ADVANCED PREPARATION AND CHARACTERIZATION OF PEDOT-BASED NONWOVEN MATERIALS FOR WEARABLE ELECTRONICS

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Abstract

Poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate (PEDOT-PSS) nanofiber-based materials represent advanced solutions for application in wearable electronics due to their biocompatibility, lightweight, permeability and improved sensitivity related to their large surface area. Since PEDOT is a conductive polymer, the electrospinning process for manufacturing thin, flexible nonwovens made of homogeneous nanofibers is not well-studied yet. In this research, we have investigated the fabrication and characterization of electrospun conductive nanofibers composed of varying concentrations of PEDOT-PSS mixed with poly(ethylene oxide) (PEO). The electrospinning technique was employed to produce these conductive nonwovens, and their morphological properties were evaluated using scanning electron microscopy (SEM). To enhance the water resistance of nanofibers, a thermal treatment was applied to remove excess PEO. The resulting samples demonstrated significant improvements in water stability, whereas untreated samples dissolved in pure water almost immediately. Electrical characterization of conductive nonwovens was performed, revealing resistivity in several hundreds of Ohm•m. To further investigate the electrical response and electrochemical behavior of the material when in contact with specific compounds, we conducted electric impedance spectroscopy (EIS) and cyclic voltammetry (CV). The EIS measurements provided insights into the impedance characteristics, while the CV analysis highlighted the occurrence of reversible faradaic reactions. Our findings suggest that the optimized PEDOT-PSS/PEO nanofibers exhibit promising electrical and electrochemical properties, making them suitable for applications in flexible electronics and wearable sensors. This study contributes to the understanding of the relationship between the fabrication process, structural morphology, and functional performance of electrospun conductive nonwovens with the potential to significantly impact the wearable technology field.

Keywords: Nonwovens, conductive polymers, electrospinning, flexible electronics

1. INTRODUCTION

The production of nanofibers has become a highly active area of research due to their unique properties and broad applications in various fields such as biomedicine, energy storage, textiles and flexible electronics, and environmental science [1–3]. Nanofibers are characterized by their high surface area-to-volume ratio, flexibility, and the ability to be tailored for specific applications, making them particularly versatile materials for diverse industrial and scientific uses. Among the different techniques for nanofiber fabrication, electrospinning has emerged as one of the most widely used and effective methods due to its scalability, versatility, and ability to produce nanofibers with customizable properties. Electrospinning involves the application of a high-voltage electric field to a polymer solution or melt, which causes the formation of a thin jet that elongates and solidifies into continuous nanofibers as the solvent evaporates and the polymer solidifies [4]. These nanofibers typically have diameters ranging from a few nanometers to several micrometers, exhibiting excellent uniformity and

purity. The primary advantage of electrospun nanofibers lies in their high surface area-to-volume ratio, which enhances their interaction with surrounding environments. Additionally, the properties of electrospun nanofibers can be fine-tuned by adjusting various parameters, including polymer concentration, solvent type, applied voltage, and collection distance [5]. The scalability and cost-effectiveness of electrospinning further enhance its industrial viability, as the process is relatively simple yet capable of producing high-quality, uniform nanofibers on a large scale. This has made electrospinning an attractive technique for various fields, particularly those requiring large-scale nanofiber production.

In recent years, conductive polymers have also gained significant attention due to their combination of electrical conductivity, mechanical flexibility, and processability [6]. These properties open up new possibilities for the development of advanced electronic devices and energy storage systems. Among the various conductive polymers, materials such as polyaniline, polypyrrole, and polythiophenes have been extensively studied. However, one of the most promising conductive polymers is poly(3,4-ethylenedioxythiophene) (PEDOT), which stands out for its exceptional conductivity, environmental stability, and ease of synthesis. PEDOT belongs to the polythiophene family and is characterized by a π-conjugated structure that imparts high electrical conductivity. The conductivity of PEDOT, measured at approximately 4380 S/cm, approaches that of indium tin oxide, a commonly used conductive material in electronic applications [7]. Unlike many other conductive polymers, PEDOT remains stable when exposed to air, moisture, and UV radiation, making it particularly well-suited for applications requiring long-term durability, such as organic electronic devices and biosensors. In addition to its stability, PEDOT's electrical and optical properties can be finely tuned through chemical doping and structural modifications. In recent years, PEDOT has found widespread use in a variety of fields, including organic electronics, energy storage, biomedicine, and wearable technology [1,2,8]. PEDOT's compatibility with flexible substrates and its biocompatibility make it an attractive candidate for flexible electronics, implantable medical devices, and bioelectronic interfaces.

Electrospinning has proven to be a valuable technique for fabricating PEDOT nanofibers, as it allows the production of nanofibers with high surface area-to-volume ratios, precise control over fiber diameter and alignment, and the ability to create complex three-dimensional structures. By electrospinning PEDOT, researchers can create bioactive interfaces with enhanced conductivity, mechanical properties, and biocompatibility, which are critical for the development of advanced biomedical devices such as biosensors, neural implants, and drug delivery systems. Significant advancements have been made in the fabrication of PEDOT nanofibers, particularly in terms of improving their conductivity and mechanical properties. Early techniques involved electrospinning insulating polymers followed by vapor-phase polymerization of PEDOT, resulting in high conductivity and resistive heating capabilities [9]. In the 2010s, researchers introduced new techniques such as oxidative polymerization and blending PEDOT with other polymers for solution-based electrospinning. These methods have further enhanced the structural stability, conductivity, and flexibility of PEDOT nanofibers [10].

In this paper, we investigate the spinnability conditions of PEDOT solutions for the fabrication of nonwoven materials. Furthermore, we characterize the electrochemical response and stability of nanofiber-based nonwovens for potential applications as wearable sensors and biosensors. In fact, one of the major limitations in the production of electrospun PEDOT-based nanofibers is related to the conductive nature of PEDOT. Therefore, being able to identify the best processing conditions for the reliable and repeatable production of nanofibers is of upmost importance in terms of industrial adoption of these materials.

2. MATERIALS AND METHODS

PEDOT:PSS PH1000 water dispersion at 1.3% (from Heraeus) was mixed with Polyethylene oxide 600 kDa (PEO, from Sigma Aldrich). The amounts of reagents used for the preparation of PEDOT-PEO starting solutions are reported in **Table 1**.

Table 1 Preparation of starting solutions made of PEDOT:PSS and PEO in deionized water

ID	Volume of PEDOT:PSS solution (ml)	Mass of PEO (mg)	Volume of deionized water (ml)	PEDOT Concentratio (mM)	PEO Concentratio (µM)
1	10.0	0.6	0.0	23.2	91.7
2	5.0	0.6	5.0	15.5	61.1
3	5.0	0.3	0.8	20.0	79.0
4	5.0	0.3	1.6	17.6	69.4
5	2.2	0.2	6.5	5.9	38.3
6	11.0	0.6	6.0	15.0	61.5
7	7.5	0.4	0.8	21.1	76.0
8	6.6	0.6	9.0	9.8	64.6
9	9.0	0.3	1.0	20.9	50.0
10	4.0	0.4	2.0	15.5	111.0

A Linari RT Advanced electrospinner has been used for the fabrication of nonwoven samples. Using the roll-to-roll configuration, 4 ml of PEDOT-PEO starting solution have been loaded in a plastic syringe, with a working distance between Al foil collector and syringe needle of 15 cm. The voltage has been set to 17 kV, and the flow rate to 0.1 ml/h. After 6 hours, the electrospinner has been stopped and the sample has been left overnight to completely dry before characterization.

2.1. Characterization techniques

Rheological analysis was performed using an DSR500-CP-4000-plus rheometer (Lamy rheology, France). The starting solutions were subjected to increasing and decreasing shea rate ramps from 10 to 500 s^{-1} for the evaluation of the viscosity. Images of nonwoven samples after the electrospinning fabrication have been collected using a scanning electron microscope (Zeiss Germany). Electrochemical characterization was performed in a naturally aerated aqueous 0.1 M sodium chloride solution (VWR, AnalaR NORMAPUR, purity >99.5%) at room temperature. Experiments were performed using a proprietary three-electrode cell suitable for exposing a fixed area of 1 cm2 of a sample. The cell configuration consisted of a sample connected as a working electrode (WE), a reference electrode (RE) of Ag/AgCl (KCl 3 M), and a platinum wire as a counter electrode (CE) in a volume of 0.250 L of test solution under static conditions. The electrochemical characterization has been carried out using a Palmsens4 potentiostat (Palmsens BV, The Netherlands).

3. RESULTS AND DISCUSSION

3.1. Solution Optimization

Figure 1a shows the results of the electrospinning tests with the PEDOT-PEO prepared starting solutions. As can be seen, when the concentration of PEO and PEDOT is relatively low the nanofiber production is successful, while if the concentrations are increased the spinning process fails. The spinnability region of starting solutions is limited on the right side due to high concentrations of PEO, which causes a marked increase of viscosity; while on top side it is limited by high concentrations of PEDOT which, being a conductive polymer, causes the electrospinning process to fail due to the disruption of the electric field between needle and collector. **Figure1b and c** show the quality of obtained nanofibers, with a uniform large area and a mean fibers diameter of 180 ±40 nm. The rheological behavior of starting solution is typical pseudoplastic, with a decrease of viscosity with increase shear rate, as shown in **Figure1d**. Using small needle size with the same

flow rate, therefore, is beneficial as the viscosity of the solution is reduced and the spinning process is promoted. Therefore, the spinnability region can be extended towards the right side of the PEO concentration recurring to smaller needles and high local fluxes, an interesting observation for increasing the output production (and, therefore, the process yield) of PEDOT-based nanofibers in industrial environments.

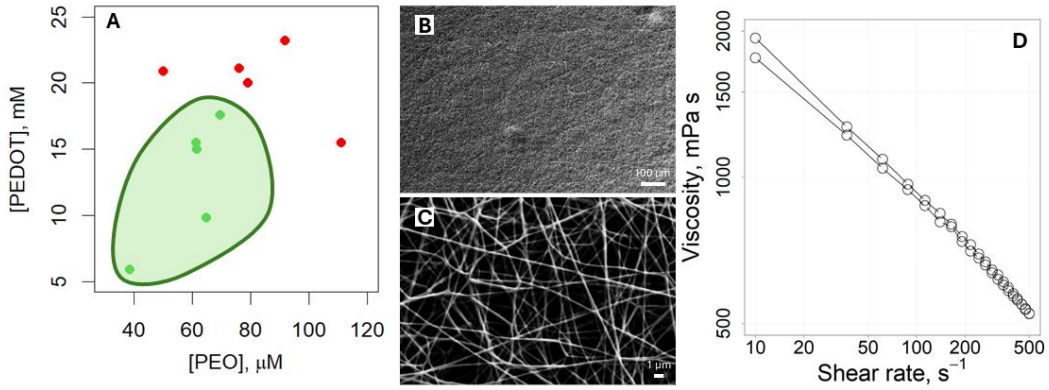

Figure 1 Characterization of the PEDOT-PEO nonwoven samples. A) spinnability as a function of PEDOT and PEO concentrations in the starting solution. B) 250X and C) 10000X SEM images of the nonwoven samples, SE 20 kV and WD 8 mm. D) Viscosity as a function of the shear rate for solution number 4 in **Table 1**.

3.2. Electrochemical Characterization

Cyclic voltammetry is a widely used technique for studying the charge/discharge process of PEDOT by measuring the current as a function of applied potential at a fixed scan rate ($mV \cdot s^{-1}$). Throughout the repeated charge/discharge process, the nonwoven material undergoes physical changes, such as swelling, shrinkage, and cracking, due to the reaction of charge carriers with the conductive polymer. The ability to maintain its mechanical integrity and preserve the cyclic voltammetry profile (**Figure 2a**) without degradation over successive testing indicates the durability of the material during measurements in aqueous media, for example for sensing applications.

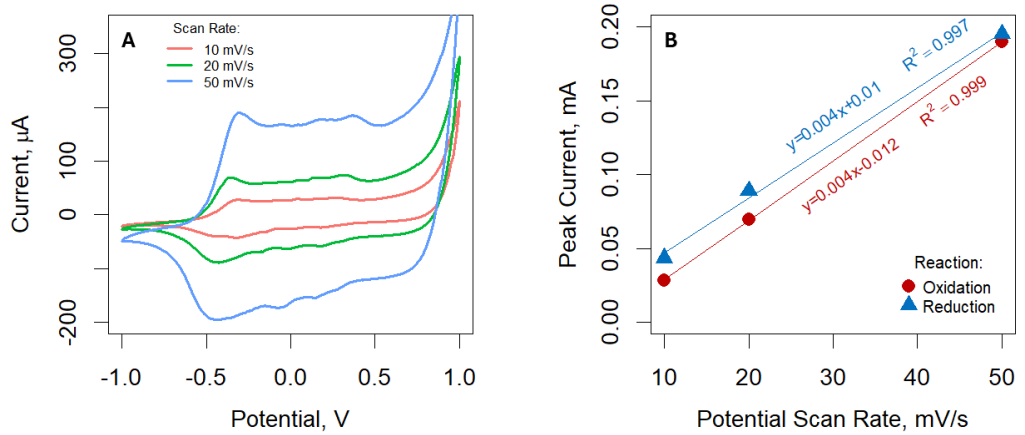

Figure 2 A) Cyclic voltammetry at different scan rate and B) linear trend of the absolute value of main current peaks

In a cyclic voltammetry experiment, the presence of symmetric peaks in the oxidizing and reducing regimes suggested the occurrence of reversible electrochemical reactions. By plotting the intensity of the main current peak as a function of the potential scan rate (**Figure 2b**) a linear relationship has been obtained, indicating the

presence of a surface-controlled process, rather than a diffusion-controlled one. This behavior is characteristic of a reaction where the redox species are adsorbed on the electrode surface rather than being freely diffusing in the bulk solution. In fact, when a redox species is adsorbed on the electrode surface, the number of available molecules for electron transfer is constant and does not depend on their diffusion from the solution to the electrode. In this case, the peak current is proportional to the scan rate, as the faster the scan rate, the more electrons are transferred per unit time. The observed linear relationship between peak current and scan rate indicates that the rate-limiting process is electron transfer at the electrode surface or adsorption/desorption of the species. Since the redox species are adsorbed, the process does not rely on diffusion from the bulk solution, and the current increases directly with the rate of potential change (scan rate). This is consistent with the very nature of nonwoven samples: nanofibers display a large surface-to-volume ratio, meaning that conducting species can easily move within the materials structure and interact at the surface of nanofibers, therefore diffusion does not represent the limiting step in the process.

4. CONCLUSION

The electrospinning experimental campaign revealed that successful nanofiber production occurs at lower concentrations of PEO and PEDOT, while higher concentrations hinder the process due to increased viscosity and disruption of the electric field. The obtained nanofibers showed uniformity with an average diameter of 180 ± 40 nm, and the starting solution exhibited pseudoplastic behavior, with viscosity decreasing as shear rate increased. By using smaller needle sizes and higher local fluxes, the spinnability region can be extended, offering a promising approach to enhance PEDOT-based nanofiber production for industrial applications. Furthermore, CV is a valuable tool for assessing both the mechanical and electrical stability of PEDOT nonwoven samples, making it particularly useful in evaluating the long-term performance and durability of nonwovens. The observed linear trend in peak current as a function of scan rate indicates that the cyclic voltammetry experiment is based on a surface-confined redox process, where the limiting process is electron transfer of the adsorbed species, not diffusion from the bulk solution. These findings indicate the PEDOT-based nonwoven samples are viable materials for the development of biological sensors and wearable electronics.

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