PRODUCTION OF PVB COMPOSITE NANOFIBRES
WITH MODIFIED SILICA NANOPARTICLES
AND CARBON NANOTUBES BY ELECTROSPINNING METHOD

PROIZVODNJA PVB KOMPOZITNIH NANOVLAKANA
SA MODIFIKOVANIM SILIKA NANOČESTICAMA
I UGLJENIČNJIM NANOČEVAIMA METODOM ELEKTROPREĐENJA

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Electrospinning is a special technology for producing polymer nanofibres from charged polymer solutions. It is a worldwide technology for forming nanofibres by utilising electrostatic forces. A detailed description of electrospinning apparatus is presented in this work. Next, the various influences of process parameters and solution parameters on the electrospun fibres are explained. In the end, the structures of the experimentally produced PVB nanocomposite fibres were examined by scanning electron microscopy (SEM). The experiments were performed with the 10 wt.% PVB/ethanol solution where the modified silica nanoparticles (mSiO2) and the oxidized single-walled carbon nanotubes (o-SWCNT) were added into the solution as reinforcement. The morphology and distribution of the electrospun nanofibres were analysed by Image-Pro Plus software.

Key words: Electrospinning, Nanofibres, Poly (vinyl butyral), morphology

Electrospredenje predstavlja posebnu tehnologiju za proizvodnju polimernih nanovlakana iz naelektrišanih polimernih rastvora. To je širom sveta rasprostranjena tehnologija za formiranje nanovlakana upotrebom elektrostatickih sila.

U ovom radu je dat detaljan opis uređaja za elektropredenje. Potom su objašnjeni uticaji raznih procesnih parametara i parametara rastvora na elektroispredena vlakna. Na kraju su strukture nanokompozitnih PVB vlakana dobijene eksperimentom ispitivane pomoću skenirajućeg elektronskog mikroskopa (SEM). Eksperimenti su se izvodili sa 10 mas.% PVB/etanol rastvorom u kome su modifikovane silika nanočestice (mSiO2) i oksidovane jednoslojne ugljenične nanocevi bile dodate u rastvor kao ojačanja. Morfologija i raspodela elektroispredenih nanovlakana su analizirane u Image-Pro Plus programu.

Ključne reči: Elektropredenje, Nanovlakna, Poli (vinil butiral), morfologija

1. Introduction

Electrospinning is a particular technology for electrostatic fibre formation from polymer solutions and polymer melts. The obtained fibres are with nanometre scale diameters, ranging from 2 nm to several micrometers with controllable pore structure and large surface area [1]. Electrospinning, a spinning technique, is a unique approach which utilises electrostatic forces for producing fine fibres from a wide variety of polymers. A high DC voltage is required to develop the electrospinning process. This process is based on the fact that in the charged polymer liquid strong mutual electrical repulsive forces overpower weaker forces of surface tension [2].

1.1. Electrospinning process

The typical set up of electrospinning device is shown in Figure 1. An electrospinning system consists of three major parts: a high voltage power supply, a spinneret and a grounded collector. This system uses a high voltage source to insert charge of a certain polarity into a polymer solution (or melt). Then, the solution is accelerated in the direction of an opposite-polarity collector. In fact, the polymer solution is placed in the capillary tube (syringe). In the process of electrospinning, this solution is held by its surface tension at the end of a capillary tube and there forms a conical shape called Taylor cone under the influence of an electrostatic field. The charged solution jet is ejected from the tip when the repulsive electrostatic forces

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overcome the surface tension forces. A speedy, unstable whipping of the jet happens in the zone between the capillary tip and collector, leading to evaporation of the solvent and drop of a polymer on the collector [2-6].

1.2. Effects of various parameters on electrospinning

The electrospinning process is merely controlled by numerous parameters which are divided into solution parameters, process parameters and ambient parameters. Solution parameters include viscosity, molecular weight, surface tension and conductivity. Process parameters consist of applied electric field, feed or flow rate and working distance (tip to collector distance). Each of these parameters is important for electrospun fibres morphology. Nanofibres of desired diameters and morphology can be produced by appropriate manipulation of these parameters along with ambiental parameters which involve temperature and humidity. An overview of these working parameters is depicted in Figure 2 [2,7].

1.3. Solution parameters

1.3.1. Concentration

A minimum solution concentration is needed for fibre formation in the electrospinning process. It has been discovered that a mixture of beads and fibres is a result of low solution concentration. Uniform fibres with enlarged diameters begin to form with the increase of solution concentration due to the higher viscosity resistance. Since it is unable to provide the flow of solution at the tip of the needle when the solution concentration is high, an optimum solution concentration is required for the successful electrospinning process. It has been found out that the increase of solution concentration causes the increase of fibre diameter [2,8].
1.3.2. Viscosity

An optimal viscosity, similar to concentration, is needed as no continuous fibres are formed at very low viscosity and with very high viscosity the ejection of jets from polymer solution is difficult to maintain. Polymer concentration, viscosity and molecular weight of polymer are in the close relationship. At low solution viscosities only beaded fibres are produced due to dominant surface tension while with increase in viscosity a continuous fibrous structure with larger diameter is obtained [2].

1.3.3. Surface tension

Surface tension plays an extremely important role in the electrospinning process. It is a function of the solvent composition of the solution. Different surface tensions depend on different solvents. Usually, the high surface tension of a solution restricts the electrospinning process due to the formation of sprayed droplets. On the contrary, uniform fibres can be obtained by diminishing surface tension. It is possible that electrospinning can appear with lower surface tension even at a lower electric field. In any case, a lower surface tension of a solvent will not always be more appropriate for electrospinning [2, 9].

1.3.4. Conductivity

Polymers are often conductive and jet formation depends on the charged ions in the polymer solution. The polymer type and the solvent used with the presence of ionisable salts have an impact on solution conductivity. It has been discovered that with low conductivity of the solution, the insufficient elongation of a jet appears and beads may be formed. A considerable decrease in the diameter of the electrospun nanofibres occurs when electrical conductivity of the solution is increased. It was approved that the jet radius is inversely related to the cube root of the electrical conductivity of the solution. The use of salts favours the fibre uniformity without bead formation [2].

1.4. Processing parameters

1.4.1. Applied voltage

The voltage, applied to the solution, is a very important processing parameter in the electrospinning process. The process begins with fibre formation that happens after reaching the threshold voltage which generates the necessary charges on the solution. Usually, a greater elongation of the solution is caused by a higher voltage as a result of greater columnic forces in the jet, producing smaller fibre diameter and rapid evaporation of solvent in this way. Additionally, bead formation can be possible at higher voltages and this varies with the polymer solution concentration and working distance [2].

1.4.2. Feed/Flow rate

The jet velocity with material transfer rate is determined by the flow (feed) rate from the syringe. The solvent will have enough time for evaporation when a flow rate is lower and a minimum flow rate of the spinning solution is always required. It has been confirmed that with an increase in the polymer flow rate the fibre diameter and the pore diameter of polystyrene (PS) fibres increase. High flow rates produce beaded fibres due to inappropriate drying time before reaching the collector [2, 10].

1.4.3. Tip to collector distance

The fibre diameters and morphology can be controlled by working distance or the distance between the tip and the collector. A minimum distance is needed to provide the fibres enough time to dry prior to reaching the collector, otherwise beads are likely to form when the distances are either too large or too short. It has been observed that plane fibres can be produced at closer distances. On the contrary, in case of silk-like polymer, cylindrical fibres have been generated with distance increasing. An optimum distance between the tip and collector is required since the dryness of the electrospun fibres happens with the evaporation of the solvent [2].

1.5. Ambient parameters

Ambient parameters that include humidity and temperature also have an impact on the electrospinning process. The influence of temperature on the electrospinning of polyamide-6 fibres in range 25°C to 60 °C has been investigated by Mit-Uppatham et al. and they discovered that with increase in temperature, fibres with decreased diameter were generated, possibly due to the decrease in the viscosity of the polymer solutions at elevated temperatures [11]. In case of the spinning polystyrene solutions it has been found that by increasing humidity small circular pores on the surface of the fibres can be formed and further increasing the humidity can cause clustering of pores. The solvent has the faster rate of evaporation at very low
humidity [2]. The effect of different working parameters on the electrospun fibre diameter is illustrated in Figure 3 [12].

![Figure 3. The effect of the working parameters on the electrospun fibre diameter](image1)

1.6. Applications of nanofibres

Electrospun fibres possess higher surface area with smaller pores compared to regular fibres. Due to these properties these fibres are well applied to various fields: tissue engineering scaffolds, filtration, protective clothing, filtration, pharmaceutical, biotechnology, nanocatalysis and environmental engineering [2].

Most of the applications of nanofibres like filtration, drug delivery, cosmetics and protective clothing are coming from their high surface to volume ratio characteristic (order of thousand). Nanofibre technology can be used to imitate naturally found biological materials in fibre form, such as collagen, silk and keratin. Research has been done to apply biodegradable nanofibres as scaffolds to tissues like bones, blood vessels and cartilages. These nanofibres behave as tissue template on which the human cells can be cultivated. Other applications of polymer nanofibres are carriers for drug delivery. It has been discovered that the drug material dissolution rate highly depends on the surface area of the carrier. Moreover, nanofibers of particular biologically active polymers can be utilised as wound dressing which prevents bacteria and dust from entering. Nanofibre technology can be also used for making medical prostheses.

Nanofibres can be used for molecular separation and filtration because of their high surface area to volume ratio. Nanofibre meshes can block chemical and biological agents because of their great potential for filtration. According to this fact, nanofibre meshes can be used as skin care masks since they prevent dust particles. Immediate transfer rate of the mask additives is accomplished with the high surface area.

Some other applications of nanofibrous membranes are worth mentioning. For example, due to the fact that the electric conductivity greatly depends on the surface area, nanofibrous membranes made from a conductive material can be utilised as electrode for batteries. They can be used as highly sensible fluorescence optical sensors as well. Some applications consider nanocomposites due to the better mechanical properties of nanofibres compared to microfibres. Figure 4 shows an overview of different applications of electrospun nanofibres [13].

![Figure 4. Applications of electrospun nanofibres in various fields](image2)
2. Experimental part

In the first set of experiments, a powder poly (vinyl butyral) (Mowital B75H, Kuraray Specialities Europe) and absolute ethanol (Zorka Pharma, Šabac) were used for preparing the 10 wt.% PVB/ethanol solution.

The electrospinning device used for the experiments in this work was Electrospinner CH-01 (Linari Engineering). First, a part of experiments was carried out with the applied voltages of 20 kV and 24 kV as the flow rate was held at $Q = 1$ mL/h. Another part of the experimental set was accomplished at the flow rate of 0.8 mL/h while the voltage was kept constant at $V = 20$ kV. The produced electrospun fibres were deposited onto the flat aluminium foil which acted as a collector. In all cases, the distance between the needle top and the collector was $h = 10$ cm.

In the next set of experiments, another powder PVB (Mowital B60H, Kuraray Specialities Europe) and absolute ethanol (Zorka Pharma, Šabac) were used for preparing the PVB solution (10 wt.%). The medium diameter of the silica nanoparticles was about 7 nm (Evonik-Degussa, Aerosil 380) and Dynasylan®AMEO, $\gamma$-aminopropyltriethoxysilane ($\text{(C}_2\text{H}_5\text{O})_3\text{SiC}_3\text{H}_6\text{NH}_2$, Degussa-Evonik), was used for the surface modification of the silica nanoparticles. The modification was carried out in toluene (Lachema, the Czech Republic).

Oxidised single walled carbon nanotubes ($\alpha$-SWCNT) were produced by catalysed chemical vapour deposition (Cheap Tubes Inc., USA). Their dimensions were 1-2 nm in the outer diameter and 3-30 µm in the length dimension. The $\alpha$-SWCNT functional content was 2.20 wt.%. As the nanoreinforcement, $\text{mSiO}_2$ and $\alpha$-SWCNT were added into ethanol with concentration of 1.0 wt.% in regard to PVB, as the reinforcement/PVB weight ratio was 0.01. This ethanol solution was sonicated for 1 hour in an ultrasonic bath (Bandelin Sonorex) in order to gain favourable dispersion of the nanoreinforcement. After the dispersion, the ethanol mixture was put into the 20 wt.% PVB/ethanol solution in order to get the final concentration of the 10 wt.% PVB/ethanol solution by mixing it on a magnetic stirrer at 200 rpm overnight. This set of experiments was performed with the applied voltage $V = 24$ kV and with the flow rate $Q = 3$ mL/h on the electrospinning apparatus.

The morphology of produced fibres from both the experiments was investigated by optical microscope OLYMPUS CX41 and MIRA3 TESCAN scanning electron microscope (SEM) at 20 kV. The average diameters of the electrospun fibres were measured in Image-Pro Plus software.

3. Results and discussion

All the produced fibres were generally narrow at low voltage of 20 kV (Figure 5(a)). On the contrary, with the increase of the applied voltage (from 20 kV to 24 kV), the PVB fibres showed an expected tendency of whipping (Figures 5(a) and 5(b)). The coiled fibre structure was also gained in reducing the flow rate (from 1 mL/h to 0.8 mL/h, Figure 5(c)).

It was observed that with the increase of the applied voltage and reducing the flow rate as well, the PVB fibre diameters tended to decrease (Figures 5 and 6). The average diameter of the electrospun PVB fibres from the optical microscopy images ranged from 1.55 µm (for $Q = 0.8$ mL/h and $V = 20$ kV) to 3.27 µm (for $Q = 1$ mL/h and $V = 20$ kV). For process parameters $Q = 1$ mL/h and $V = 24$ kV, the mean diameter of PVB fibres was 2.02 µm. From the histogram of fibre diameter distribution it can be noticed that the majority of the fibre diameters was in the range 1.5 µm - 1.6 µm when the flow rate was decreased to $Q = 0.8$ mL/h (Figure 6). With this flow rate, the population of fibres had the smallest diameters compared to other processing conditions.

![Figure 5. Optical microscopy images of PVB fibres (scalebar 50 µm): (a) $Q = 1$ mL/h and $V = 20$ kV, (b) $Q = 1$ mL/h and $V = 24$ kV, (c) $Q = 0.8$ mL/h and $V = 20$ kV](image-url)
Small structures of PVB nanofibres can be detected with SEM usage since they are invisible through an optical microscope (Figure 7). Some beads can be noticed in a greater quantity in the image of PVB/o-SWCNT fibres (Figure 7(c)), possibly due to inappropriate dispersion of o-SWCNT. With the applied voltage $V = 24$ kV and with the flow rate $Q = 3$ mL/h the average diameter of the electrospun fibres from the SEM images ranged from 281 nm (for PVB/o-SWCNT fibres) to 523 nm (PVB fibres). The average diameter of PVB/mSiO$_2$ fibres was 313 nm (Figure 8). Compared to the neat PVB fibres the smaller values of the diameters possibly happened as a consequence of the chemical interaction of mSiO$_2$ with PVB. Apparently, by introducing the conductivity with o-SWCNT the diameter decreased in the PVB/o-SWCNT fibres [14, 15].
4. Conclusion

Electrospinning presents a technology for producing polymer nanofibres from polymer solutions or melts and it is becoming popular in 21st century. The produced polymer fibres are in diameter between 2 nm and several micrometers.

The morphology of the electrospun PVB fibres with the effects of flow rate $Q$ and applied voltage $V$ were investigated. The produced fibres were narrow at $V = 20$ kV and $Q = 1$ mL/h, but they started to whip with increasing the voltage and decreasing the flow rate. The diameters of the fibres were the smallest with the decreased flow of $Q = 0.8$ mL/h.

In another experiment, the lower values of the diameters compared to the neat PVB fibres were probably a result of the chemical interaction of mSiO$_2$ with PVB. The cause of the diameter decrease in the PVB/o-SWCNT fibres may be the conductivity introduction with o-SWCNT.

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6. References


