COMPOSITE ELECTROSPUN FIBROUS STRUCTURES BY DIFFERENT FIBER GENERATORS

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Abstract

A combination of electrospinning, a well-known technology for producing nanofibrous structures, and carbon nanotubes is presented in this work. Electrospinning is technology offering many arrangement options. The needleless electrospinning with three different types of fiber generating electrodes (spinners) was used to produce electrospun polymeric nanofibers doped with carbon nanotubes. The study is focused on description of electrospinning process with different types of spinners with respect to final fiber morphology represented by fiber diameters. The comparison between production of blank AC and DC electrospun nanofibrous layers and nanofibrous layers reinforced with carbon nanotubes is studied here as well.

Keywords: Electrospinning, composite nanofibers, carbon nanotube

1. INTRODUCTION

The process of electrospinning has to be based on high voltage source. Until now, mostly DC (direct current) high voltage sources have been used in the industry and in laboratories [1]. Only a few publications, for example [2, 3], have studied application of AC (alternating current) high voltage sources for the electrospinning process. In both cases, the electric forces are applied to polymer solution or polymer melt to drive the fiber spinning process. The DC electrospinning requires a grounded collector to achieve the electrical potential difference and can be used in needle or needle-less form. On the other hand, the AC electrospinning is needleless and collectorless [2]. Alternately charged nanofibrous groups from successive emissions attract each other so they are working as the virtual collector.

The parameters, that can be changed, can be divided into two groups [4]: material conditions and process conditions. Material conditions are type of polymer, its molecular weight, concentration in solution, temperature of melts, surface tension, viscosity and electrical conductivity of used polymer solution or melt, additives, etc. Among process parameter belong applied voltage, working distance (for DC electrospinning), type and shape of spinning electrode, type of collector and of course ambient conditions, such as room temperature and humidity.

The electrospinning modifications influenced by material or process conditions changes are for example these: fiber orientation (alignment), fiber patterning, type of spinning electrode, 3D fibrous objects by change, porous fibers, hybrid yarns or nanofibrous yarns [5].

The production of composite nanofibers requires not only special polymer solution preparation but it also follows different tendencies during AC or DC electrospinning process. The carbon nanotube addition into solution change not only material conditions, but also process parameters have to be adapted. The type of spinning electrode can have influence on the final DC electrospun fiber morphology, even if there is no addition of other materials into the used polymer solution [6]. The AC electrospinning also reacts very sensitively to changes of material condition, because the relaxation time is very important parameter here.

The comparison of so called blank samples of polymeric nanofibers produced by DC and AC electrospinning with composite nanofibers reinforced by carbon nanotubes is presented in this article. Also different types of spinning electrodes for DC electrospinning of simple polymer fibers and composite fibers are compared.

2. MATERIALS AND METHODS

The Poly(vinyl butyral) (PVB, Mowital B60H, Kuraray America, Inc., with an average molecular weight of 60,000) was used in a form of 10wt% solution in ethanol. The solution for composite nanofibers electrospinning contains carbon nanotubes (MWNTs, Sigma-Aldrich; purity >95 %; length 5 μm; diameter 6-9 nm) in 2.5 wt% of polymer dry matter. The dispersion of nanotubes was carried out by ultrasound (ultrasonic exposure time 90 s, ultrasonic power 175 W, ultrasonic frequency 20 kHz) in ethanol and then the polymer was added.

The prepared solutions were electrospun by DC and AC electrospinning. For DC electrospinning, the needleless electrospinning device based on rotating cylinder wetted in solution bath was used. Three different spinning electrodes - rollers were used for DC electrospinning of blank PVB solutions and composite solutions: a smooth roller, a roller with spikes and a string roller. The spinning rollers were made of electrically conductive material. The string cylinder produces fibers on strings that are stretched in the axis of the roller. There are a total of 4 strings uniformly distributed over the circumference of the cylinder. The roller with spikes contains 6 rows of spikes around the perimeter of the roller, each row consisting of 9 spikes. There are 54 spikes on the roller surface. The smooth roller does not have any special shaping. The spinning electrode was connected to direct current high voltage source and a collector in the form of metal plate was grounded. The spunbond nonwoven supporting material was placed under the collector. The process parameters for direct current electrospinning were: spinning electrode to collector distance - 17 cm; spunbond speed - 5 cm/min.; spinning roller frequency - 9 rpm; ambient air humidity - 27 %RH; ambient temperature - 21 °C; spinning electrode roller applied electrical voltage - 56 kV (positive polarity).

The AC electrospinning was done on device consisting of hollow rod spinning electrode by which polymer solution was dosed. The inner electrode diameter was 4 mm and the rod was made of aluminium. The alternating current electrospinning experiments were conducted using a high voltage transformer (24,000 V/100V ratio) powered by a 0-230 V variable transformer. The voltage applied on the rod spinning electrode was 24 kV at the frequency of 50 Hz.

The composite fibers were studied by thermogravimetric analysis (TGA) performed on instrument Q500 (TA Instruments, USA). The thermogravimetric analysis was carried out in a reactive atmosphere, e.g. in synthetic air, which was composed of 20% oxygen and 80% nitrogen. The platinum pans with a volume of 100 µl were used as a sample holder. The TGA set up was: temperature speed - 20 °C/min; maximum temperature - 670 °C; synthetic air flow - 60 ml/min; weight of each sample - 10 mg.

3. RESULTS AND DISCUSSION

All the solutions were electrospun by all of the electrospinning techniques described above. DC electrospinning of blank samples did not produce a uniform layer. The electrospinning was possible, but only from the edges of the roller. The AC electrospinning had no problems. The DC electrospinning of composite solution has the same tendency; the smooth roller did not achieve a uniform layer. The best sample, according to the electrospinnability and with respect to the structure and amount of defects in the layer, seems to be a sample made with a string roller. The scanning electron images representing all the DC electrospun samples can be seen in **Figure 1** and **Figure 2**, the AC electrospun samples images are shown in **Figure 3**. The average fiber diameter was calculated by means of image analysis from three hundred individual fiber measurement in each sample.

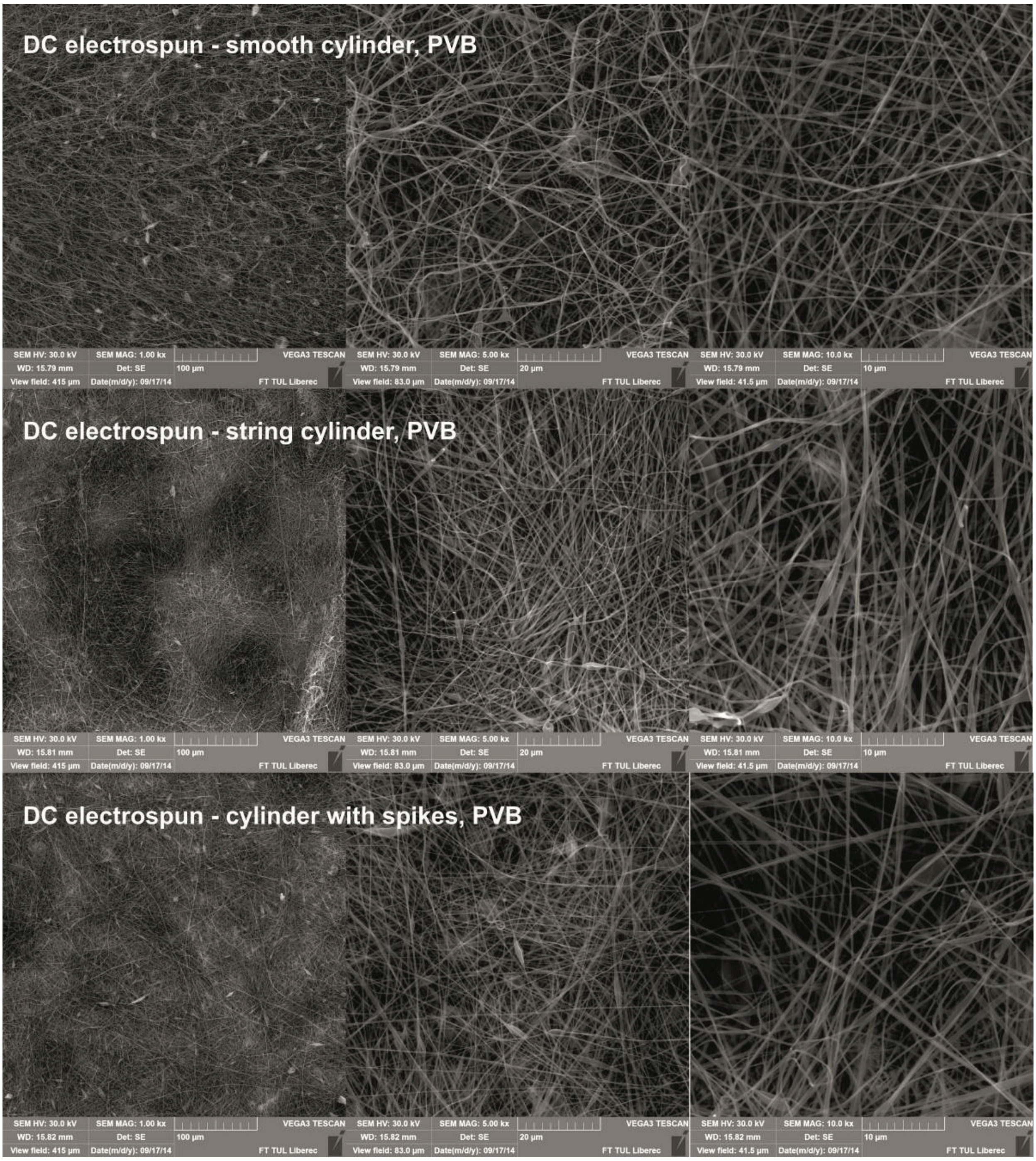

Figure 1 Scanning electron images of DC electrospun PVB fibrous layers produced by means of smooth and string cylinder and cylinder with spikes as a spinning electrode. There are three different images for each sample. Scale bar from left: 100 µm; 20 µm and 10 µm

The average diameter of blank samples (PVB) produced by DC electrospinning were: smooth roller - diameter 266 ± 66 nm; string roller - 244 ± 79 nm; roller with spikes - 267 ± 95 nm. The average composite fiber (with 2.5wt% CNTs) diameters for DC electrospun samples were: smooth roller - diameter 657 ± 252 nm; string roller - 869 ± 342 nm; roller with spikes - 500 ± 232 nm. It is necessary to note, that the electrospun nanofibrous layer made by roller with spikes contains many defects uniformly distributed in the structure. AC electrospun blank PVB fibers average diameter was 607 ± 187 nm and AC electrospun composite fibers average diameter was 695 ± 185 nm.

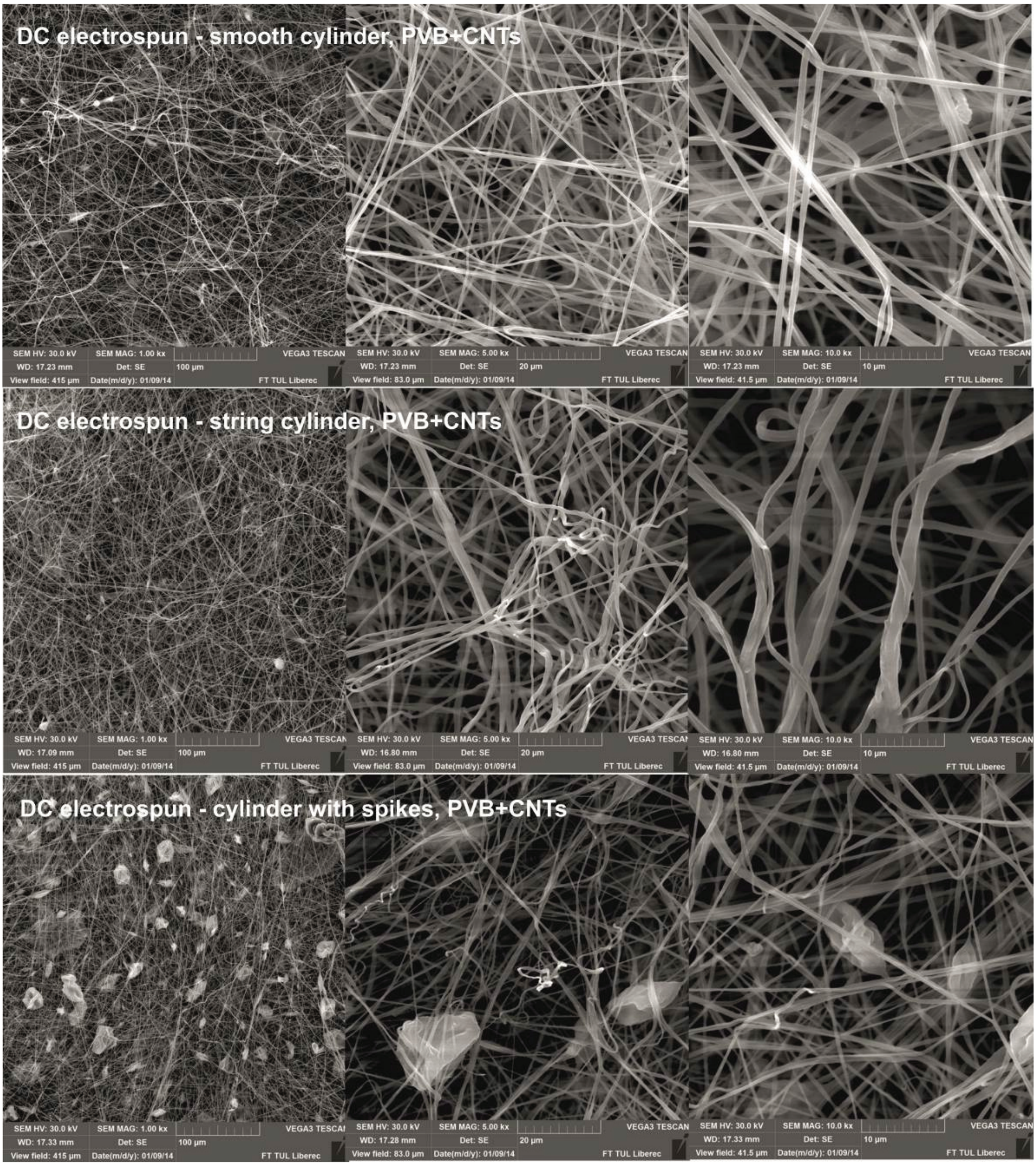

Figure 2 Scanning electron images of DC composite electrospun fibrous layers produced by means of smooth and string cylinder and cylinder with spikes as a spinning electrode. There are three different images for each sample. Scale bar from left: 100 µm; 20 µm and 10 µm

It is obvious, that carbon nanotubes addition increases the fiber diameter. The fact is clear mainly for DC electrospinning. When the AC electrospinning is taken into consideration, the fiber average diameters are not so significantly different. The comparison of three spinning electrode cylinders for DC electrospinning showed different final fiber morphology for composite nanofibers only. The blank samples did not have significant differences in the average fiber diameters.

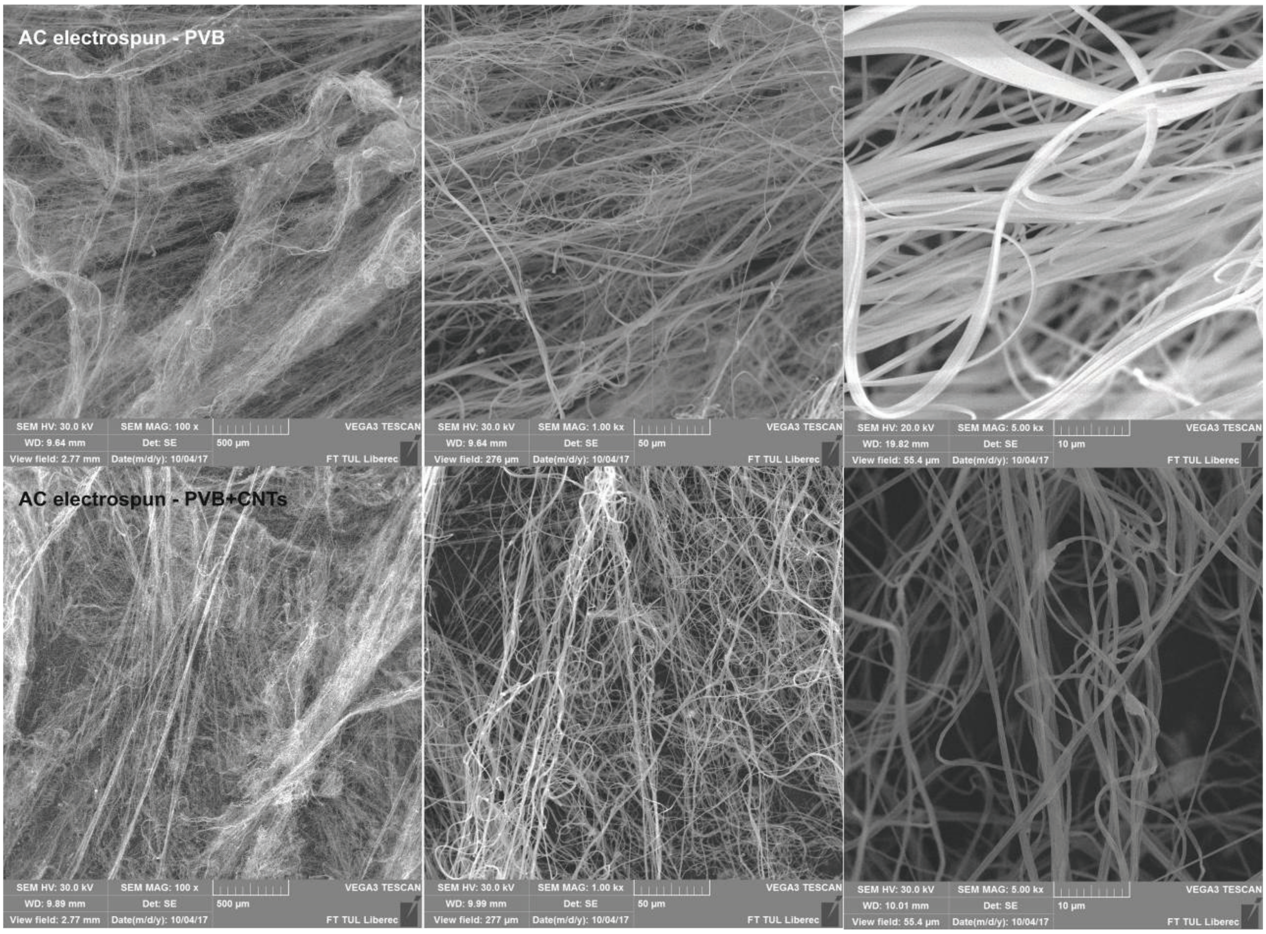

Figure 3 Scanning electron images of AC electrospun fibrous layers produced from PVB solution (upper) and composite PVB solution with carbon nanotubes (lower). There are three different images for each sample. Scale bar from left: 500 μm; 50 μm and 10 μm

However, diameters of composite nanofibers are significantly different. It is obvious that spinning electrode roller geometry influenced not only fiber diameter but complete fiber layer morphology. The smallest average fiber diameters were produced by the roller with spikes but contained the most defects. The largest average fiber diameters were measured on the string roll, but the fibrous layer was the most homogeneous and almost defect-free. This is apparently due to the different distribution of the electric field on the spinning electrodes. When carbon nanotubes were in the spinning solution and increased the electrical conductivity of the solutions, the spinning electrode geometry appeared to be more pronounced.

The distribution of electric field intensity on spinning electrodes was simulated using the Comsol Multiphysics software. This simulation should help to better understand the electrical field's occurrences between the spinning electrode and the collector and thus explain the morphology differences in final fibrous composite structures made by DC electrospinning. The simulation was created as a graphical interpretation of the electrical potential and the intensity of the electric field. In the simulation this set up was used: Neutral environment; the spinning electrode charged at 56 kV; the grounded collector; the spinning electrode holder made from a non-conductor. The colour of final graphical results (see **Figure 4**) represents an electrical potential, the contours represent the intensity of the electric field and the arrows represent the field lines of the electric field.

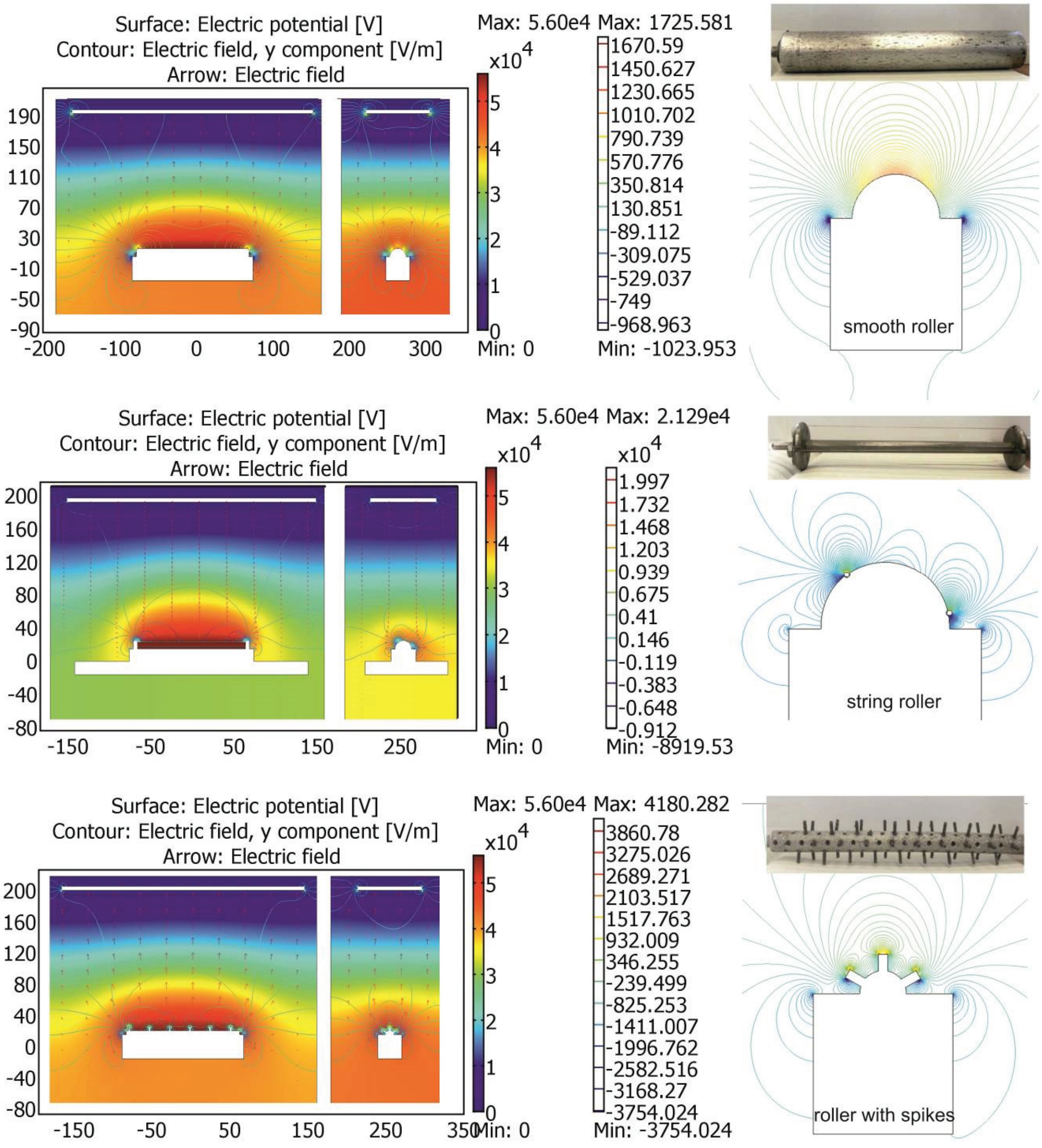

Figure 4 Examples of graphical results from simulation of electric field distribution for DC electrospinning with three different fiber generators - cylinder electrodes: smooth roller (upper), string roller (middle), roller with spikes (lower). Photos of the cylinder electrodes used for the real experiments are enclosed with each simulation results

The concentration of the electric charge is the most significant in the areas that are formed by the edge, not the smooth surface. In these places, Taylor cones are formed more preferably than on smooth surfaces. Blue contours illustrate the locations where the highest electrical charge concentration is associated with the value of the field strength. For the roller with spikes, the field intensity is highest at the top of each spike. On a smooth roller, the intensity is greatest at the edges. Practically it means that Taylor cones are formed mainly at the edges of the spinning electrode. This helps explain the differences in the final morphology of the fibers made from these spinning electrodes.

All the composite electrospun fibers contain carbon nanotubes because of their uniform grey colouring, but the amount of carbon nanotubes inside the final fibrous material is not necessarily the same as in the spinning solutions. According to TGA analysis, there is not significant influence of used spinning electrode geometry. The resulting final CNTs content in the composite fibrous samples produced by different electrospinning methods were: smooth cylinder - 1.39±1.11 %; string cylinder - 1.17±0.45 %; cylinder with spikes - 1.40±0.27 %; AC electrospun sample - 2.21±0.22 %.

4. CONCLUSIONS

This paper compares the electrospinning of polymer and composite fibers from different spinning electrodes, as well as direct current electrospinning and alternating current electrospinning. Optimal DC electrospinning of PVB solution, where a uniform layer with almost no defects was formed, was produced using the string roller. The lowest quality electrospun material was from the smooth roller. Although the roller with spikes has produced fine fibers due to the high intensity of the electrical field on the spikes, many defects have also been produced. This is supported by a graphical simulation of the distribution of the electric field on individual spinning electrodes. Whereas on the smooth roller the electric charge concentrated mainly on the edges of the spinning electrode, in the case of the string roller, the distribution of the electric field was more uniform. In the production of composite fibers by these processes, significant differences were observed between the resulting fiber diameters. The amount of defects increased in the nanofiber layer not only with the change of the spinning electrode but also with the presence of carbon nanotubes in the polymer solution. The results of TGA analysis showed that nanofibers did not incorporate the whole amount of carbon nanotubes from the solution, but only about half of them. In the case of AC electrospinning on the other hand, almost the whole amount of carbon nanotubes was present in the resulting fibers. The study of the production of composite nanofibres using different types of spinning generators for DC electrospinning and different types of electrospinning (DC versus AC) will continue with the change in the amount of carbon nanotubes added to the basic spinning solution.

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