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Research article

The electrospinning of less common polyamides via direct and alternating current

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Abstract. This paper presents a method for direct and alternating current electrospinning of polymeric solutions of three less common polyamides (nylons). Homopolyamide PA 8, heteropolyamide PA 6|9 and semi-aromatic amide (phthalamide) PA 6(3)T were dissolved in the formic acid and dichloromethane mixture, which have proved to be a suitable solvent for various other linear polyamides. The dependence of the viscosity, electrical conductivity, and spinnability via the direct (DC) and alternating current (AC) technology on the solution concentration was observed. Scanning electron microscope images of the prepared nanofibers were acquired and consequently analyzed for fiber defects, followed by measuring the fiber diameters. The differences in the nanofiber quality of DC layers and AC plumes were discussed. Finally, the optimal concentrations for the electrospinning of the examined solutions were determined. The communication follows our previous work and extends the number of electrospinnable polyamides, thus facilitating future research in this area.

Keywords: *nanomaterials, polyamide, electrospinning, polymer synthesis, industrial applications*

1. Introduction

Synthetic linear polyamides (nylons) are a group of chemically related polymers containing amide groups (–CONH–) and aliphatic chains or aromatic cores. The increasing length of the chain (or the number of cores) alters the properties of polyamides, such as polarity, tensile strength, glass transition temperature, melting point, solubility, wettability, or gas permeability [1]. A number of PA types allow for sorting them into logical groups (homopolyamides, heteropolyamides, aromatic polyamides) with defined and gradually changing properties. It can be harnessed for choosing the most suitable polyamide for a particular application. The polyamide nanofibers evince good thermal, mechanical, and chemical resistance, thus allowing for their application in demanding sectors [2]. Polar polyamides (*e.g.* PA 6 and PA 6|6 [3, 4]) are usually soluted in formic acid or a formic and acetic acid mixture. However, less polar PAs require more expensive solvents, thus limiting their industrial potential. Behler *et al*. [5] found that the formic acid and dichloromethane mixture can be used as a universal solvent for PAs. Our previous work showed that it is possible to electrospin the PA 4, PA 6, PA 11, PA 4|6, PA 6|6, PA 6|10, and PA 6|12 from the solvent using direct (DC) or alternating current (AC) technology [6]. The advantage of the method is the possibility of producing different nanofibrous materials without needing solvent or set-up alteration. It also allows DC and AC electrospinning. While both technologies produce polymeric nanofibers [7, 8], the differences are evident in terms of the final structure of the material, thus impacting its application [8]. This paper extends the range of DC

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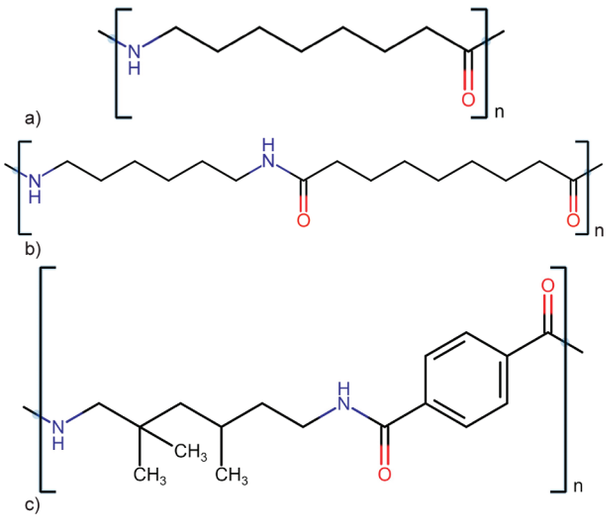

Figure 1. Chemical structures of repeating units – PA 8 (a), PA 6|9 (b), and PA 6(3)T (c) made in online software Chem-Space.

and AC electrospinnable polyamides by three less common types: PA 8, PA 6|9 [9], and PA 6(3)T [10] (Figure 1). The described method is suitable for producing PA nanofibers for filtration [11] or solid-phase extraction sorbents [12].

2. Experimental section

2.1. Materials and preparation of the solution

PA 8 was synthesized at the Department of Polymers – UCT Prague. Monomer η-capryllactam (Fluka AG – Buchs, Switzerland) was distilled under reduced pressure before use. The η-capryllactam was polymerized in a sealed ampoule in 1 mol% of ε-aminocaproic acid at 250 °C for 96 hours. The yield of polymer: 99,7%; viscosity average molar mass M_v = 24500 g/mol; melting temperature (differential scanning calorimetry, DSC) 194 °C.

The PA 6|9 (CAS 27136-65-8) and PA 6(3)T (CAS 25497-66-9) were purchased from Scientific Polymer Production Inc. (New York, NY, USA), the formic acid (CAS 64-18-6) and dichloromethane (CAS 75-09-2) from Penta s.r.o. (Prague, Czech Republic). Sets of 6, 8, 10, 12, 14, and 16 wt% solutions were prepared by dissolving the polyamides in a mixture of formic acid and dichloromethane at a weight ratio of 1:1. They were stirred for 24 hours on a magnetic stirrer at standard laboratory conditions.

2.2. Methods

Viscosity and electrical conductivity

A HAAKE Rotovisco (Thermo Fisher Scientific, Prague, Czech Republic) rheometer with a C35/1°Ti L cone was used to assess dynamic viscosity. Each measurement lasted 30 s in continuous mode, and the shear rate was increased linearly from 300 to 3000 1/s. A Eutech Instruments CON 510 (Eutech Instruments – Thermo Fisher Scientific Inc., Landsmeer, The Netherlands) with a K10/6MM8 was used for the determination of the conductivity of the solutions. The measurements were repeated three times at a temperature of 21 °C.

Electrospinning system

An AU-60P0.5-L (Matsusada Precision, Ōtsu, Japan) positive voltage source was used for the DC electrospinning, and a KGUG 36 transformer (ABB, Prague, Czech Republic) with an ESS 104 regulator (Thalheimer-Trafowerke, Ostrava, Czech Republic) at a frequency of 50 Hz (sinusoidal wave) was used for the AC electrospinning. The setups for both methods were identical: a steel rod (diameter 10 mm) was used as the positive electrode, upon which a droplet of the polymeric solutions was deposited and subsequently electrospun. A steel plate was used as the fiber collector (grounded for the DC, electrically neutral for the AC system) at a distance of 100 mm from the electrode top. The paper [6] describes the electrospinning setup in more detail. The supplied voltage was 30 kV for the DC and effective 30 kV for the AC methods. The electrospinning process took 30 s for each sample. The relative humidity during electrospinning was 40%, and the temperature was 21 °C.

Scanning electron microscopy

A Q150R ES rotary-pumped coater (Quorum, Lewes, UK) was used to coat the nanofibers with a 10 nm thick deposit of gold. A Vega 3 scanning electron microscope (TESCAN, Brno, Czech Republic) was employed at a 10 kV accelerating voltage. ImageJ freeware (version 1.52a, Bethesda, MD, USA) was used to measure the fiber diameters (200 for each sample).

3. Results and discussion

3.1. Viscosity and electrical conductivity

All tested solutions' dynamic viscosities and conductivities increased with the concentrations (Figure 2). The dynamic viscosity of the PA 8 was higher due to its higher molecular weight. The lower conductivity of PA 6(3)T was caused by lower moisture content in the PA 6(3)T compared to more polar

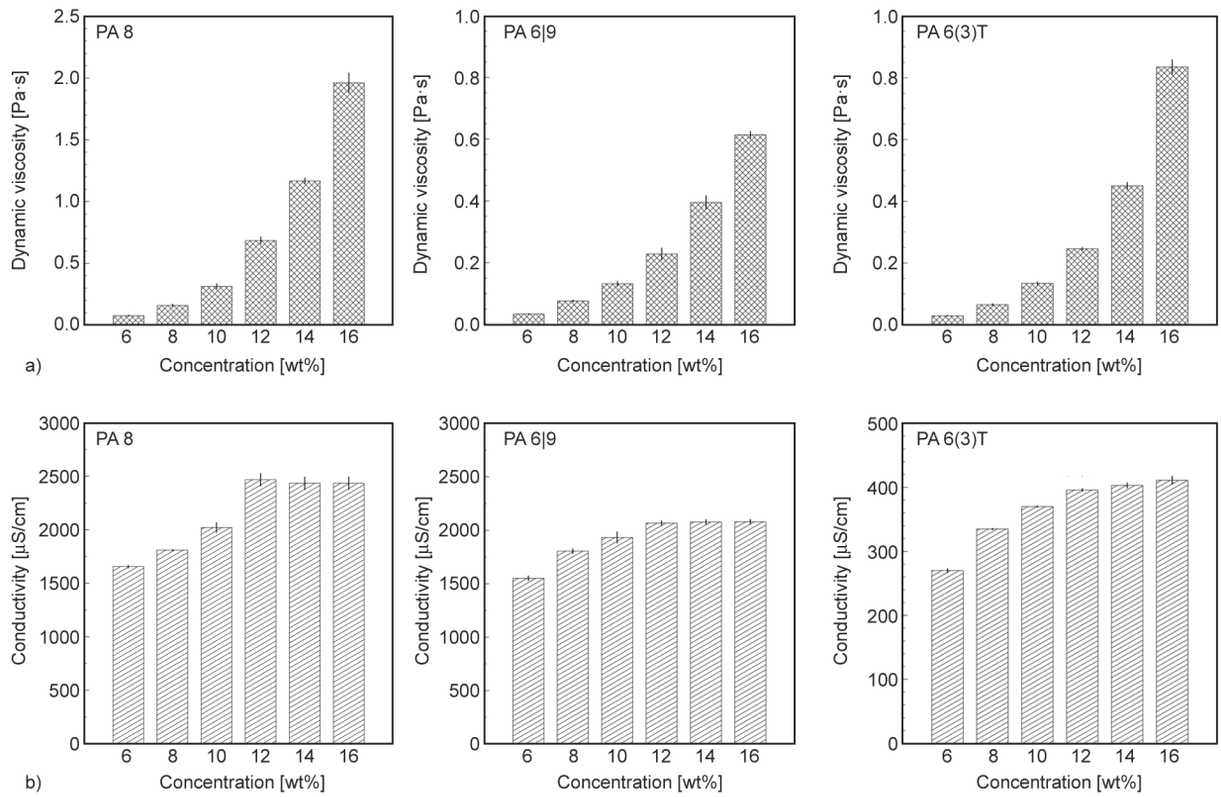

Figure 2. Dynamic viscosity at a shear rate of 500/s (a) and conductivity (b) of the solutions.

PA 8 or PA 6|9. The decreased formic acid dissociation rate led to the solution's lower conductivity.

3.2. DC and AC electrospinning

Prepared polyamide solutions were spinnable via both the DC and AC technologies. The collector's surface covered with fibers of the DC electrospun layers was highest for the 8% PA 8 and 10% PA 6|9 and PA 6(3)T solutions (Figure 3). Above or below these concentrations, the layers covered a smaller area and were less homogeneous. The lower concentration determined for the PA 8 was caused by the higher molecular weight, which corresponded to the viscosity measurements.

3.3. Fiber diameters and defects

The SEM images showed that the quality of the DC- and AC-fabricated fibers was standard for all the samples except the fibers produced from the 12, 14, and 16 % PA 8 solutions via the DC electrospinning. A fibers and ribbons mixture was observed for the 12% PA 8. At 14 and 16%, samples consisted entirely of ribbons (Figure 4a and Figure 4b). This phenomenon was not observed for the samples of the same solutions produced via the AC method. While the isolated occurrence of ribbons in AC samples was observed, they were sporadic and never formed a compact structure (Figure 4c). It was caused by the lower momentum of AC fibers, which flight to the collector was accelerated by lower energy via the ionic wind. In contrast, the DC fibers were accelerated by stronger electrostatic force and were flattened by impact with the collector. This phenomenon was observed only for solutions of higher concentrations, where the initial polymeric streams from Tylor cones were thicker due to the higher viscosity of solutions.

The fiber diameters and the standard deviations of all three polyamide layers increased with the increasing concentration of the solutions (see Table 1). Concerning the deviations, the estimation of the differences between the fibers prepared via the DC and AC approaches from identical solutions was inconclusive. The significant increase in the fiber diameters of the 14 and 16% PA 8 solutions was caused by the creation of ribbons (only major diameters were measured).

4. Conclusions

The paper presents a method for the DC and AC electrospinning of PA 8, PA 6|9, and PA 6(3)T solutions. The dynamic viscosity and conductivity of the solutions were measured to support observed facts.

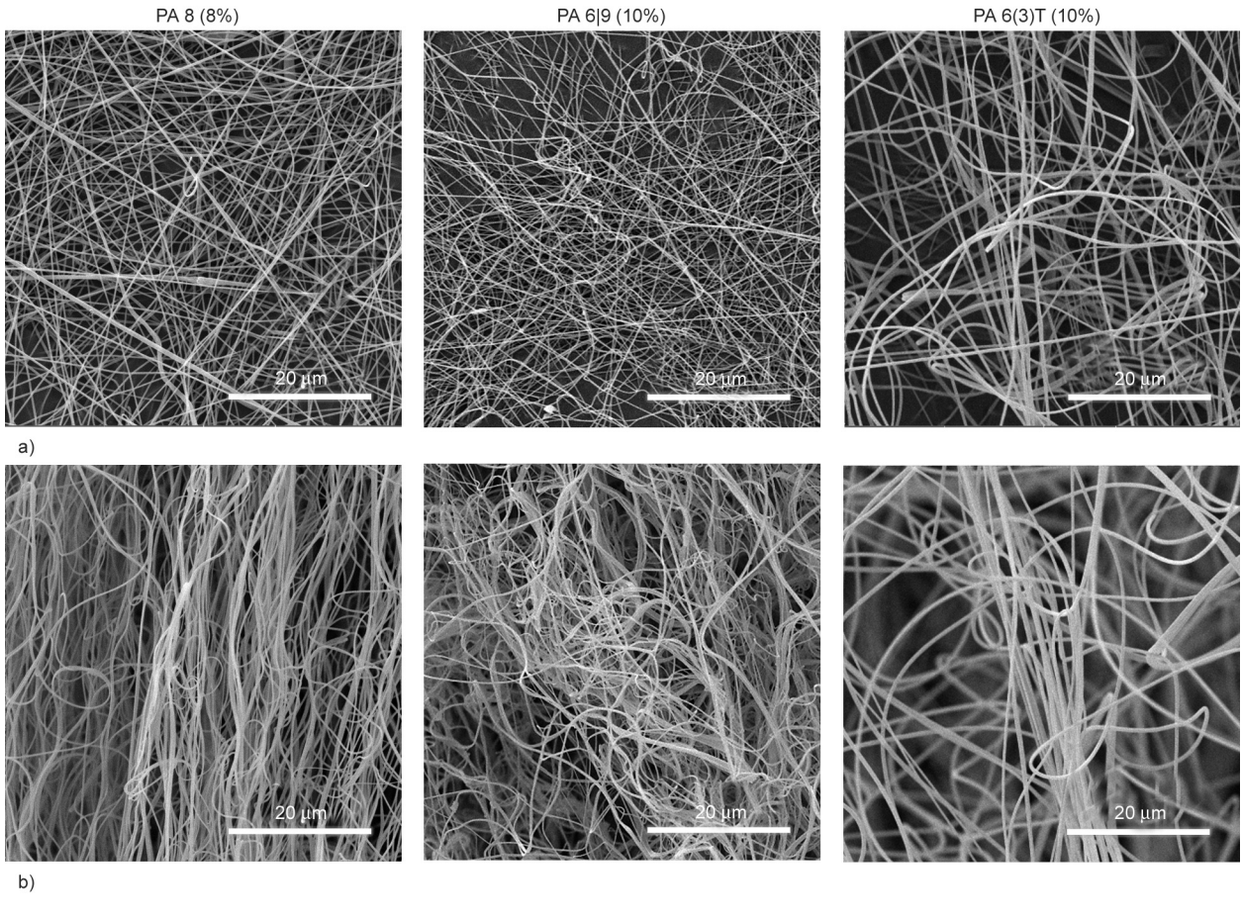

Figure 3. SEM images of the DC (a) and AC (b) electrospun PA 8, PA 6|9, and PA 6(3)T nanofibers.

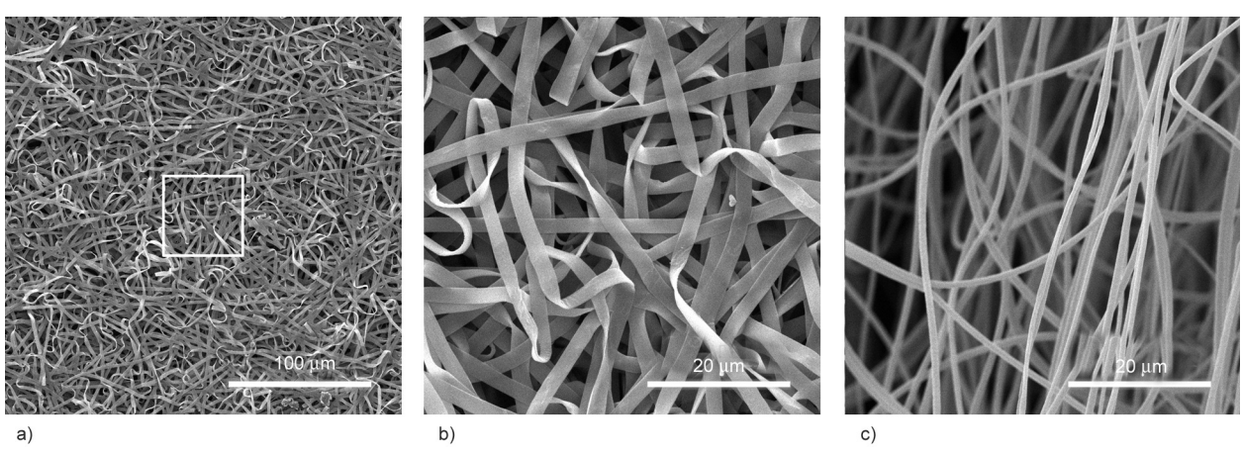

Figure 4. The DC electrospun PA 8 (16%) consisted of ribbons (a); the white square specifies the location of the detail shown in the (b), whereas the AC electrospun structure of the PA 8 (16%) showed no ribbon content (c).

Table 1. The dependence of the average fiber diameters on the polymeric solutions concentration (± standard deviation).

Concentration [wt%]	PA 8		PA 6|9		PA 6(3)T	
	DC [nm]	AC [nm]	DC [nm]	AC [nm]	DC [nm]	AC [nm]
6%	185±43	176±59	126±24	140±39	176±39	194±45
8%	213±41	250±75	149±26	214±56	239±47	244±46
10%	340±66	286±59	207±44	245±71	359±97	484±90
12%	413±79	359±55	277±43	263±81	834±168	532±117
14%	2077±250	674±142	315±47	413±178	977±250	789±278
16%	2273±186	951±308	670±169	486±176	1217±143	984±401

The most suitable of the tested solutions were 8% PA 8, 10% PA 6|9, and 10% PA 6(3)T, of which the DC-produced nanofiber layers and the AC-produced nanofiber plumes were observed to be the most voluminous and homogeneous. The SEM images showed no defects in the fibers at the same time. The lower concentration for PA 8 was caused by its higher molecular weight, which corresponded with the viscosity measurements. The DC spinning of the 14 and 16% PA 8 solutions resulted in the production of exclusively ribbon structures, which was not observed for the AC spun samples because the carrying speed of AC fibers to the collector was lower than for the DC spun fibers. Considering the previous results of PA electrospinning, it was confirmed that the used solvent system is suitable for the DC and AC electrospinning of synthetic linear polyamides.

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