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Needleless Electrospinning of PAN Nanofibre Mats

Brezigelno elektropredenje PAN nanovlaknatih kopren

Original Scientific Article/*Izvirni znanstveni članek*
Received/*Prispelo* 08-2017 • Accepted/*Sprejeto* 10-2017

Abstract

Polyacrylonitrile (PAN) is one of the few waterproof polymers that can be spun from relatively safe solvents, facilitating the use of PAN nanofibre mats in diverse medical and biological applications, such as tissue engineering and cell growth promotion. PAN, on the other hand, is significantly harder to use in electrospinning than polyethylene glycol and other water-soluble biopolymers. In our recent study, we thus varied spinning and material parameters for PAN dissolved in dimethyl sulfoxide (DMSO) and studied spinnability, as well as the resulting nanofibre mat morphologies, using a "Nanospider Lab" needleless electrospinning machine. The results were examined using confocal laser scanning microscopy and atomic force microscopy. On the one hand, the images show that the relative humidity in the chamber plays a significant role: excessively high values may cause undesired fibre connections between oppositely charged parts of the Nano-spider, creating cotton-candy-like structures that impede the free flow of fibres to the substrate and thus the creation of the desired nanofibre mat. On the other hand, the PAN concentration in the spinning solution is crucial: similar to the electrospinning of other (bio-)polymers, no fibres are formed if the polymer concentration is too low. Third, the PAN material itself affects the nanofibre creation process, illustrating that not every PAN is ideal for electrospinning.
Keywords: polyacrylonitrile, electrospinning, nanospinning, nanofibre mat, spinning parameters

Izvleček

Poliakrilonitril (PAN) spada med redke vodoodporne polimere, ki jih je mogoče oblikovati v vlakna s pomočjo relativno varnih topil, kar omogoča uporabnost PAN nanovlaknatih kopren v različnih medicinskih in bioloških aplikacijah, kot sta tkivno inženirstvo in spodbujanje razraščanja celic. V primerjavi s polietilenglikolom in drugimi vodotopnimi biopolimeri je elektropredenje PAN nanovlaken veliko težje. V predstavljeni študiji so raziskani vplivi procesnih parametrov in parametrov raztopine PAN v dimetilsulfoksidu (DMSO) na predilnost in morfologijo nanovlaknatih kopren, izdelanih z brezigelno elektropredilno napravo »Nanospider Lab«. Nanovlaknate koprene so bile proučevane s pomočjo konfokalne laserske vrstične mikroskopije in mikroskopije na atomsko silo. Ugotovljeno je bilo, da ima relativna zračna vlaga v predilni komori pomembno vlogo, saj previsoke vrednosti vlage lahko povzročijo neželeno oblikovanje sladkorni peni podobnih struktur iz nanovlaken, ki poveže nasprotno nabite strani Nanospiderja, kar ovira prost pretok nanovlaken do podlage in ustvarjanje želene strukture nanovlaknate koprene. Poleg tega je ključnega pomena tudi koncentracija PAN v predilni raztopini: podobno kot pri elektropredenju drugih (bio-)polimerov se nanovlakna ne oblikujejo, če je koncentracija polimera prenizka. Tretjič, tudi narava samega PAN vpliva na oblikovanje nanovlaken, kar kaže, da ni vsak PAN idealen za elektropredenje.
Ključne besede: poliakrilonitril, elektropredenje, predenje nanovlaken, nanovlaknata koprena, parametri predenja

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DOI: 10.14502/Tekstilec2017.60.290-295

1 Introduction

Electrospinning is one of the primary spinning processes that results in fine polymer fibres with diameters in the range of several ten to several hundred nanometres. In needleless electrospinning, polymers are often spun from solutions, a process that is technically easier than melt electrospinning. Several polymers, however, cannot be dissolved in non-hazardous solvents. Polyacrylonitrile (PAN) is a material that can be dissolved in dimethyl sulfoxide (DMSO), a solvent that must be handled with care, but does not cause problems in biological or medical applications.

PAN is thus a typical material used in electrospinning [1, 2]. In most cases, it is used in a two-step process for the creation of carbon nanofibres [3–5]. Alternatively, it can be used to incorporate inorganic components, such as MgO or ZnO [6–8]. Additionally, PAN is one of the few water-resistant polymers that can be spun from non-toxic solvents (DMSO). This is not only important in terms of "green" electrospinning, i.e. electrospinning without strong acids or poisonous solvents, but also for planned applications in medical or biotechnological areas. Cell growth experiments have, for example, revealed strong evidence of the presence of acetic acid in PA6 nanofibre mats that were prepared using this acid more than a year earlier [9]. A solvent such as DMSO is thus more preferable.

However, studies regarding the effect of PAN spinning and material parameters on the resulting nanofibre mats are scarce [10–12]. Reports regarding the effect of the solution and spinning parameters on the spinnability of the solution and the resulting fibre morphology are lacking, particularly for the needleless electrospinning of PAN in a wire-based geometry.

Our article provides an overview of the effect of different polymer concentrations in DMSO, different base materials and the variation of spinning parameters on the spinning process and resulting nanofibre mats.

2 Experimental

PAN solutions were prepared with PAN concentrations ranging from 5% to 20% in DMSO (min. 99.9%, purchased from S3 Chemicals, Germany) by stirring for two hours at room temperature (higher concentrations were not dissolved completely). Different PAN-based materials were used as a base for the spinning solution. The easiest available source of PAN is yarn from this material. To facilitate the testing of the electrospinning process with PAN without the need to find pure PAN pellets, two different PAN yarns were tested: "Super Star" from H. S. Wuppertal (Germany) and "Pade" (from Andreas Hoffmann Garnhandel & Textilspulerei (Germany)).

Electrospinning was performed using a "Nanospider Lab" needleless nanospinning machine (Elmarco, Czech Republic). A polypropylene (PP) fibre mat (purchased from Elmarco) was used as a substrate. The spinning parameters, such as high voltage, electrode-substrate distance, carriage speed, etc. were varied to find the optimum conditions for different spinning solutions. The selected parameters are shown in Table 1.

Table 1: Parameter ranges for the electrospinning process

Parameter	Value
Voltage [kV]	40–80
Current [mA]	0.09–0.12
Nozzle diameter [mm]	0.6–1.5
Carriage speed [mm/s]	200
Substrate speed [mm/min]	0
Ground-substrate distance [mm]	50
Electrode-substrate distance [mm]	240
Temperature in chamber [°C]	22–24
Rel. humidity in chamber [%]	31–33

To reduce relative humidity during the spinning process, dry (oil- and water-free) compressed air was fed into the spinning chamber. After waiting for up to 90 minutes, a relative humidity of 30–35% was reached after starting from a relative humidity of approximately 65%.

The nanofibre mat morphologies were studied using a VK-9000 (Keyence) confocal laser scanning microscope (CLSM) with a nominal magnification of 2000 x and a FlexAFM Axiom atomic force microscope (AFM) (Nanosurf).

Figure 1: Needleless electrospinning of a PAN solution with undesired cotton-candy-like polymer connections between the high voltage electrode and substrate

3 Results

The most critical parameter for the electrospinning of PAN is the relative humidity in the spinning chamber. In the presence of high humidity, cotton-candy-like polymer connections are formed between the high voltage electrode and the substrate (Figure 1).

Depending on the solution and spinning parameters, significant deviations occur between the different spinning processes. In the worst case scenario, cotton-candy-like polymer connections were formed between the high voltage area at the bottom of the chamber and the grounded area at the top, immediately after switching on the high voltage (Figure 1). This leads to no nanofibre mat being formed on the substrate, as nearly all fibres are caught in these 3D structures. This behaviour is significantly different from the electrospinning of typical biopolymers from aqueous solutions [13, 14].

On the other hand, it is possible to form even, straight nanofibres on the substrate with the ideal spinning and solution parameters. Figure 2 gives an example of electrospinning with a voltage of only 40 kV and a carriage speed of 100 mm/s, in contrast to the other experiments depicted in Figures 3-5, which used 80 kV and a carriage speed of 200 mm/s. The other spinning and environmental parameters are identical to those given in Table 1. Both areas were found on the same substrate after the identical spinning process at randomly chosen positions. This example indicates the importance of carefully selecting the ideal spinning parameters to avoid undesired irregularities, such as the significant modification in mat density depicted in Figure 2 in the created nanofibre mat.

Figure 3 depicts CLSM images of nanofibre mats created from "Pade" yarn. PAN concentrations of less than 10% resulted in a pure electrospraying process without any fibre formation. The results of these experiments are thus not depicted here. For PAN concentrations higher than 14%, both tested nozzles (0.6 mm and 0.9 mm), as well as a particularly large nozzle (1.5 mm in diameter), tended to clog after short periods of time, thus impeding the normal spinning process for more than a few minutes.

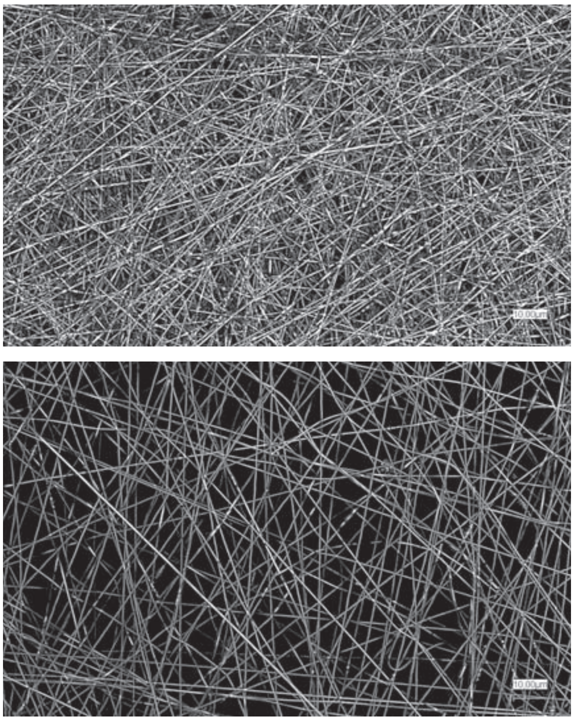
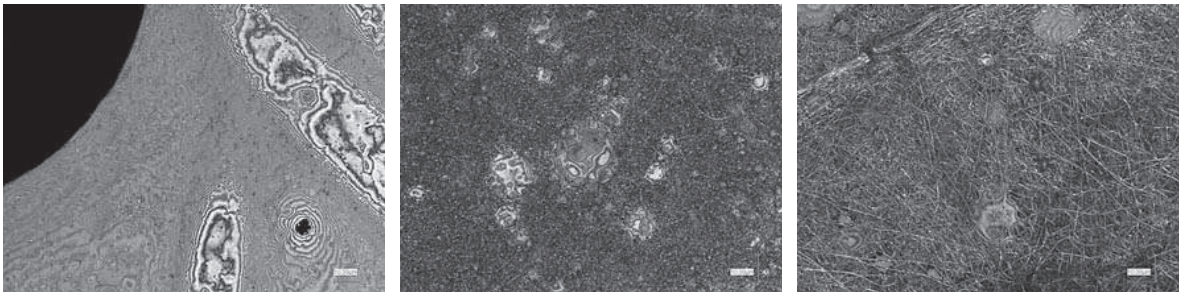


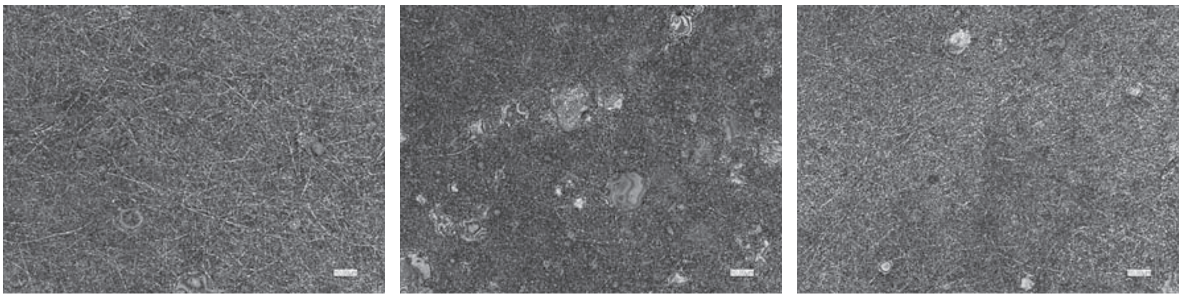
Figure 2: CLSM images of nanofibre mats of different densities, found at randomly chosen positions of the nanofibre mat, produced by needleless electrospinning from a PAN concentration of 14% dissolved in DMSO, using a voltage of 40 kV, a nozzle diameter of 0.6 mm, and a carriage speed of 100 mm/s at 23 °C and 32% relative humidity

For PAN concentrations of 17% and 20%, however, very fine nanomats could be achieved by spinning for short periods of time (not depicted in Figure 3).
Figure 3 shows the results of electrospinning with a 10–14% concentration of “Pade” PAN in the spinning solution, using a 0.6 mm nozzle, and the residual spinning and ambient parameters as given in Table 1. Observing the spinning process with a 10% concentration of PAN suggests that the material is sprayed rather than spun. The CLSM image underlines this observation: apparently, a fine membrane is built instead of a fibre network, similar to previous experiments using low-concentrated chitosan [15]. Mostly fibres are formed using a PAN concentration of 12%, while some areas are still coated by membranes. A clear fibre network is visible by increasing the PAN concentration further to 14%. Again, however, some membrane-like parts can be identified.
By changing the dissolved yarn, the experiments resulted in different findings, as can be seen in Figure 4. With the “Super Star” material as a base for the spinning solution, fibre creation begins already at a 10% PAN concentration in the solution. By using higher concentrations, the fibre mats become denser, and the fibre diameters become more regular (from approximately (450 ± 110) nm to (330 ± 30) nm). We assume that the increase in membrane density can be attributed to an increased DMSO concentration in the spinning chamber, as this effect is always visible after spinning for several hours and vanishes again after waiting approximately half an hour.
In previous studies of other polymers, we found that the molecular weight of the respective polymer had a significant effect on the nanofibre mat morphology. Particularly in a comprehensive study of polyethylene glycol (PEG) that tested diverse spinning and solution parameters, the molecular weight, as well as the polymer concentration in the solution, could be shown to significantly modify the spinning results [14, 16]. Nanofibres were found to form ideally from molecular weights of approximately 600 kDa, while smaller molecular weights led to inhomogeneous fibre mats, short and thick fibres or even electrosprayed droplets instead of fibres. On the



10% “Pade” 12% “Pade” 14% “Pade”

Figure 3: CLSM images of PAN nanofibre mats created from “Pade” yarn with PAN concentrations of 10%, 12% and 14% in the spinning solution, using a 0.6 mm nozzle and the spinning and ambient parameters as given in Table 1



10% “Super Star” 12% “Super Star” 14% “Super Star”

Figure 4: CLSM images of PAN nanofibre mats created from “Super Star” yarn with PAN concentrations of 10%, 12% and 14% in the spinning solution, using a 0.6 mm nozzle and the spinning and ambient parameters as given in Table 1

other hand, using higher molecular weights increased the viscosity, so that the necessary polymer concentrations to form fibres could no longer be achieved. By comparing previous studies with the results shown here, it seems obvious that both yarns contain PAN with different molecular weights. Apparently, not each PAN yarn serves as a good base for an electrospinning solution.

On the other hand, further experiments with "Super Star" PAN yarns show that this material is quite stable against modifications to the polymer content in the solution, to spinning parameters and even to the relative humidity in the spinning chamber. This thus offers an inexpensive and easily available alternative for the electrospinning of PAN.

AFM images were taken to compare the morphology of the nanofibres themselves. Figure 5 shows images of PAN nanofibre mats created from "Pade" yarn with a PAN concentration of 20% in the spinning solution and from "Super Star" yarn with a PAN concentration of 14% in the spinning solution, respectively. Different fibre diameters are clearly visible. Additionally, the nanofibre mat created from "Super Star" yarn shows distinct longitudinal grooves in the upper fibres, indicating that they actually consist of two, three or more single fibres on the dense fibre background.

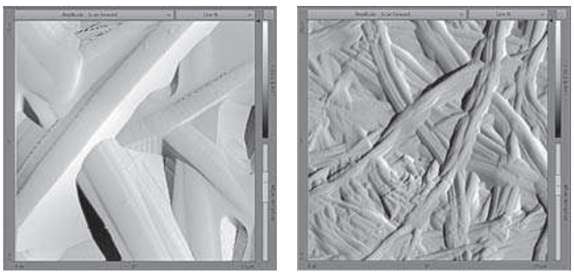


Figure 5: AFM image of PAN nanofibre mats created from "Pade" yarn with a PAN concentration of 20% in the spinning solution (left) and from "Super Star" yarn with a PAN concentration of 14% in the spinning solution, respectively (right)

Interestingly, the thick fibres created from a "Pade" concentration of 20% partly show a transverse rib structure that we assume can be attributed to the rapid polymerisation process. More pronounced transverse rib structures are, for example, well-known from the pulsed laser treatment of man-made fibres [17].

4 Conclusion

For needleless electrospinning using PAN, finding the ideal spinning and solution parameters is crucial for the creation of optimum nanofibre mats. In particular, the relative humidity in the spinning chamber was shown to have a significant effect on the spinning results. Additionally, a well suited PAN material as a base for the spinning solution and the ideal polymer concentration in the solution are necessary to reliably create nanofibre mats instead of membranes or sprayed patterns. The morphologies of single fibres were studied using AFM, and showed fibre-agglomerates for thinner fibres created from lower PAN concentrations and partly transverse rib structures on thicker fibres spun from the highest possible PAN concentration. Finally, electrospinning from DMSO-based solutions results in increased DMSO contents in the spinning chamber, which may cause higher amounts of membrane-like areas. This limits the possible spinning duration if the spinning chamber is not ventilated sufficiently.

Acknowledgement
The authors gratefully acknowledge the FH Basis programme of the federal German state of North Rhine-Westphalia for funding the "Nanospider Lab" and "FlexAFM Axiom" AFM.

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