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Electrostatic fabrication of polymer nanofibers

Abstract. *Fabrication process of nanofibers from the liquid polymer solution using electrospinning is described in the paper. In the experiments, polyvinylidene fluoride (PVDF) and dimethylformamide (DMF) were used as a polymeric material and a solvent, respectively. Additionally, the results of the measurements of diameters of obtained fibers, current-voltage characteristics of the process and calculation of resistivity of liquid polymer are presented.*

Streszczenie. *W pracy przedstawiono proces elektrostatycznego wytwarzania nanowłókien z roztworu ciekłego polimeru. W procesie elektroprzędzenia w roli polimeru i rozpuszczalnika użyto odpowiednio polifluorek winylidenu (PVDF) i dimetyloformamid (DMF). Dodatkowo badania obejmowały pomiary średnic otrzymanych włókien, charakterystyk prądowo-napięciowych procesu oraz wyznaczenie rezystywności ciekłego polimeru (**Elektrostatyczne wytwarzanie nanowłókien polimerowych**).*

Keywords: electrospinning, electrostatics, nanofiber, polymer.
Słowa kluczowe: elektroprzędzenie, elektrostatyka, nanowłókna, polimer.

Introduction

Electrospinning is an electrohydrodynamic process used for the production of nanofibrous materials for many modern applications. The most important are tissue engineering and biomedical applications (e.g. drug delivery, wound healing), sensors for diagnostics, electronics, filtration purposes and energy harvesting systems [1-7]. In general, this process enables to manufacture nanofibers using an electrically charged stream of polymer solution. The diameters of the obtained polymer fibers range from submicron to nanometer values. This process has been successfully used to produce various types of fibres – natural, synthetic, biodegradable, nondegradable and their mixtures [8]. The main advantages of this process in comparison to other conventional fiber-forming methods (e.g. mechanical drawing, phase separation) are low cost and simplicity of the experimental system.

The process of electrospinning is influenced by many parameters. The basic factors influencing the quality of nanofibers obtained are the properties of the polymer solution (e.g. resistivity, viscosity), the arrangement of the measuring system (e.g. type of collector used, capillary-collector distance, solution flow rate) and the environmental conditions in which process is carried out (e.g. humidity, temperature).

During electrospinning, a strong electric field causes a continuous jet of a polymer solution to be formed and moved from the capillary or nozzle towards the oppositely charged grounded electrode – a collector. In the case of weak or absence of any electric field the polymer droplet is held at the capillary tip by surface tension of the liquid. When a strong electric field is applied to the polymer solution, as the surface tension is balanced by the electrostatic forces, the droplet elongates and develops into so called Taylor cone. When the strength of the electrical field is sufficient to overcome the surface tension of the liquid, a fine fiber jet is ejected from the tip of the Taylor cone. As the fiber jet moves in the air, the solvent evaporates and solid polymer fibers are deposited on a grounded collector.

Electrospinning makes it practically possible to produce fibers from a huge number of polymeric materials. The most important limiting factor for the production of fibers is the application of the right solvent. Sometimes it is necessary to use a mixture of solvents to obtain fibres with desired morphological properties In our work we present the process of manufacturing poly(vinylidene fluoride) (PVDF) fibers.

PVDF is a semi crystalline polymer which is chemically and mechanically stable. It also exhibits high thermal stability and aging resistance. This material is the most frequently chosen polymer for various applications because of its unique properties such as flexibility, biocompatibility, and piezoelectric properties. In general, piezoelectricity is the internal feature of the material that generates electrical potential because of stress or deformation. PVDF has five different crystalline phases and the polar β phase is crucial and the most desirable from the point of view of piezoelectric properties of the material [9]. Electrospinning gives great opportunities to obtain β phase during the production of PVDF nanofibers. PVDF nanofibers are widely used in many applications such as nanogenerators, water treatment, membrane distillation, gas separation, pollutants removal [10-13].

Experimental section

The paper focuses on the electrostatic fabrication of PVDF nanofibers. For this purpose, electrospinning was carried out in the measuring system presented in Fig. 1.

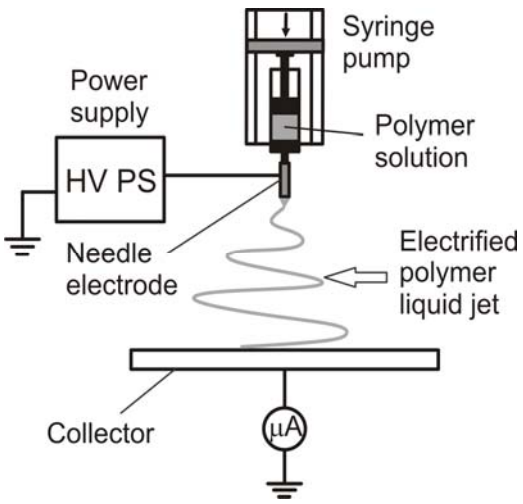

Fig.1. Scheme of the experimental system for the fabrication of polymeric nanofibers and measurement of current-voltage characteristics of electrospinning process

Moreover, this system (i.e. after a slight modification – the grounded collector by a current meter) made it possible to determine the current-voltage characteristics of the electrospinning for various measurement conditions. A

polymer solution was supplied to a metal capillary using a syringe pump (Model NE-300, New Era Pump Systems Inc., USA). A capillary was a surgical needle made of stainless steel with an external diameter varying from 0.5 to 0,9 mm. A capillary was connected to a positive high voltage source (Model SP/EW50P12.0Y17, Glassman High Voltage Inc., USA). A stainless steel plate (200 mm by 200 mm) was positioned under the needle as a collector, which was electrically grounded and covered with a thin aluminum foil. The collector was located at a fixed distance of 120 mm away from the capillary tip. PVDF was dissolved at a concentration of 15 and 20% (w/w) in dimethylformamide (DMF). The electrospinning was carried out at room temperature 22±2°C and a humidity of 45±3%. The flow rate of the polymer solutions was regulated in the range from 0.1 to 1 ml/h and the voltage in the range from 7 to 16 kV, respectively.

The morphology of the prepared nanofibers was observed using OPTA-TECH MB-200 (Poland) optical microscope. In order to determine the electrical parameters of a polymer solution (i.e. electrical resistivity), resistance measurements were performed in the system shown in Fig. 2. Resistance measurements were carried out using resistance meter Trek 152-1.

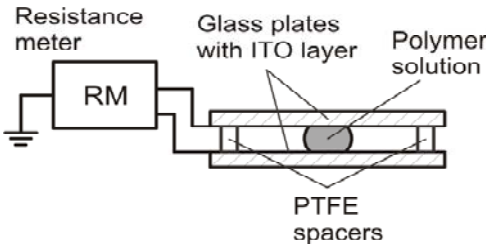

Fig.2. Scheme of the system for measuring the resistance of a polymer solution

Results and discussion

The image of the Taylor cone and the nanofibres produced during electrospinning was shown in Fig. 3.

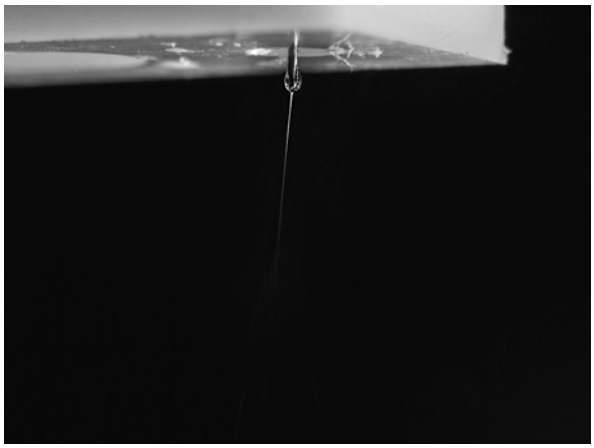

Fig.3. Image of polymeric nanofibers using electrospinning method. Results obtained for PVDF concentration c=20%, applied voltage U=+12 kV, distance between the capillary and collector l=120 mm, and flow rate v=1 ml/h in the air

As can be seen, at the end of the capillary there is a drop of polymer solution which transforms into the Taylor cone from which single nanofibres are extracted towards the collector.

In our experiments most manufactured electrospun nanofibers showed a round cross section with a quite smooth surface. A single PVDF nanofiber with regular shape was presented in Fig. 4.

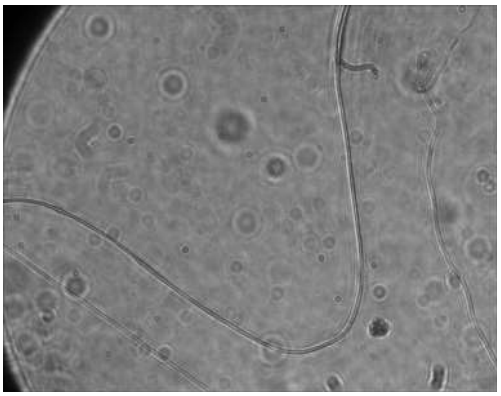

Fig.4. Optical image of a single PVDF fiber with a regular morphological form. The individual dots visible in the image are the impurities of the laboratory slide. Results obtained for capillary diameter d=0.5 mm, applied voltage U=+12 kV, distance between the capillary and collector l=120 mm, and flow rate v=1 ml/h in the air

However, some fibers had beaded morphologies. Beaded fibers can be observed for practically all polymers during electrospinning [14]. In general, this effect is due to processing variables – the applied voltage, and the distance between the capillary and collector. Other parameters such as solution flow rate, polymer concentration, solution viscosity and conductivity were constant during our tests. PCDF nanofibers with beads were shown in Fig. 5. It should be noted that the structure of fibres with beads is not due to poor electrospinning performance and is in some cases desirable and used for particular applications [15].

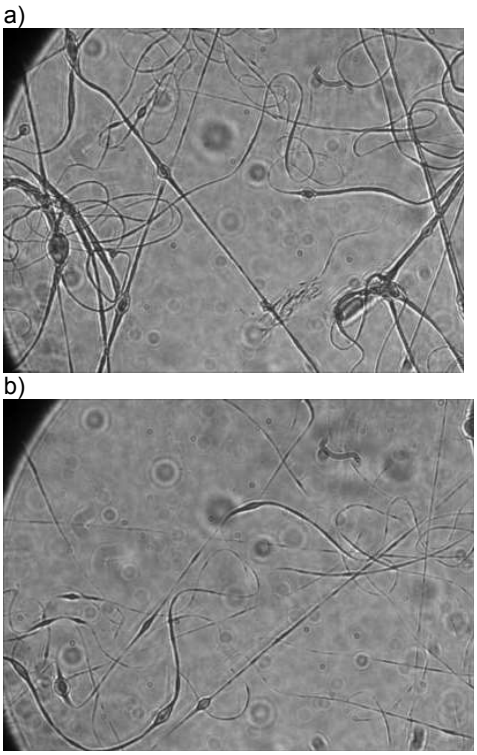

Fig.5. Optical image of PVDF fibers with beaded morphology. Results obtained for capillary diameter d=0.5 mm, applied voltage U=+14 kV, distance between the capillary and collector l=120 mm, and flow rate v=1 ml/h in the air: a) PVDF concentration c=20%, b) PVDF concentration c=15%

During experiments, it was noticed that the diameter of the PVDF fibres fabricated D_f was in the range of 700 to 1200 nm regardless of the capillary diameter, flow rate of polymer solution, and the capillary supply voltage. The results of diameter measurements for different conditions of electrospinning were shown in Fig. 6. As can be seen in Fig. 6, for increasing flow rate of polymer solution there was a decrease in the diameter of the produced fibers for all cases. The most significant difference in the value of fiber diameter was observed for applied voltage and PVDF concentration equal to +10 kV and 15%, respectively. For the other test cases the fibres obtained had diameters below 1000 nm regardless of the flow rate of polymer solution. It should be noted that the above results were obtained for a capillary diameter of 0.5 mm, but similar effects were observed for other capillary diameters. The observed some differences were insignificant.

Our research has confirmed that electrospinning process is a stable nanofiber production process for different power supply conditions, capillary diameters and flow rates of the polymer solution.

The dependence of the so-called start and stop voltage (V_{start} and V_{stop}) of the spinning process for different polymer concentrations on the capillary diameter was shown in Fig. 7.

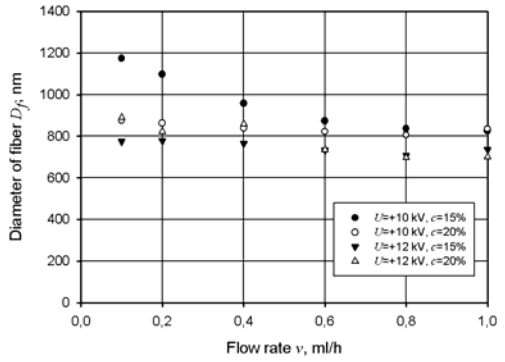

Fig.6. Influence of the flow rate of polymer solution on the diameter of fibers for different conditions of the process. Results obtained for capillary diameter d=0.5 mm, distance between the capillary and collector l=120 mm in the air

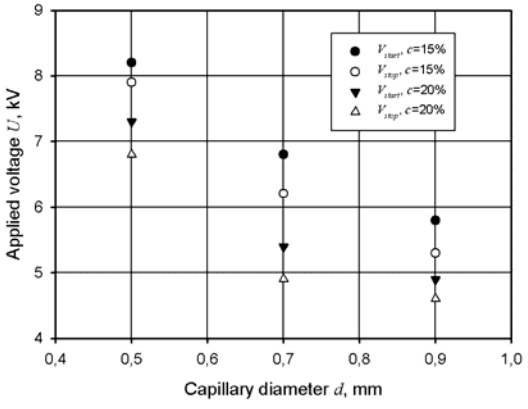

Fig.7. Influence of capillary diameter d on the behaviour of electrospinning process. Results obtained for applied voltage U=+12 kV, distance between the capillary and collector l=120 mm, and flow rate v=1 ml/h in the air

V_{start} determines the voltage value for which a single or many fibers develop from the Taylor cone. As can be seen from Fig. 7, the increase in the capillary diameter leads to the decrease in the value of both voltages. This effect is most likely due to electrodynamic processes occurring when high voltage is supplied to a capillary filled with a polymer solution.

The increase in polymer concentration leads to the increase in these voltages, which can be directly related to changes in surface tension of the polymer solution, i.e. for higher polymer concentrations, the surface tension of the solution is increased. It was also seen that V_{start} and V_{stop} graphs show a hysteresis character, which also confirms the occurrence of dynamic phenomena of electrospinning.

In the next step of our research, current-voltage characteristics of electrospinning were determined. The results of measurements of I-U characteristics were obtained in the measuring system presented in Fig. 1. It should be pointed out that the characteristics were strictly defined by the resistance of the polymer solution.

Examples of I-U graphs obtained for different polymer concentrations and flow rates of a polymer solution were shown in Fig. 8. All measurements were carried out in the voltage range for which the electrospinning was a stable process.

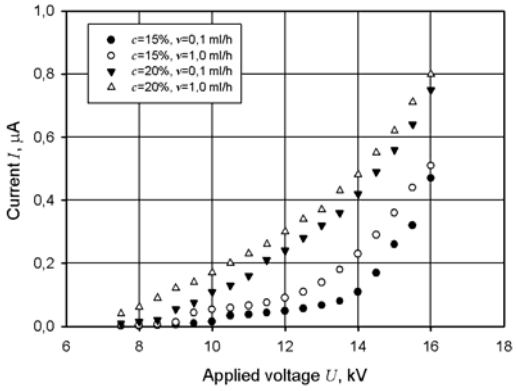

Fig.8. Current-voltage characteristics of electrospinning. Results obtained for capillary diameter d=0.5 mm, distance between the capillary and collector l=120 mm in the air

From these result it was concluded that an increase in flow rate from 0.1 ml/h to 1 ml/h led to an increase in current for the same supply conditions. This effect was most likely due to the shortened evaporation time of the solvent from the polymer solution. As a result, a solution with a lower resistance was obtained. Our results also showed that for lower polymer concentration values higher current values were obtained for the same values of capillary supplying voltages. In this example, the polymer concentration directly defined the value of polymer solution resistance and I-U characteristics.

In the last part of the tests, measurements of the resistance of a polymer solution R were made in the system shown in Fig. 2. In order to calculate the resistivity ρ, glass plates covered with a conductive layer of ITO (Indium Tin Oxide) as measuring electrodes were used. These plates made it possible to determine the surface of a drop of a polymer solution S at a given distance between the electrodes h.

The resistivity value of the polymer solution ρ was calculated from the equation:

$$\rho = R \cdot \frac{S}{h} \tag{1}$$

where: ρ – calculated resistivity, R – measured value of the resistance of the polymer solution, S – surface of a drop of the polymer solution, h – distance between electrodes (i.e. glass plates covered with ITO layer).

The results of the studies on the resistivity of a polymer solution were presented in Table 1.

Table 1. Resistivity values of the polymer solution used in electrospinning. The results obtained for the measurement voltage U_m=100 V

Measurement duration t, s	PVDF concentration c=15%		PVDF concentration c=20%	
	Measured resistance R, Ω	Calculated resistivity ρ, Ωm	Measured resistance R, Ω	Calculated resistivity ρ, Ωm
15	1.2×10^5	6.6×10^3	1.1×10^5	6.9×10^3
60	1.4×10^5	7.7×10^3	2.4×10^5	1.5×10^4

As can be seen in Table 1, the results of the calculated polymer resistivity indicated that the main factor influencing its value was the content of a solvent (with conductive properties) in the prepared polymer solution. Differences in the obtained resistivity values are more visible for longer measurement times. The increase in polymer concentration from 15 to 20% led to an increase in the resistivity value by one order of magnitude for a measurement time of 60 seconds. For the measurement time of 15 s no significant differences were observed. This effect can probably be explained by the complexity of the solvent evaporation process from a polymer drop placed between the glass plates for short measurement times.

Conclusions

The presented studies confirmed that electrospinning is a very complex process. In order to run this process properly, many aspects need to be taken into account, including the correct combination of a solvent and a polymer and its concentrations, power supply conditions, environmental conditions, etc.

The main aim of the work was to develop a system for electrostatic fabrication of nanofibers from liquid polymer solution. The efficiency of the system was checked during the measurements of the nanofibers diameters. The results presented in the paper confirmed the possibility of manufacturing PVDF nanofibres with diameters below 1000 nm using electrospinning. All experiments were carried out under controlled conditions of air temperature and humidity and it was found that the occurrence of minor changes in these factors led to changes in properties of fiber surface – during our research, we obtained both fiber forms, i.e. without and with beads. Some circulations were also observed during the tests. This also made it difficult for the fibres to settle on the collector.

The major challenge of the electrospinning process seems to be the optimization of the process parameters to achieve desirable nanofiber morphology and properties. An electric field may affect the occurrence of beaded morphologies or even inhibit polymer jet initiation. Further research in this area is planned. The morphologies of the obtained nanofibers will also be examined in detail using a scanning electron microscopy (SEM).

Another our goal was to convert PVDF into nanofibers using electrospinning. The proposed solution may increase the piezoelectric properties of the tested material. Tests of piezoelectric properties of the obtained fibres will be the subject of our further tests. The addition of particles increasing the potential piezoelectric effect to the polymer solution is also considered. There are planned activities aimed at the optimization of process parameters in order to obtain fibers with desired piezoelectric properties.

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