Andrzej Krupa,
Arkadiusz Tomasz Sobczyk,
*Anatol Jaworek

Surface Properties of Plasma-Modified Poly(vinylidene fluoride) and Poly(vinyl chloride) Nanofibres

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

*Institute of Physics,
Pomeranian Academy in Słupsk,
ul. Arciszewskiego 22, 75-200 Słupsk, Poland

Abstract
The paper presents electrospinning technology used for the production of polymer nanofibrous mats. Surface properties of polymer nanofibrous mats electrospun from poly (vinylidene fluoride) (PVDF) and poly (vinyl chloride) (PVC), and modified in dielectric barrier discharge (DBD) are presented. The contact angle of the polymer mats un-modified and modified in DBD generated plasma were compared. The plasma modification decreased the contact angle for water from 134° to 40°, for PVDF, and close to zero in the case of PVC. It was also observed that the contact angle decreased with an increase in the discharge power and discharge time, leading to an improvement of adhesion properties of the mat.

Key words: *nanofibrous mat, electrospinning, plasma modification, poly(vinylidene fluoride), poly(vinyl chloride), dielectric barrier discharge.*

Introduction

Electrospinning is a process of production of fine polymer fibres of submicron diameter by imposing electrical shear stress on the surface of the polymer-solution jet flowing out from a capillary nozzle. The electric field that causes the stress is established by connecting the metal capillary to a high voltage supply, and grounding the counter electrode, which is a collector for the fibres. Polymer fibres of diameter smaller than a couple of hundred nanometers are obtained after evaporation of the polymer solvent. Nowadays electrospinning is the most effective method of the production of polymer nanofibrous mats of relatively uniform density composed of fibres of nearly the same diameter [1, 2]. Most of the papers published on the subject of electrospinning are intended for the production of nanofibres for various nanotechnology applications, with an increasing number of applications in biotechnology [3]. Nevertheless, recently, problems regarding the fabrication of nanocomposite membranes for gas cleaning applications [4 - 9] have also been explored. In order to solve the problem of the filtration of submicron particles, including nanoparticles, spores, bacteria or viruses, for example in industry, the environment and health protection systems, non-woven nanofibrous filtration mats can be used [4]. The significance of the filtration of submicron particles, irrespective of their source, has increased in recent years because they are very dangerous to human health due to the high penetration of such particles to lower airways, and because such particles are extremely difficult to remove by conventional methods.

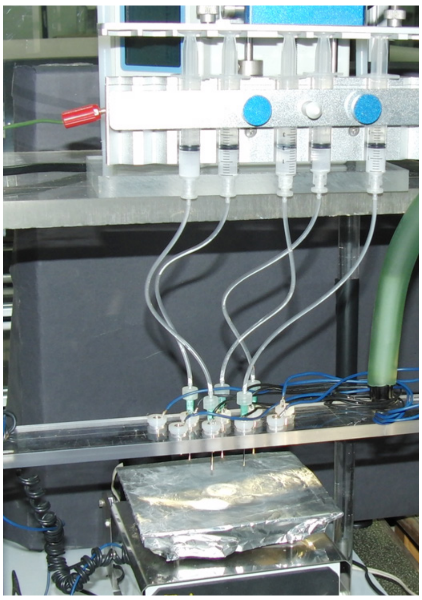

Figure 1. Multinozzle electrospinning system with moving table for polymer non-woven mat production.

In this paper, we used electrospinning technology for the production of nanofibrous filtration mats in the form of non-woven fabric. The goal of the research was to modify the surface properties of polymer nanofibrous mats electrospun from PVDF and PVC, and modified by dielectric barrier discharge (DBD). The hydrophilic properties of polymer mats un-modified and modified in electrically generated plasma (DBD) were compared.

Experimental

Production of polymer nanofibrous mats

A photograph of the multinozzle electrospinning system with a moving table for the production of a polymer non-woven mat is presented in ***Figure 1***. A polymer solution was supplied to the nozzles using a Fusion 200 High Precision Dual syringe pump with a 10 syringe support (Chemyx Inc, USA). Each capillary nozzle, which was made from a metal hypodermic needle with an outer diameter of 0.5 mm was connected to a positive voltage source (DC power supply, SPELLMAN SL300 30kV, USA). During the process of electrospinning, the polymer jet flowing out from the capillary nozzle was elongated, forming a thin thread, which became thinner due to solvent evaporation. In order to increase the surface of the mat produced, a multinozzle system was used in the experiments. A plume of polymer fibres produced by electrospinning from a single nozzle and multinozzle system is presented in ***Figure 2***. Two passive

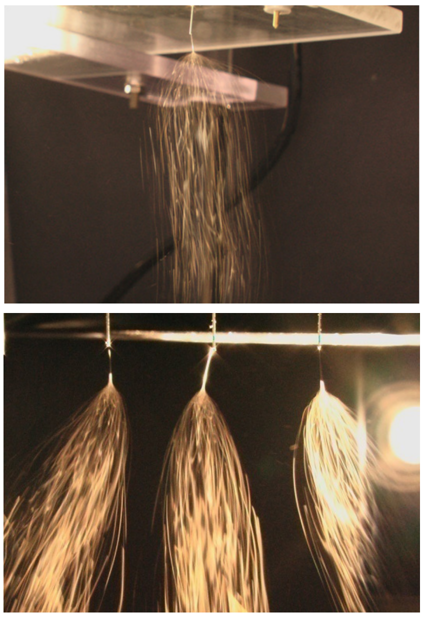

Figure 2. Single nozzle and multinozzle electrospinning plumes (PVDF for non-woven mat production) - exposure 1/50 s)

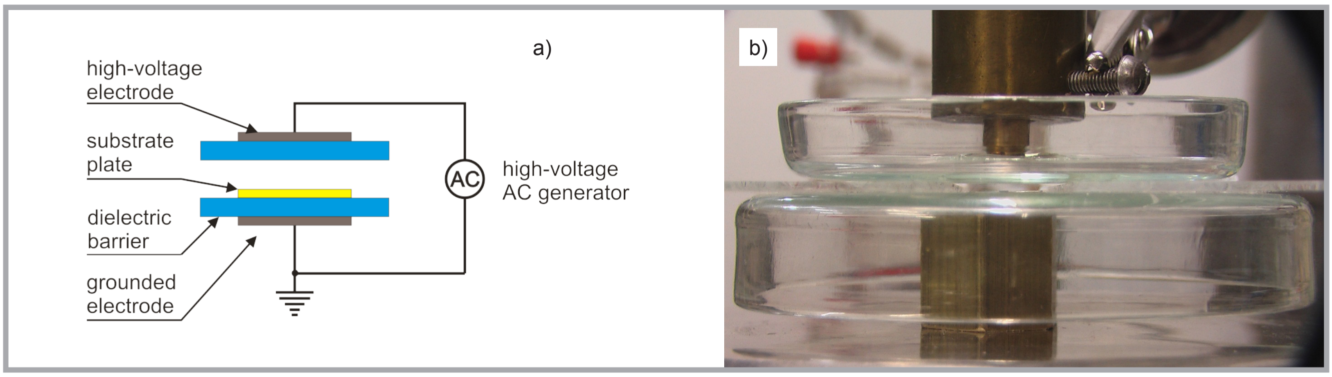

***Figure 3.** Experimental setup for plasma modification of a nanofibrous mat by DBD a) schematic, b) photograph of plasma reactor.*

nozzles were placed on both sides of the nozzles row in order to make the electric field more uniform and abate the effect of electrostatic repulsion of the fibres. The electrospun fibres were deposited onto a flat collector (square metal plate of 15 cm edge) covered with a thin aluminum foil. The collector was placed on a grounded, horizontal table, which was periodically turned 90° in order to obtain a uniform fibrous deposit. The distance between the nozzle tip and table was about 120 mm. The nanofibre mats were electrospun from poly(vinyl chloride) (PVC) and poly(vinylidene fluoride) (PVDF) polymers. The molecular weight of the PVC and PVDF used in the experiments was 233.0 and 455.0 kDa, respectively. Both polymers were purchased from Sigma-Aldrich (USA). The PVC was dissolved in a 1:1 dimethylformamide (DMF) and tetrahydrofuran (THF) mixture by stirring at room temperature to obtain a 9% solution. A 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. DMF, THF and acetone were purchased from CHEMPUR, and DMAC from Sigma-Aldrich (USA). The electrospinning was carried out at room temperature 20 ± 1 °C and a humidity of 45 - 50%. The flow rate of the polymer solutions was 1 ml/h, and the voltage was 12 and 14 kV for PVC and PVDF, respectively.

The morphology of the nanofibrous filtration mats produced by electrospinning was tested under a Zeiss EVO 40 scanning electron microscope (SEM) (Germany) and NIKON Eclipse TS-100F (Japan) optical microscope. The diameter of the PVC and PVDF fibres produced was in the range of 600 to 800 nm, and 400 to 600 nm, respectively.

In this specific experimental case, samples of fibres for plasma treatment were collected onto microscopic cover glasses 0.15 mm thick and with a surface of 324 mm^2, placed on the aluminium collector.

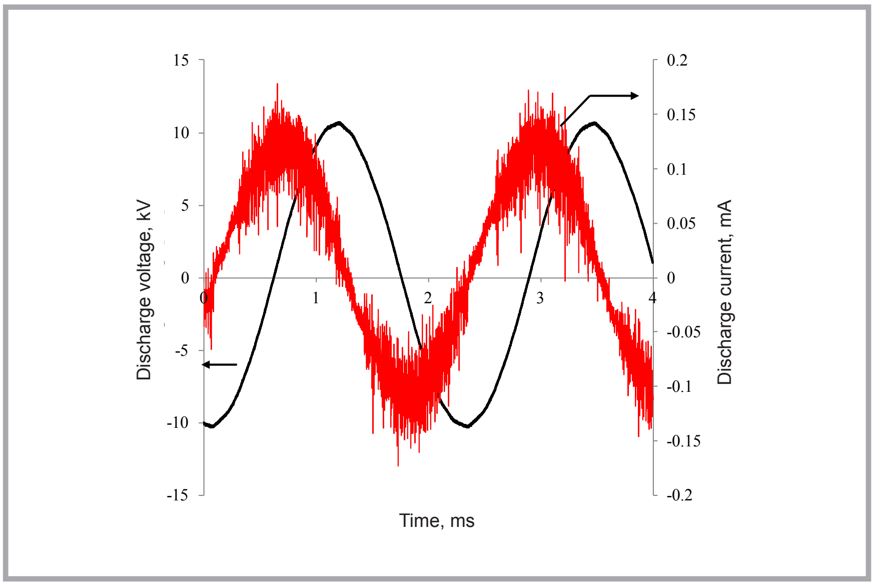

***Figure 4.** Example of waveforms of the excitation voltage and discharge current during DBD plasma treatment of a PVDF mat. Frequency 500 Hz. Discharge power 1.95 W.*

Plasma treatment

Due to their chemical and mechanical resistance, PVDF and PVC are often used as materials for nanofibrous mats. Such mats are also considered as a carrier of low – temperature nanoparticle catalyst, for example Ag, Au, Pd, Cu, Ni and metal oxides (MgO, TiO_2, Al_2O_3 etc.) [10]. A material with a large specific surface area and high adhesion to different media (particles) have to be used for this purpose. The morphology of a nanofibrous mat with fine fibres and small gaps between them guarantees effective interactions between the reactant and catalyst deposited onto these nanofibres; such a nanocomposite material is valuable for continuous-flow chemical reactions or biological processes [11]. Because PVC and PVDF have hydrophobic properties, the deposition of nanoparticles from water suspension is ineffective. The modification of the contact angle of such mats is therefore required. In this paper dielectric barrier discharge was tested as a technology for surface property modification.

DBD is a type of electrical discharge generated between two plane-parallel or co-axial cylindrical electrodes that are supplied with alternating high voltage of high frequency. For effective DBD generation, the electrodes are additionally separated with a solid dielectric barrier placed on one of the electrodes, on both, or in the middle between them. The DBD used for the plasma treatment of nanofibrous mats was generated in a reactor formed by two circular flat electrodes made of copper, with a surface area of 165 mm^2 supplied with alternating high voltage of high frequency in the range from 0.5 to 2.3 kHz. A scheme of the setup used for DBD generation and a pho-

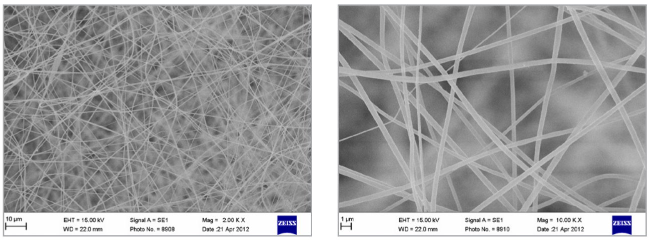

Figure 5. *SEM images of an unmodified nanofibrous mat from PVC for two magnifications.*

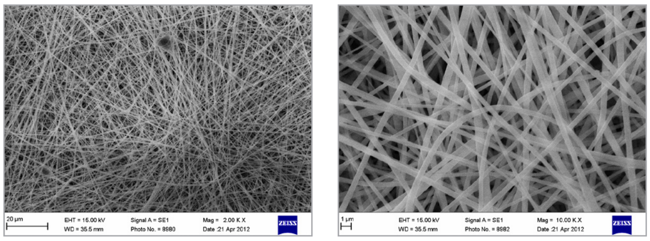

Figure 6. *SEM images of a nanofibrous mat from PVC after DBD plasma treatment for 120 s. Discharge power 4 W.*

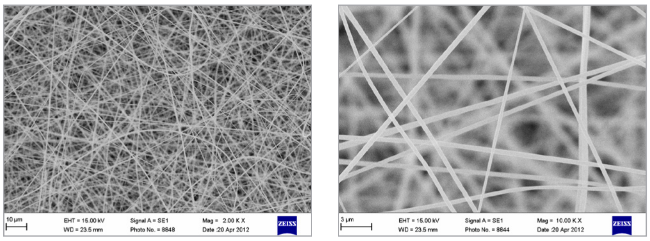

Figure 7. *SEM images of an unmodified nanofibrous mat from PVDF for two magnifications.*

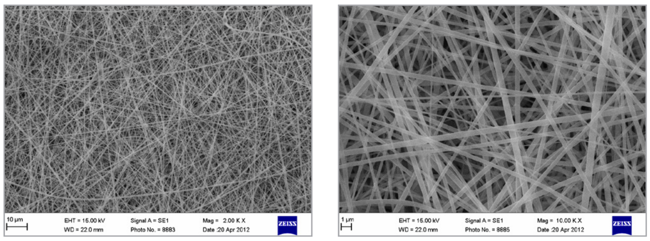

Figure 8. *SEM images of nanofibrous mat from PVDF after DBD plasma treatment for 120 s. Discharge power 4 W.*

tograph of such a system are shown in ***Figure 3***. An example of the waveforms of excitation voltage and discharge current during DBD plasma treatment of the PVDF mat is presented in the ***Figure 4***. The electrodes were supplied from an HV power source - Trek Model PMO4015A. The RMS value of the supply voltage varied from 7.3 to 8 kV, depending on frequency. The discharge current was set between 0.17 and 0.6 mA, and the discharge power was in the range from 1.2 to 5 W. The noise signals superimposed on the current sinewave is due to many faint streamers generated in the interelectrode gap. The phase shift between the current and voltage waveforms is about 90°, which indicates the capacitive character of the discharge with only low energy dissipated for the heating of gas and dielectrics.

Two glass sheets of a thickness of 1.8 mm covering each electrode were used as the dielectric barrier. The gap between these glass sheets was about 0.6 mm. For the plasma treatment microscopic glasses with deposited polymer nanofibrous mats were placed onto the lower glass. The plasma treatment lasted 60 or 120 s. The morphology of nanofibrous mats deposited onto microscopic glasses before and after the plasma treatment was investigated using a scanning electron microscope - Zeiss EVO 40 (Germany). The elemental composition of the fibrous mats was determined by the Energy-Dispersive Spectroscopy method (EDS) using a spectrometer - Bruker Quantax 400 (USA), with a detector - SDD X - flash 5010, 10 mm^2, 125 eV. Due to the limited sensitivity of this detector, only the elements of atomic abundance higher than 0.1 at.% were identified. Due to the polymeric composition, small diameter of individual fibres, and small matt thickness (tens of µm), the measuring signal was collected from the depth of electron beam penetration, which is usually up to about 5 µm.

The static contact angle for water was measured using the sessile drop method. Measurements were carried out at a temperature of 20 °C. A distilled water drop of 10 µl was placed on the surface matt using a pipette. For each sample, four drops were placed at different locations on the mat and the mean value from this measurement was used as a point of the presented in ***Figure 12*** (see page 39).

Results

SEM images of unmodified and DBD plasma-modified nanofibrous mats are shown in ***Figures 5 – 8***, with each sample presented for two magnifications. Nanofibrous filtration mats produced by the electrospinning method consist of fibres of a diameter in the range from 400 to 800 nm, estimated from the photographs. The mats produced by electrospinning from PVC and PVDF were of high porosity and uniform density, which allowed to obtain uniform pressure drop distribution over the entire surface of the filter. No significant changes in fibre morphology were observed under a SEM after plasma treatment. The only changes noticed was an increased packing of the fibres.

EDS measurements showed that the most abundant elements in un-treated fibres (besides carbon) were chlorine Cl (30 at.%) in PVC, and fluorine F (55 at.%) in PVDF. Changes in the atomic concentration of the three main elements of electrospun nanofibres: carbon, oxygen and chlorine in PVC, and carbon, oxygen and fluorine in PVDF, after plasma treatment in air for a time of 60 and 120 s versus the discharge power, are shown in ***Figures 9*** and ***10*** (see page 38), respectively. After plasma treatment for 120 s, the content of Cl and F decreased from 30 to 28.5% and from 55 to 50%, respectively. The percentage of oxygen increased from 0.5 to 1.6% and from 0.6 to 1.1%, for PVC and PVDF, respectively, which is probably an effect of the reaction of oxygen radicals with the polymers, and it can be supposed that oxygen is responsible for the increased hydrophilic properties of the polymer mats. It was shown in literature that plasma generated by dielectric barrier discharge incorporate oxygen into its molecular structure and creates some oxygen-containing functional groups on the PVC and PVDF surface, which improves the wettability of the surface [12, 13].

Wetting properties of the mats were investigated by measuring the contact angle for distilled water before and after plasma treatment. The contact angle formed by a drop of distilled water raw and plasma-modified nanofibrous mats

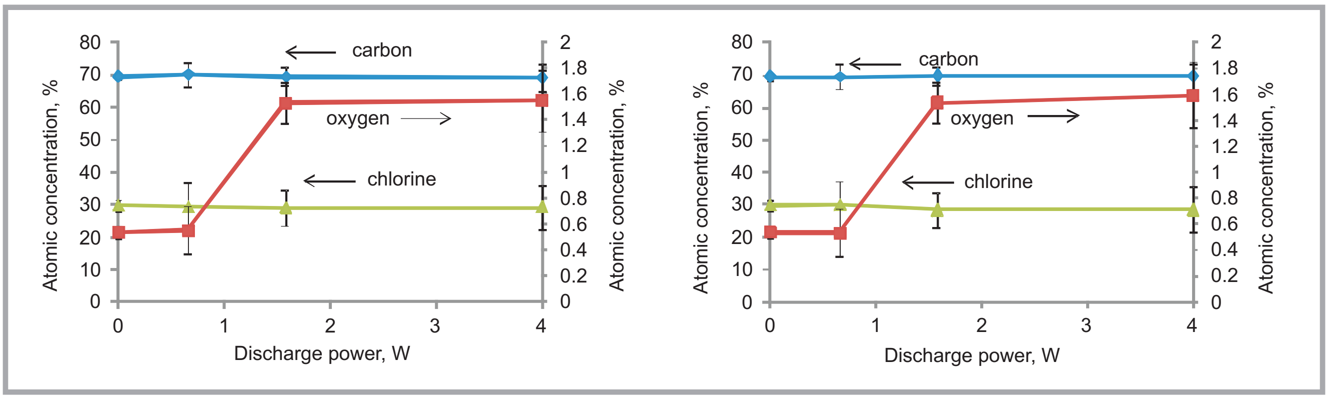

__Figure 9.__ Changes in atomic concentration of carbon, oxygen and chlorine in PVC electrospun nanofibres after a) 60 s and b) 120 s of plasma treatment, measured by EDS.

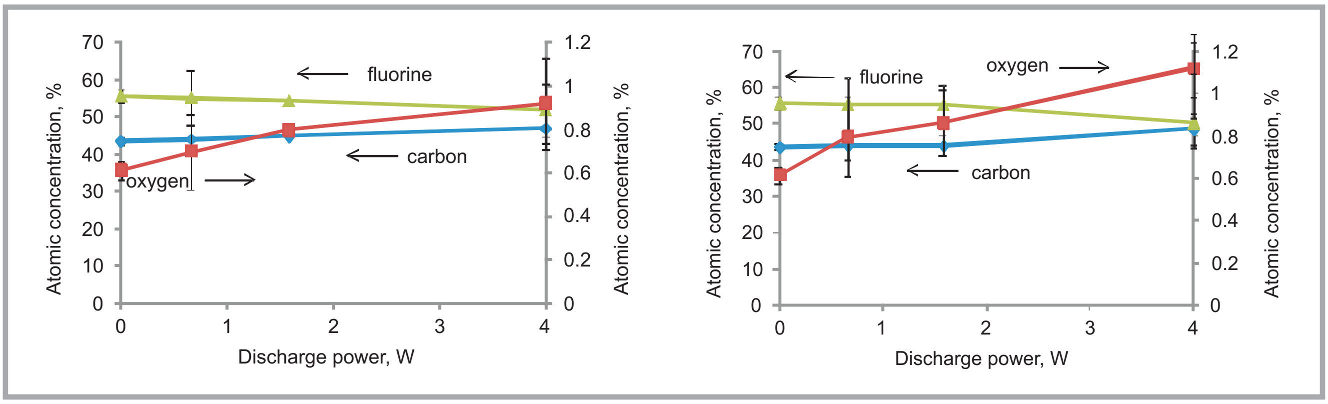

__Figure 10.__ Changes in atomic concentration of carbon, oxygen and fluorine in PVDF electrospun nanofibres after a) 60 s and b) 120 s of plasma treatment, measured by EDS.

was determined from photographs by the method of sessile drop. Examples of droplets settled onto a PVDF mat for various contact angles are shown in ***Figure 11***. The effect of discharge power on the magnitude of the contact angle is shown in ***Figure 12***. Each measuring point is the mean value from 4 measurements made for each fibrous sample. For example, the contact angle to the nanofibrous PVDF mat decreased from about 130 to 20° after plasma treatment in DBD with a power of 4 W for 120 s (***Figure 12.a***). The contact angle to the PVC (***Figure 12.b***) nanofibrous mat decreased from about 130 to below 2° after plasma treatment in DBD with a power of 4 W for 120 s. For the discharge lasting 60 s and for a power of 5 W the lowest value of the contact angle was about 67°.

In DBD in air, the microstructure (porosity) of the fibre surface is modified due to positive ion bombardment, whereas due to the reaction of polymer with negative ions of oxygen, the physical and chemical properties of the polymer are changed as an effect of forming polar oxygen groups, which increase the wettability of the material. A lower contact angle gives information about increased surface energy, which results in increased adhesion force [14, 15]. Nanofibrous filtration mats can be applied for the removal of nanoparticles and submicron particles from gases, such as spores, bacteria, viruses or other inorganic contaminants in air-conditioning systems. Plasma-modified filtration mats of a smaller contact angle can be used for the filtration of fine water aerosol.

Summary

The paper presents electrospinning technology used for the production of nanofibrous mats and an experimental investigation of the modification of PVDF and PVC electrospun nanofibrous mats using low-temperature plasma generated by Dielectric Barrier Discharge (DBD). The effect of the discharge power and time of plasma treatment on the wettability of the mats was determined. A nanofibrous filtration mat produced by the electrospinning method consists of fibres of a diameter in the range from 400 to 800 nm. The mats produced by electrospinning from PVC and PVDF were of high porosity and uniform distribution, which allows to obtain a uniform pressure drop distribution over the entire surface of the filter.

Changes in the water contact angle occurring after DBD plasma treatment were observed. With an increase in the discharge power and discharge time, the contact angle decreased, resulting in an improvement in adhesion properties of the mat. The water contact angle for the PVDF electrospun nanofibre mat was initially about 134°, but after plasma treatment, for a discharge power of about 2.5 W and time of 60 s, it decreased to 40°. In the case of the plasma treatment of PVC for 60 s, the electrospun nanofibres mat lost its hydrophobic properties.

No significant changes in the morphology of the nanofibre mat were observed after plasma treatment. The only morphological effect in the experiments noted was the increased packing of fibres. Slight changes in the atomic concentration of carbon, oxygen and chlorine for PVC mats and fluorine for PVDF mats were also observed. After plasma treatment for 120 s, the content of Cl and F decreased from 30 to 28.5% and from 55

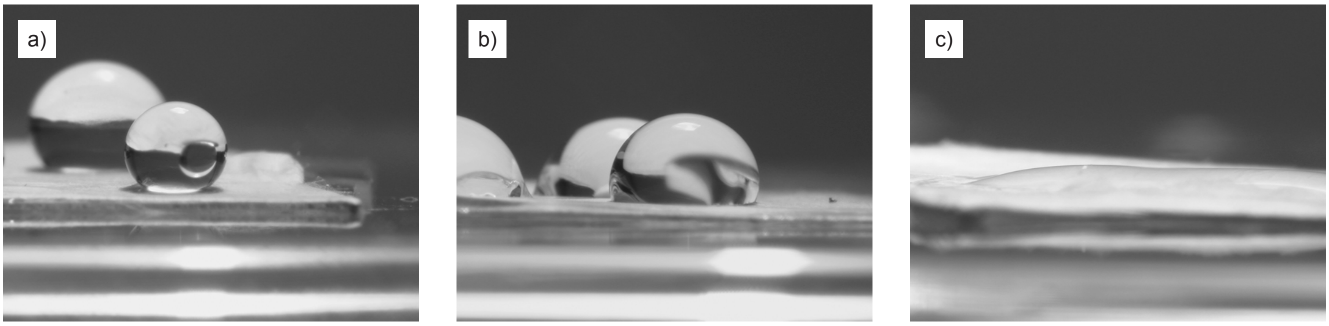

***Figure 11.** Distilled water droplets on a PVDF nanofibrous mat: a - raw mat, b - plasma modified mat for 60 s, c - plasma modified mat for 120 s. Discharge power 4 W; a) power = 0 W (untreated), b) discharge power = 4 W, time = 60, c) discharge power = 4 W, time = 120 s.*

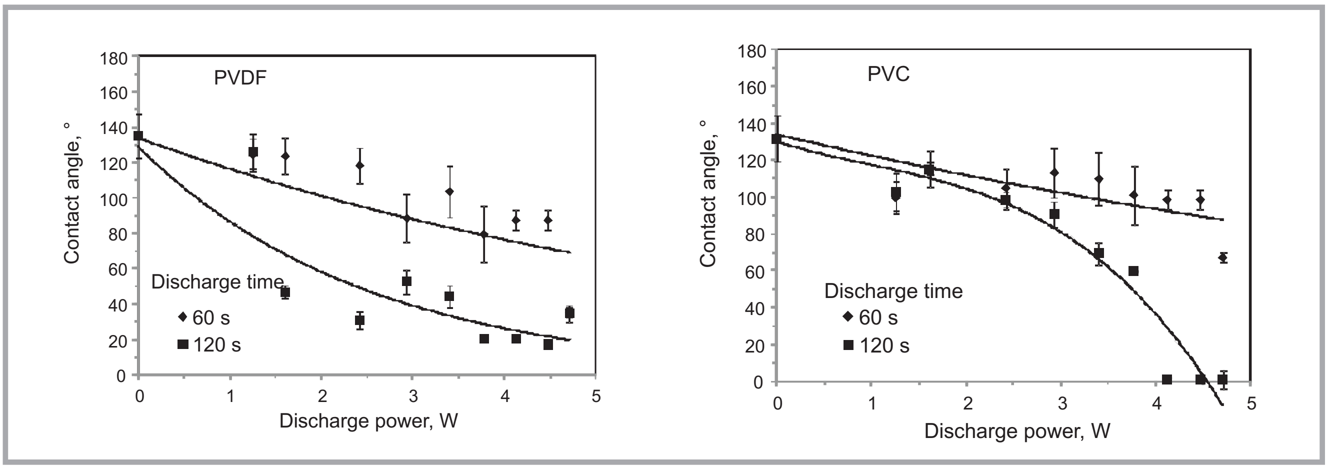

***Figure 12.** Changes in contact angle formed by a drop of distilled water on a plasma-treated polymer nanofibrous mat vs. discharge power, for double plasma treatment.*

to 50%, respectively, while the percentage of oxygen increased from 0.5 to 1.6% and from 0.6 to 1.1% for PVC and PVDF, respectively.

Acknowledgement

The research was supported by the Polish Ministry for Science and Higher Education within the project No. 4169/B/T02/2009/37.

References

1. Doshi J, Reneker DH. Electrospinning process and application of electrospun fibers. *Journal of Electrostatics* 1995; 35: 151-160.
2. Ramakrishna S, Fujihara K, Teo W E, Lim T Ch, Ma Z. An introduction to electrospinning and nanofibers. In: *Word Scientific* 2005, Singapore.
3. Teo WE, Ramakrishna S. A review on electrospinning design and nanofibre assemblies *Nanotechnology* 2006; 17: R89-R106.
4. Ramakrishna S, Fujihara K, Teo W E, Yong T, Ma Z, Ramaseshan R. Electrospun nanofibers: solving global issues. *Materials Today* 2006; 9: 40-50.
5. Jaworek A, Krupa A, Lackowski M, Sobczyk AT, Czech T, Ramakrishna S, Sundarrajan S, Pliszka D. Nanocomposite fabric formation by electrospinning and electrospraying technologies. *Journal of Electrostatics* 2009; 67, 2-3: 435-438.
6. Jaworek A, Krupa A, Lackowski M, Sobczyk AT, Czech T, Ramakrishna S, Sundarrajan S, Pliszka D. Electrospinning and electrospraying techniques for nanocomposite non-woven fabric production. *Fibers and Textiles in Eastern Europe* 2009; 17, 4: 77-81.
7. Jaworek A, Krupa A, Sundarrajan S, Pliszka D, Ramakrishna S. Mechanical Properties of an Electrospun Polymer Fibre-Metal Oxide Nanocomposite Mat. *Fibres & Textiles in Eastern Europe* 2012; 20, 2: 25-27.
8. Neubert S, Pliszka D, Góra A, Jaworek A, Wintermantel E, Ramakrishna S. Focused deposition of electrospun polymer fibers. *Journal of Applied Polymer Science* 2012; 125: 820-827.
9. Sundarrajan S, Pliszka D, Jaworek A, Krupa A, Lackowski M, Ramakrishna S. A novel process for the fabrication of nanocomposite membranes. *Journal of Nanoscience and Nanotechnology* 2009; 9, 7: 4442-4447.
10. Sundarrajan S, Ramakrishna S. Fabrication of nanocomposite membranes from nanofibers and nanoparticles for protection against chemical warfare stimulants. *Journal of Material Science* 2007; 42: 8400–8407.
11. Naim MN, Bakar NFA., Iijima M, Kamiya H, Lenggoro IW. Electrostatic Deposition of Aerosol Particles Generated from an Aqueous Nanopowder Suspension on a Chemically Treated Substrate. *Japanese Journal of Applied Physics* 2010; 49: 06GH17:1-6.
12. Li R, Chen J. Surface modification of poly (vinyl chloride) by long-distance and direct argon RF plasma. *Chinese Science Bulletin* 2006; 51, 5: 615—619.
13. Tendero C, Tixier C, Tristant P, Desmaison J, Leprince P. Plasma surface modification of poly vinyl chloride for improvement of antibacterial properties. *Biomaterials* 2006; 27: 44–51.
14. Wolf R, Sparavigna AC. Role of Plasma Surface Treatments on Wetting and Adhesion, *Engineering* 2010; 2: 397-402.
15. Balazs DJ, Hollenstein C, Mathieu HJ. Surface modification of poly(vinyl chloride) intubation tubes to control bacterial adhesion: teflon-like and pluronics. *European Cells and Materials* 2002; 3. Suppl. 1: 7-8.

Received 03.12.2012 Reviewed 03.07.2013