



Development of a novel pressure sensing material based on polypyrrole-coated electrospun poly(vinylidene fluoride) fibers



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ABSTRACT

Conductive polypyrrole-coated poly(vinylidene fluoride) (PVDF/PPy) fibers with diameters ranging from 500 nm to 1 μm were prepared through pyrrole (Py) oxidative polymerization on electrospun PVDF membrane. The influence of polymerization conditions on structures and properties of PVDF/PPy composites were investigated. The electrical conductivity and PPy content enhanced significantly with increasing Py concentration due to the conducting polymer layer formation that completely coated the PVDF fiber surfaces. The effect of dynamic load on electrical conductivity of PVDF/PPy composites has been registered. The maximum electrical sensitivity was observed for the composites containing 50 wt.% of PPy content, for which the relative conductivity increases around 40-fold with applied compressive stress. This behavior can be explained by the fact that during compressive stress, the contact between PVDF/PPy fibers increases to form new conducting pathways and, hence, the relative conductivity of the polymer composites enhances significantly. It was also observed that the electrical conductivity is almost the same as its previous value after the loading being released. The PVDF/PPy composite properties produced by the method described in this study have showed interesting possibilities for pressure sensor developments.

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1. Introduction

Over the last few decades, interest in developing fibrous membranes based on intrinsically conducting polymer (ICP), such as polypyrrole (PPy) and polyaniline (PANI), has increased significantly because of their specific properties associated with porous structure (high surface area and controlled porosity) which are important in many technological application varieties. Pyrrole or aniline direct polymerization in the presence of natural or synthetic insulating polymer fibers is one of the most used methods to produce conducting polymeric fibrous materials (CPFM). These materials can also be obtained by electrospinning technique due to its manufacturing versatility and simplicity. CPFM can be normally produced by: (i) direct technique, in which fibers are electrospun from a conducting polymer dispersion [1–4] or a mixture comprising of insulating polymer and ICP dispersed in a common solvent [4–10]; and (ii) indirect method, in which the insulating fibrous membrane is firstly prepared by electrospinning and after coated

with PPy or PANi through pyrrole or aniline oxidative polymerization [11–13]. CPFM have been recognized as being relevant for sensing applications, e.g., gas sensors, pH sensors, humidity sensors, biosensors, amperometric sensors, pressure sensors and others due to their high surface area, high sensitivity and flexibility.

Recent effort has been made on developing high sensitive pressure sensors with fast and linear response, reliability and low cost for robotics, touch-sensitive switches, prosthetic devices and remote control systems [14,15]. Pressure sensing materials are normally composed of insulating polymer matrix, such as unsaturated rubbers, thermoplastic rubbers or insulating fibrous polymer membranes and conductive filler, including, carbon nanotubes, carbon black (CB), PPy or PANi as the conductive disperse phase [16]. Under pressure, the electrical conductivity of these systems enhances due to conducting polymer particle arrangements, forming a conductive polymer network. In addition, when the pressure is released, the conductive pathway is discontinued, and the electrical conductivity must be returned to the initial value to that without pressure [17,18]. On the other hand, there are others polymeric systems, e.g. CB composites, in which the electrical conductivity decreases when a pressure is applied [23]. In addition, pressure sensitivity depends on the sensing material structure and properties (insulating polymer matrix and conductive filler) and also on the test conditions, such as temperature, and applied compressive or tensile forces [24].

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In this context, poly(vinylidene fluoride) (PVDF) is a suitable polymer matrix to prepare conducting polymer composites due to its excellent mechanical properties, high dielectric permittivity, ease for processing, resistant to chemicals and unique pyroelectric/piezoelectric properties. Because of these remarkable properties, PVDF is used to prepare conducting polymer composites for self-regulated heaters, over-current protectors, conducting electrodes and highly sensitive pressure sensors.

Several works in the literature have described PVDF/PPy or PANi film productions by different processes, which include mainly solution and melt processing [19–23]. Moreover, few works have reported the use of PVDF/PPy or PANi blends for pressure sensing applications [24,25]. Radhakrishnan and Kar [25] have reported a technique to decrease the impedance without affecting the piezosensitivity of PVDF by blending it with PANi. In that work, electrically conductive PVDF/PANi blends were prepared through a solution casting method, at room temperature, after dissolving both components in N,N-Dimethylacetamide (DMA) as a common solvent. The sensitivity was dependent on the composition, dopant type as well as the electric polarization of PVDF/PANi blends. The PVDF/PANi blends containing PANi content in the range of 10–15 wt.% showed higher piezo-sensitivity than other blend compositions. In another work, Patil et al. have prepared PVDF/barium titanate (BaTiO_3)/PANi composites by conventional powder processing method. The hybrid PVDF/ BaTiO_3 /PANi composites showed good piezo-sensitivity [24].

However, to our best knowledge, there are no studies concerning to the polypyrrole-coated poly(vinylidene fluoride) (PVDF/PPy) fiber preparations by electrospinning method to develop conducting fibrous composites for pressure sensitive transducers. The main advantage of using conducting polymer-based electrospun membranes for pressure applications is due to their PVDF piezoelectric and inherent properties of conducting polymer with the compressive characteristic of fibrous network structure. Therefore, in order to produce conducting PVDF/PPy fibrous composites with suitable properties for sensing applications, the focus of this study was to prepare a new conducting composite through pyrrole (Py) oxidative polymerization on the PVDF fiber surfaces, by using ferric chloride hexahydrate ($\text{FeCl}_3 \cdot \text{H}_2\text{O}$) as oxidant. The synthesis condition influences, such as oxidant-to-monomer molar ratio, monomer concentration and reaction time on the structure and physical properties was investigated to evaluate PVDF/PPy conducting fibrous composites effectiveness as a pressure sensor.

2. Experimental

2.1. Material

Pyrrole (Aldrich; 98%) was distilled under vacuum and stored in a refrigerator. Iron (III) Chloride Hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (analytical grade, Vetec) was used without further purification. Poly(vinylidene fluoride) (PVDF) commercially designated Solef 11010/1001 was kindly supplied by *Solvay do Brasil Ltda*. Dimethylformamide (DMF) (99.8%) and acetone (99.5%) were purchased from Synth.

2.2. PVDF fiber membrane preparations by electrospinning

Fibers were electrospun from PVDF dissolved in DMF/acetone mixture at 25 °C and room humidity of 54%. In a typical procedure, PVDF was dissolved in DMF by stirring for 4 h at 40 °C, resulting in a solution of 25 wt.%. After cooling to room temperature, acetone was added to the solution under stirring in a DMF/acetone 75/25 proportion in weight. About 5 mL of the solution was added in a syringe needle with internal diameter of 0.5 mm. The solution was pumped

using a syringe pump (KD-100, KD Scientific) at 2.5 mL h⁻¹ flow rate. The fibers were collected on a copper plate (90 mm × 150 mm) covered with aluminum foil. The electric field was generated using a high voltage supply (Testtech), which generates DC fields from 0 to 30 kV. The positive pole was connected to the syringe needle and the collector plate was grounded. PVDF fibers were obtained using an electric potential of 15 kV and needle-collector distance of 24 cm.

2.3. Polypyrrole coating

PPy-coated PVDF fibers (PVDF/PPy) were prepared through pyrrole (Py) oxidative polymerization using Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), as oxidant at room temperature. Firstly, dried PVDF fibrous membranes with 30 mm of diameter were immersed in Py aqueous solution (0.06 L) with concentration ranging from 0.01 to 0.1 mol L⁻¹ under stirring. After 10 minutes, an appropriated amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ dissolved in 0.05 L distilled water was slowly added. In order to find suitable conditions, polymerization was held using different oxidant-to-monomer molar ratios (2/1, 4/1 and 6/1) and reaction times (0.5–6 h). After the reaction, the PVDF/PPy composites were thoroughly washed with distilled water in order to extract the byproducts and wastes of the reaction and vacuum dried at room temperature. The pure polypyrrole was also synthesized following the same reaction conditions.

2.4. Characterization

The PPy and PVDF/PPy electrical resistivity were measured using the four probe standard methods with a Keithley 6220 current source to apply the current and a Keithley Model 6517A electrometer to measure the potential difference. For high-resistivity samples, as PVDF membrane, the measurements were performed using a Keithley 6517A electrometer connected to a Keithley 8009 test fixture. Sample measurements were performed at least six times at room temperature.

PVDF and PVDF/PPy composite micrographs were analyzed by using Scanning electron microscope (SEM), Zeiss-Evoma-15. The samples were coated with gold in a Sputter Coater (Bal-Tec-SCD-050) and observed using an applied tension of 10 or 15 kV according to the magnification.

The carbon, hydrogen and nitrogen elemental analysis was performed on a Perkin-Elmer CHN 2400 instrument. The combustion process was held at 925 °C using 99.995% of pure oxygen.

Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) was performed in a Bruker spectrometer, model TENSOR 27, by accumulating 32 scans at 4 cm⁻¹ resolution, ranging from 4000 to 400 cm⁻¹ for PVDF and 4000 to 600 cm⁻¹ for PPy and PVDF/PPy composites.

The X-ray photoelectron spectroscopy (XPS) measurements of the PVDF, PPy and PVDF/PPy composites were obtained using a ESCA3000 V.G spectrometer with an MgK α (1253.6 eV) operating under high vacuum at 10⁻⁹ mbar.

Thermogravimetric analysis (TGA) was performed on a STA 449 F1 Jupiter[®] (Netzsch) instrument. The samples were heated from 35 to 700 °C, at a heating rate of 10 °C min⁻¹, less than 50 cm³ min⁻¹ of nitrogen flow.

The electrospun PVDF and PVDF/PPy composite tensile properties ranging from 100 to 550 μm of thicknesses were performed in a Dynamic mechanical analyzer (Q-800, TA Scientific) equipped with clamp for films. The analysis was performed six times for each sample, with 3 mm min⁻¹ speed at room temperature. The tensile strength, elasticity and stretching modulus at break were calculated from the stress-strain curves.

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