ALTERNATING CURRENT ELECTROSPINNING OF PA 6 USING ADDITIVES IN FORM OF OXOACIDS

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Abstract

Nanofibrous materials are currently in transition between laboratory and industrial-scale production. The main factor that hinders transition speed is relatively low productivity compared to widely used technologies such as melt-blown or force-spinning. One possible solution is to use a different technology than a typical direct current electrospinning (DC). It is possible to electrospin solutions using another high-voltage source – providing alternating current energy (AC). The potential of AC technology lies in increased productivity of the process and the possibility of electrospinning solutions containing a high dose of additives (15-30 % wt.) such as hydroxyapatite, graphene, active carbon, ceramics, clay particle, aluminium or metallic oxides. When using AC technology, some problems can arise. The main one is the transition of a working solution that spins well in small laboratory DC systems or industrial-scale Nanospider™ machines driven by direct current. It is usually required to modify the solution to improve the spinnability of the solution in the AC system. In our case, we experienced the problem in the spinnability of PA 6 when using the so-called "overflow electrode" that enables the spinning of polymer for a more extended time (multiple hours). The initial solution of PA 6 did not produce a nanofibrous layer but technologically unprocessable small flakes. We show that minor modification of solutions using oxoacids can lead to significant improvement of the nanofibrous product. The results are presented in the form of SEM images and histograms showing the change in diameters of nanofibers.

Keywords: Electrospinning, polyamide 6, nanofibers, oxoacids

1. INTRODUCTION

Materials with high added value are currently increasing in demand. Currently, there is a wide range of technologies that can provide such materials. In general, we can divide the technologies as mentioned above into two primary groups. The first one contains systems initially designed to produce fibers with diameters in the range of micrometers, such as melt-blown [1], which are currently modified to provide fibers with decreased diameter, leading to approximately 500 nm [2]. The second group is represented by the processes that are directly aimed at the production of nanofibers. The most well-known approach for the production of nanofibers is electrospinning [3]. Since then, most experiments/systems have been driven by direct current power sources [4]. Recently, the so-called alternating current (AC) electrospinning has been discovered [5]. Initially, experiments with AC electrospinning contained electrically active collectors similar to the DC systems [6]. The modification of the AC system was done by our group, removing the electrically active collector [7]. This seemingly small change brings a whole new set of possibilities for the concept of electrospinning. By its nature, AC electrospinning produces a nanofibrous structure that spontaneously creates a tube-like structure that contains almost no charge due to a constant change in polarity, leading to self-discharging. This structure is subsequently blown away from the electrode (to a specific place where the electrode is aimed at) by so-called ionic wind [8]. Without the necessity to use the electrically active collector (for the neutralization of charge), fibers can be used to coat any object of desired shape [7]. It is necessary to mention that the AC variant of electrospinning also brings a new challenge that can be represented by the required (often) modification of electrospun solution. The solution that works well on the DC system can manifest difficulties during the transfer

to the AC electrospinning due to its nonstatic nature. The rapid change of polarity and constant change of the voltage gives only a limited time [9] for actual electrospinning, and polymeric solution needs to be able to offset the spinning process in this limited window. This paper presents an example of such modification based on the spinning of Polyamide 6 (PA 6). We show that adding multiple oxoacids can lead to a major improvement of the spinning process and provide nanofibrous materials of good quality. The level of quality is dependant on the used oxoacid.

2. METHODS

The technologically sustainable long-term AC electrospinning of Polyamide 6 can be arranged using a pump with an overflowing effect. This method provides more solutions than can be electrospun at a given time, so the whole body of the electrode is always coated with the solution. The new solution flows down - back to the reservoir. Without this overflow effect, the dry parts of the electrode are slowly covered by a growing mass of the dried polymer. This leads to diminishing quality of the electrospinning and subsequent end of the stable process.

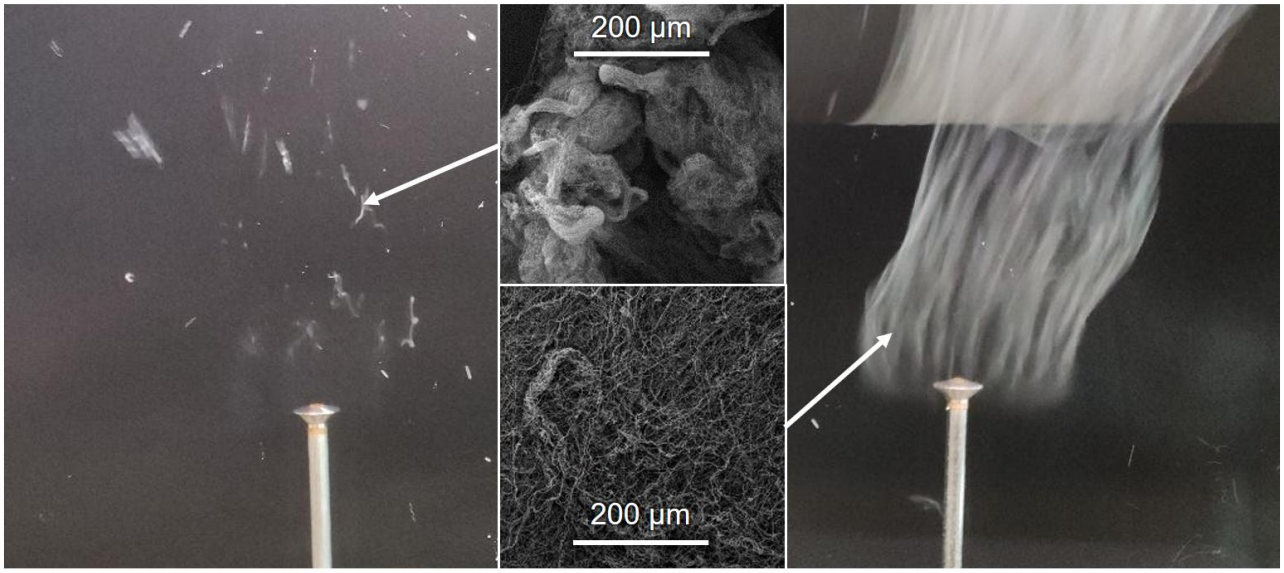

Figure 1 AC electrospinning of basic PA 6 solution (left) and one enhanced by an oxoacid (right) with corresponding details of the nanofibres

Materials and preparation of solutions

The experiments used the basic solution of PA 6 – Ultramid B27 (M_w 66360 g/mol, D=3.2) provided by the BASF company. The polymer was dissolved in a mixture of two organic acids, namely formic acid (Penta Chemicals) and acetic acid (Penta Chemicals), mixed in weight ratio 1:1. The basic solution contained 10% (wt.) PA 6. For the following experiments with additives, the set of oxoacids that expanded our previous research [10] were chosen: nitric acid (Penta Chemicals), phosphoric acid (Penta Chemicals), and p-toluenesulfonic acid monohydrate (Sigma Aldrich).

Table 1 List of additives successfully improving the quality of AC electrospinning of PA 6

Acid	Formula	Concentration [mol/l]
nitric	HNO_3	0.441
phosphoric	H_3PO_4	0.863
p-toluenesulfonic	$C_6H_4(CH_3)SO_3H$	0.298

Table 1 shows the various additives and their respective concentration in the basic solution of PA 6. It is worth mentioning that the dose of additives was always very small. Only a few drops are required to modify the relatively high volume of a basic solution (for example, 300 ml). The values in **Table 1** represent the optimal dose of the additive. A smaller dose does not sufficiently affect the spinning quality. Exceeding the optimal value also depresses the production of quality materials.

Electrospinning system

The quality of electrospinning was ensured by the use of a custom-made screw pump [7]. The fresh polymer was constantly overflown from the top of the electrode and over the edge, where maximal electrical intensity can be found. The signal (type and frequency) was provided by the Owon AG 1022 and transformed to high voltage values by TREK 50/20 high-voltage amplifier. All experiments were performed using the same 42 kV and 50 Hz settings.

3. RESULTS

The solvents were electrospun using the screw-pump mentioned above and high voltage power source TREK. Each sample was collected using a PMMA (polymethyl methacrylate) plate. Samples were examined using an SEM microscope.

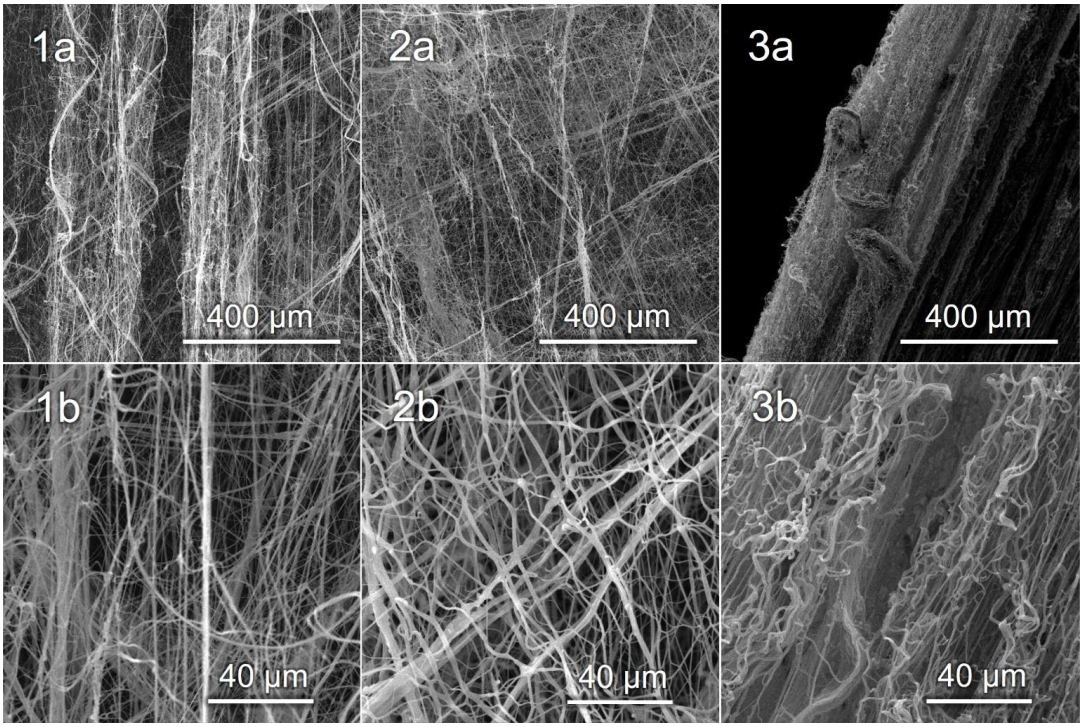

Figure 2 Nanofibrous products provided by basic solution of PA 6 enhanced by nitric (1a, 1b), phosphoric (2a, 2b) and p-toluenesulfonic acid (3a, 3b).

The materials produced using enhanced solutions (optimal dose) produced the process-able fibrous layers in all cases (**Figure 2**). The morphology and diameters of the fibers differ, and they are shown in histograms (**Figure 3**). Each oxoacid created a different structure of the fibers. Compared to previously tested oxoacids (sulfuric and methanesulfonic) published in [10], the quality of the fibrous product was decreased. The relatively significant differences in the diameters of nanofibers were caused by the nature of AC electrospinning that does not provide constant energy through the whole half-wave of the signal.

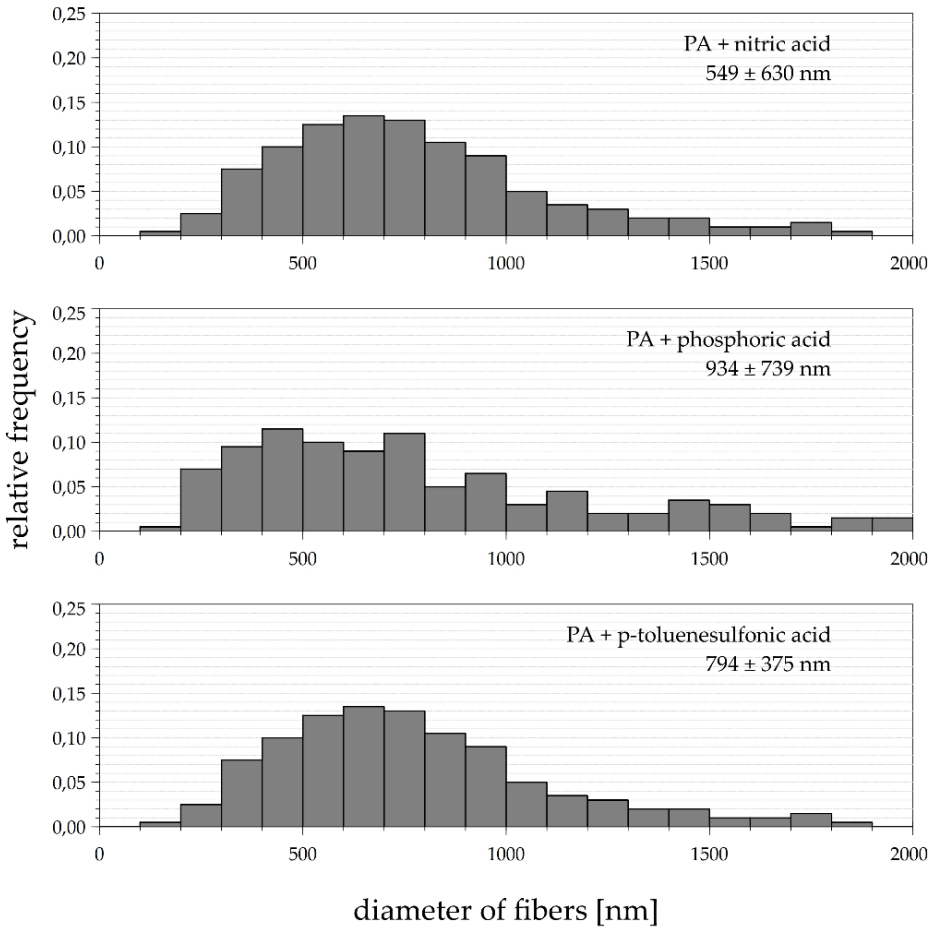

Figure 3 Histograms of fibrous diameters for each modified PA6 solution. Figures represent the solution enhanced by nitric, phosphoric and p-toluenesulfonic acid with a corresponding average diameter and standard deviation.

The positive influence on the spinnability of Polyamide 6 with additive in the form of oxoacids might be explained by the physical bonding of the carboxyl groups of the acids to the amide groups of the polymer. Each oxoacid can dissociate in the basic solution and create ions in the solution. Dissociated acid particles are probably able to interact with the electrically imbalanced CONH group in amides. Although no covalent bond is created, the dissociated particles can influence the properties of polyamide macromolecules through relatively weak but numerous interactions between the amide group and dissociated ions. This might lead to a virtual increase in molecular weight, number of entanglements or improve macromolecule stability in changing alternating current electric fields. This behavior was not observed when using different chemicals as additives that change the physical properties of solutions, such as viscosity or conductivity (salts or surfactants).

4. CONCLUSION

The presented work shows that oxoacids can improve the spinnability of PA 6 solutions for AC electrospinning systems and can lead to a fibrous material with acceptable diameters and structures. We have shown that acids that can dissociate can improve AC electrospinning when using an overflowing system (improving the sustainability of the process). The theory explaining this behavior was also mentioned. Further research could improve the spinnability of various polymers using AC field and optimization of fibrous diameters and morphology of produced nanofibrous layers and bulky structures.

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REFERENCES

[1] DRABEK, J., ZATLOUKAL, M. Meltblown technology for production of polymeric microfibers/nanofibers: A review. *Physics of Fluids.* 2019, vol. 31, 091301.

[2] ELLISON, J., PHATAK, A., GILES, D., MACOSKO, CH., BATES, F. Melt blown nanofibers: Fiber diameter distribution and onset of fiber breakup. *Polymer.* 2007, vol. 48, pp. 3306-3316.

[3] RAMAKRISHNA, S., FUJIHARA, K., TEO, W., LIM, T., MA, Z. *An Introduction to Electrospinning and Nanofibers*. Singapore: World Scientific Publishing Co, 2005. ISBN 981-256-415-2.

[4] DOSHI, J., RENEKKER D.; Electrospinning process and application of electrospun fibers. *Journal of electrostatics* 1995, vol. 35, pp. 151-160.

[5] KESSICK, R., FENN, J., TEPPER, G. The Use of AC Potentials in Electrospraying and Electrospinning Processes. *Polymer*. 2004, vol. 45, pp. 2981–2984.

[6] MAHESHWARI, S., CHANG, H.-C. Assembly of Multi-Stranded Nanofiber Threads through AC Electrospinning. *Adv. Mater.* 2009, vol. 21, pp. 349–354.

[7] POKORNY, P., KOSTAKOVA, E., SANETRNIK, F., MIKES, P., CHVOJKA, J., KALOUS, T., BILEK, M., PEJCHAR, K., VALTERA, J., LUKAS, D. Effective AC Needleless and Collectorless Electrospinning for Yarn Production. *Phys. Chem. Chem. Phys.* 2014, vol. 16, pp. 26816–26822.

[8] WANG, J., ZHU, T., CAI, Y., ZHANG, J., WANG, J. Review on the recent development of corona wind and its application in heat transfer enhancement. *International Journal of Heat and Mass Transfer*. 2020, vol. 152.

[9] FARKAS, B., BALOGH, A., CSELKÓ, R., MOLNÁR, K., FARKAS, A., BORBÁR, E., MAROSI, G., NAGY, Z. Corona alternating current electrospinning: A combined approach for increasing the productivity of electrospinning. *International Journal of Pharmaceutics*. 2019, vol. 561, pp. 219-227.

[10] KALOUS, T., HOLEC, P., JIRKOVEC, R., LUKAS, D., CHVOJKA, J. Improved spinnability of PA 6 solutions using AC electrospinning. *Materials Letters.* 2021, vol. 283.