

Electrospun natural rubber fibers-based flexible conductive membranes

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ABSTRACT

In recent years, the technique of electrospinning has been used to develop a novel class of micro- and nanoscale materials based on fibrous structures. Several polymers, in particular elastomers, that have been implemented in this process rely on properties such as elasticity, flexibility, biocompatibility, and low cost. Herein, we describe for the first time the electrospinning of natural rubber fibers without polymeric matrix to obtain self-standing non-woven mats and oriented elastomeric fibers. The fibers average diameters were approximately 5.5 μm . Polyaniline (PAni) was deposited on the membrane surface in order to enhance the conductive properties making easy the charge transportation. We have obtained biocompatible and flexible fibrous materials using natural rubber, this research opens up possibilities of using micro and nanofibers of only-natural rubber in many applications including sensors preparation.

Keywords: Electrospinning; Fiber technology; Microstructure; Polymer; Sensors.

1. INTRODUCTION

Electrospinning is a process that uses electric fields to produce nonwoven materials with high porosity, large surface area, small diameters, and uniform fibers; there is great industrial and scientific interest in these materials because of their many potential applications [1-3], as membranes for drug delivery [4], for tissue engineering [5], for water treatment [6], for food packing applications [7], sensors [8, 9] and others. A typical electrospinning setup comprises a syringe pump to control the solution flow rate, a syringe with a small-diameter metallic needle, a high-voltage power supply, and a grounded collector plate (Fig. 1) [10, 11].

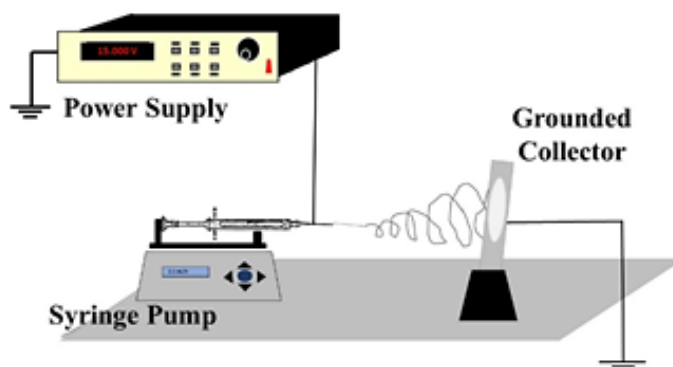


Figure 1: Schematic illustration of the homemade electrospinning setup using a syringe pump with single syringe, a high-voltage power supply and a grounded collector plate.

Researchers are increasingly shifting their attention toward the use of polymeric materials in order to obtain sub-micron and nanometer fibers by electrospinning [12-13]. Of the polymers that have been utilized, elastomers are attracting

increasing interest, and their use could be an important strategy in the development of flexible electrospun mats. Silicone rubber [4,17] and synthetic rubbers such as polybutadiene rubber (BR) and polyisobutylene-isoprene rubber (IIR) [11] have been used to produce electrospun fibers containing inorganic fillers such as silver nanoparticles (AgNPs) [11] and a europium (Eu^{3+})-like luminescent filler [18], more recently fluorescent polymer/acrylonitrile butadiene rubber (NBR) blends [19] and epoxidized natural rubber [20] have been studied.

Natural rubber (NR) is a unique elastomeric material whose flexibility, biocompatibility, elasticity, and low cost have led to its widespread use [21-24]. In recent studies, NR has been used to produce many materials such as thermo-mechanical actuators [25], nanocomposites to be used as gas barriers [26], shape memory polymers [27], and polymer networks used for environmental gas recognition [28, 29]. By combining the properties of NR with the electrospinning technique, it is possible to obtain highly flexible fibers and nonwoven porous mats with good mechanical resistance and elasticity. However, the production of electrospun fibers using only natural rubber has not yet been explored.

Recently, authors have reported attempting to electrospinning a blend of natural rubber (non-vulcanized) and polycaprolactone (PCL) using a maximal ratio of 50% of natural rubber in a PCL matrix [30]. Sithornkul et. al. reported electrospinning a blend of vulcanized NR and acrylonitrile-butadiene-styrene to investigate the parameters of electrospinning [31]. Mascia et al. produced binary blend of an epoxidized natural rubber and PLA using compatibilizer ENR-g-JM [32], still using PLA like matrix Cosme et al. developed a blend from PLA/ epoxidized natural rubber but without compatibilizer [33]. A number of challenges must be addressed when electrospinning NR: for example, it is difficult to obtain the ideal process parameters, such as solution flow, voltage, distance between the collector and the injector. Moreover, the amount of water present in the NR latex increases the time required for drying and evaporation of the solvent during the electrospinning process, i.e. when the fibers are deposited over the collector losing their fiber characteristic becoming a film material. Here, we report the development of a new material based on electrospun NR fibers. We have produced organic fibers deposited on a collector or substrate in an oriented arrangement; these fibers show high linearity and submicron size. We have also produced self-standing non-woven mats from Polyaniline-coated natural rubber ($\text{NR/PAni}_{\text{Fibers}}$) as a possible new material to apply in the sensors industry.

2. MATERIALS AND METHODS

NR membranes were prepared using latex collected from different rubber trees (*Hevea brasiliensis*) of the RRIM 600 clone in Indiana City, Sao Paulo State, Brazil (Fig. 2a). After extraction, the latex samples were stabilized with ammonium hydroxide (2% v/v). The stabilized latex was centrifuged at 14000 rpm (15,340 g) in a Microhemato Bench Centrifuge (Model 2410, Fanem) to separate out the solid rubber phase. After centrifugation, the latex was separated into three phases (Fig. 2b): the solid rubber phase (cream phase), composed mostly of isoprene monomers and containing approximately 60–40% dry rubber; the serum phase, composed of approximately 1.0 to 1.8% protein, 1.0 to 1.2% carbohydrate, 0.4 to 1.1% neutral lipids, 0.4 to 0.5% polar lipids, 0.4 to 0.6% inorganic lipids, 0.4% amino acids and amines, various other components, and 50 to 60% water; and the bottom fraction, which contained a portion of the monomers and metal ions obtained from interactions between the plant and soil [15]. The rubber cream phase was removed and annealed at 50 °C until completely dry.

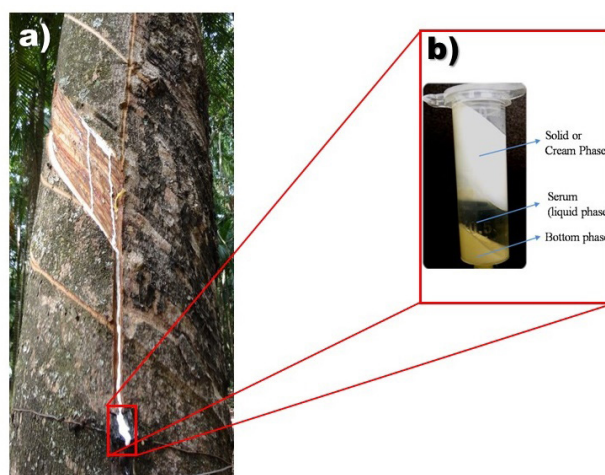


Figure 2: a) Latex extracted from *Hevea brasiliensis* from different trees was collected. b) Latex separated into three phases (cream phase, serum and, bottom phase).

To prepare the solution for electrospinning, the dried rubber phase was diluted in toluene to a concentration of 20.0 mg mL⁻¹ under constant stirring for 48 h to form a rubber solution (NRL). To confer an electrostatic charge to the NRL, was added 30 wt% of analytical-grade ethanol (Labsynth Products for Laboratories) to the dried rubber/toluene mixture.

The electrospinning system was composed of a high-voltage (15kV) power supply (Spellman Bertan Series 225), a syringe pump (Cole Parmer) with a flow rate of 0.50 mL h⁻¹, and a plastic syringe equipped with a 23-gauge metallic needle. To prevent problems with the solution outflow, a 50-W halogen lamp was included in the system, to maintain a temperature of approximately 40 °C to prevent the solvent from evaporating before the fibers reached the collector, which was placed a distance of 0.1 m from the needle. An evaluation of the optimal parameters for producing natural rubber fibers (NR_{Fibers}) is presented in the Supporting Information. To analyze the structural and thermal behavior of the electrospun fibers, membranes by casting were produced. The 10 mL of the solution previously prepared for electrospinning was poured into a glass petri dish (φ 90 mm), then was dried in an oven above 65 °C for 12 h in order to evaporate the solvent content.

To polymerize the PANi was used the MacDiarmid method [34, 35]. The aniline was acquired by Labsynth and was previously distilled. The polymerization process was performed using a 5:1 molar ratio of monomer:oxidant. In this sense, the mats were immersed in 0.2684 mol of the aniline and 300 mL of 1M HCl (hydrochloric acid). In another beaker 0.0505 mol of (NH₄)₂S₂O₈ (Ammonium persulfate) were solubilized in 200 mL of 1M HCl, then the oxidant solution was added slowly in the first solution maintaining the temperature at 0 °C, 20 minutes under constant stirring. The mats were withdrawn, washed with 1M HCl and dried in desiccator.

Characterization of the electrospun fibers was performed using optical microscopy (OM) to evaluate the morphology of the materials produced. A Carl Zeiss optical microscope with a digital camera (AxioCam MRC5) and a nominal magnification of up to 1500x was used. In addition, a scanning electron microscope (SEM; Carl Zeiss, EVO LS 15) was used to perform a complementary study of the structural properties of the NR_{Fibers}. FT-IR spectroscopy with mode ATR (model Tensor 27, Bruker) was performed in the range from 600 to 4000 cm⁻¹ with 64 scans and 4 cm⁻¹ spectral resolution in order to evaluate whether electrospinning modified the polymeric structure of NR_{Fibers} compared to that of common NR membranes prepared by casting (annealed at 65 °C in the oven during 12 h). The thermal behavior was studied by TGA (model 209, Netzsch). After the polyaniline coating, the UV-Vis spectrometer (model 1800, Shimadzu) was carried out to confirm the emeraldine form of the conductive polymer. For evaluate the fibers conductive properties was used the DC with a Keithley Source (Model 617Programmable Electrometer) by the two-point method applied from -0.5 to 0.5V.

3. RESULTS AND DISCUSSIONS

A self-standing non-woven mat of neat natural rubber (porous membrane) microscopy image is shown in Fig. 3a. The image shows the high porosity into the fibrous mat. The preparation of fibrous membranes results in increased surface area and shows great promise for the production of implanted devices, drug delivery systems, and biological filters.

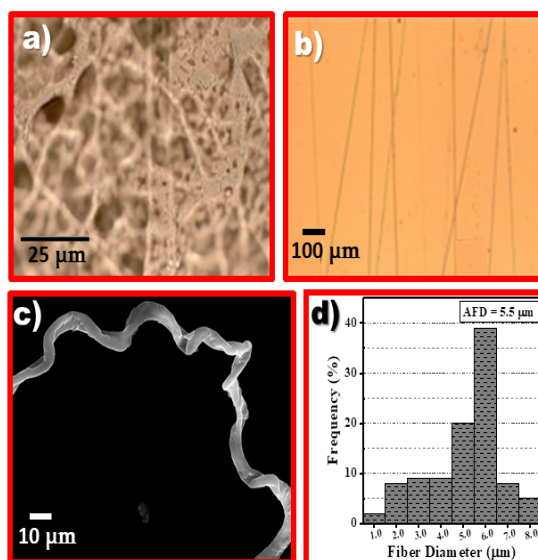


Figure 3: a) Optical micrograph of self-standing non-woven mat of neat natural rubber (NR_{Fibers}) produced with increase 1000x. b) Optical micrograph of oriented fibers produced with increase 400x. c) SEM image of isolated fibers electrospun with magnification of 2000x. d) Histogram of fibers diameter distribution for the NR_{Fibers}.

In addition, when a rotary collector was used to control the mats porosity (i.e., to ensure uniformity), oriented fibers were obtained (Fig. 3b). The characteristics of the fibers was observed, mainly the linearity and the fiber thickness, varied under the different electrospinning parameters tested (Supporting Information).

To produce oriented fibers, we used a rotary collector (30 rpm) on which the fibers were deposited onto coupled glass slides (Fig. 4a). To produce self-standing non-woven mats, the fibers were deposited on a stationary stainless-steel plate (Fig. 4b). The SEM micrograph (Fig. 3c) shows the morphology of a single fiber at a magnification of 2000x. A relatively smooth surface is observed, with well-formed fibers. ImageJ® software was used to measure the fiber diameter and revealed that the NR_{Fibers} deposited in self-standing mats had an average diameter of 5.5 μm.

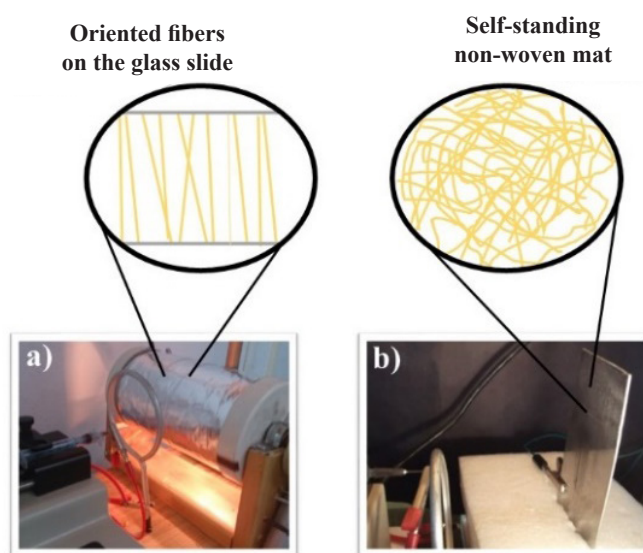


Figure 4: a) Rotary collector for deposit the oriented fibers on glass slides, was used a rotation of 30 rpm in this collector. b) The stainless-steel plate for deposit the self-standing non-woven mats.

Fig. 5 shows FT-IR/ATR spectra for NR (casting membranes) and NR_{Fibers} (self-standing mats). The spectra show vibrational bands characteristic of cis 1,4 poly-isoprene. The bands between 3666 and 3105 cm⁻¹ can be attributed to water vapor. The absorption bands at 3007, 2929 and, 2849 cm⁻¹ can be assigned to various functional groups of NR: asymmetric stretching of C=C and CH in the -CH₃ region and symmetric stretching of CH in the -CH₂ region, respectively. The band at 1659 cm⁻¹ arises from C=O symmetric stretching, the band at 1447 cm⁻¹ from C=C stretching, the band at 1375 cm⁻¹ from angular deformation (δ), and the band at 839 cm⁻¹ arises from angular deformation of the C=CH group [15, 36, 37]. There are no observable differences between the NR and NR_{Fibers} spectra, indicating that electrospinning generated no structural modifications and that the elastomeric properties, such as flexibility and elasticity (mechanical resistance), of the natural rubber polymer were maintained.

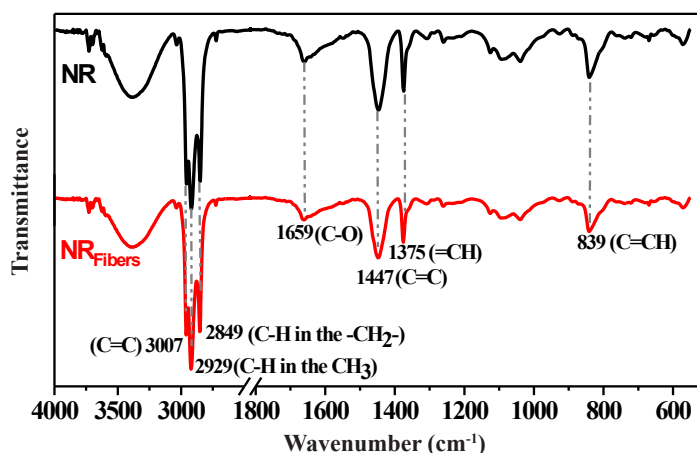


Figure 5: FT-IR spectra of natural rubber) produced by casting method (NR and natural rubber fibers produced by electrospinning (NR_{Fibers}).

In addition to the similarity of the FTIR spectra for both samples, the thermal similarity was also observed in Fig.6. The profile of the curves were very similar with a displacement of 2 °C in the main degradation stage of the NR (as seen in the DTG peaks), which is related to polyisoprene degradation [15, 38]. Two peaks (432 and 494 °C) were observed for the electrospun sample, which may have occurred due the stretching of the rubber chains during the electrospinning process.

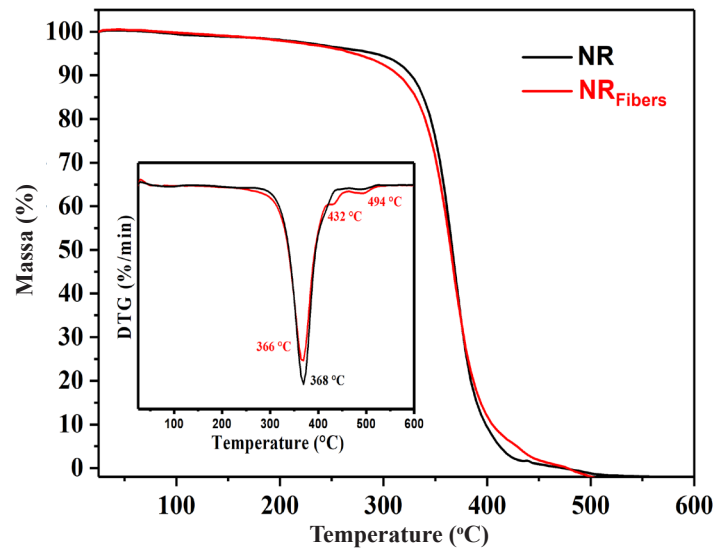


Figure 6: TGA and DTG curves for NR (casting membranes) and NR_{Fibers} (electrospun mats).

The produced mats present properties to be applied in different materials, including the sensors can be easily produced with this flexible mat. Then, the electrospun mat was coated with PANi, a polymereasily synthesized, chemically stable at room temperature conditions, high conductivity, and low cost [39]. To verify the presence of polyaniline in the conductive state (emeraldine salt), UV-Vis spectroscopy analysis was performed. Fig. 7 shows the presence of PANi absorption bands at 408 nm and 799 nm, which refers to the π bond transition in the benzenoids unites and the excitonic transitions for the polymer protonation, respectively [28, 30].

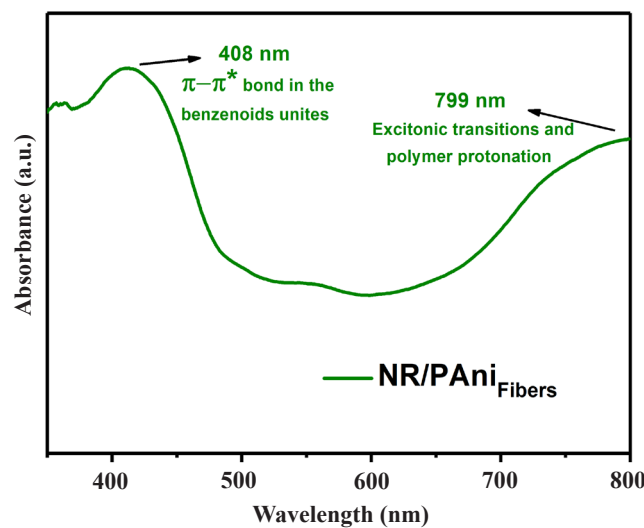


Figure 7: UV-Visible spectrum of the natural rubber/polyaniline fibers (NR/PANi_{Fibers}) showing the presence of polyaniline on fibers.

The Figure 8 shows the current–voltage (I–V) characteristics of the NR_{Fibers} and the NR/PANi_{Fibers} at room temperature in the potential range –0,5 V to +0,5 V. The linear dependence of current on voltage indicated an ohmic behavior of NR/PANi_{Fibers}. Inserted in the figure above is possible observe the values of resistivity and conductivity calculated by the following equations (1) and (2) respectively:

$$R = \rho \frac{l}{A} \tag{1}$$

$$\sigma = \frac{1}{\rho} \tag{2}$$

where R is the electrical resistance of membranes (Ω), ρ represents the electrical resistivity ($\Omega.m$), l is the sample length (m), A is referent the cross-section area of the sample (m^2) and, σ represents the electrical conductivity ($S.m^{-1}$).

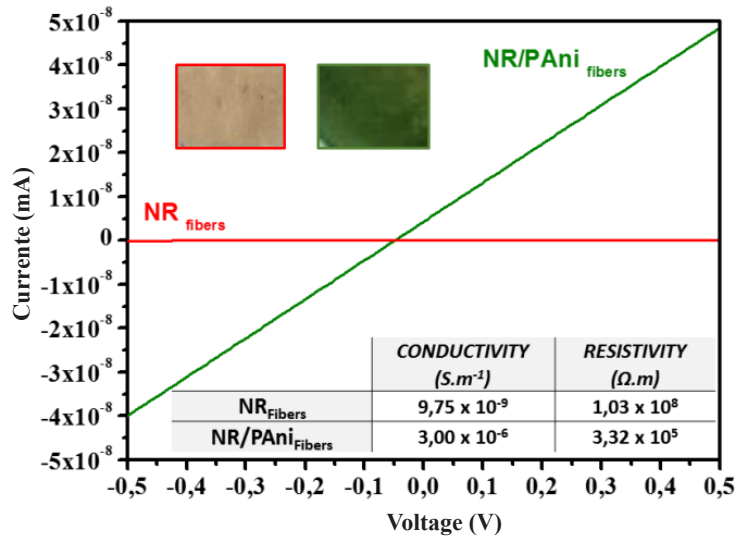


Figure 8: Shows the current–voltage (I–V) characteristics of the natural rubber fibers (NR_{Fibers}) and the natural rubber/polyaniline fibers (NR/PANI_{Fibers}). In detail are showing the photography of the electrospun membranes before and after add polyaniline; the table shows the conductivity and resistivity values for both samples.

As expected, the natural rubber fibers show high resistivity around to $1 \times 10^8 \Omega.m$ which qualifies the membranes as insulating materials. After PANi deposition the resistivity decrease to $3.32 \times 10^5 \Omega.m$ as well as increases the conductivity to $3.0 \times 10^{-6} S.m^{-1}$. It is known that the conductivity of solid materials is caused by the number of carriers and the mobility of these carriers. The conjugated polymers have a large number of carriers, but a low mobility. For this reason, lead in low conductivity orders [40].

In this sense, the materials described in this paper reached values of electrical conductivity in the semiconductor range around to $10^{-6} S.m^{-1}$ for NR/PANI_{Fibers}, and can be applied as melamine (1,3,5-triazine-2,4,6-triamine) sensor [41]; ammonia sensors [42, 43]; radiation sensors [44]; H₂S and SO₂ sensors [45] and strain sensor [46].

It was observed from the I–V curve that the NR/PANI_{Fibers} has ohmic behavior increased the current from 3.90×10^{-8} mA to 4.77×10^{-8} mA as the voltage increased. It is expected that the PANi molecules be incorporated into the natural rubber fibers, i.e. into the porous surface due the fibers presence.

4. CONCLUSIONS

Oriented fibers and self-standing non-woven mats were prepared from NR by electrospinning, and their morphological, structural and thermal properties were characterized. The average diameter of the NR fibers was approximately $5.5 \mu m$. Self-standing, non-woven mats fabricated using an organic polymer (such as NR) could lead to the production of biocompatible and flexible fibrous materials. Moreover, highly oriented fibers will improve the homogeneity and uniformity of porous mats. Through the study is possible to suggest the application in sensor, as confirmed by the electrical characterization after the polyaniline deposition.

5. ACKNOWLEDGEMENTS

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