PEO as spinnable polymer and spinning-agent for non-spinnable materials

Timo Grothe
Fachhochschule Bielefeld

Johannes Brikmann
Fachhochschule Bielefeld

Andrea Ehrmann
Fachhochschule Bielefeld

PEO AS SPINNABLE POLYMER AND SPINNING-AGENT FOR NON-SPINNABLE MATERIALS

Timo Grothe[1], Johannes Brikmann[1], Andrea Ehrmann[1]
[1] Bielefeld University of Applied Sciences, Faculty of Engineering and Mathematics, Bielefeld (Germany)

Abstract

PEO (poly(ethylene oxide)) with high molecular weight is an excellently spinnable polymer for needleless electrospinning. With its interesting chemical and physical properties, it has a wide potential spectrum of usage, such as in drug delivery or in the biotechnology sector. Depending on the desired application, PEO can be used in its original water-solvable form or can be crosslinked to create water-resistant fabrics. With average fiber diameters of 400 nm - 2 µm, these nanofiber-mats have improved properties in comparison with other production methods, e.g. high fiber strength and nearly defect-free fibers which allow studying the pure material's parameters.

PEO, however, can also be used as a spinning-agent for many non-spinnable materials, such as graphite, PEDOT:PSS, TiO_2, or aloe vera. In this way, either composite fibers from both spinning partners are created, or non-solvable particles are integrated into a nanofiber-mat.

The article gives an overview of spinning parameters for pure PEO and electrospinning different combinations with PEO as spinning partner, depicting the large differences between several conductive, semiconductive and isolating materials.

Introduction

PEO can be used as single material in diverse applications, such as medicine and pharmaceutics, green wood stabilization, or skin creams and toothpaste. Additionally, PEO can serve as a coating for fibers prepared from other materials [1,2]. In electrospinning, it can also support spinning other materials which cannot be spun solely or which do not form fibers properly, e.g. aloe vera, graphite, cellulose, collagen, or PVDF [3-5]. Alternatively, it can be used as single material in electrospinning [6,7].

The focus of this article is the co-spinning process of PEO and other materials which cannot be spun solely, such as polymers with low molecular weight building droplets instead of fibers [6] or inorganic materials, especially TiO_2 – which is an important part of textile-based dye-sensitized solar cells – and graphite – which may serve as a thin conductive electrode in smart textiles.

Experimental

PEO with a molecular weight of 600 kD was purchased from S3 Chemicals. The powder was stirred with distilled water for 2 hours until no more clusters were visible. Solutions contained PEO contents of 5 %. In the experiments described here, 6 % of TiO_2 (P25) or graphite powder, 22 % of PEDOT:PSS (Clevios SV 3) or 15 % of aloe vera were added.

Electrospinning was performed using the needleless nanospinning machine “Nanospider Lab” (Elmarco, Czech Republic). Spinning parameters were in the ranges given in Table 1. Tests were performed with 5-10 ml of spinning solution.

Table 1. Parameter ranges for the electrospinning process.

Parameter	min	max
Voltage / kV	55	75
Current / mA	0.08	0.25
Nozzle diameter / mm	0.9	
Carriage speed / (mm/s)	100	
Substrate speed (mm/min)	10	
Ground-substrate distance / mm	50	
Electrode-substrate distance / mm	220	230

Optical evaluation of the nanomats was done using a confocal laser scanning microscope (CLSM) VK 9000 by Keyence. Images shown here have a nominal magnification of 2000 x.

Results

Firstly, TiO_2 was co-spun with PEO (600 kD). Fig. 1 depicts the results. Spinning the TiO_2 in this way is apparently possible.

Fig. 1. TiO_2-PEO nanofiber mat.

Next, different approaches were made to extract the TiO_2 by evaporating the PEO. For a first investigation of the necessary temperatures, the PEO was investigated by DSC (differential scanning calorimetry) using pure powder and nanofiber mats produced from aqueous solutions with PEO (600 kD) concentrations of 4 % and 8 %. Fig. 2 depicts the results. In all cases, melting occurs below 80 °C. The different temperatures can be attributed to different degrees of crystallinity.

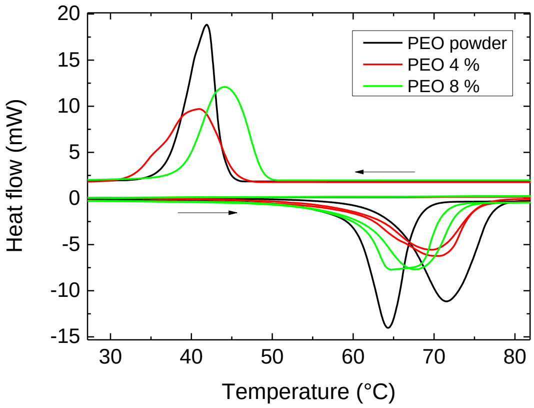

Fig. 2. DSC measurements of PEO powder and nanofiber mats.

Thus, the nanofiber mats co-spun from PEO and TiO_2 were carefully heated up to 85 °C. The result is depicted in Fig. 3. Apparently, the nanofiber structure is not preserved during heating and evaporating the PEO.

Nevertheless, the resulting fine layers were sintered and dyed afterwards which was possible without problems (Fig. 4). In this way, very fine and even TiO_2 layers for the possible use in dye sensitized solar cells (DSSCs) could be prepared; however, the procedure is much too time-consuming if no nanofibers are received.

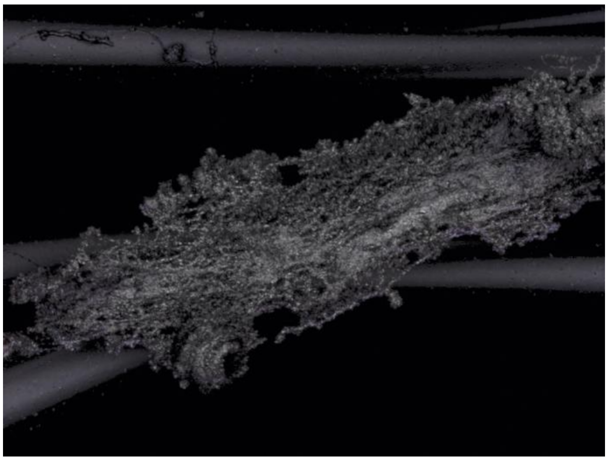

Fig. 3. TiO_2-PEO nanofiber mat after heating at 85 °C.

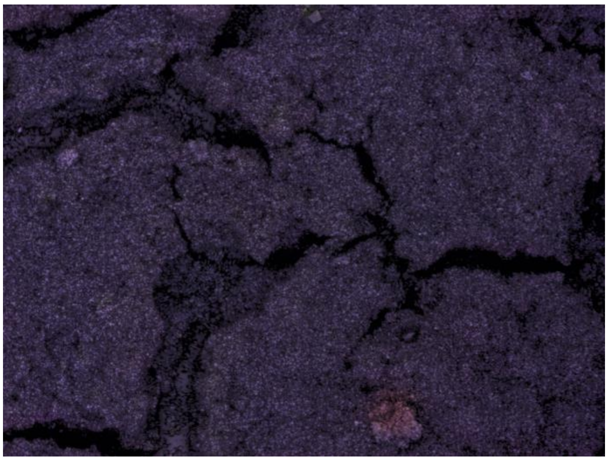

Fig. 4. TiO_2 prepared by nanospinning after sintering and dying.

As a next step, we tried to co-spin PEDOT:PSS with PEO. Spinning pure PEDOT:PSS resulted in droplets only on the substrate, while by co-spinning both materials, a regular nanofiber mat was produced (Fig. 5). First tests with low concentrations of PEDOT:PSS (22 %) resulted in non-conductive nanospun mats, thus future tests will concentrate on investigating how high the PEDOT:PSS concentration can be until fiber formation is disturbed.

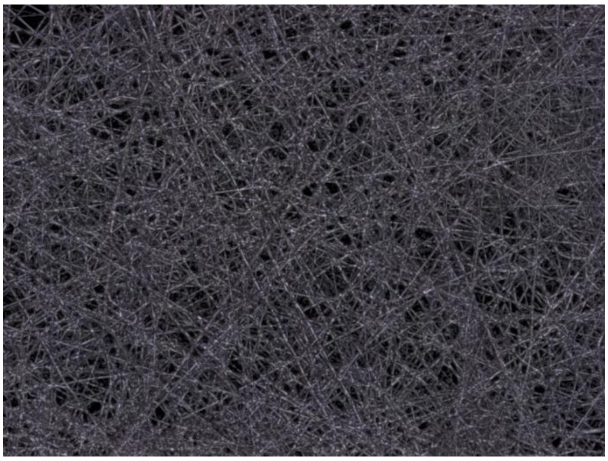

Fig. 5. PEDOT:PSS-PEO nanofiber mat.

Spinning aloe vera is also complicated, while co-spinning this material in combination with PEO results in dense and even nanofiber mats. Fig. 6 depicts one of the mats gained by nanospinning, with the thinner fibers produced by PEO and the thicker ones stemming from the aloe vera. Opposite to PEO-TiO_2 fiber mats, both materials are not intermixed here but build independent fibers.

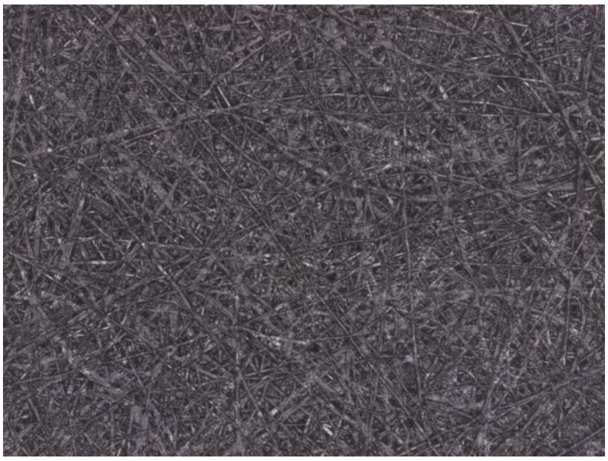

Fig. 6. Aloe vera-PEO nanofiber mat.

This effect is even stronger when co-spinning PEO and graphite. Fig. 7 depicts the results of such an experiment. The graphite flakes are clearly visible, lying on the PEO nanofiber mat and being integrated in it. The mat is not conductive due to the missing percolation paths. Higher concentrations of graphite are thus necessary if a conductive fine layer shall be created. Additionally, the adhesion between graphite and PEO or another spinning agent must be tested to ensure that the graphite particles are bonded on the surface and cannot be washed or rubbed off easily.

Fig. 7. Graphite-PEO nanofiber mat.

Discussion

PEO has proven its ability to serve as a spinning agent for many other materials. While large particles, such as graphite, can only be adhered to a nanospun mat, other materials, such as aloe vera, are forced to form nano-fibers in the presence of PEO. TiO_2 and PEDOT:PSS, on the other hand, seem to be incorporated in the PEO nanofibers.

The possibility to use PEO or other polymers as spinning agents enables spinning materials which are actually not spinnable. In this way, nanofiber mats can be produced from a broad variety of materials.

Nevertheless, the water solubility and the low melting point of PEO must be taken into account. Depending on the planned application, these properties may be supportive or disadvantageous.

Summary

To summarize, we have shown the possibility to use PEO as spinning agent for diverse materials in electrospinning, resulting in nanofiber mats with different properties, depending on the spinning partner.

Future research will concentrate on defining more possible spinning combinations for diverse applications.

Acknowledgements

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