ABSTRACT: This study deals with a new combination of alternating current (ac) electrospinning and bubble electrospinning. Research devoted to the combination of these two methods for the preparation of nanofibrous and microfibrous mats has been carried out. The design, construction, and description of bubble electrospinning are described in this article. The final morphologies of the fibrous layers produced by these methods have been compared with other well-known electrospinning methods. The bubble electrospinning and ac electrospinning aspire to become new technologies that could be utilized in various technical areas and tissue-engineering applications.

INTRODUCTION

Bubble electrospinning is a novel method which has recently joined the family of very progressive technologies of electrospinning. Bubble electrospinning offers a lot of advantages in the electrospinning production of submicron fibers. Bubble electrospinning was first mentioned in the study of He and Liu in 2012.1 The electrospinning method uses electric forces to overcome the surface tension on the surface of the resulting bubbles. These bubbles occur on the surface of the polymer solution with the aid of forced air. The electric forces form Taylor cones from which the fibers are produced. The surface tension depends on the geometry and size of the bubbles. The surface tension of the bubbles may be expressed by the following Young–Laplace equation: \( \sigma = \frac{1}{4}r\Delta P \), where \( \sigma \) is the surface tension, \( r \) is the radius of the bubble, and \( \Delta P \) is the pressure difference.2

During the electrospinning process, some difficult-to-control bubbles are created on the surface of the solution. Nevertheless, this phenomenon has no negative impact on the industrial production of fibers, including fiber deposition characteristics, morphology, and productivity of the process.2

The process of the electrospinning method was an impulse for the design of the first electrospinning equipment in the lab that could be modified in the future or become the basis for a new bubble electrospinning equipment. This device and its electrospinning technology could find use in technical applications, for example, in the mass production of filters with fine fiber yarns.3 Its application may also be found in the medical field for creation of new composite nanofibrous scaffolds for tissue engineering.4 The study describes in detail the devices for producing fibers by bubble electrospinning. The described experiment compares the productivity and the structures produced by the technology of alternating current (ac) bubble electrospinning with well-known direct current (dc) bubble and needle electrospinning.

Possible usage of ac high voltage for electrospinning is discussed in the patent US 2005/0067287.5 This patent shows the potential of ac electrospinning for production of contact lenses. Remarks of the potential use of this method can be found in patents US 2003/0226750 and US 2011/0018174, dealing with the composition of ac-produced nanoibers, and in CZ 2012/304137, the patent for collectorless ac electrospinning process which forms the so-called nanoibrous plume.6 Ac electrospinning does not require an electrically
expressed counter electrode. The fibers are conveyed through the space to the collector only by their kinetic energy obtained by alternating polarity and subsequent self-organization at the beginning of the production process. Placing onto the collector in the form of a layer is realized solely by adhesion.

**EXPERIMENTAL PART**

**Materials.** Poly(vinyl alcohol) (Mowiol 18-88, Mw 130,000, Sigma-Aldrich) and distilled water have been used for preparing the working solutions.

**Structure Fabrication.** Poly(vinyl alcohol) (12% w/w) in distilled water has been used for electrospinning by all technologies. The solution is stirred for 24 h at the temperature of 22 °C. A concentration of 12% w/w poly(vinyl alcohol) has been chosen on the basis of the best electrospinning process and the final morphology of the fibrous layer. For ac and dc bubble electrospinning, identical equipment was used (Figure 1), and the needed respective high voltage source was connected (Figure 1). The device was further composed of transformer (ABB-KGUG 36, 0.7 bar) and a precision pressure-reducing valve (MS-LRP/B-FESTO, 0.05–0.265 bar). The overall voltage controller (ABB-KGUG 36, 0–37 kV effective value) with a conversion ratio of 36 000/230 V was used, from which the spinner was supplied with a voltage of 37 kV and a frequency of 50 Hz. The output voltage was controlled by a Thalheimer-Trafowerke ESS 104 variable transformer designed for 230 V ac input and an output of 0–250 V. The maximum output voltage was 440 V with a capacity (kVA) of 1.2 (scheme of electrical circuit—Figure 2). The polymer dosing was 50 mL/h, and the air flow rate was 1 L/min. In this case, the collector was electrically neutral.

For the ac bubble electrospinning, a dc voltage source (Spellman-SL 300, 0–100 kV) was used, from which a current of positive +21 kV polarity was applied to the spinner. The polymer dosing was 4 mL/h, and the air flow rate was 0.3 L/min. The negative voltage on the collecting collector was −10 kV.

For the dc needle electrospinning, a dc voltage source (Spellman) was used, and a needle (1.2 × 40 mm) with a positive voltage of +20 kV served as the spinner. The nanofibers were deposited on the collector in the form of a negatively charged electrode with a voltage of −10 kV at a distance of 150 mm from the needle spinner. The polymer dosing was 4 mL/h. The difference between the dosing rates for dc and ac electrospinning is caused by specific requirements of technologies mentioned above. The productivity rate of ac spun nanofibers is higher than in the dc variant and requires higher feeding rates. Explanation for different high-voltage settings of ac and dc systems can be explained by our effort for achieving best quality electrospun nanofibers.

The process was realized at the temperature of 22 °C and a relative air humidity of 50%.

**Scanning Electron Microscopy Analysis.** The dry samples (10 × 10 mm) were sputter-coated with gold (10 nm) by a coater (Q150 R-Quorum) and observed by a scanning electron microscope (Tescan Vega 3 SB Easyprobe).

**Morphology Characterization.** The study of the morphology of the individual samples was carried out using the image analysis software (NIS Elements-Nikon). To measure porosity, the binary thresholding of scanning electron microscopy (SEM) images was used. The selected threshold was 20.300 with standardized contrast for all images. The magnification of all images was 15.000X. To measure the fiber diameters, five SEM images (magnification 10.000X) from each technology were taken from different locations of the respective sample. For each sample, 1000 fiber diameters were measured for different fibers. These measured values were further subjected to statistical analysis.

**Visualization of the Electrospinning Process.** The emergence of Taylor cones and subsequent fluid jets of polymer solution in the electric field was visualized using a high-speed camera (Speed Camera Olympus-13) at a scanning speed of 5000 fps. The recording took place at a distance of 450 mm from the observed object.

**Productivity Study.** Determination of productivity was carried out by weighing samples of the nanofibrous layer created by the respective technology in 1 h. For each technology, 10 samples were measured, and afterward, the values were averaged.

**RESULTS AND DISCUSSION**

With all tested technologies, we have managed to create nanofibrous layers with a homogeneous structure that confluent the collector. The ac electrospinning of bubbles has proven to be functional. The average porosity of these layers ranged from 67 to 71%. Morphology characteristics of the materials were studied by SEM (Figure 3) and then analyzed by the image analysis software. The specific values (Figure 3) of the mean fiber diameter are as follows: dc bubble electrospinning—265 ± 56 nm; dc needle electro-
spinning—248 ± 76 nm; ac bubble electrospinning 227 ± 84 nm. The results show that the fiber diameter values are not significantly different for individual technologies, even though ac bubble electrospinning shows the lowest value. Nanofibrous layers are homogeneous without any major structural defects.

Another studied attribute was the productivity of individual technologies.

The results for individual technologies (Figure 4) are as follows: ac bubble electrospinning—2.03 ± 0.11 g/h; dc bubble electrospinning—0.31 ± 0.05 g/h; dc needle electrospinning—0.27 ± 0.03 g/h. These results are supported by the study of the generation of Taylor cones and subsequent polymer jets in the electric field, where the average number of emitted polymer jets for individual technologies is represented.

Figure 3. Comparison of the fiber diameter: upper part—SEM images comparing the structure of nanofibrous layers; the scale bar is 5 μm; lower part—histogram comparing average fiber diameters produced by a different electrospinning technology.

Figure 4. Comparison of productivity: upper part—high-speed camera images capturing the generation of Taylor cones and subsequent polymer jets in the electric field represented by red dots; the scale bar is 1 mm; lower part—a histogram comparing the productivity values of individual technologies.
by the images of the electrospinning process from a high-speed camera (Figure 4). Individual jets are marked with red dots. The number of polymer jets is shown in Figure 4: ac bubble electrospinning—8; dc bubble electrospinning—2; dc needle electrospinning—1. It is clear that the ac bubble electrospinning provides several times higher productivity in comparison with comparative technologies.

The ac variant of bubble electrospinning is more productive because it provides the polymer solution with a high hydrodynamic instability that promotes the formation of polymer jets. Compared to the dc variant, the degree of this instability is unchanged, which is due to the constant change of polarity of the system.

Although dc bubble electrospinning sometimes provides a greater number of jets (larger surface area with more curvature) during the process of electrospinning, the productivity is very similar. The number of average polymeric jets is usually the same (one to four jets). We can support this with productivity of dc needles and dc bubble electrospinning mentioned above.

## CONCLUSIONS

A new ac bubble electrospinning method was introduced, and its technical solution has been described. This study has proven that the bubble electrospinning technology is able to produce nanofibers from poly(vinyl alcohol) solution of the same quality structure as conventional electrospinning methods. A clear advantage of ac bubble electrospinning in the form of multiplicity of productivity compared to the dc variant of bubble electrospinning has been manifested. This advantage extends the possibility of use of bubble electrospinning technology to produce ultrafine fibers in other industries. The future research of ac bubble electrospinning will focus on a more thorough description of the dependence of this method on the rheological and chemical properties of superfluous polymer solutions.

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### Notes

The authors declare no competing financial interest.

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