ELECTRODE FOR CONTINUOUS PRODUCTION OF COMPOSITE NANOFIBER MATERIAL USING AC-ELECTROSPINNING METHOD

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Abstract

Composite nanofiber materials offer advanced properties and functions applicable in many fields, especially in medicine. Nowadays, these materials are mainly fabricated using the DC electrospinning technology with multi-spinnerets electrodes designed for such purpose. For the novel, highly effective AC electrospinning method, spinnerets distance needs to be increased enormously in order to avoid mutual affecting of virtual collectors created around each of the spinnerets. This fact limits the efficient usage of multi spinnerets types of electrodes for production of composite nanofiber materials using the AC electrospinning technology. Here we show, that two independent polymeric solutions can be effectively supplied to a single unique AC electrode and electrospun in order to fabricate bi-component nanofiber structure. This new electrode was designed using a CAD software with relation to the results of electric field distribution analysed in the Autodesk Simulation Mechanical. The manufactured electrode was experimentally verified for simultaneous AC electrospinning of PVAc and PVB solutions, both with EtOH solvents. SEM scan of fabricated material proved a bi-component structure of the final product. Our results demonstrate the new, experimentally verified technology for simultaneous electrospinning of two independent polymeric solutions from a single electrode and fabricating of composite nanofiber material of advanced mechanical properties. Based on the kind of polymeric solution spun, this represents new possibilities for various applications, e.g. tissue engineering, filtration and others.

Keywords: AC-electrospinning, AC-spinneret, AC-electrode, Composite nanofibrous material

1. INTRODUCTION

Nanofibrous materials are used in numerous applications, especially in medicine, e.g. tissue engineering, air, water and blood filtration, glaucoma treatments, and others [1]. This is primarily because of the specific surface and mechanical properties of nanofibrous textile structures. For further usage of these modern materials, more efficient means of nanofiber production needs to be introduced and applied. Industrial production of various nanofibrous materials is nowadays based mainly on the electrostatic spinning technology (DC electrospinning) [2]. This technology offers many spinable polymeric materials and the spinning process control for obtaining materials of required parameters. The alternating current based technology (AC electrospinning) that was introduced in 2012, shows promising parameters in producibility and spinning process stability. In comparison to DC electrospinning, the AC electrospinning enables more efficient production of nanofibers from main technological polymeric materials [3]. A cost-effective production of nanofibrous materials using this new technology indicates the potential in usage of nanofibrous materials for wide spectrum of applications. Requirements of more advanced applications can be reached by composite nanofibrous materials with enhanced mechanical, chemical, hydrodynamic, and other properties [4, 5]. There are various types of electrodes designed for production of composite nanofibrous materials using the DC electrospinning [2]. For production of co-axial nanofibrous materials, there were developed electrodes for the DC electrospinning technology [6, 7]. This work describes the design and parameters of the unique AC electrode that enables continuous production of composite nanofibrous material.

2. THEORY OF AC-ELECTROSPINNING

The AC-electrospinning is a collector-less type of electrical based technology of nanofibers fabrication. A time-varying electric field creates between the AC-charged electrode and a virtual collector, which is formed in the electrode surroundings by emitted oppositely charged ions [3]. Similar to DC electrospinning, this field is a source of electric forces. Over-critical values of electric forces destabilize the polymeric surface and creates Taylor cone from which the fibre is elongated [8]. Due to the massive evaporation of the solvent, extremely low fibre diameters can be achieved. Created nanofibers form smoke-like structure that is wafted by an electric wind. Fibres can be easily collected on various types of collectors or on textile structures to produce unique textile materials, e.g. hybrid nanoyarn. The electrodes for AC-electrospinning are described in [9]. An AC-spinneret consists of two basic parts: tube and a spinning head. The first invented AC-electrospinning head was of conic shape. Electric field intensity is very important parameter during the spinning process. This parameter is dependent not only on applied voltage but also on curvature of the spinning head. Electric field intensity influences lot of parameters of created nanofibers such as diameter and their productivity. FEM analyses of electric field are used during design of the electrode heads. Electric field intensity is the highest at the spinning zone due to higher curvature of the rounded conic edge, see **Figure 1**. That is why the spinning process takes place primarily at the spinning zone after covering it with polymer solution and apllying appropriate value of high voltage. Because of the polarity change frequency 50 Hz in this electrospinning process, some of the created nanofibers may be attracted back to the electrode and end up in the surrounding area of the electrode or on the electrode itself. Despite this does not occur in significant amount, it may cause destabilizing of the process in a long-term operation. In order to maintain the spinning process stable, the amount of delivered solution is higher than the spun one. The unspun polymeric solution then flows over the outer surface of the electrode back to the reservoir, see **Figure 2**. Compact polymeric layer ensures nanofibers collected on the electrode to be dissolved again.

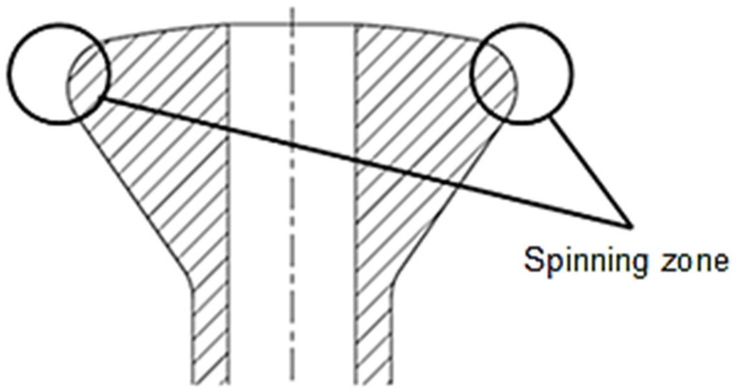

Figure 1 Scheme of the basic AC electrode shape

3. ELECTRODE DESIGN AND ANALYSIS

Design of the AC electrode must reflect the presence of the virtual collector present in this technology [10]. The electrode virtual collector interfere negatively with neighbour one with distance under 150 mm. Due to that, it is not possible to use typical multi-spinnerets electrodes in pursuit of producing mixed nanofiber material. It was therefore necessary to design electrode with two spinning heads which forms single virtual collector. This unique electrode consists of two cone-shaped spinning heads, three tubes for the transport of two different polymeric solutions and electrode housing. Polymeric solutions are transported to the electrode by external pumping system connected to the electrode housing. Electrode can be completely dissembled for easy maintenance after the operation. The electrode design prevents any contact or mixing of used polymeric solutions during the spinning process. High voltage is applied to the electrode housing and distributed by means of tubes and heads made of stainless steel. Two exchangeable sets of spinning heads with different electric field distribution were designed in order to influence the spinning process and the structure of final material. Design of the spinning heads geometry was derived from results of series of analyses of electric field. These analyses were processed in the Autodesk simulation mechanical 2015 software. The main parameter monitored was the distribution of electric field around spinning heads. For this purpose, the 2D axisymmetric model was created, see **Figure 3**. The geometry of the electrode was placed into quarter circle air-surroundings. Series of analyses were carried out and their results were reflected into the geometry design. Electric field potential in the spinning zones have to be remarkably higher then on the top of separation tube. Two sets of spinning heads with different electric field distribution were designed. Spinning heads of each set are design with equal electric field potential on the top and the bottom head. The difference in the electric field potential between each set is $1000\ V/mm$.

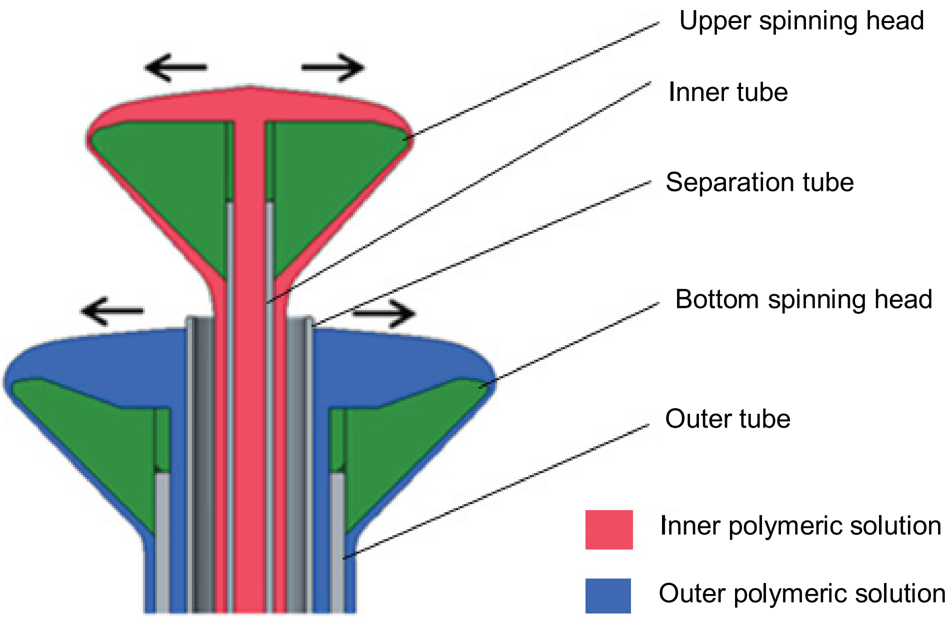

Figure 2 Scheme of the AC electrode for composite nanofiber production

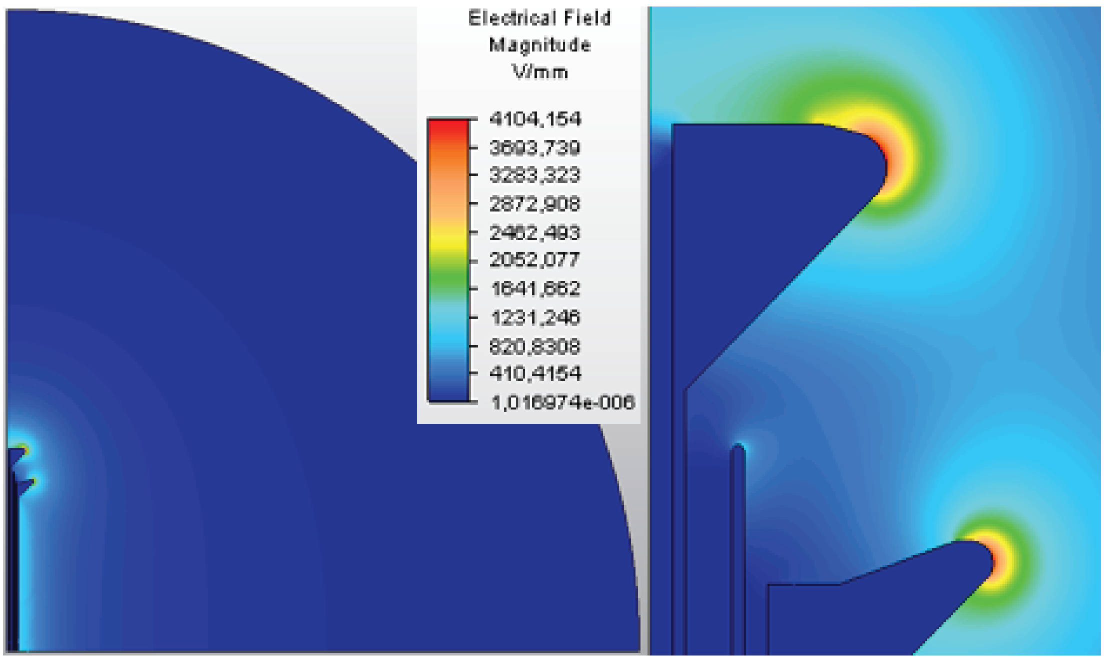

Figure 3 Electrical field distribution of the 2D asymmetrical model of the AC electrode (applied voltage: 30 kV). **Left**: full model. **Right**: detailed view of the spinning heads

4. EXPERIMENT

The manufactured prototype of the designed electrode was experimentally verified in the spinning process on an AC-electrospinning testing device in laboratories of Technical University of Liberec. Firstly, a sufficient sealing of electrode canals avoiding any leakage and solutions mixture was tested. This was proven by dosing two 10% (wt) polymeric solutions of PVB (Kuraray) with average molecular weight 60.000 dissolved in ethanol, where one solution was coloured by Prussian blue. These polymeric solutions have been circulating through the electrode for more than 20 minutes without any sign of colour-change that has proved sufficient sealing of the electrode tubes. Secondly, a combination of above mentioned PVB solution and 22.5% (wt) solution of PVAc (polyvinyl acetate - Carl Roth) with molecular weight 55.000-70.000 dissolved in ethanol was successfully tested in the AC electro-spinning process. Detail of the electrode heads from this test are depicted in **Figure 4**. The spinning process was maintained stable for more than 20 minutes under conditions 23°C and relative humidity 37%. The nanofibrous material was collected on a rotating drum with a spunbond. The measured productivity of this nanofibrous material was 0.5 g/min. The electrode was also tested with combination of 10% solution of PVB in ethanol and 10% solution of PVA (polyvinyl alcohol - Sloviol R) with average molecular weight 130.000 dissolved in H_2O. In this case, it was not possible to run the process for longer than several minutes due to the extensive coagulation of one of the solution and difficulties with continuous polymeric circulation. During all carried out experiments was one of the tested polymeric solutions subsidised by Prussian blue in order to increase a contrast of the material in SEM scan of the final nanofibrous material. The spinning process from both electrode heads was confirmed visually during all carried out experiments.

Figure 4 Detail view of the electrode heads under the AC-electrospinning process (upper head - PVAC solution, bottom head - PVB solution).

5. DISCUSSION

Collected samples of manufactured nanofibrous material were analysed by SEM and FT-IR spectroscopy. Selected SEM scan of PVB-PVAc sample is shown in **Figure 5**. It is supposed that the distinctive difference in the fibres diameter in the sample indicates presence of both polymeric materials. Diameters of fibres fabricated with electrode heads set of equal electrical field on the spinning zones were measured using the NIS-Elements software. The mean value was 920 nm with standard deviation 520. It is supposed that higher value of the standard deviation, reflecting flat distribution function of fibre diameter, is caused by presence of two various materials in the sample. However, presence of two polymeric materials in the fabricated nanofibrous layer was proved by the FT-IR spectroscopy. FT-IR spectroscopy was carried out on Nicolet™ iS™ 10 FT-IR spectrometer by ATR method on Ge-crystal with resolution 1 cm^{-1} and range 4000-700 cm^{-1}.

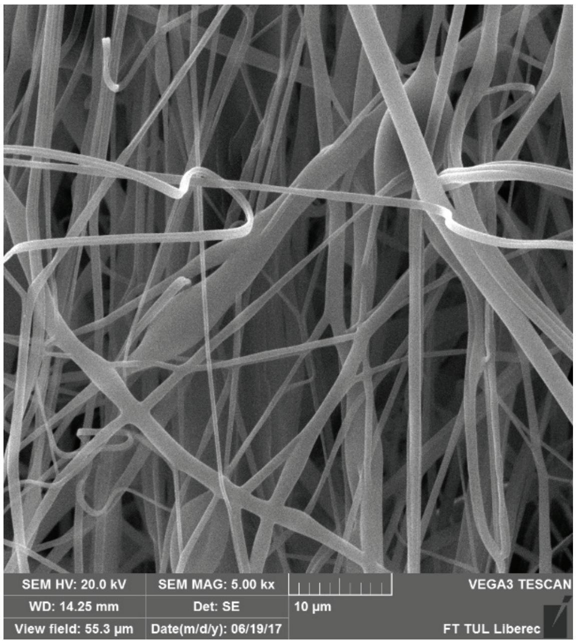

Figure 5 PVB-PVAc sample SEM scan

Results of FT-IR are shown in **Figure 6**. It shows the spectre of examined sample together with library-based spectres of PVB and PVAc. Distinctive marks of each library-based material in the spectre of the studied material proved the presence of both polymeric materials in the sample.

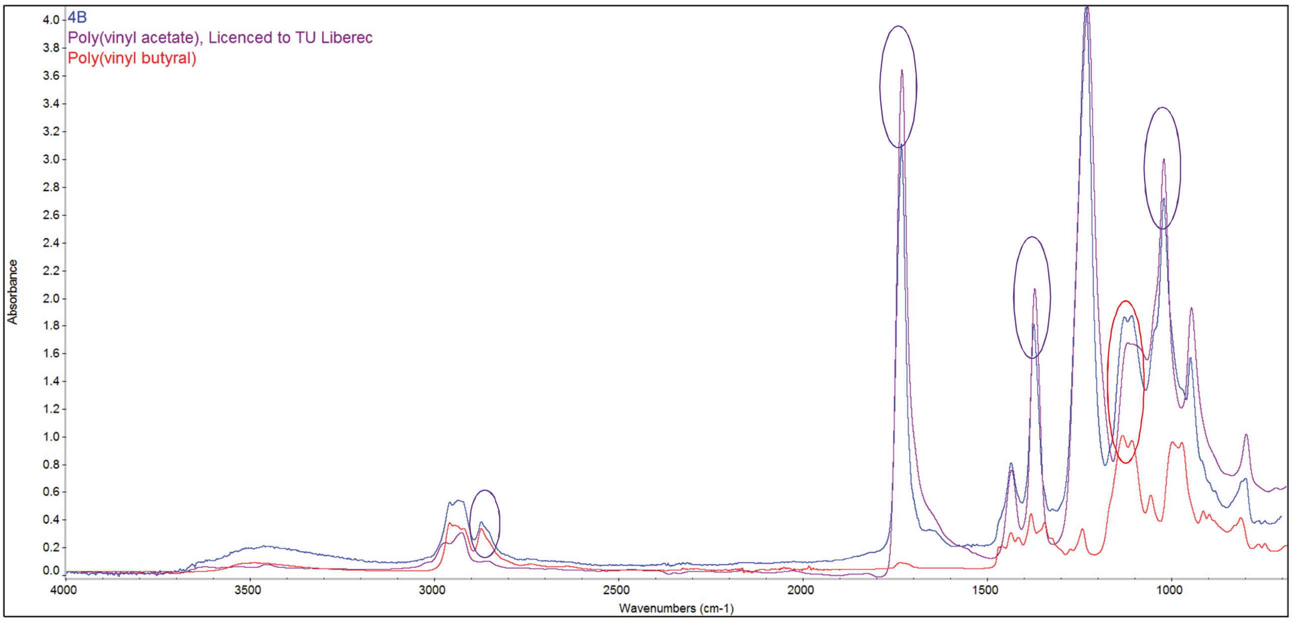

Figure 6 Comparison of spectres of examined sample (4B), PVAc and PVB. Significant features of particular material in the spectre of the fabricated nanofibrous material are marked in the graph

6. CONCLUSION

The newly designed electrode was analysed, manufactured and successfully tested on a laboratory AC-electrospinning device at Technical University in Liberec. It shows that the AC-electrospinning technology can be used also for production of composite nanofibrous materials of advanced mechanical and chemical properties. The electrode geometry was designed according to results of electrical field analyses and tested for selected polymeric solutions. Experimental verification proved the ability of simultaneous spinning of PVAc and PVB polymeric solutions continuously without any detected obstacles. The presence of both material components in the fabricated nanofibrous layer was proved by FT-IR spectroscopy and visually during the electrospinning process. In the case of electrospinning of PVB (dissolved in ethanol) and PVA (dissolved in H_2O), the process became unstable after several minutes due to extensive coagulation. Despite of avoiding any contact of polymeric solutions on the electrode, extensive solvent evaporation during the fibre formation may contaminate other polymeric solution and thus negatively affect the polymeric solution properties. It is therefore suggested to use polymeric solutions based on the same solvents only. However, under these preconditions it is possible to run the AC electrospinning continuously with the productivity approx. 0.5 g/min. Thanks to replaceable heads of the electrode it is also possible to design another special set of spinning heads that reflects the required electrical field intensity for particular polymeric materials. Another work will be also focused on investigation of the relation between final material structure and spinning heads electric field distribution. The described model represents a useful tool for such purpose. The upcoming research will be therefore subjected to further testing of spinning heads with specific geometry as well as new polymeric solutions for production of composite AC-electrospun nanofibrous materials useful for various medical applications.

ACKNOWLEDGEMENTS

The research presented in this article was supported by the Ministry of Education, Youth and Sports in the framework of the targeted support of the "National Programme for Sustainability I" LO 1201 and the OPR&DI project "Centre for Nanomaterials, Advanced Technologies and Innovation", CZ.1.05/2.1.00/01.0005.

This publication was written at the Technical University of Liberec as part of the project "RESEARCH AND DEVELOPMENT OF DEVICES FOR PRODUCTION OF NANOFIBROUS MATERIALS USING AC-ELECTROSPINNING PROCESS" with the support of the Specific University Research Grant, as provided by the Ministry of Education, Youth and Sports of the Czech Republic in the year 2017.

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