PLA – based electrospun structures

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Abstract. Polymer matrix (MATER-BI) electrospinning tests were carried out under various process conditions. Structures with a diversified morphology have been obtained. Changing the parameters of electrospinning process (mainly voltage and solution concentration) resulted in products with different morphology.

1 Introduction

Electrospinning is a technique patented by Anton Formhals (for the first time, the use of electrospinning was recorded in 1934), who was first to describe the process of cellulose acetate polymer fibers in the early years of twentieth century [1]. Electrospin is a process in which electrostatic forces are used to produce fibers and nanofibers [2]. This technique allows the production of natural as well as synthetic fibers from polymer solutions with a diameter ranging from 10 to 1000 nm. Process is usually carried out at room temperature and may be characterized (comparing to other polymer processing techniques) as a low energy amount consuming and utilised on basic, primitive electric devices [3]. Depending on the polymer type used, process conditions, machine set up as well this method allows to create versatile structures with enhanced, intrinsic structure arrangement (i.e. smooth, homogenous fibers, porous fibers, beaded fibers) [4].

The material used in the research is a granulate with the trade name MATER-BI EF51L and MATER-BI HF03A2 produced by the Italian concern Novamont.

Utilizing the electrospinning process needs understanding several phenomena related to electrostatics, fluid rheology, and polymer solution properties such as: solvent evaporation rate, surface tension and conductivity. Process is vastly influenced by a set of factors resulting from simultaneous and permanent (during whole process) interaction among all above mentioned phenomena.

To quantify factors, those phenomena were divided into three groups consisting of easily – to control parameters:

- a) equipment parameters: collector type, needle diameter, voltage applied, solution flow rate, distance between nozzle tip and collector.
- b) parameters of the solution: electrical conductivity, surface tension, viscosity, dielectric permittivity.
- c) ambient parameters: humidity and temperature.

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2 Materials and methods

The aim of the conducted research was to obtain nanofibres with a developed specific surface area. For this purpose, a series of polymer solutions from two materials (MATER-BI EF51L and MATER-BI HF03A2) was prepared in a chloroform (CHCl₃). The surface morphology of the obtained fibers was determined by scanning electron microscopy (SEM).

2.1 Characterization of reagents

The material used in the research is a granulate with the trade name MATER-BI EF51L and MATER-BI HF03A2 produced by the Italian concern Novamont. These granules are produced from natural agricultural products which ensure the return of polymer basic components to environment in the process of biodegradation and composting without the release of pollutants. Thus, reduces greenhouse gas emissions as well as energy and non-renewable resources escesive usage. From polymer processor point of view, it is a thermoplastic starch mixed and grafted with biodegradable polyesters to increase flexibility and resistance to moisture, it is also completely biodegradable and compostable material. Due to its enhanced mechanical properties it is used as a packaging material for the production of packaging films, thermoformed trays and containers, foamed moldings and foamed material filling free spaces in transport packaging, as well as for the production of bags for biodegradable waste intended for composting [5]. Polymers solutions MATER-BI (EF51L and HF03A2) were prepared in chloroform, manufactured by "CHEMPUR" company with mean molecular mass 119.38 g/mol and purity 99.5%. Polymers used during tests is a granulate available under the name of MATER-BI EF51L and MATER-BI HF03A2 manufactured by Novamont. Their most signifiacant properties are listed in the Table 1.

Table 1. MATER-BI EF51L and MATER-BI HF03A2 physical parameters.

Parameter	Value	
	MATER-BI EF51L	MATER-BI HF03A2
Melting temperature, °C	167	113
Elongation at break, %	180	400
Density, g/cm ³	1.23	1.28
MFR (2.16 kg, 190°C), g/10 min	4	-
MFR (5.0 kg, 160°C), g/10 min	-	2.5

2.2 Sample preparation

The tests were carried out on a series of solutions differing in concentrations (shown in Table 2).

Table 2. Concentration of polymer solutions used for the electrospinning process.

	Concentration of the solution	Material
Sample 1	9.7%	MATER-BI HF03A2
Sample 2	12.2%	MATER-BI HF03A2
Sample 3	12.7%	MATER-BI EF51L
Sample 4	17.9%	MATER-BI HF03A2
Sample 5	19.5%	MATER-BI HF03A2
Sample 6	19.8%	MATER-BI EF51L

For each sample the preparation procedure was as follows:

- 1) Weighting of desired polymer matrix quantity
- 2) Measured volume of solvent (20 ml CHCl_3).
- 3) The prepared mixture was left on a magnetic stirrer to accelerate the dissolution of the granulate at room temperature.
- 4) The prepared solution was placed in a syringe that was part of the Fluidnatek LE-10 system.

2.3 Research system

The tests were carried out on the FLUIDNATEK LE-10 equipment from the Spanish company Bioinicia. It consists of three main parts:

- infusion pumps with syringe and nozzle,
- collector for fiber collection,
- high voltage supply.

Fig. 1. FLUIDNATEK LE-10.

The morphology of the obtained materials was made on the basis of analysis of images obtained from the scanning electron microscope SEM - VEGA Tescan 3.

2.4 Scanning Electron Microscope investigation

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

3 Results and discussion

Two systems were investigated: polymer matrix MATER-BI (EF51L and HF03A2) (Novamont). A set of solutions were prepared to cover substantial range of concentrations (9.7%, 12.2%, 12.7%, 17.9%, 19.5%, 19.8%). Electrospinning process was conducted using the following set-up settings:

- Collector to nozzle distance: 27 cm (fixed in all experiments);
- Flow rate: 0.8 ml/h (fixed in all experiments);
- Temperature/humidity – uncontrolled; recorded in each experiment after spinneret was collected steadily (average temperature value: 21°C, humidity around 45%);
- Voltage: range 6.5–8.0 kV changed in 0.5 kV step;
- Magnification: 1000x.

Fig. 2a. Concentration influence on the structure type of electrospun polymer structure at 6.5 kV.

Fig. 2b. Concentration influence on the structure type of electrospun polymer structure at 7.0 kV.

Fig. 2c. Concentration influence on the structure type of electrospun polymer structure at 7.5 kV.

Fig. 2d. Concentration influence on the structure type of electrospun polymer structure at 8.0 kV.

Two groups of structures were acquired (fibered and spheres) and thus the discussion is divided into two sections. As a preliminary observation a fact that no significant differences between two polymers has to be withdrawn. Comparing SEM micrographs on figs 3a–3c and figs 4a and 4b one can easily notice that fiber/spheres formation is unresponsive to substrate. According to manufacturer’s data (Table 1) those two plastics differ in MFR, melting temperature, what is an indicator of their differences in chemical nature and/or chain length. Those two factors have also an influence on the so called “electrospinnability” – an ease of process execution and structure type formation. In case of two investigated materials those differences may be neglected. Comparison of SEM

micrographs presented on the Fig. 2a–2d indicates that increasing polymer concentration leads to creation fibers. In all instances, at constant voltage, a “critical” value of concentration of about 12.7% is a determinant below which creation of spheres is promoted. Around 12.2% beaded fibers are observed whereas above 12.7% only fibers were detected. This observation is sobnsistent with literature announcements [6–9]. When analysing influence of voltage to the acquired structures one can easily withdraw an observation from figs 3a–3c that at low voltages, fibers are uncontinoues. This fact is illustrated on Fig. 3a which may be a result of (still) low polymer concentration promoting creation of beaded structures. What is more, low values of spinning voltage may be acceptably high to create fibers but not sufficiently high to stretch the fibers in the spinneret. Satisfactory conditions (concentration and applied voltage) were provided for samples which structures were depicted on the Fig. 3c. As it is clearly seen, fibers have much more uniform surface (smooth, uniform diameter), beaded character almost not observed.

Fig. 3a. Fibered structures obtained during electrospinning of MATER-BI EF51L type at 12.7%.

Fig. 3b. Fibered structures obtained during electrospinning of MATER-BI EF51L type at 19.8%.

Fig. 3c. Fibered structures obtained during electrospinning of MATER-BI HF03A2 type at 17.9%.

Fig. 4a. Spheres obtained during electrospinning of MATER-BI HF03A2 at 9.7%.

Fig. 4b. Spheres obtained during electrospinning of MATER-BI HF03A2 at 12.2%.

Figures 4a and 4b shows spherical structures obtained at low polymer concentration. The important feature is creation of uniformly shaped spheres at low concentration, with practically no influence of applied voltage value on the sphere diameter (refer to Fig. 4a). On the other hand, being in the vicinity of “critical” concentration (12.2% – Fig. 4b) allows to observe transitional state. For 7.5 kV and 8.0 kV spheres are observed, for 7.5 kV beaded fibers whereas lower voltages allowed creation of fibered structures coexisting with spheres. Taking into consideration that all other conditions remained unchanged (also ambient: humidity and temperature) that is an interesting case of non-stationary structures being a result of stable process.

4 Conclusions

- On the basis of conducted tests, a reliable possibility to create openwork structures from the MATER-BI materials solution was demonstrated;
- Slight alternation of applied voltage allowed to create structures different in their morphology and dimensions. Authors were aware of the fact to apply voltage in range appropriate for fibers electrospinning (to avoid beads or electrospaying). Above study allowed to analytically describe electrospinning of commercially available material of huge application potential. Figures 3a–3c (with particular reference to Fig. 3c) indicate the dependence of the formation of homogeneous fibers. A higher value of the applied voltage determines the obtaining of a more-aesthetic and ordered look.
- As the concentration increases, the affinity for fiber growth increases. At a concentration of 9.7%, in each of the applied voltages, beads were obtained, whereas at the concentration of 12.7% fibers were obtained.
- An unstable structure was obtained while carrying out a stable electric grinding process (Fig. 4b) at (applied voltages: 6.0 kV, 6.5 kV, 7.0 kV, 7.5 kV, 8.0 kV and concentration 12.2%).

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