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Electrospinning of Polymer Fibres Using Recycled PET

Attila GERGELY,[1] József KÁNTOR,[2] Enikő BITAY,[3, 4] Domokos BIRÓ[5]

[1] *Sapientia Hungarian University of Transylvania, Faculty of Technical and Human Sciences Târgu Mureș, Department of Mechanical Engineering, Târgu Mureș, Romania, agergely@ms.sapientia.ro*

[2] *Elitex Prodexim Kft., Ceuașu de Câmpie, Romania, jkantor106@gmail.com*

[3] *Sapientia Hungarian University of Transylvania, Faculty of Technical and Human Sciences Târgu Mureș, Department of Mechanical Engineering, Târgu Mureș, Romania*

[4] *Transilvanian Museum Sociaty, Cluj Napoca, Romania, bitay@eme.ro*

[5] *Sapientia Hungarian University of Transylvania, Faculty of Technical and Human Sciences Târgu Mureș, Department of Mechanical Engineering, Târgu Mureș, Romania, dbiro@ms.sapientia.ro*

Abstract

The effective recycling of polymer materials remains unresolved to this day, and this has had a devastating effect on the environment. This study examines an alternative method to PET recycling that is the generation of polymer fibers and fiber mats for filtration applications. The electrospinning instrumentation used in this study had to be designed and built in order to carry out the research. We have managed to produce PET fibers with 200-600 nm diameter, and free-standing fiber mats that could potentially be used in filtration applications.

Keywords*: polymer fiber, electrospinning, recycling, PET.*

1. Introduction

The recycling of poly(ethylene terephthalate) (PET) is an urgent problem, since this material is exclusively used for the packaging of water and refreshing drinks. In the United States of America 12.7 % of the generated garbage was polymeric based materials in 2012 [1, 2]. Only 9 % of the polymeric material was recycled, and 30 % of this was PET bottles [3]. Recycled PET is used in many areas, such as in the automotive-, packaging-, textile industry, container manufacturing and foil production [4]. However, recycled PET cannot be used in the medical industries, in the manufacturing of protective clothing and some filtration applications [5, 6].

The PET material used to manufacture plastic bottles is semi crystalline, has good mechanical properties, is resistant to environmental effects and the products keep their shapes up to 70 °C [7, 8]. The manufacturing of plastic bottles involves the contact of PET with different additives and other material, thus recycled PET cannot be used in medical applications. Due to the increasing air pollution [9] and the advantageous mechanical properties of recycled PET [10], it could be potentially used in filtration applications.

There are several products that use polymer fibers in filtration applications. One of the methods that is capable of producing polymer fibers with nano- and micrometer range diameter is electrospinning. There are two way to generate polymer fibers with electrospinning: melt- and solution electrospinning [11]. Melt electrospinning requires the polymer to be molten. Thus, this process has high energy requirements. Additionally, the polymer fibers produced have relatively high diameter, in the micrometer range. Furthermore, the method seems to provide poor control over the fiber diameter [12]. Recycled PET fibers with melt electrospinning have resulted in fiber diameters of 30 μm [8]. In contrast to the mentioned disadvantages solution electrospinning has lower energy requirement and has proved a better in control of the produced polymer fiber diameter [10].

Figure 1. shows the schematics of a solution electrospinning instrument. The instrument has 3 major components: a high DC power supply, a

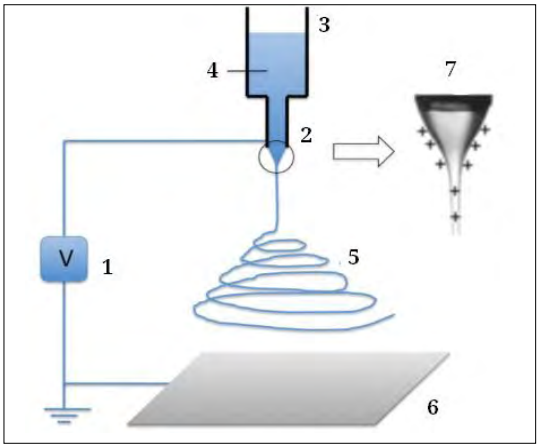


Figure 1. *Solution electrospinning setup* **[14]**. *1: high voltage power supply, 2: spinneret, 3: syringe, 4: polymer solution, 5: liquid jet, 6: collector, 7: Taylor cone*

container that holds the polymer solution, with a small opening, and a collector that is used to collect the polymer fibers. Solution electrospinning requires an electric field that charges and drives the charged polymer jet from the small opening of the container to the collector. In the process, the solvent, used to produce the polymer solution evaporates and the polymer fibers deposit on the collector in random orientation, with diameters in the nano- and/or micrometer range, producing a porous membrane (**Figure 2.**) **[11, 13]**.

The container is usually a syringe holding the polymer solution and is connected to a needle, serving as the small opening, with tubing. The needle is set to positive potential whereas the collector is set to either ground or negative potential. Due to the positive potential at the needle, the polymer solution becomes positively charged. The positive charges repel one another, and when the repelling forces become greater than the surface tension of the polymer solution a charged polymer jet is generated. The so-called Taylor cone that forms in the process is shown in **Figure 1. [15]**. During the travel of the charged polymer jet from the needle to the collector, almost all of the solvent evaporates, and the jet elongates, resulting the polymer fiber **[11, 13]**.

Strain et al. **[10]** used the solution electrospinning process to generate polymer fibermats from recycled PET. They used Coca-Cola PET bottles, trifluoroacetic acid (TFA) and dichloromethane (DCM) to prepare the polymer solution. The electrospinning parameters were set as follows: distance between the needle and the collector was 250 mm, the inner diameter of the needle was 0.6 mm, the flow rate was varied between 5, 10 and 20 µL/min, the applied potential difference was varied between 7 and 12 kV, whereas 10, 15 and 20 wt% polymer solution concentrations were used.

They produced polymer fibers with average fiber diameters between 0.4 and 4.3 µm. The authors concluded that the lower the polymer solution concertation the smaller the produced fiber diameters. The produced porous polymer membranes were used to manufacture a filtration device to filter cigarette fumes. The results show that the weight of a polymer membrane, produced by polymer fibers with 0.4 µm diameter, increased by 43 times after the filtration. Stain et. al concluded that the smaller the polymer fiber diameter the better the mechanical and filtration properties of the resulting fibermats. This result shows the potential use of recycled polymer fibermats in air filtration application. The publication generated great interest in the use of recycled PET in filtration applications. Since the original publication, recycled PET fibermats have been used in water filtration application too **[16]**.

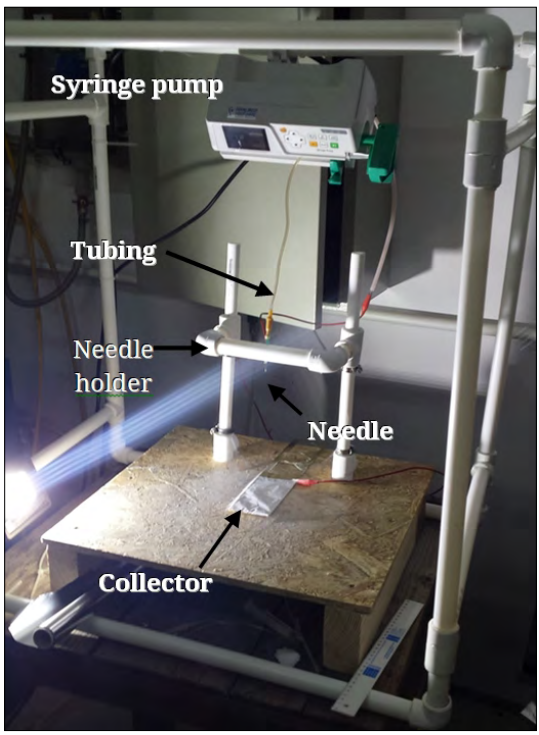


Figure 2. *The electrospinning equipment built for this project*

This study aims to investigate the effect of solution electrospinning parameters, such as polymer solution concentration, flow rate, applied potential difference, distance between needle tip and collector and the inner diameter (ID) of the needle, on the diameter of the produced recycled PET fibers and membrane morphology.

2. Experimental

2.1. Polymer solution

In the experiments Carpatica sparkling water bottles made of transparent PET were used. The bottles were washed with ethanol and were cut into squares of 10×10 mm^2. Solutions of PET with various concenteations were prepared in trifluoroacetic acid. The vials were placed on a shaker at 400 rpm. The PET completely dissolved in 15–90 minutes, depending on the concentration.

2.2. Electrospinning

Electrospinning was performed with an electrospinning instrument built within this project. The PET solutions were dispensed from 5 ml syringes through a 1/16 inch inner diameter polytetrafluoroethylene (PTFE) tube and a needle. The syringes were paced in a syringe pump, while the needles were inserted into the needle holder of the instrument. Positive high potential was connected to the needle and the collector was attached to the ground potential. The electrospinning was performed for 8 minutes per sample.

2.3. Scanning electron microscopy (SEM)

SEM imaging was carried out with a JEOL JSM-5200 scanning electron microscope at 10 kV potential and 1000x, 5000x and 10000x magnification. At x10000 magnification images were taken from three different spots of the fiber mats.

The fiber sizes were measured with the ImageJ software. The 10000x magnification images were used for fiber size measurement and at least 10 measurements were taken per image. In the case of beaded fibers at least 30 beads were measured per image.

3. Results

3.1. Instrumentation designing and building

The goal was to design an instrument that was easy to build and customize **Figure 2.** shows the instrument. The syringe pump was placed above the needle on a separate stand. The syringe was mounted in the pump, while the needle was placed in the needle holder. The syringe and the needle were connected with a PTFE tube. The collector was placed below the needle and the needle-collector distance could be adjusted. The image doesn't show the voltage source.

Figure 3. shows a porous PET fiber mat and its SEM image. It is white instead of transparent and it resembles a thin plastic foil. However, looking at the SEM image it can be seen that it's actually porous which is caused by the random orientation of the PET fibers.

3.2. Design of experiments

The list of electrospinning parameters used in the experiments can be seen in **Table 1.** Out of the plethora of factors the effects of PET concentration (C), volumetric flow rate (F), voltage (V), needle-collector distance (D), and the inner diameter of the needle (ID) on the electrospinning process were studied.

The conditions were created from the variation of these parameters in the following way:

- The effect of V was studied with the experimets 1, 2 and 3. C = 10 wt%, F = 15 µL/min, D = 250 mm, ID = 0.8 mm, and V = 15, 20 and 25 kV.
- The effect of F was studied with the experiments 2, 4, and 5. C = 10 wt%, V = 20 kV, D = 250 mm, ID = 0.8 mm, and F = 15, 30 and 45 µL/min.
- The effect of D was studied with the experiments 2, 8 and 9. C = 10 wt%, V = 20 kV, F = 30 µL/min, ID = 0.8 mm and D = 200, 250 and 300 mm.
- The effect of D was studied with the experiments 4, 6, and 7. C = 10 wt%, V = 20 kV, F = 15 µL/min, D = 250 mm and ID = 0.8, 0.55 and 0,3 mm.
- The experimental design was created with 5, 10 and 15 wt% solutions in mind, however the 15 wt% solution couldn't be spun which was due to its high viscosity.

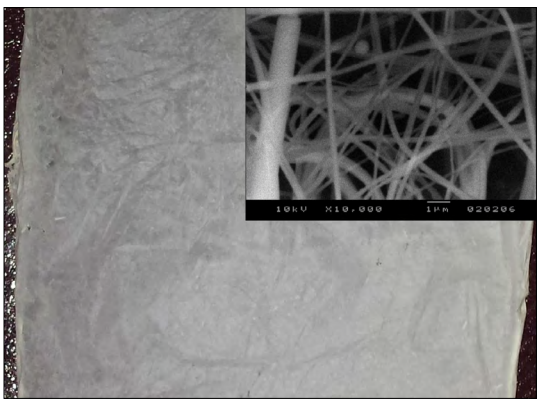


Figure 3. *PET fiber mat and its SEM image*

Table 1. *Performed electrospinning experiments*

No.	C (wt %)	F (µL/min)	V (kV)	D (mm)	ID (mm)	Fiber diameter (nm)	Bead diameter (µm)
1	10	15	15	250	0.8	289.6 ± 98.8	0 ± 0
2	10	15	20	250	0.8	502.8 ± 263.9	0 ± 0
3	10	15	25	250	0.8	452.4 ± 165.6	0 ± 0
4	10	30	20	250	0.8	322.4 ± 151.3	9.73 ± 4.40
5	10	45	20	250	0.8	359 ± 112.5	0 ± 0
6	10	30	20	200	0.8	549.3 ± 236.1	0 ± 0
7	10	30	20	300	0.8	407.1 ± 169.9	11.60 ± 3.85
8	10	15	20	250	0.55	297 ± 106.7	7.69 ± 2.42
9	10	15	20	250	0.3	377.4 ± 138.8	0 ± 0
10	5	15	15	250	0.8	126 ± 49	4.5 ± 1.3
11	5	15	20	250	0.8	0 ± 0	5.5 ± 0.8
12	5	15	25	250	0.8	118 ± 165.6	3.5 ± 1.1
13	5	30	20	250	0.8	283.5 ± 192.2	5.5 ± 1.7
14	5	45	20	250	0.8	171 ± 80.5	4.2 ± 2
15	5	30	20	200	0.8	295.9 ± 225.8	4.9 ± 2.4
16	5	30	20	300	0.8	346 ± 132.2	5.9 ± 2.1
17	5	15	20	250	0.55	159.7 ± 92.2	5.9 ± 1.9
18	5	15	20	250	0.3	245.9 ± 75.8	0 ± 0

3.3. Results of SEM examination

3.3.1. The effect of electrospinning parameters on fiber diameter

In the following the effect of the process parameters on the cross-sectional diameter of the produced PET fibers is discussed. The experiments were carried out with 5 and 10 wt% solutions, and the plots in **Figures 4–7**.

Figure 4. shows the PET fiber diameters as a function of V.

In **Figure 4.** it can be seen that in case of a C = 10 wt% solution by increasing the applied voltage, the PET fiber diameter also increased. At 15 kV fibers with 289.6 ± 98.8 nm diameter were produced while at 25 kV the average fiber diameter was 452.4 ± 165.6 nm. At 20 kV the PET fibers were a bit thicker with a diameter of 502.8 ± 263.9 nm, which had a large deviation. These results match well with the data reported in the literature **[10]**. According to an explanation found in the literature the higher voltage generates a stronger electric field, which increases the local volumetric flow rate at the tip of the needle and this leads to the increase of fiber size. In case of C = 5 wt% this effect wasn't as strong as it had been for the 10 wt% solution. On the other hand at V = 15 kV the average diameter of PET fibers was 126 ± 49 nm, and beading also occurred with bead sizes of 4.5 ± 1.3 µm. At 20 kV there were barely any fibers and the bead sizes were 5.5 ± 0.8 µm. At 25 kV the morphology consisted of beaded fibers and standalone beads. The average fiber diameter was 118 ± 165.6 nm. Voltage had a low influence on fiber diameter at C = 5 wt%.

The F vs. fiber diameter plot can be seen in **Figure 5.**

The general trend reported in the literature is that higher volumetric flow rates lead to thicker fibers. The results shown in **Figure 5.** indicate that for C = 10 wt% the increase in fiber diameter occurred between F = 30 and 45 µL/min. The

increase of fiber diameter was due to a larger amount of solution getting into the solution jet at the higher flow rates. For C = 5 wt% the increase of fiber size with higher F did not occur, however there weren't many fibers to begin with, and instead beads formed. The bead sizes were 5.5 ± 0.8 µm, 5.5 ± 1.7 µm and 4.2 ± 2 µm at 15, 30 and 45 µL/min respectively.

Figure 6. shows the fiber diameter-D plot.

It can be seen that at C = 10 wt% the diameter vs. D plot had a minimum value at D = 250 mm. For D = 200 mm needle-collector distance the average fiber diameter was 549.3 ± 236.1 nm, for D = 250 mm it was 322.4 ± 151.3 nm, and for D = 300 mm it was 407.1 ± 169.9 nm. According to the literature at short needle-collector distances there is only a short time for the evaporation of the solvent, resulting in wet fibers which have a relatively large diameter. As the distance increases, the fibers are able to dry out more, and the fiber diameters decrease. Further studies are necessary to explain the difference between our results and the results reported by others.

At C = 5 wt% there was a similar tendency, but in this case there were also beads forming. The bead diameters were similar for all three experi-

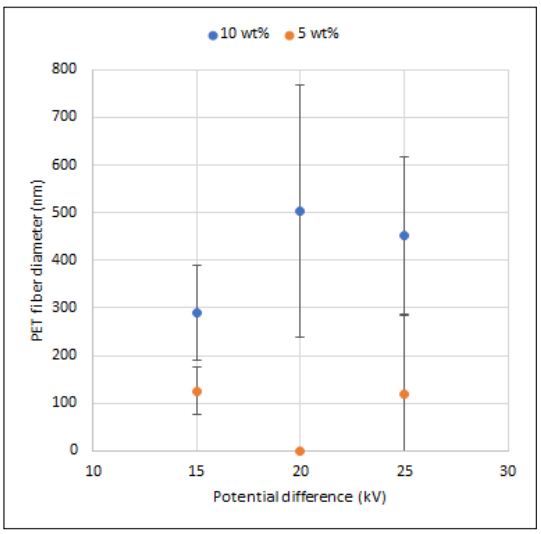


Figure 4. *The effect of V on the fiber diameter. F = 15 µL/min, D = 250 mm, ID = 0.8 mm*

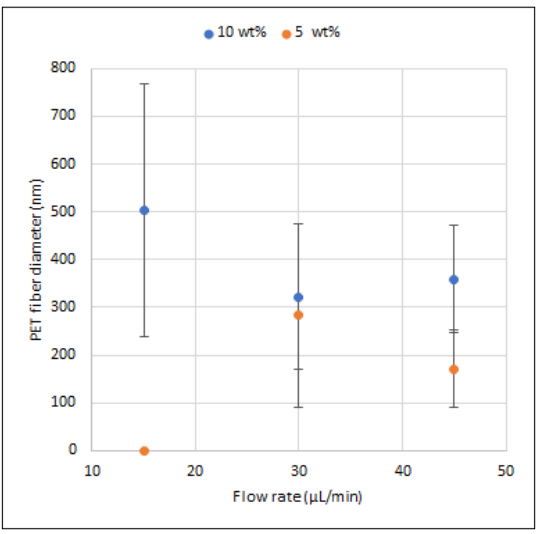


Figure 5. *The effect of F on the fiber diameter. 20 V = kV, D = 250 mm, ID = 0.8 mm*

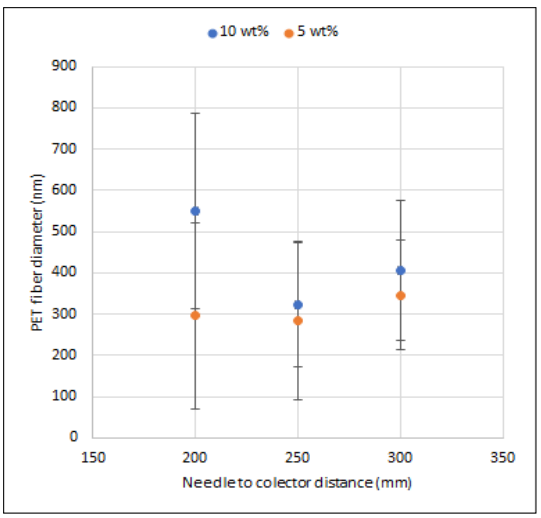


Figure 6. *The effect of D on the fiber diameter. V = 20 kV, F = 30 µL/min, ID = 0.8 mm*

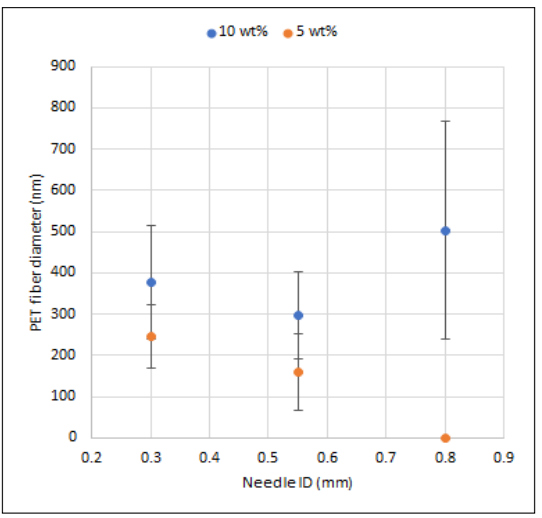
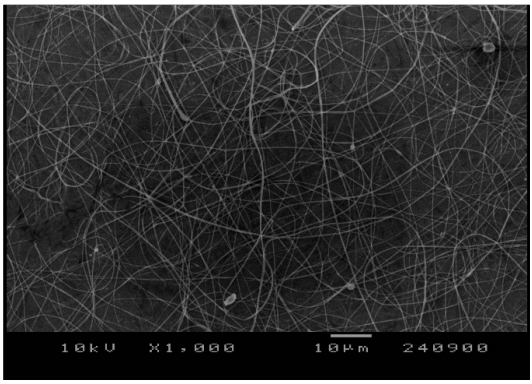
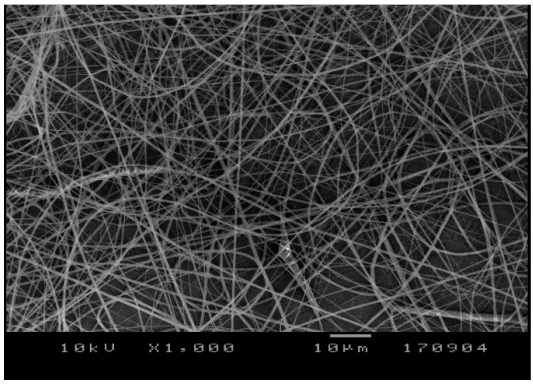


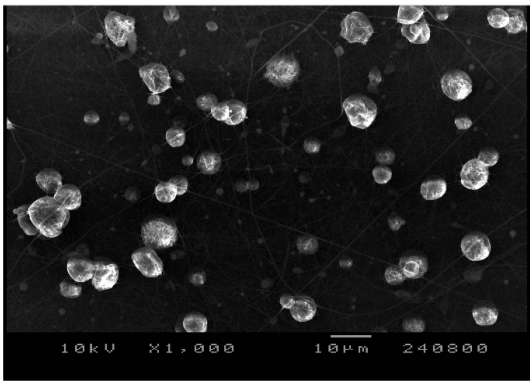
Figure 7. *The effect of ID on the fiber diameter. V = 20 kV, F = 15 µL/min, D = 250 mm*



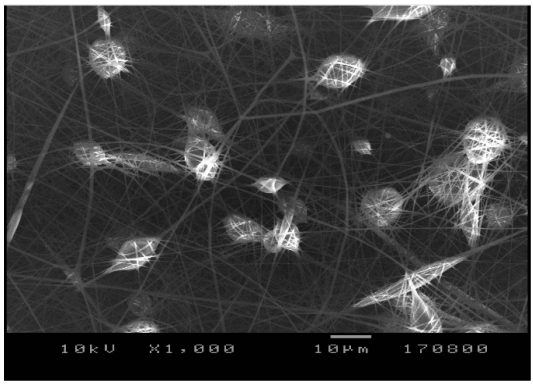
C = 5 wt%, ID = 0,3 mm



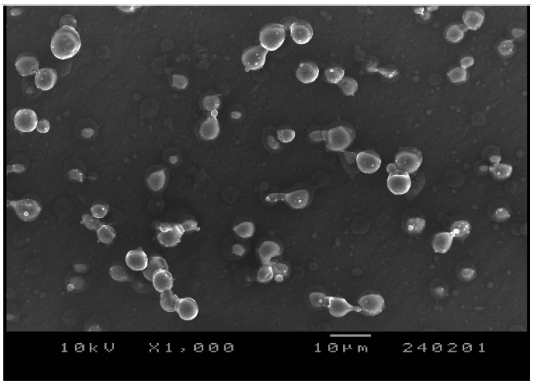
C = 10 wt%, ID = 0,3 mm



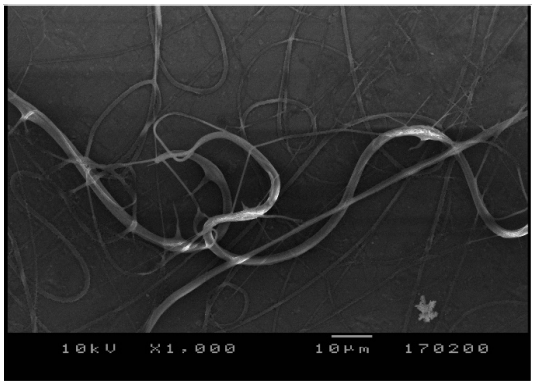
C = 5 wt%, ID = 0,55 mm



C = 10 wt%, ID = 0,55 mm



C = 5 wt%, ID = 0,8 mm



C = 10 wt%, ID = 0,8 mm

Figure 8. *SEM micrographs of beaded PET fibers in function of ID. C = 5 and 10 wt%, V = 20 kV, F = 15 μL/min, and D = 250 mm*

ments, 5.9 ± 2.1 at μm D = 200 mm, 5.5 ± 1.7 μm at D = 250 mm and 5.9 ± 1.9 μm at D = 300 mm.

The fiber diameter vs. ID plots are shown in **Figure 7.**

As the plots indicate, experiments with lower ID did not produce thinner fibers. In both cases – C = 5 and 10 wt%, at 0.3 mm ID the fiber diameters were 245.9 ± 75.8 nm and 377.4 ± 138.8 nm – larger than in case of a 0,55 mm ID: 159.7 ± 92.2 nm and 297 ± 106.7 nm. It should be noted that at C = 5 wt% and ID = 0.3 mm beads weren't produced, while in all other experiments with C = 5 wt% the mats contained beads. Interestingly at C = 5 wt%, ID = 0.8 mm there were beads with 5.5 ± 0.8 μm diameter, and no fibers. However at C = 10 wt% and ID = 0.8 mm there weren't any beads, and the PET fibers had diameters of 502.8 ± 263.9 nm.

Generally speaking **Figures 4–7.** indicate that fiber diameter is strongly influenced by the concentration of the PET solution. It should be emphasized that, as confirmed by the literature at lower concentrations beaded fibers or standalone beads appear.

3.3.2. The effects of electrospinning parameters on fiber mat morphology

The investigation of the fiber mat morphology showed that at 5 wt% PET concentration – with one exception – beaded fibers were produced or in ceration cases almost exclusively beads. At 10 wt% concentration beading occurred in experiments 4, 7, and 8, but most of these were attached to fibers. These results are in accordance with those reported in the literature, i.e. beads are less likely to form at higher solution concentrations.

In **Figure 8.** SEM images of the electrospun fiber mats can be seen, in function of various ID values, with C = 5 and 10 wt%, V = 20 kV, F = 15 μL/min, and D = 250 mm.

4. Conclusions

In summary it can be stated that the designed electrospinning instrument is capable of producing PET fibers. In addition the effects of electrospinning parameters on fibers created from the recycled Carpatica sparkling water bottles were investigated. The results are in good agreement with the data published in the literature from a qualitative perspective. PET fibers with 200–600 nm diameters were successfully spun. The produced fiber mats can potentially be used in filtration applications.

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