PLASMA MODIFICATION OF POLYACRYLONITRILE POWDER OR SOLUTION PRIOR ELECTROSPINNING

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Abstract

The process of electrospinning can be influenced strongly by a change in the electrical conductivity of the spinning solution. Plasma-mediated modification of organic polymer powders is known to alter their surface polarity. The introduction of plasma-modified powders into the liquid phase may introduce novel routes for charge formation within the resulting dispersion. In addition, plasma generated directly within the spinning solution is also capable of producing an ample amount of charged species, contributing to increased conductivity. The magnitude of these effects is still rather unexplored, especially for non-aqueous solutions which are used in electrospinning recipes. In the presented work, three distinct approaches of plasma modification were investigated for the preparation of electrospun polyacrylonitrile (PAN) mats from PAN/dimethylformamide (DMF) solution. PAN powders were modified either by Ar/N_2 radiofrequency jet or by dielectric surface barrier discharge in air, both operated at atmospheric pressure. In addition, the same RF jet was used to modify the PAN/DMF solution. A thorough analysis of achieved changes on treated powders, solution as well as electrospun fibers was performed, including confocal microscopy, SEM, EDS, XPS, surface free energy evaluation of powders, and solution viscosity, zeta potential, and electrical conductivity. Modified powders exhibited increased oxygen content, mainly on their surface. The polar component of the surface free energy was higher for the dielectric barrier discharge modification. Prepared solutions had higher viscosity values, and higher conductivity, but lower values of zeta potential. The electrospinning process resulted in fibers with slightly bigger diameters than the reference.

Keywords: Plasma modification, polyacrylonitrile, PAN nanofiber, DCSBD, electrospinning

Abbreviations: Polyacrylonitrile (PAN); dimethylformamide (DMF); diffuse coplanar surface barrier discharge (DCSBD), radiofrequency jet (RF jet); scanning electron microscopy (SEM); confocal microscopy (CM); energy dispersive spectroscopy (EDS); X-ray photoelectron spectroscopy (XPS); contact angle (CA); surface free energy (SFE)

1. INTRODUCTION

Polyacrylonitrile has found wide applications in the field of textile and fibrous material production [1], polymer electrolyte precursors for lithium batteries [2], ultrafiltration membranes [3], or air filters [4]. Various approaches of electrospinning and post-processing of the spun fibers allow the PAN as the precursor for the production of

carbon fibrous materials with enhanced physical properties [4,5]. In this work, the effect of plasma modification on PAN powder or PAN/DMF solution was investigated. Plasma modification can deliver a functionalization of PAN powder surface, providing different physical-chemical properties of solution with the shift of the working conditions for the electrospinning to the more economical range (necessary applied voltage). The ultimate goal was to improve the quality of electrospun PAN nanofibers, which are intended to be used for further preparation of 3D hybrid materials for photoelectrochemical decomposition of the water. This process would involve the carbonization/calcination of prepared PAN mats, thus their quality is essential for a favorable output.

2.   MATERIALS AND METHODS

2.1   Materials

PAN (Mr 150 000) was purchased from Sigma Aldrich, DMF (p.a.) by Penta Chemicals. SFE liquids: glycerol (99.5 % p.a.), ethylene glycol (p.a.), and formamide (p.a.) were provided via Penta Chemicals. 1-bromonaphthalene (≥ 95 %) and diiodomethane (stabilized, for synthesis) were purchased via Sigma Aldrich. Deionized water (conductivity 18.18 µS/cm at 13 °C) was prepared at Masaryk University using RO 1-1CC unit by MEMSEP Ltd. For XPS, EDS, and SEM, copper tape for SEM was purchased at Edlin. Substrates for CA and SFE were microscopic slides from Paul Marienfeld.

2.2   Methods

2.2.1 Plasma modification

Plasma modification of PAN powders and PAN solutions was processed using an atmospheric RF jet and DCSBD device. RF jet was operated with the flow of the argon/nitrogen mixture, powered by the frequency of 13.56 MHz and applied power within the interval of 100-150 W. RF jet was used to modify sole PAN powder, as well as to modify PAN dispersed in DMF solution. In the first case, PAN powder was placed in a polypropylene container with the orifice on the top for the jet positioning. The gas flow mixed the powder with the plume jet of generated plasma. In the second case, the solution was placed in a glass vial with the RF jet nozzle placed above the solution level. The DCSBD plasma was operated at atmospheric pressure ambient air. It was powered with a frequency of 15 kHz with a power range of 300-350 W. The powder was sifted over the electrode and covered with a polycarbonate plate to prevent material loss due to the generated ionic wind. For each plasma method, treatment times of 10 s, 30 s, and 60 s were investigated.

2.2.2 Solution preparation

Pristine and plasma-modified PAN particles were placed into the DMF for 8.5 wt% solution preparation. The mixture was placed on the magnetic stirrer and homogenized for 2 h at 800 rpm. For the RF jet-modified solutions, the solution was plasma-modified directly after the mixing process finalization.

2.2.3 Electrospinning

The electrospinning procedure was placed in a semi-closed box using needle-to-plate geometry. The automatic pump was dosing the PAN/DMF solution using the 0.25 ml/h. The ring electrode was placed around the body of the syringe. The applied power was varied for stable fiber production using modified solutions. The distance between the needle tip and the counter electrode (aluminum foil on the plastic plate) was 15 cm. Electrospinning time was 30 min. The PAN/DMF solutions used for mat preparation were 2 days old.

2.2.4 Material characterization

The surface topography characterization was carried out via CM (Olympus LEXT OLS4000 3D Laser microscope with LEXT software) and SEM (Tescan Mira II). Modified and reference powders were compared,

as well as electrospun fiber mats. For SEM, samples were placed on the copper tape and covered by 40 nm Au/Pd layer using magnetron sputtering as a charging prevention. Chemical changes of modified materials were studied with EDS (Tescan Mira II) and XPS (Kratos Axis Supra spectrometer, equipped with a monochromated source, Al/Ag anode). The EDS gave information about the material volume changes in elemental composition. XPS provided information mainly on surface chemistry changes induced by plasma modification. The EDS measurement conditions were: working distance 15 mm, voltage 10 kV, beam intensity 12.0, magnification 1000×. High-res XPS spectra were acquired with a charge neutralization overcompensated mode at 20 eV. The spectra fitting was processed in CasaXPS software using subtraction of the Shirley-type background to obtain individual Gaussian-Lorentzian-shaped components with a fixed Gaussian-Lorentzian percentage of 30%. Binding energy values were taken from the literature. The Zeta potential of PAN/DMF solutions was measured by dynamic light scattering instrument Litesizer DLS 500 by Anton Paar using the 6 ml solution with 20 mg of unmodified/modified PAN. The resulting value is averaged from three measurements. Electrical conductivity was measured for 8.5 wt% PAN/DMF solutions using a Mettler Toledo Five EasyPlus Conductometer with a stainless-steel probe calibrated with 84 µS/cm standard solution. The measurement times were 0 h (directly after the preparation), 1 h, 2 h, 3 h and 4 h. For each time, three measurements were taken to get the final average value. The viscosity measurement was done by Anton Paar Modular Compact Rheometer 102 using a plate-plate configuration with a plate diameter of 20 mm, distance of 0.1 mm, at 25 °C. The shear rate was stated to 100 points. Powder surface free energy was measured by the sessile droplet method (SEE system, Advex Instruments). Before the modification, powders were fixed on glass plate using double-sided scotch tape. The droplet volume was 2 µl. CA for DMF was calculated from five droplets, and SFE was calculated from three droplets using a six-liquid Owens Wendt regression model.

3.   RESULTS AND DISCUSSION
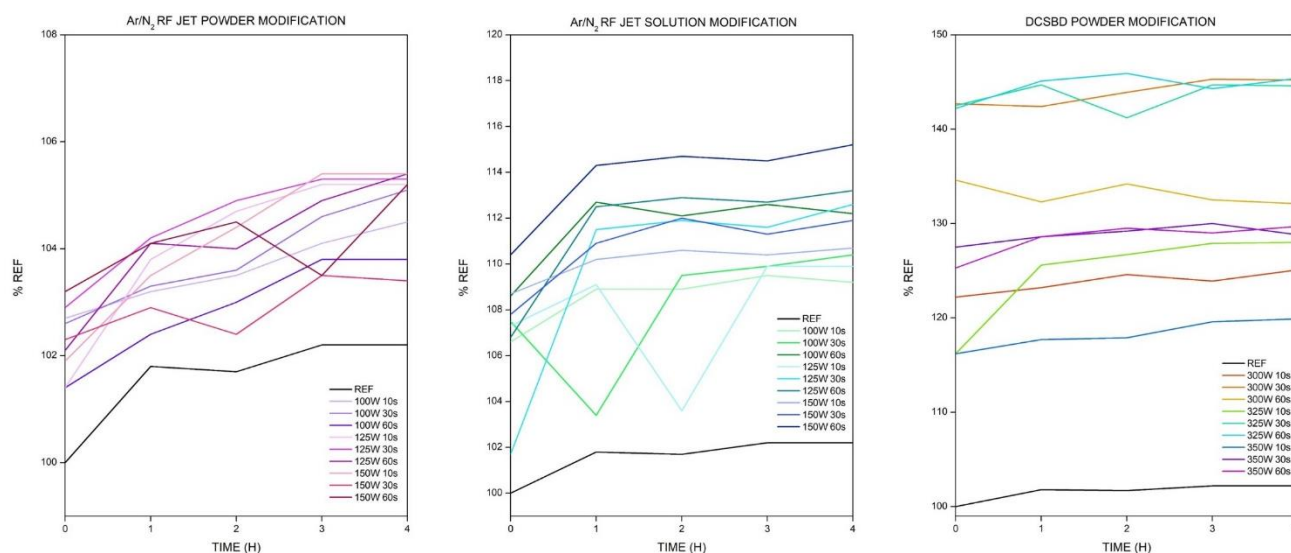
Figure 1 Evolution of PAN/DMF relative conductivity over time from the modification for all three plasma treatment methods. The initial reference conductivity is set to 100%.

An increase in the conductivity of freshly prepared solutions was observed for all types of plasma modification (see **Figure 1**). The conductivity continued to gradually increase with the time from the treatment. The most pronounced effect exhibited DCSBD. Treatment at 325 W resulted in an immediate conductivity increase of 27%, 41%, and 45% for 10 s, 30 s and 60 s modifications, respectively. The presence of conductivity growth suggests the existence of ongoing secondary chemical reactions. The viscosity of the solutions was higher for plasma-modified samples. DCSBD showed a trend of rising viscosity value with the modification time. The RF

jet did not provide any correlation between the viscosity and applied power or modification time. The highest viscosity was measured for the RF jet. The reference sample exhibited values under 120 mPa.s, and samples with modified powders varied within the interval of 120-150 mPa.s. The RF jet modified solution with 150 W (60s) had the highest viscosity ≈ 170 mPa.s. This may be caused by the increase of the solution temperature during the treatment, leading to evaporation of some DMF (the temperature varied from 33 to 64 °C) or conformation changes [7]. The stability of the solutions and the charge of the particles were evaluated by zeta potential measurement. The zeta potential of plasma-modified samples was shifted to a more positive value. The reference value of -9.3 mV increased slightly after the RF jet powder modification to -9.0 mV and -8.0 mV for 100 W (60 s) and 150 W (60 s), respectively. RF jet modification of PAN/DMF solution provided considerable zeta potential change to -1 mV. DCSBD changed zeta potential to -2.2 mV and -0.8 mV for 325 W (30 s) and 325 W (60 s), respectively. The change of the zeta potential (and thus the particle mobility) is connected to the polar group presence on the PAN particles. The values between ± 10 mV are frequently connected to phenomena such as low stability, coagulation, and sedimentation, these were not observed. The lack of such behavior can be attributed to the presence of van der Waals bonds [8] on the PAN material. As stated below, the increased representation of the SFE polar component is getting pronounced for DCSBD modification, however, no sample exhibited a higher value of this component in comparison to the van der
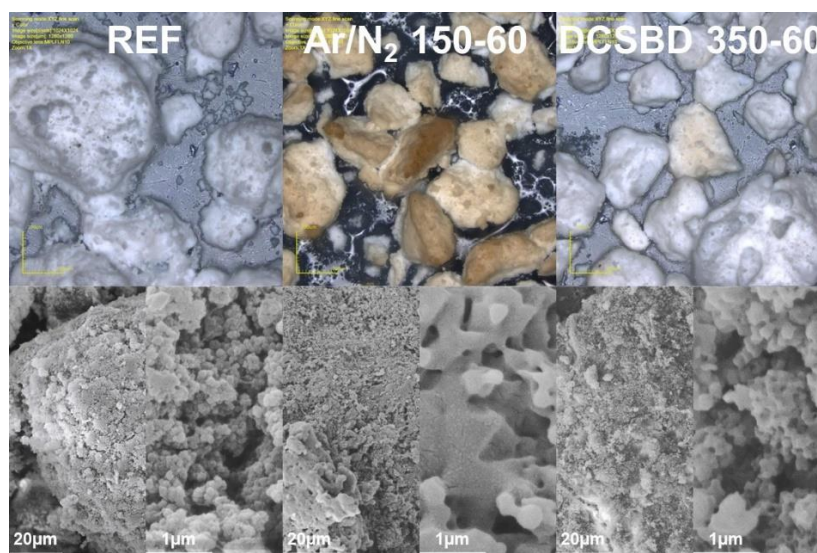
Figure 2 CM (top row) and SEM (bottom row) topography for REF sample, Ar/N$_2$ RF jet powder modified sample and DCSBD modified sample: SEM pictures: on the left mag. 2k, on the right detail mag. 50k.

Waals component. Confocal microscopy revealed the change of the particle surface color after the exposition to plasma for 60 s. **Figure 2** shows the PAN powder turned from white to dark yellow after RF jet modification. The color change appears also after the DCSBD modification but was not as remarkable as for the RF jet. In [9], the thermal coloration reaction of PAN is explained by the presence of tertiary C-H structures. **Figure 2** shows the microstructure of the PAN powder particles in SEM with a significant change of shape for Ar/N$_2$ RF jet plasma modification, especially for 50k magnification. This can be connected to the locally increased temperature during the modification that led to the melting of the material. For shorter exposure times the effect was less pronounced. On the other hand, DCSBD modification did not affect powder's topography as the RF jet. EDS analysis showed the changes mainly in the oxygen content. In comparison to reference with O of 2.1 at%, RF jet modification using 150 W for 60 s has 3.6 at%. Samples modified by DCSBD exhibited an increase with increasing time of the exposure as well as with the increase of applied power. Namely from 4.2 at% to 6.1 at% for 325 W (varied from 10 s to 60 s, respectively) and from 5.7 at% to 7.4 at% for 60 s (varied from 300 W to 350 W, respectively). This can be connected to the bulk material changes and oxidation. A more surface-sensitive XPS analysis confirmed oxygen content increase. The reference sample showed

4.85 at% of oxygen. The highest oxygen of 23.5 at% was measured for DCSBD 325 W (60 s). The O content has increased with a longer DCSBD modification time. In contrast, RF jet modification provided its highest O content of 18.3 at% for the lowest applied power 100 W (60 s). For 150 W (60s) it decreased to 15.5 at%. Measured carbon and nitrogen content on the surface varied more significantly when compared to their variation within the material volume. While EDS spectra showed the C content within the interval of 71.4 to 78.6 at%, the XPS spectrum showed 77.6 at% for the reference and the interval of 59,4 to 68,2 at% for plasma-modified samples. This observation indicates the presence of surface-selective oxidation of PAN particles, leading to C=O/C-N=O/O-C=O groups production [2,3,5,6,7,8]. The extreme case of oxidation is the thermal cyclization of PAN where the C≡N group changes to C=N group. The process of cyclization is recognizable by the color change [9,10]. These chemical changes produce more polar groups on the top of the PAN surface, which in turn would affect the wettability properties [16], [17]. For DCSBD, a polar component of the surface free energy had enhanced representation next to the van der Waals component. This effect is for RF jet not as strong as for DCSBD. The less significant change in the polar component of surface free energy can be connected to the lower values of oxygen content on the particle surface that is discussed below as the reason for the new polar group presence on PAN material. SFE for reference is 49 mJ/m^2. For RF modification it was in the interval 51-61 mJ/m^2 and for DCSBD (except the 60 s modification, where it was 45-50 mJ/m^2) varied from 60 to 64 mJ/m^2. Finally, the impact of solution modification on the electrospinning process was investigated. The necessary voltages for homogeneous filament electrospinning were: 9 kV for reference solution, 8.7 kV for DCSBD 325 W(60 s), 8.3 kV for Ar/N$_2$ RF jet modification of dry powder at 150 W (60 s), and 8.0 kV for Ar/N$_2$ RF jet modification of solution at 150 W (60 s). The nanofibers from modified PAN materials had bigger diameters, namely 299, 362, and 295 nm for DCSBD, RF powder, and RF solution modification, respectively. In comparison, the reference fibers had an average diameter of 245 nm. Using RF-modified powder for electrospinning resulted in undesirable beads formation, as visible in **Figure 3**. EDS showed that the content of N was constantly ≈21-22 at% for all spun mats. The content of O was variable, the reference sample has 1.8 at%. In comparison to the reference the DCSBD, RF powder, and RF solution-modified samples contain 2.7at%, 2.9 at%, and 3.2 at%, respectively. This reveals that part of the oxygen atoms was lost in the material during the electrospinning process. The most significant change is for the DCSBD sample from 6.1 at% to 2.7 at%.
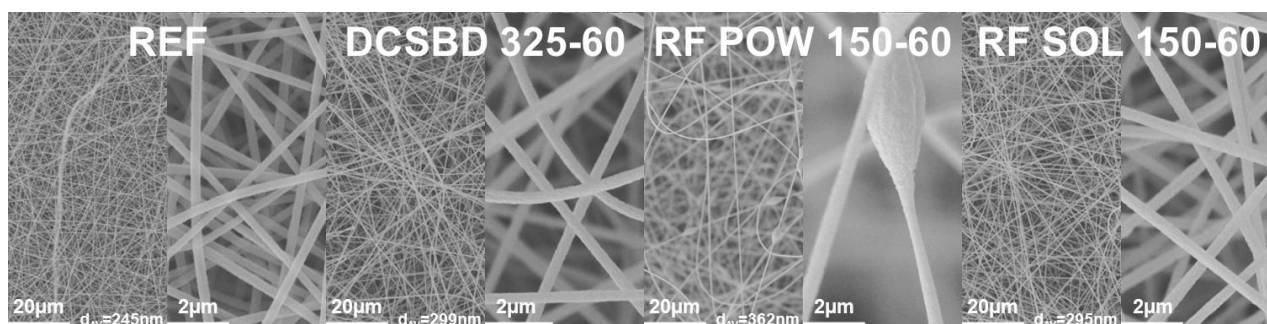
Figure 3 SEM topography for electrospun mats: REF sample; DCSBD 325 W-60 s; Ar/N$_2$ RF jet powder modification 150 W-60 s and Ar/N$_2$ RF jet solution modification 150 W-60 s - on the left mag. 2k, on the right detail mag. 20k.

4. CONCLUSION

The polyacrylonitrile powder was modified using two types of plasma devices, RF plasma jet using a mixture of argon and nitrogen and a dielectric coplanar surface barrier discharge device using ambient air. The DCSBD device provided the powder product with a higher surface oxygen content 23.5 at% in comparison to 4.9 at% for the reference, higher polar component of SFE without the destruction or decomposition of the powder particles. As-prepared solutions exhibited increased conductivity by up to 45%. These solutions are suitable

for electrospinning, producing fibers with a slightly bigger diameter 299 nm. Increased thickness can offer the robustness of the material for further intended application - carbonization.

ACKNOWLEDGEMENTS

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