

SOLUTION BLOW SPINNING OF POLYMERIC SOLUTIONS CONTAINING BENIGN SOLVENTS

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Abstract

In recent years, the solution blow spinning (SBS) process has gained interest due to its numerous advantages like high production rate or absence of high voltage for nanofiber fabrication. This technology utilizes coaxial nozzle systems, polymeric solution and high-velocity gas or airflow. One of the SBS research directions is represented by a potential *in situ* application of nanofibrous wound dressings of SBS in medicine. The spun polymeric solutions for SBS are usually prepared using toxic solvents due to the suitable properties required for spinning like high vapor pressure. Regarding the prospective medical application, ensuring that the spinning method poses no harmful effects is crucial. This statement contradicts the use of toxic solvents. Replacing toxic solvents with so-called nontoxic benign solvents seems to be a suitable solution. However, benign solvents pose a problem for the SBS process in terms of evaporation. It must be compensated for by one of the technology parameters e.g. nozzle diameter. This paper presents the results of SBS process of polymeric solutions based on aliphatic polyesters containing benign solvents such as ethyl acetate and acetone. The influence of a change in nozzle diameter on the SBS process is shown. The morphology of the produced fibers was studied using scanning electron microscopy. According to the results, the process of replacing toxic solvents with environmentally friendly ones is not trivial and it is still necessary to address this issue to obtain optimal fiber morphology using the SBS method and solutions containing benign solvents.

Keywords: Solution blow spinning, *in situ* application, benign solvents

1. INTRODUCTION

Research interest in nanomaterials has increased over the last two decades. One of the main focuses is directed towards nanofiber materials for their excellent properties like high surface ratio or light weight. With the increasing popularity trend of nanofibers, research is also shifting towards the technologies of their production. The newly investigated technique is referred to as solution blow spinning (SBS) [1]. Unlike electrospinning, this method operates without the need for electrical power or an electrically conductive collector, relying instead on a high-speed air flow to generate fibers, as describe by Dadol et al. [2]. In the SBS process, fibers are produced using a coaxial nozzle system such as in a commercial airbrush. The outer nozzle delivers a high-speed air flow that surrounds a polymer solution flowing through the inner nozzle toward the device outlet. At the nozzle tip, the polymer solution forms a droplet, which is stretched and elongated into a fiber form by aerodynamic forces. The resulting nanofibers are finally deposited onto a collector. This method offers a major advantage for the relatively safe application of nanofiber wound dressings directly at the site of application (*in situ*) [3].

For this possible application, the polymer used for fiber production must be both biocompatible and in some cases biodegradable as well [4], such as polycaprolactone (PCL). However, in the case of direct application, non-toxicity requirements must also be imposed on the solvents used in the spinning solution. During spinning, it is necessary for the solvent to evaporate as quickly as possible for the formed fiber to solidify. The evaporation rate is defined based on the saturated vapor pressure. For rapid evaporation, it is advisable to

use solvents with high saturated vapor pressure. Solvents that can dissolve PCL, such as dichloromethane (DCM) or chloroform, meet this condition. The toxicity of these solvents presents a major obstacle to their application in *in situ* nanofiber deposition. A potential approach to mitigate this issue is the substitution of toxic solvents with so-called benign solvents e.g. ethyl acetate (EtOAc) or acetone (Ac). The U. S. Food and Drug Administration (FDA) has issued toxicity classifications and recommendations for the use of various solvents via list [5]. This topic has received limited attention in the available scientific literature.

However, the disadvantage of benign solvents is low saturated vapor pressure, which has a negative effect on the spinning and fiber formation process. This deficiency can be compensated by adjusting other parameters of the SBS process. One such parameter is the diameter of the spinning nozzle, which can affect the capillary pressure within the solution droplet at the nozzle tip as well as the droplet's surface area. In theory, proper adjustment of this parameter can enhance the spinnability of the solution. In this work, the SBS process of PCL solutions using EtOAc and Ac with small addition of DCM is shown. During the spinning process of the prepared solutions, nozzles of three different diameters were used – 0.2, 0.3 and 0.5 mm. The influence of the nozzle diameter change was then studied. The produced fibers and layers were investigated using scanning electron microscope (SEM). The mean values of fiber diameters were evaluated using SEM images. The results showed that it is possible to produce fibers from polymeric solutions containing benign solvents using different spinning nozzle diameters.

2. MATERIALS AND METHODS

For the experiments, PCL (Mw = 45 000) was purchased from Corbion (Netherlands). Solvents – Ac and DCM were purchased from Penta (Czech Republic). Solvent EtOAc was obtained from Carl Roth (Germany). The granular form of PCL was dissolved in the solvents, respectively, at relevant weight ratios (wt%). The mixtures were left to stir overnight on the magnetic stirrer at 300 rpm. For a complete list of prepared solutions, see **Table 1**.

Table 1 List of prepared PCL solutions containing benign solvents

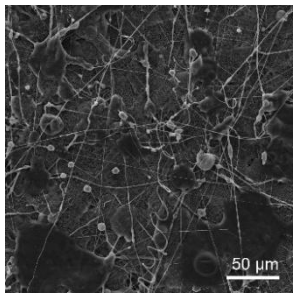
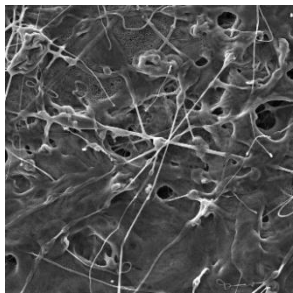
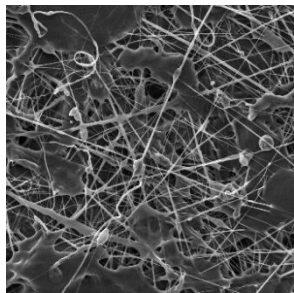
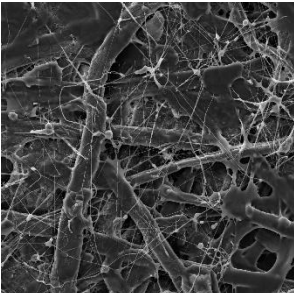
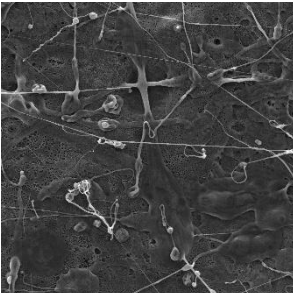
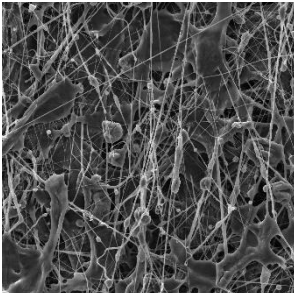
Solution label	PCL content (wt%)	Benign solvent	Second solvent	Solvent ratio
A	14	EtOAc	-	-
B	14	EtOAc	DCM	9 : 1
C	14	EtOAc	DCM	8 : 2
D	14	EtOAc	DCM	7 : 3
E	12	Ac	-	-
F	12	Ac	DCM	9 : 1

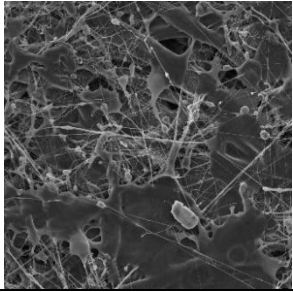
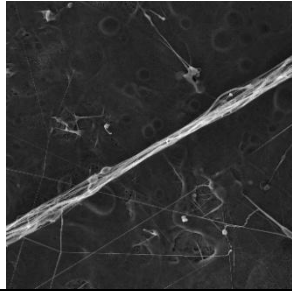
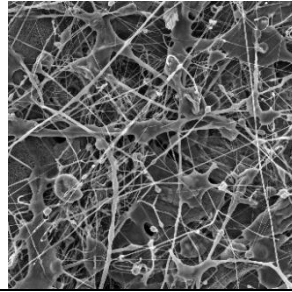
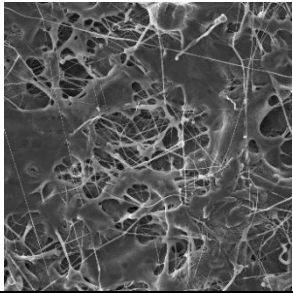
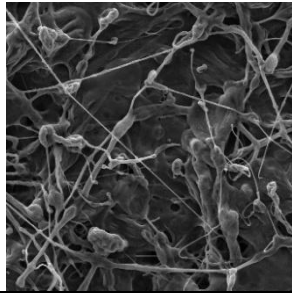
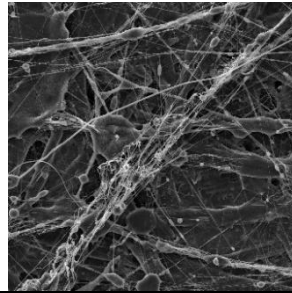
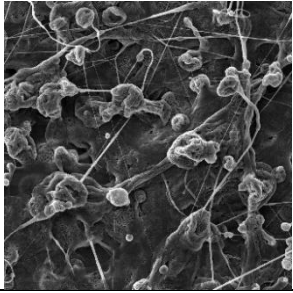
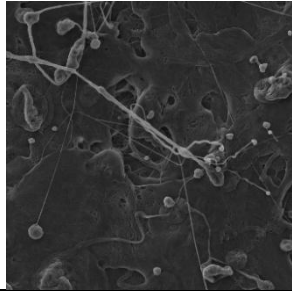
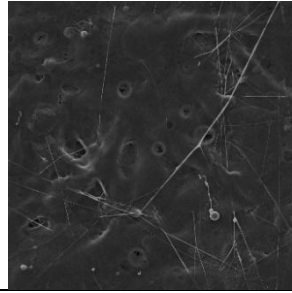
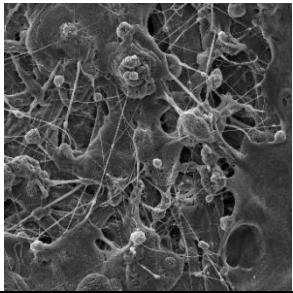
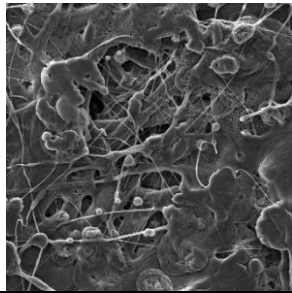
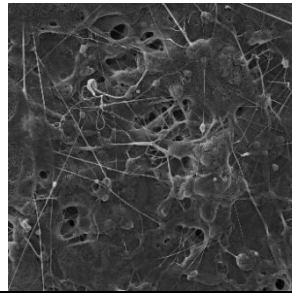
The solutions were spun using a commercial airbrush, the Fengda BD-180 (Fengda, China), and a compressor, the Fengda AS-186 (Fengda, China). The SBS process was executed under the following conditions: an air pressure of 1.8 bar, a nozzle diameter of 0.2, 0.3 and 0.5 mm and a working distance (distance between a nozzle outlet and collector) of 10–15 cm. The produced fibers were collected on a black paper. Subsequently, the samples from each material were cut. The samples were then placed on a metal target and coated with a thin gold layer using a Quorum Q150R Plus coater (United Kingdom). The samples were then examined using scanning electron microscope (SEM) Vega S3B (Tescan, Czech Republic). The SEM images were taken and later analysed to evaluate fiber diameters according to change in spinning nozzle. The nanofiber diameters were evaluated from five SEM images, each with a magnification of 3,000× or 5,000×, for every sample using ImageJ (USA). The mean value (MV) and standard deviation (SD) were then calculated from at least 40 fiber diameter values.

3. RESULTS AND DISCUSSION

The fibers were successfully produced from certain solutions containing benign solvents using different nozzle diameters (0.2, 0.3 and 0.5 mm). The solvents were chosen according to FDA recommendation [5] of solvents for pharmaceutical use. For a more detailed description of the SBS process of the solutions with benign solvents see **Table 2**. The table also shows SEM images of prepared fibers using SBS method and the MV of fiber diameter with SD depending on the change in nozzle diameter. The final fibers show beaded structures and droplets in the whole layers are found. During the spinning process, the solutions containing pure benign solvents (A – 14 wt% PCL in EtOAc and E – 12 wt% PCL in Ac) exhibited slow evaporation in some cases, leading to the formation of solution droplets and their collection on the collector. This is most likely caused by low saturated vapor pressure. The addition of a small amount of toxic solvent DCM of different ratios was necessary due to its suitable vapor pressure values for more rapid evaporation. Based on observations and subsequent examination of SEM images, it was found that the addition of DCM supports fiber formation. This is most likely due to the reasons mentioned above.

Table 1 Description of fiber production using SBS method with a change of spinning nozzle diameter for the solutions containing benign solvents. **Green indicates** that the solution forms a fibrous layer that is visible to the naked eye. **Orange represents** solutions that do not form a fibrous layer visible to the naked eye but can be observed using SEM. **Red marks** solutions that do not form fibers. The scale is 50 μm for each SEM image.

Solution	SBS process dependent on the change of spinning nozzle diameter		
	0.2 mm	0.3 mm	0.5 mm
A – 14 wt% PCL in EtOAc	White compact layer without visible fiber structure	White compact layer without visible fiber structure	Visible fiber structure forms on the edge of the collector
SEM images of A			
MV \pm SD [nm] of A	531 \pm 307	N/A	779 \pm 424
B – 14 wt% PCL in EtOAc/DCM (9 : 1)	Visible fiber structure forms on the edge of the collector	White compact layer without visible fiber structure	Visible fiber structure forms in the collector's middle
SEM images of B			
MV \pm SD [nm] of B	425 \pm 339	N/A	705 \pm 471

C – 14 wt% PCL in EtOAc/DCM (8 : 2)	Visible fiber structure forms on the edge of the collector	Visible fiber structure forms on the edge of the collector	Visible fiber structure forms in the collector's middle
SEM images of C			
MV ± SD [nm] of C	440 ± 307	N/A	924 ± 662
D – 14 wt% PCL in EtOAc/DCM (7 : 3)	Compact droplets form in the layer and fibers around them	White compact layer without visible fiber structure	Visible fiber structure forms in the collector's middle
SEM images of D			
MV ± SD [nm] of D	679 ± 441	2438 ± 1395	341 ± 309
E – 12 wt% PCL in Ac	Formation of the droplets, no visible fiber structure	White compact layer without visible fiber structure	Visible bundle of fibers
SEM images of E			
MV ± SD [nm] of E	1167 ± 804	N/A	N/A
F – 12 wt% PCL in Ac/DCM (9 : 1)	Visible fiber structure forms on the edge of the collector	White compact layer without visible fiber structure	Visible fiber structure forms on the edge of the collector
SEM images of F			
MV ± SD [nm] of F	441 ± 290	618 ± 441	N/A

Most solutions could be spun using nozzles with diameters of 0.2 and 0.5 mm. A nozzle with a diameter of 0.3 mm provided positive spinning results only for the solution D – 14 wt% PCL in EtOAc/DCM (7 : 3) and F – 12 wt% PCL in Ac/DCM (9 : 1). It is assumed that, in the case of a 0.2 mm nozzle, the droplet formed at its end is small enough for its surface to be destabilized by the air flow and subsequently drawn into fiber. The capillary pressure resisting the aerodynamic force will be the highest of all the nozzles used, but the smallest droplet size may play a positive role in the formation of nanofibers. On the other hand, in the case of a nozzle with a diameter of 0.5 mm, the opposite may be true. The droplet will have the largest diameter and surface area, while the capillary pressure will be lowest. This will allow the air flow to destabilize the surface of the droplet, thereby elongating the fiber. When using a 0.3 mm nozzle, its surface area will not be as large as when using a 0.5 mm nozzle. However, it will be larger than a droplet created by a 0.2 mm nozzle. The opposite will be true for capillary pressure. The surface area and capillary pressure can therefore contribute to the resistance of the droplet to air flow. This results in a lower probability of the solution becoming fibrous. However, this theory requires further investigation. It was noted that, except for solution 14 wt% PCL in EtOAc/DCM (7 : 3), an increase in nozzle diameter corresponded to an increase in the mean fiber diameter. This trend is likely related to the larger droplet surface area generated at the nozzle tip. A wider nozzle promotes a more substantial initial liquid flow with higher volume and inertia, which resists deformation and elongation [2]. As a result, for a given air flow rate and polymer concentration, the reduced extensional forces lead to the formation of fibers with larger diameters.

4. CONCLUSION

This paper presents the results of spinning polymer solutions containing benign solvents – ethyl acetate and acetone – using the SBS method. PCL solutions of two concentrations in pure benign solvents or in a combination of benign solvent and DCM (for enhancing the solution spinning properties) were spun using a commercial airbrush. The effect of changing the diameter of the spinning nozzle to 0.2, 0.3, and 0.5 mm was also monitored. As can be seen from the SEM images, five of the six solutions were successfully spun using the above-mentioned nozzle diameters. The 0.5 mm nozzle was identified as the most effective configuration for fiber formation. The solutions that generated the greatest quantity of fibers with minimal droplet defects were 14 wt% PCL in EtOAc, 14 wt% PCL in EtOAc/DCM (9 : 1) and 14 wt% PCL in EtOAc/DCM (8 : 2) using the 0.5 mm nozzle. These solutions appear to be suitable candidates for further investigation for medical use. Nevertheless, additional analytical investigations, such as infrared spectroscopy and differential scanning calorimetry, are essential to characterize the chemical structure and microscopic organization of the polymer matrices in the fibers as it can play a major role in the potential biodegradation of the material. Moreover, preliminary *in vitro* biological assays are required to evaluate the potential cytotoxicity or biocompatibility of these materials.

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REFERENCES

- [1] Y. GAO *et al.*, “Recent progress and challenges in solution blow spinning,” *Mater. Horiz.* Feb. 2021, vol. 8, no. 2, pp. 426–446. Available from: <https://doi.org/10.1039/D0MH01096K>.
- [2] G. C. DADOL *et al.*, “Solution blow spinning (SBS) and SBS-spun nanofibers: Materials, methods, and applications.” *Materials Today Communications*. 2020, vol. 25, p. 101656. Available from: <https://doi.org/10.1016/j.mtcomm.2020.101656>

- [3] Y. GAO *et al.* "A portable solution blow spinning device for minimally invasive surgery hemostasis." *Chemical Engineering Journal*. May 2020, vol. 387, p. 124052, Available from: <https://doi.org/10.1016/j.cej.2020.124052>.
- [4] L. S. NAIR and C. T. LAURENCIN, "Biodegradable polymers as biomaterials," *Progress in Polymer Science*, vol. 32, no. 8, pp. 762–798, Aug. 2007, Available from: <https://doi.org/10.1016/j.progpolymsci.2007.05.017>.
- [5] C. for D. E. and Research, "Q3C Tables and List Rev. 4." Accessed: Oct. 17, 2025. [Online]. Available: <https://www.fda.gov/regulatory-information/search-fda-guidance-documents/q3c-tables-and-list-rev-4>