Polymer 55 (2014) 5727–5733

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Electrospun composite poly(lactic acid)/polyaniline nanofibers from low concentrations in $CHCl_3$: Making a biocompatible polyester electro-active

William Serrano, Anamaris Meléndez, Idalia Ramos, Nicholas J. Pinto*

Department of Physics and Electronics, University of Puerto Rico at Humacao, Humacao, PR 00792, USA

ARTICLE INFO

Article history:
Received 11 July 2014
Received in revised form
28 August 2014
Accepted 6 September 2014
Available online 16 September 2014

Keywords:
Electrospinning
Nanofibers
Diode

ABSTRACT

Nanofibers of poly(lactic acid) (PLA) blended with polyaniline (PANi) were fabricated via electrospinning at much lower PLA concentrations (~1wt%) in $CHCl_3$ than reported before using a more efficient technique of preparing the solutions. The polymer nanofibers had diameters in the range 10 nm–300 nm. Nanofibers prepared with a 3 wt% PLA/PANi solution were conducting and were used to fabricate a diode which was electrically characterized and exhibited a low turn-on voltage and a rectification ratio of 500. The device characteristics were analyzed using the standard thermionic emission model of a Schottky junction and yielded an ideality factor of 1.6 and a barrier height of 0.49 eV. Using a simple circuit, the diode was able to rectify a low frequency alternating current signal with an efficiency of 10%. The ability to engineer insulating PLA into nanofibers that are electro-active extends the range of applications of this biocompatible and biodegradable polyester to include electronic devices that have reduced toxicity.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The design of degradable and electrically conductive polymers is an important field of study for biomedical applications [1]. Poly(-lactic acid)—PLA is a thermoplastic aliphatic polyester that is biocompatible and biodegradable, with lactic acid being a typical harmless byproduct of decomposition. PLA can be produced via processing starch and although it is an electrical insulator, it is mechanically robust and environmentally stable and has therefore attracted interest in passive electrical applications such as biomedical implants (screws), controlled drug delivery, kitchen variety commodity products and 3-D printing [2]. Commercial PLA has a hard grainy morphology, but is readily soluble in organic solvents and can be cast into thin films, fibers, foams or other forms. Fibers typically have a larger surface to volume ratio compared to films and are thus technologically advantageous for sensor applications. One common technique of making PLA fibers is using electrospinning [3–7]. Composite fibers of PLA blended with conducting polymers have also been fabricated via this technique [8,9]. In all of these experiments however, the PLA concentration in solution was 8wt% or higher, reducing the possibility of obtaining PLA fibers that are electrically conducting to be used in devices and sensors. The motivation for the present work is therefore to fabricate nanofibers of this biodegradable polymer that are electrically conducting so that they can be used in active electronic devices such as diodes, sensors and in 3D printing of PLA based products.

In this work we have used the electrospinning technique to fabricate nanofibers of PLA blended with the conducting polymer polyaniline doped with camphor-sulfonic acid (PANi-CSA) at concentrations as low as 1 wt% of PLA in chloroform ($CHCl_3$). PANi-CSA is a common conducting polymer that is easy to synthesize and is also soluble in $CHCl_3$ in the doped conducting form. By controlling the evaporation of the solvent in the blend solution prior to electrospinning, while keeping the amount of PANi-CSA fixed, extremely fine fibers of the blend could be produced at low PLA concentrations than previously reported *and that were electrically conducting*. Electrospinning nanofibers of PLA at low concentrations increased the probability of making them conducting, used less material and made the fabrication of devices economical. The fibers were used to fabricate a diode, and represent the first use of these composite fibers as the *active* material in an electronic device, where PLA provides the mechanical stability of the fibers and PANi-CSA provides the conducting pathway. A diode was selected as a prototype device as it forms the basic building block in complex electronic circuits, especially in power supplies. The standard thermionic emission model of a Schottky junction was applied to

* Corresponding author. Tel.: +1 787 850 9381.
E-mail address: nicholas.pinto@upr.edu (N.J. Pinto).

http://dx.doi.org/10.1016/j.polymer.2014.09.015
0032-3861/© 2014 Elsevier Ltd. All rights reserved.

analyze the diode characteristics and the device was used to rectify an alternating current (AC) low frequency signal. The ability to fabricate insulating PLA into *nanofibers* that are electro-active extends the range of applications of this biocompatible and biodegradable polyester to include electronic devices and sensors capable of operating under low power requirements. The benefit of obtaining nanofibers of biodegradable polyester that are conducting (via the incorporation of a small fraction of a conducting polymer) is the ability to fabricate devices that are environmentally less toxic and hence very desirable. In addition, making biodegradable polyester like PLA conductive can also lead to its use in biocompatible applications such 3-D printing of conducting screws for bone repair.

2. Experimental

PLA (MW 60,000) was purchased from Sigma–Aldrich and used as received. For fiber preparation, the following concentrations of PLA in $CHCl_3$ (in wt%) were prepared: 1,3,5,7 since previous studies included concentrations >8 wt%. The solutions prepared above are labeled Part A for future reference in this manuscript. The insulating emeraldine base polyaniline (PANi-EB) was synthesized via the oxidative polymerization of aniline in acidic media at 0 °C and converted to the base form by washing in 1 M ammonium hydroxide [10,11]. The resulting polymer was dried in air and 100 mg of PANi-EB was then mixed with 129 mg of camphor-sulfonic acid (CSA) in a mortar and pestle and slowly dissolved in 10 ml of $CHCl_3$ via constant stirring. In this doping process, the polymer has a deep green color and represents the conducting salt form of polyaniline i.e. PANi-CSA [12,13]. Once dissolved, the solution was filtered using a 0.45 μm syringe filter and is labeled Part B for future reference in this manuscript. The two polymers were dissolved separately in $CHCl_3$ in order to have a uniform particle free solution when they were mixed together.

In a process (weigh and mix) used by us in the past to fabricate polymer nanofibers, the two Parts prepared above were mixed in the following proportion in order to fabricate fibers via electrospinning [14]: 0.85 g of Part A was mixed with 0.11 g of Part B. Since the two Parts have a common solvent, a homogeneous solution was obtained after stirring for a few minutes. Thus for example, the solution labeled 1wt % PLA/PANi-CSA consists of 0.85 g of the 1 wt% PLA/$CHCl_3$ solution and 0.11 g of the PANi-CSA/$CHCl_3$ solution. The mass ratio of PLA to PANi-CSA in the electrospun fibers using this process were: 28, 85, 142 and 198, for the 1, 3, 5 and 7 wt% solutions respectively. The pure solution of PLA in $CHCl_3$ and the blends with PANi-CSA were then used to prepare fibers using the electrospinning technique [15,16]. No fibers were formed from the pure PANi-CSA/$CHCl_3$ solution due to the low molecular weight of PANi. The fibers formed using the blend solutions were relatively short and ill-defined; they also contained a large fraction of PLA and were non-conducting, hence they could not be used in devices. In a novel and modified process that resulted in the formation of long fibers at low PLA concentrations in $CHCl_3$, 0.45 g of Part A was mixed with 0.50 g of Part B in a vial to obtain a homogeneous solution, the vial was then placed on a balance and 0.5 g of the solution was evaporated. This resulted in a larger fraction of the blend solution containing PANi-CSA when compared to the previous process. In this modified process, while the PLA concentrations were changed from 1 wt% to 7 wt%, the PANi-CSA concentration was kept the same in each blend solution. After evaporation of 0.5 g, the solution in the modified process was still seen to be homogenous (since both polymers were dissolved in a common solvent) with no polymer precipitation for all concentrations studied. The resulting solution prepared via this modified process was then electrospun and it yielded PLA nanofibers that were conducting (for the 3 wt% PLA/$CHCl_3$ concentration) and from which devices and sensors could be fabricated and tested. The mass ratio of PLA to PANi-CSA in the electrospun fibers using the modified process were: 0.52, 1.57, 2.62 and 3.66, for the 1, 3, 5 and 7 wt% solutions respectively.

Fibers fabricated from the 3 wt% PLA solution using the modified process were used in device fabrication as they were longer and better defined that those obtained from the 1 wt% PLA solution, and more importantly, they were conducting. The device reported here is a diode fabricated from the electrospun fibers and a pre-patterned *n*-doped Si/SiO_2 substrate [14]. External contacts were made to the diode using gold wire and silver paint. The currents and voltages were supplied and measured using a Keithley Model 6517A electrometer and a SRS model DS335 synthesized function generator was used for AC signal excitation to the diode. The input and output signals were recorded on an Agilent Technologies DSO-X 2012A digital storage oscilloscope.

3. Results and discussion

The preparation of PLA nanofibers at low polymer concentrations in $CHCl_3$ than previously reported required the use of a conducting polymer (PANi-CSA) and a modified technique as mentioned earlier to assist in fiber formation. Since the two polymers were soluble in a common solvent (i.e. $CHCl_3$), it is important that they do not phase separate or chemically interact with each other in order to obtain the desired fibers of the polymer blends. One way to verify this was to measure the UV/VIS spectra of the blends in solution prior to electrospinning and compare it to that of pure PANi-CSA. Fig. 1 shows the UV/VIS spectra of the PLA/PANi-CSA blend solutions prior to electrospinning for different PLA concentrations in $CHCl_3$. UV/VIS spectra of pure PANi-CSA and pure PLA in $CHCl_3$ were also measured and included for comparison in Fig. 1. The spectrum for PLA is constant in the frequency range studied. From Fig. 1 we see that regardless of the PLA concentration, the spectra of the composite PLA/PANi-CSA solutions at various concentrations are similar to that of pure PANi-CSA, and include a broad absorption valley in the range 450 nm–650 nm that is

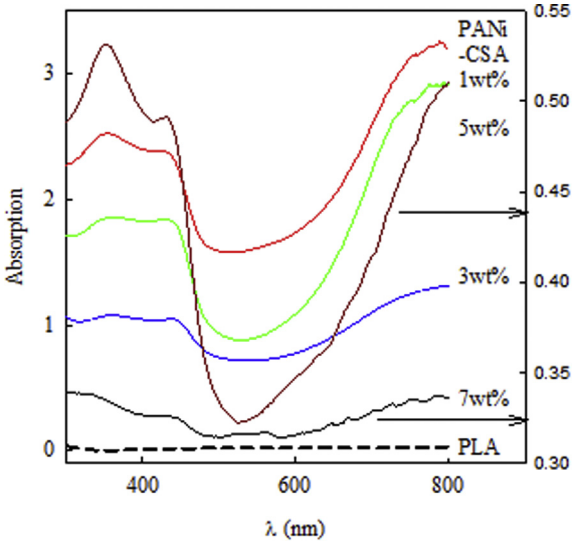

Fig. 1. UV/VIS absorption spectra of the solutions prepared from various PLA/PANi-CSA concentrations (wt%) in $CHCl_3$ prior to electrospinning. Also included are the absorption spectra for pure PANi-CSA (red) and pure PLA (dashed). The absorption spectrum of PLA is flat in the frequency range since it is transparent in the visible wavelength range. The scale for 5 and 7 wt% is to the right. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Download English Version:

https://daneshyari.com/en/article/5180708

Download Persian Version:

https://daneshyari.com/article/5180708

Daneshyari.com