Unique properties of Ecoflex® electrospun structures

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Abstract. Electrospinning of biodegradable poly(butylene adipate-co-terephthalate) has been performed. Alternation of process parameters resulted in slight changes in the surface structure morphology of the obtained fibres which was evaluated by using scanning electron microscopy (SEM).

1 Introduction

In recent years, a stable increase in production and demand for biodegradable plastics can be observed. This fact can be linked to the European Union regulations regarding the storage and recycling of plastics waste but also increasing ecological awareness of the society. The biggest advantage of this type of plastics is their ability of biodegradation which their synthetic counterparts mostly are lacking. One of those materials is poly(butylene adipate-co-terephthalate) (PBAT) which is a commercially available material known as Ecoflex®, from BASF. This polymer blend is widely used in agriculture due to its short degradation rate which is 6 weeks in soil but also flexibility which makes it a perfect material for mulch films which are of great importance in agriculture production as indicated by the annual market demand in the amount of 2×10^6 tones [1]. Another feature that allows the wide use of this material is its biosorbability in human body which, together with its fast biodegradability, allows it to be used in the form of a modern drug carrier system [2]. the use of this material in specialist areas may require other methods of processing than injection or extrusion. One of such methods is electrospinning which can be used in production of nanostructures with controlled morphology from a solution or molted polymer (melt spinning). This method is widely used in medicine for drug carriers where the active compound can be implemented in the polymer matrix when it's being dissolved or tissue scaffolds but also for production of filters with highly developed specific surface which is the biggest advantage of this technique [3]. The purpose of this work is to determine parameters for the electrospinning process required to obtain Ecoflex® based mats with a fixed morphology and fiber diameter.

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Fig. 1. Diagram of the electrospinning process [3].

2 Materials and methods

2.1 Characterization of reagents

The experiments were carried out using a series of solutions containing different concentrations of the polymer (refer to table 1. Solvent used in the tests was chloroform (CHF) from "CHEMPUR", 99.5% purity. Granules of poly(butylene adipate-co-terephthalate) (PBAT) were acquired from BASF, under the manufacturer's name: Ecoflex® F Blend C1200. Ecoflex® is one of the commercially available materials made of aliphatic-aromatic monomers due to condensation reaction of butadienol, terephthalic acid and adipic acid [4]. The characteristics of the material is shown in the table 1.

Table 1. Ecoflex® F Blend C1200.

Parameter	Value
Density, g/cm ³	1.25–1.27
Melting temperature, °C	110–120
Tensile elongation at break, %	560/710
MFR (2.16 kg, 190°C), g/10 min	2.7–4.9

2.2 Procedure for the solutions preparation

For each of the tested solutions, the preparation procedure was as follows:

1. Ecoflex® granulate was weighed by using the analytical balance
2. Addition of measured solvent volume – 20 cm³ of CHF

3. Prepared solution was placed on a magnetic stirrer to accelerate the dissolution rate of the granulate at room temperature.
4. The prepared clear solution was poured to the syringe and placed in the electrospinning set pump

Table 2. Concentration of PBAT in the solutions used for electrospinning process.

Sample number	Concentration
1	17%
2	19%

2.3 Research system

Polymer solutions electrospinning has been carried out using a Bioinicia FLUIDNATEK LE-10 device (Fig. 2). This device consists of the following elements: two infusion pumps for feeding the polymer solution from a syringe, a DC power supply with two electrodes, injector with interchangeable nozzles and a grounded collector in the form of a galvanized steel plate where the fibres are collected. The solution is fed to the injector from where it exits through the nozzle. Exiting solution is subjected to an electric field which forces the resulting capillary to extend to form a Taylor cone which is extended further in the shape of a fibre. The fibre moves towards the collector in a spiral motion along the force lines of the electrostatic field, at the same time reducing its diameter [5].

Fig. 2. FLUIDNATEK LE-10.

2.4 Parameters regulation

There were seven parameters (among all) identified as crucial for the process and put under investigation. All of them may be divided into three groups:

- **Electrospinning equipment parameters:**
 - Distance of the nozzle to the collector - The distance between the needle and the collector affects the electrospinning process by directly influencing

the electric field which is the motor force of it. Extending the distance leads to weakening the electric field which gives the jet more time for stretching but may also lead to more instabilities in the form of none homogenous diameter of the fibres. On the other hand, shortening of the distance leads to higher intensity of the field but also shortens the time of solvent evaporation [4, 5].

- Rate of the polymer solution feed – the rate of polymer solution feeding affects the formation of the Taylor cone but also the time for polarisation of the solution. High feeding rate of the solution may cause dripping from the dispensing nozzle without the formation of a suitably thin thread or even the Taylors cone. Too low speed, however, may lead to the thread breaking or clogging the solution dispensing nozzle because of the solvent evaporation [6].
- Electric field strength – Intensity of the electric field defines the rate of the electrospinning process. Usage of higher voltage leads to better stretching of the solution jet, resulting in higher Coulomb interactions and the generation of greater fibre diameters. Too high tension increases the tendency to form beads or fibres with uneven diameter. Lower voltage, lower acceleration and weaker electric field favours the formation of thinner nanofibers [3].
- Needle diameter – Usage of different needles diameters may lead to certain changes in the fibres diameter. It has been found that reducing the inner diameter of the nozzle can result in a reduction in fibre diameter and clogging. This phenomenon is caused by the increase in the surface tension of the droplets but also reducing the time of exposure to atmosphere during the electrospinning [3, 4].
- **Solution parameters:**
 - Concentration - is one of the most important parameters of the solution defining the morphology of the electrospun fibres but also other parameters of the solution like viscosity, surface tension and conductivity. Too low concentration of polymer in the solution may lead to the formation of droplets or beads on string, at the optimal concentration, a homogeneous fibre of constant diameter is created over its entire section. The last structure can be obtained when concentration is higher than the optimal one. In this case, the product of the process is a ribbon [3, 5].
- **Ambient parameters:**
 - **Humidity** – affects the electrical conductivity of the solution but can also affect the morphology of the structures. With an increase in humidity to about 30–50%, the fibres become thinner but can also lead to forming pores on the spun structures which is connected to the quick evaporation of the solvent [5]. This is a desirable phenomenon, because it is possible to use a lower voltage, with solutions even with increased viscosities but can also allow to obtain a porous structure in a simple way changing only the humidity [3, 5].
 - Temperature – affects some properties of the solution but also the electrospinning process. Increase in the temperature over a certain point may lead to a decrease of the viscosity and surface tension of the polymer solution which leads to obtaining thinner fibres [5]. Increase of the temperature in the chamber where the electrospinning takes place changes the rate of evaporation of the solution, by reducing

its viscosity. At higher temperatures the electrospun fibres are more homogeneous in diameter but also thinner [5].

2.5 SEM investigation

Scanning electron microscope was used to investigate the morphology of the process products. It was carried out using VEGA Tescan 3, gun voltage 5.0 kV, magnification rate is mentioned on the respective pictures and text. Surface of the samples were gold sputtered (Kressington 108 sputter coater) for 60s and 40 mA current before SEM investigation.

3 Results and discussion

3.1 Morphology

Table 3. Process parameters for different Ecoflex solutions used for electrospinning process.

Figure number	Concentration, %	Voltage, kV	Distance, cm	Flow rate, cm ³ /h	Mean radius, μ m
3a	17	7.5	19	0.5	7.5
3b	17	7.5	20	1.0	5.7
3c	17	7.5	21	1.5	9.75
3d	17	24	20	1.0	6.2–20
4a	19	8.0	21	0,6	10.2
4b	19	9.0	21	0,6	4.8
4c	19	10.5	21	0,6	6.8
4d	19	18.5	21	1.7	8–18

Ecoflex® is one of the polymer materials ascribed in the literature as “easy to electrospin” material [2, 7] but also with a wide field of applications. This statement is very true but lack of comprehensive data about electrospinning of on the pure material, made us to perform some experimental testing. Tests have shown that even a slight change in the concentration of the polymer may result in obtaining structures of different morphology and affect the process. Concentrations lower than 17% were not tested as it was impossible to create Taylor cone and thus obtain smooth electrospinning process. It must be mentioned, that highly concentrated solutions (20% and more) were much more viscous defeating processability. For each solution four attempts were made differing mainly in applied voltage value. First three tests (for each concentration) were performed at appropriate values (for fuibers spinning) whereas the last sample was collected under voltage 2–3 times higher. Figs 2 and 3 represent structures examined by scanning electron microscope. Temperature and humidity were not controlled but their values during experiment remained unchanged (temperature 21°C and humidity 44%). Despite literature reports the ambient parameters had no effect on the structure. In conditions of such high humidity (30% and more) no porous structure was observed [5]. This observation may mean that the material is not sensitive to humidity changes during the electrospinning proces. As it can be seen on figures 3 and 4, all fibres reveal smooth surface without noticeable signs of porosity. Secondly, their diameter is uniform what is confirmed by standard deviation value, referring to the last column of table 3. Obviously, latter fact mustn’t be applied to the structures acquired at 24 kV (17% solution) and 18.5kV (19% solution) due to intentional voltage “overdrive”. Even though voltage was changed in 1kV steps, in 19% solution (please refer to Fig. 2), no significant changes in structure was observed. Still, fibres were smooth and uniform with no signs of beds,

uncontinuous phenomena or any other signs indicating non-stationary process. Fibres collected on different collector-nozzle distance (fig. 3) also remain unchanged. That may not be a surprising fact as the distance changed only slightly but still stability of the process is high. Those observations are confirmed by data collected in table 3 – diameter of all investigated fibres varies from 6–10 μm (except “overdriven” samples).

Fig. 3. SEM photos of 17% Ecoflex® solution: a) Voltage 7.5kV, Distance 19 cm, flow rate 0.5 cm^3/h ; b) Voltage 7.5kV, Distance 20 cm, flow rate 1.0 cm^3/h ; c) Voltage 7.5kV, Distance 21 cm, flow rate 1.5 cm^3/h ; d) Voltage 24 kV, Distance 20 cm, flow rate 1.0.

Those collected at very high voltage reveal remarkably scattered distribution of fibre diameter but still, taking into consideration fact that applied voltage was 2–3 times higher, overall appearance is quite satisfying.

This is an interesting fact, as in literature one can find remarks on increasing voltage much above normal. Usually this operation results at least in bedded fibres. Despite non-uniform distribution, none of the fact was observed here.

Fig. 4. SEM photos of 19% Ecoflex® solution: a) Voltage 8.0kV, Distance 21 cm, flow rate 0.6 cm^3/h ; b) Voltage 9.0kV, Distance 21 cm, flow rate 0.6 cm^3/h ; c) Voltage 10.5kV, Distance 21 cm, flow rate 0.6 cm^3/h ; d) Voltage 18.5 kV, Distance 21 cm, flow rate 1.7

4 Conclusions

- External conditions do not affect the process and morphologic structures of the spun material.
- Even in case of an overdrive, the material is still fibrous and there's no problem with identification of fibers (no thickening or joints).
- Materials are smooth with well-formed morphology regardless of process conditions.
- Humidity does not affect the formation of porous structures as with some materials.

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