Solid State Phenomena *Online: 2008-10-01*
ISSN: 1662-9779, Vol. 140, pp 127-132
doi:10.4028/www.scientific.net/SSP.140.127

Electrospray Nanocoating of Microfibres.

A. Jaworek[1, a], A. Krupa[1, b], A.T. Sobczyk[1, c], M. Lackowski[1, d], T. Czech[1, e], S. Ramakrishna [2, f], S. Sundarrajan [2, g] and D. Pliszka [2, h]

[1] Institute of Fluid Flow Machinery, Polish Academy of Sciences, Fiszera 14, 80-952 Gdansk, Poland

[2] National University of Singapore, Nanoscience & Nanotechnology Initiative, Faculty of Engineering, Block E3, 05-29, 2 Engineering Drive 3, Singapore 117576

e-mail: [a] jaworek@imp.gda.pl; [b] krupa@imp.gda.pl; [c] sobczyk@imp.gda.pl; [d] mala@imp.gda.pl; [e] czech@imp.gda.pl; [f] seeram@nus.edu.sg; [g] nnisubra@nus.edu.sg; [h] nnidp@nus.edu.sg

Keywords: nanocoating, electrospray, microfibers, nanotechnology

Abstract. The paper presents experimental results of electrospray deposition of nanopowder onto microfibers. The process is designed to form fibrous filters with an enhanced collection efficiency in the submicron range by covering the fabric with a catalytic material. Polyamide fibres were coated with Al_2O_3, ZnO, MgO, or TiO_2 nanoparticles. The structures obtained were porous at the nanometer scale which increased the total surface area of the catalyst.

Introduction

Electrospraying is a method of liquid atomisation achieved by subjecting a liquid to electrical stress at a capillary nozzle. The liquid meniscus maintained at high electric potential elongates into a jet and disrupts into fine droplets. The droplets obtained by this method are charged and can be of submicron size. The size of the droplets and their production rate can be readily controlled by adjustment of the liquid flow rate and the voltage applied to the nozzle. Since the last decade, there is increasing interest in the application of electrospray processes in nanotechnology [1-4]. It was discovered by many authors that the deposition efficiency of a charged spray onto an object is significantly higher than for an uncharged spray. In the case of nanotechnology applications, the droplets can be directly deposited onto a substrate which facilitates surface coating or direct writing in a submicron scale. The process of jet formation and its disintegration into droplets is known in the literature as the mode of spraying [5, 6].

The spraying modes can be categorized into two groups:

1. Dripping modes, in which only fragments of liquid are ejected from the capillary outlet by the deformation and detaching of the liquid meniscus. These fragments can be formed as large regular drops (dripping mode), fine droplets (microdripping mode) or a single or multiple spindles (spindle and multispindle modes), or irregular fragments of liquids.

2. Jetting modes by which the meniscus elongates into a long fine jet, The jet can be smooth and stable (cone-jet mode) or can move in any regular way: rotate around the capillary axis (precession mode) or oscillate in a plane (oscillating mode). Sometimes a few jets on the circumference of the capillary can be observed (multijet mode). The case when the jet branches is known as a ramified jet.

In this paper the experimental results of deposition of nanopowder on microfibers using electrospraying are presented. The aim of the process is the formation of fibrous filters with enhanced collection efficiency in the submicron range by covering a tight unwoven fabric with a catalytic material. The deposited metal-oxides used as catalyst will facilititate the production of materials for protective technologies such as masks, garments, or respirators. The currently used

materials are not very efficient in giving protection against small-sized biological agents or chemical compounds, and they are frequently heavy. The composite materials made from nanoparticles deposited onto nanofibers and sandwiched between two layers of fabric will provide light weight, low cost, and breathable structures with improved protection, duration and performance.

Experimental

The experiments were carried out in a system consisting of a stainless-steel capillary nozzle and an aluminium plate (a gutter) (Fig. 1).

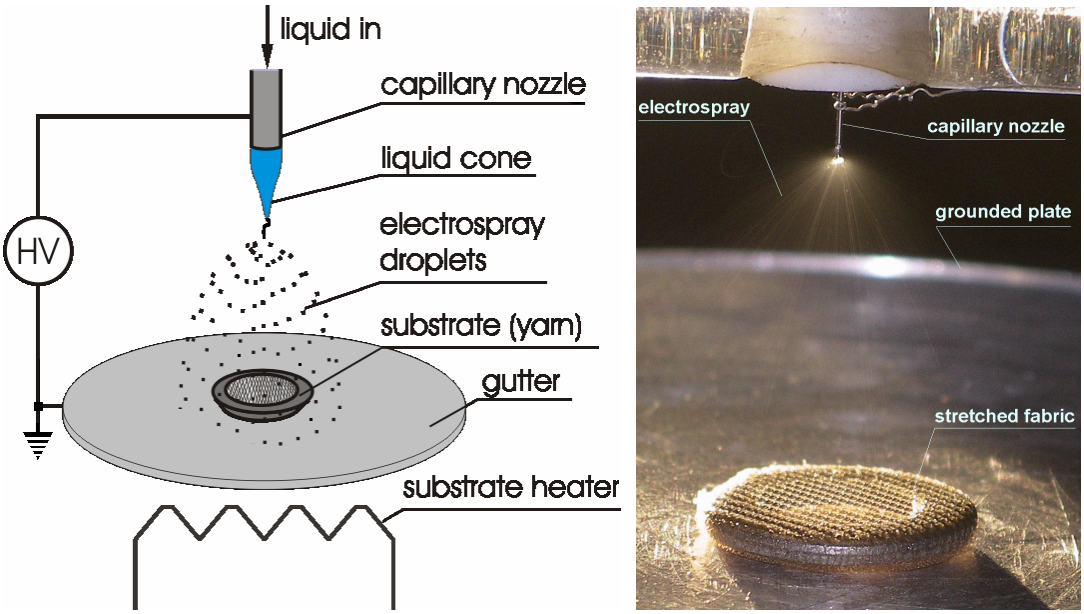

Fig. 1. (a) schematic of experimental stand, (b) photograph of electrospray system.

The dimensions of the capillary were 0.45 mm o.d. and 0.25 mm i.d. and a length of 10 mm. The distance between the nozzle tip and the plate was 25 mm. The diameter of the aluminium plate was 150 mm. The substrate was a commercial fabric made of woven 30 μm diameter polyamide fibres stretched over a small 1 mm thick metal ring of o.d 15 mm and i.d 10 mm.
The nozzle was connected to a high voltage supply, SPELMANN SL600W/30kV/PN, of positive polarity with the plate electrode earthed. An electric heater under the plate facilitated the liquid's evaporation. The spray plumes were recorded using a SONY DSC-F585V CCD camera. Metal oxides suspensions of Al_2O_3, ZnO, MgO, and TiO_2 in methanol supplied from Chempur (Poland) were used in the experiments. The liquid was supplied from a syringe mounted above the capillary nozzle. MgO particles of pure grade 40.3 g/mol were purchased from POCH Gliwice (Poland); TiO_2 particles of molecular weight of 79.90 g/mol were supplied by Eurochem BGD (Poland); Al_2O_3 particles of 99.9% purity, and ZnO particles of 99.0% purity were purchased from Alfa Aesar. The suspensions were electrosprayed for about 15 minutes at an estimated flow rate of 20 ml/h. The structures obtained were examined with a Zeiss EVO-40 scanning electron microscope.

Results and discussion

In the experiments, the suspended particles in methanol were electrosprayed and deposited onto 30 μm diameter polyamide fibres. The cone-jet and multijet spray modes are shown in Figs. 2a and b. The smaller droplets in the multijet mode produced smaller particle agglomerates. The results presented were obtained for the multijet mode. Low particle concentration and the ease of solvent

evaporation enabled a uniform tight layer to be deposited on the fibres. The layer morphology varies depending on the structure of deposited particles.

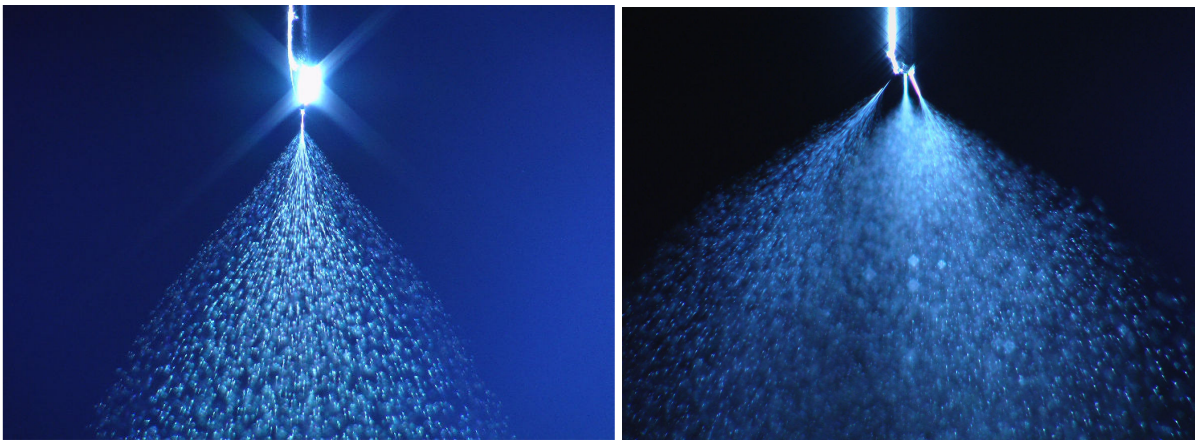

Fig. 2. (a) cone-jet mode of electrospraying (voltage 5.1 kV), (b) multijet mode of electrospraying (voltage 7.8 kV). Liquid: MgO suspension in methanol. Electrode distance: 20 mm, exposure: 3 μs.

Figs. 3 to 6 show SEM micrographs of the fragments of the layers consisting of Al_2O_3, ZnO, MgO, and TiO_2 particles deposited onto the polyamide fibres.

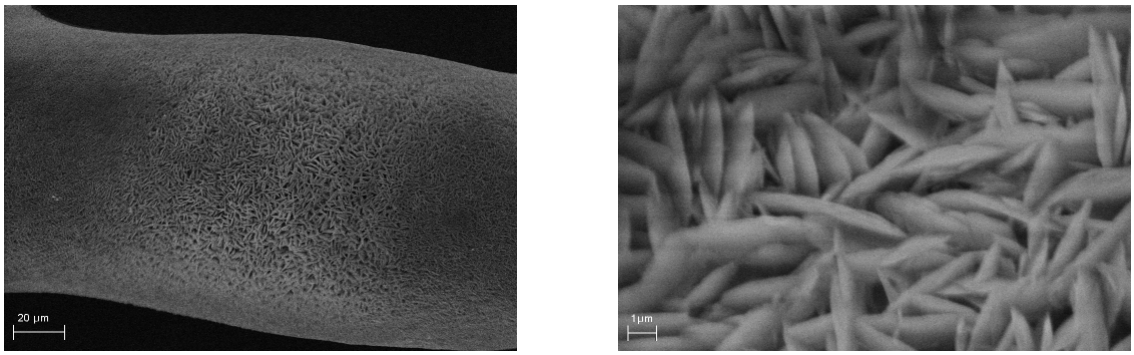

Fig. 3. SEM images of Al_2O_3 layer deposited by electrospraying onto a 30 μm dia polyamide fibre. (Al_2O_3 suspension in methanol, voltage=24 kVdc).
Left: a fragment of the coated fibre. Right: the spindle-like structure of the deposit

The layers are formed despite the dielectric nature of the fibre. This is due to a thin film being formed on the fibre by the methanol-metal-oxide suspension before complete evaporation of the solvent. The film is sufficiently conducting for the electrical charges to leak to earth. Because the electric field lines terminate on the rear of the fibre it is almost evenly covered over the whole surface. It was observed that each material forms a different porous structure on the fiber after evaporation of the solvent. The Al_2O_3 layer shown in Fig. 3 was uniform and composed of spindle-like particles a few μm long and 1 μm in diameter.

The ZnO deposit was irregular, and composed of ZnO flakes about 1-2 μm across as show in Fig 4. The flakes were deposited on the fibre in island-like groups.

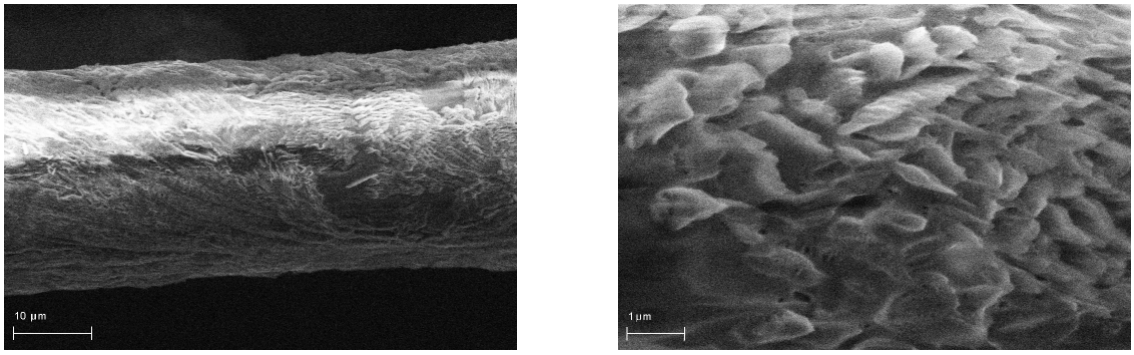

Fig. 4. SEM images of ZnO layer deposited by electrospraying on a 30 µm dia polyamide fibre. (ZnO suspension in methanol, voltage=25 kVdc).
Left: a fragment of the coated fibre. Right: the flaky structure of the deposit.

The MgO particles which are shown in Fig. 5 formed a tight deposit on the fibre which was composed of individual particles having a size of about 100-200 nm.

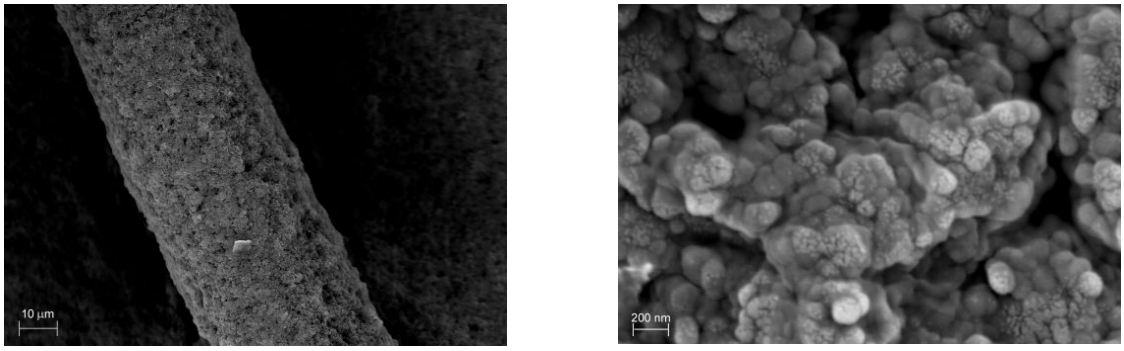

Fig. 5. SEM images of MgO layer deposited by electrospraying on a 30 µm dia polyamide fibre. (MgO suspension in methanol, voltage=5.1 kVdc).
Left: a fragment of the coated fibre. Right: the crystalline structure of the deposit.

The TiO_2 particles deposited onto the polyamide fibres formed a thin and irregular deposit as given in Fig. 6. The particles forming the layer were not strongly adherent to the polyamide and the layer was not uniform. Only small agglomerates of particles with a size of about 100-200 nm can be observed on the substrate

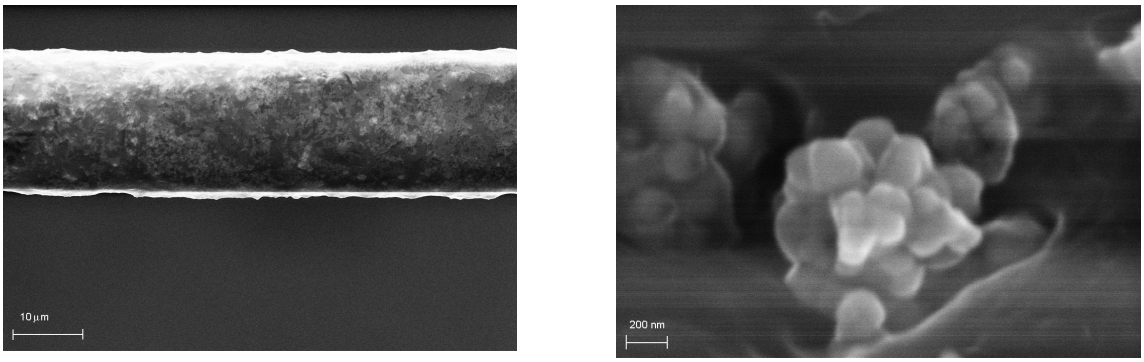

Fig.6. SEM images of TiO_2 layer deposited by electrospraying on a 30 µm dia polyamide fibre. (TiO_2 suspension in methanol, voltage=15 kVdc).
Left: a fragment of the coated fibre. Right: the crystalline structure of the deposit.

Formerly, electrospraying was used for covering various materials, usually metal or Si substrates, with thin layers. Usually, the deposit is formed from a precursor. Only a few papers have presented the results of deposition of layers directly formed with metal oxides. These papers are summarized in Table 1.

Layer // substrate	Particles size (sinter temperature)	Solvent	Flow rate (spray time)	References
alumina (Al_2O_3) // Al	100 nm (100-250^{o}C)	ethanol or ethanol + butyl carbitol	0.8 ml/h or 1.5 ml/h (60 min)	[7]
silica (SiO_2) // glass	20 nm	ethylene glycol	36 ml/h	[9]
	5 nm	ethylene glycol	22 ml/h	[8]
zirconia (ZrO_2) // polymer sponge;	410 nm (1450^{o}C)	ethanol + 0.5% dispersant	3.3 ml/h (2 h)	[14]
zirconia (ZrO_2) // zirconia;	410 nm (1500^{o}C)	ethanol + 0.5% dispersant	0.36 ml/h (153 s for 100 layers)	[10]
zirconia (ZrO_2) // silicone release paper	200 nm	butyl acetate + ethanol	0.6-45 ml/h (0.2 g/h)	[11]
zirconia + alumina composite (Al_2O_3+ZrO_2) // quartz	500 nm (Al_2O_3), 400 nm (ZrO_2) (1200^{o}C)	glycerol (for alumina), olive oil (for zirconia) + 1 wt% dispersant	0.25-250 ml/h	[12]
titania (TiO_2) // FTO glass	500 nm (TiO_2 nanorods)	ethanol	1 ml/h	[13]

Table 1. Metal oxides electrosprayed from a suspension as submicron layers.

The structure of the Al_2O_3 layer on an Al substrate obtained by Chen et al. [7] was composed of individual particles of the sol of about 100 nm. The morphology of SiO_2 particles deposited on a glass substrate by Jayasinghe and co-workers [8,9] was grainy. The grains of a size of hundreds of nm were built from the sol particles 5 or 20 nm. Wang et al. [10] and Teng et al. [11] produced zirconia structures which were formed from irregularly arranged particles. A composite material consisting of Al_2O_3 and ZrO_2 particles was produced by Balasubramanian et al. [12]. The TiO_2 layer produced by Fujihara et al. [13] was composed of nanorods about 500 nm long. Other layers were produced by the use of various kinds of precursors [14].

Summary

The paper provides experimental results of electrospray deposition of nanoparticles of metal-oxide on a polyamide fibre. The structures are porous on the nanometer scale which increases the total surface area of the catalyst. The reason for choosing electrospraying as a method of deposition is that an electrospray can operate in atmospheric conditions and deposit uniform micro- and nano-thin films on large areas with an easily controlled deposition rate and film thickness by controlling he voltage and liquid flow rate. Electrospraying is a single-step, low-energy, and low-cost material processing technology, which can deliver products possessing unique properties. The substrate is not damaged after the spraying process. Optimization of the processing conditions will result in a low number of voids, flaws and cracks in the coating and give a sufficiently good homogeneity of the layer.

Acknowledgements

The work was co-sponsored by Polish Ministry of Science and Higher Education Project Grant 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] S. Ramakrishna, K. Fujihara, W.E. Teo, T.Ch. Lim, Z. Ma: *An introduction to electrospinning and nanofibers* (World Scientific, Singapore 2005)
[2] A. Jaworek: J. Mater. Sci. Vol. 42 No.1 (2007a), p. 266
[3] A. Jaworek: Powder Technol. Vol. 176 No.1 (2007b), p. 18
[4] W.E. Teo, S. Ramakrishna: Nanotechnology Vol. 17 (2006), p. R89
[5] A. Jaworek, A. Krupa: J. Aerosol Sci. Vol. 30 (1999a), p. 873
[6] A. Jaworek, A. Krupa: Exp. Fluids Vol. 27 (1999b), p. 43
[7] C.H.Chen, M.H.J. Emond, E.M. Kelder, B. Meester: J. Schoonman, J. Aerosol Sci. Vol. 30 No.7 (1999), p. 959
[8] S.N. Jayasinghe: Physica E Vol. 33 (2006), p. 398
[9] S.N. Jayasinghe, M.J. Edirisinghe, D.Z. Wang: Nanotechnology Vol. 15 (2004), p. 1519
[10] D.Z. Wang, M.J. Edirisinghe, S.N. Jayasinghe: J. Am. Ceram. Soc. Vol. 89 No.5 (2006), p. 1727
[11] W.D Teng., Z.A. Huneiti, W. Machowski, J.R.G. Evans, M.J. Edirisinghe, W. Balachandran: J. Mater. Sci. Lett. Vol. 16 (1997), p.1017
[12] K. Balasubramanian, S. N Jayasinghe., M. J. Edirisinghe: Int. J. Appl. Ceram. Technol. Vol. 3 No.1 (2006), p. 55
[13] K. Fujihara, A. Kumar, R. Jose, S. Ramakrishna, S. Uchida: Nanotechnology Vol. 18 (2007), paper No. 365709
[14] Q. Z. Chen, A. R. Boccaccini, H.B. Zhang, D.Z. Wang, M.J. Edirisinghe: J. Am. Ceram. Soc. Vol. 89 No.5 (2006), p. 1534