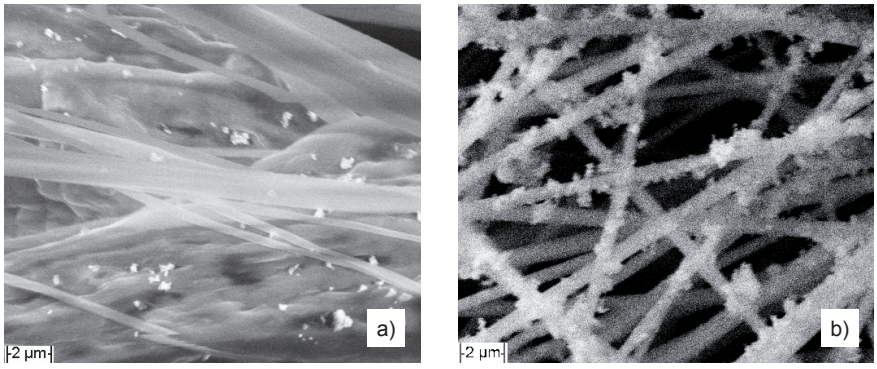

Figure 4. *SEM images of PVC electrospun fibres with deposited Al_2O_3 nanoparticles (particle concentration: 0.6 wt.%): a) Simultaneous electrospinning and electrospraying process; b) Postspinning deposition.*

nozzles were used over a rotating drum simultaneously. In each case, after the particles were deposited, the fabric was dried at a slightly elevated temperature, for example, at 45 °C or in a vacuum chamber before its inspection under a scanning electron microscope.

Examples of spray plumes, the multijet modes of electrospraying and the electrospinning of PVC solution are shown in ***Figures 2.a*** & ***2.b***, respectively. In the multijet mode the droplets are small and allow the generation of smaller particles than for other modes. The number of spray jets during multijet spraying was 4 to 6. Due to mutual electrostatic repulsion, the jets were symmetrically distributed around the capillary rim. For a total flow rate of 1 ml/h, for example the flow rate of each of the 5 jets was 0.2 ml/h, which is favourable for generating submicron droplets. The results presented were obtained for the multijet mode. Low particle concentration and ease of evaporation of the solvent enabled the deposition of particles on the fibres. The structure of the mats differs depending on the size of polymer fibres and the structure of particles deposited.

SEM images of PVC electrospun nanofibres with deposited nanoparticles of MgO, Al_2O_3, and TiO_2 are presented in ***Figures 3, 4*** & ***5***, respectively. Results obtained for simultaneous electrospinning and electrospraying processes are shown on the left, and for post-spinning deposition on the right. PVC was dissolved in a dimethylformamide and tetrahydrofuran mixture (1 : 5 : 5). An addition of dimethylformamide to the spinning solution improves the fibre structure and reduces the fibre diameter [11, 12].

SEM pictures of electrospun nanofibres with electrosprayed TiO_2 nanoparticles deposited during the postspinning process onto PSU and nylon nanofibres are shown in ***Figures 6.a*** & ***6.b,*** respectively. ***Figure 7*** presents two magnifications of SEM images of electrospun nylon nanofibres with ZrO_2 nanoparticles deposited during the postspinning process.

From these experiments it can be concluded that the postspinning deposition forms a denser deposit of particles on the surface of the mat, but in the simultaneous electrospinning/electrospraying process the particles are more uniformly distributed between the fibre layers. No significant difference in the process of particle deposition for various polymers in the postspinning deposition was noticed. The mass percentage of nanoparticles in the nanocomposite membrane determined from the solution, suspension concentrations and flow rates was about 3%.

It was observed that there is an optimal viscosity of the polymer solution to be spun, at which the fibre is homogeneous and beads within the fibres are not produced, confirming the earlier results of Doshi and Reneker [13] obtained for PEO, and Zong et al. [14] for poly(D,L-lactic acid). Beads are sometimes formed within the electrospun fibres as an effect of local higher dilution of the polymer solution and incomplete solvent evaporation. Earlier results obtained by Jaworek et al. [15] for water-glycol mixtures showed that the diameter of the jet decreases at higher viscosities of the liquid, which should also indirectly indicate a decrease in fibre diameter. Son et al. [16]

noticed that a higher dielectric constant of the solvent used for the polymer solution helps to decrease the diameter of electrospun fibres. During the experiments, it was also observed that the multijet mode of spraying is more effective for nanofibre coating than the cone-jet mode, resulting in denser and more uniform coverage of fibres.

Conclusions

This paper provides experimental results of electrospray deposition of metal-oxide nanoparticles on electrospun PVC, PSU and nylon nanofibres. The nonwoven mats obtained are porous, with the nanoparticles deposited on them increasing the total surface area when the particle-catalyst is deposited. The reason for choosing electrospray is that it is is single-step, low-energy, and low-cost material processing technology which can operate in atmospheric conditions at an easily controlled production rate by setting the voltage and flow rate. The materials are not damaged during the spraying and spinning processes. In order to improve the electrospinning process, the solvent mixture used has to be composed of two components: an easily evaporating solvent which facilitates cone and jet formation at the nozzle outlet, and a low-evaporation rate solvent which allows further jet elongation.

The technologies tested can be applied for the production of nanocomposite nonwoven fabrics which could serve, for example, as a filtration mat with improved efficiency due to catalytic material incorporated, electrodes of high specific surface area for fuel cells, or scaffolds for tissue regeneration. Filter mats produced from electrospun fibres enable gas flow through the filter but remove particles of nanometer size. When catalytic material is deposited onto the fibres, the mat can also operate as a simultaneous nanoparticle filter and device for removing harmful gases.

Discussing the economic aspects of the technology presented, it should be noted that the throughput of electrospraying and electrospinning techniques is rather low, which prevents their commercialisation. One of the possible solutions is using multinozzle systems, which multiply the number of electrospinning jets. Electrospinning from a drum covered with spinning solution seems to be the more economically viable due to a higher production rate.

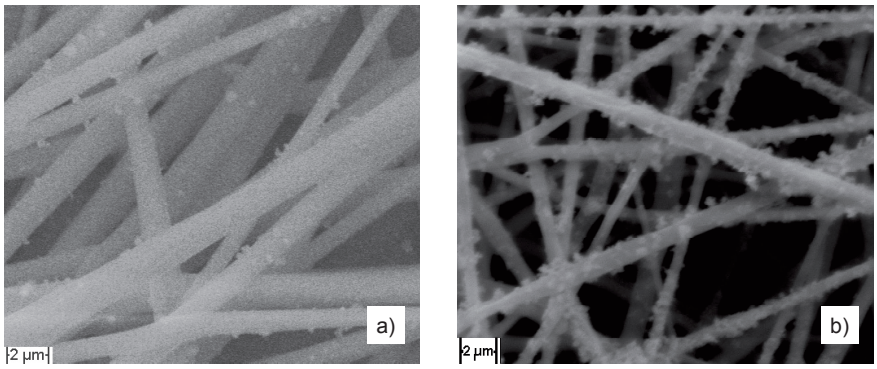

Figure 5. *SEM images of PVC electrospun fibres with deposited TiO_2 nanoparticles (particle concentration: 0.6 wt.%): a) Simultaneous electrospinning and electrospraying process; b) Postspinning deposition.*

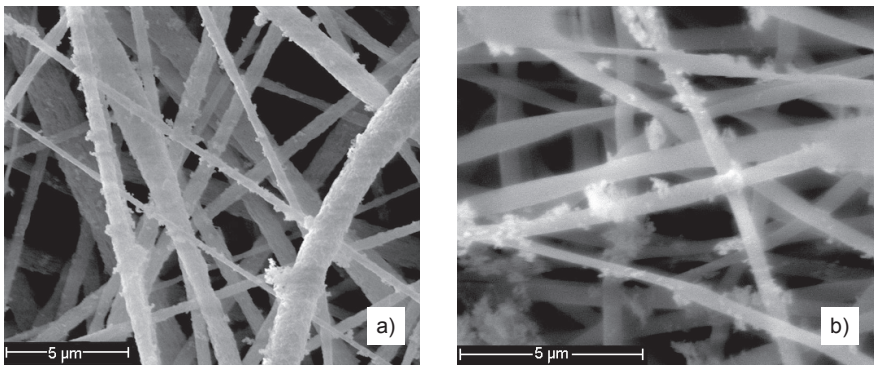

Figure 6. *SEM images of electrospun fibres with TiO_2 nanoparticles (particle concentration: 0.6 wt.%) deposited during the postspinning process: a) PSU nanofibres, b) Nylon nanofibres.*

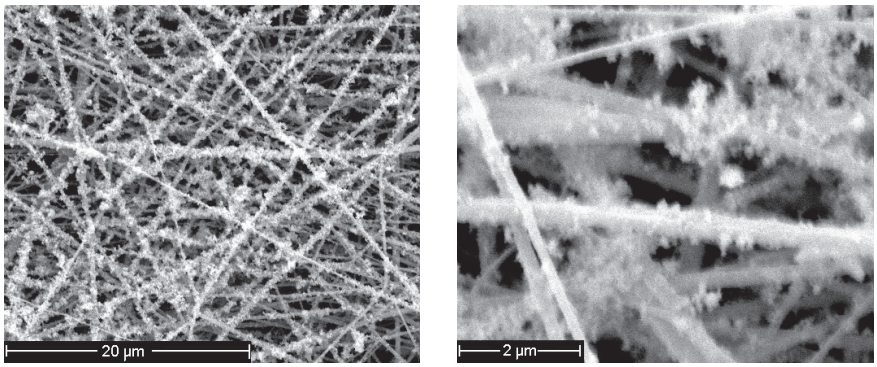

Figure 7. *SEM images of electrospun nylon nanofibres with ZrO_2 nanoparticles (particle concentration: 0.6 wt.%, multijet mode, 8 kV, flow rate: 0.3 ml/h) deposited during the postspinning process, for two magnifications.*

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