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# MORPHOLOGY AND THERMAL STABILITY OF ELECTROSPUN NANOFIBERS BASED ON POLYMER NANOCOMPOSITE WITH METHYLIMIDAZOLIUM IONIC LIQUID

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**Abstract:** New composite materials were prepared by electrospinning/casting method aiming the preparation of membranes for fuel cell application. Non-woven nanofiber mats of poly(styrene sulfonic acid-co-maleic anhydride) (PSSAMA)/poly(vinyl alcohol) (PVA)/Ionic liquid (IL) blends were prepared by electrospinning using water as solvent. The mass ratio PSSAMA/PVA = 2/3 was employed and 1-Butyl-3-methylimidazolium trifluoromethanesulfonate (BMIM TfO) was used as IL, in the content of 10, 30, and 50 wt% concerning the polymers. Scanning electron microscopy (SEM) showed that these materials are dense structures formed by nanofibers which can act as composite filler and proton conducting elements. SEM micrographs revealed also that the addition of the smaller amount of BMIM TfO to the blend decreases the average diameter of the fiber up to 76 nm when compared with fibers prepared without any IL (average diameter = 123 nm), and the global effect of this addition of IL is the reduction of the average diameter of the fibers of the PSSAMA/PVA mixture. Thermogravimetric analyses (TGA) showed that nanofibers on set degradation temperature was not altered up to 30 wt% of IL (295 °C), but it decreases to 260 °C when 50 wt% of BMIM TfO was added to the fiber.

**Key Words**: SEM and thermal analysis, electrospinning, ionic liquid, morphology, nanocomposite, nanofibers, polymer materials.

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#### **1 INTRODUCTION**

Composites can be defined as multiphase materials made by joining at least two different materials of different properties using physical methods. Each component contributes with its properties to the final material. A composite consists of at least two parts, one is reinforcement and the second is the matrix. The composite may contain metals, ceramics, and other polymers as a matrix and as reinforcement. These kinds of materials are usually better materials if compared to the material without any filler. For example, the addition of 30 wt% of glass fibers to a polymer matrix of nylon 6 allows us to obtain a polymer composite with an elastic modulus six times higher than nylon 6 without any filler.

There are a lot of polymer materials prepared as commercial composites in which mechanical, thermal, or electrical properties are improved as compared with the corresponding polymer. Many composites have been prepared up to our days, but the use of nanotechnology has shown new possibilities to obtain new composite materials as the result of different and unique morphology of nanophases that can significantly impact the properties.

In the last years, the area of nanotechnology has shown the growth of new techniques of preparation of nanostructures with different morphologies like solid nanorods, nanowires, hollow nanocylinders, nanofibrils, nanospheres and micelles, nanofiber webs, foams with nanostructured walls and pores, and nanopatterned materials with application in nanocatalysts.

Among these new techniques of nanostructured materials preparation, electrospinning has appeared as a promising method. By this method, it is possible to obtain different polymer structures with nano or micromorpholoay which could be very difficult to be prepared by other techniques or methodologies. An example of this, is the production of polymer nanofibers that can be used in many applications such as, for instance, in semiconductors technology, protective clothing, filtration membranes, energy harvesting, energy storage, electrical and electronic devices, smart structures, 4D printing, biomedical scaffolds, bio-mimetic, sensors, actuators, nanoelectronics, ceramics materials, and composite nanofiller. This technique can form highly porous structures and the large surface-tovolume ratio of nanofibers are special properties that improve the performance [1-7].

Concerning our body, the Extracellular Matrix (ECM) plays important roles in the wound healing process. Nanofibers have various innate properties that make them promising candidates for the wound healing applications. Electrospinning as nano/submicron fiber development method has gained a lot of attention in the past few decades for the preparation of highly porous biomaterials for wound healing applications or tissue engineering research [8-9].

The food industry is developing natural antimicrobial materials for food preservation applications more sustainable and environmentally friendly by using electrospun antimicrobial hybrid mats, in which those natural antimicrobials as silver, gold, titanium dioxide, zinc oxide, copper oxide, etc. are trapped within nanofibers fabricated by electrospinning [10-12].

In many studies, the electrospinning uses toxic solvents, halogenated, hazardous or carcinogenic, but now using green solvents or benign solvents is possible integrating polymers materials and additives too, i.e., over the years by this technique the production of polymeric fibers via solution, emulsion, suspension, and in situ crosslinking electrospinning is feasible like as a green electrospinning. In this regard, ionic liquids are molten salts in the liquid state, which are composed of ions: cations and anions, nonvolatile nature and high thermo chemical stability, that are emerging as a greener solvent option and for example in the Biopolymer processing the cellulose is one of the best alternatives to conventional polymers since it is non-toxic, biocompatible, biodegradable, and the most abundant renewable biopolymer on the planet. Lignocellulosic biomass is the most abundant renewable resource on earth that can be transformed into biochemicals and biofuels for partially substituting the fossil resource. In this context the ionic liquids exhibit many advantages in biomass pretreatment and conversion because of their high catalytic efficiency, high solubility, unique molecular structure, recyclable property, and a brief perspective on possible challenges and strategies for the sustainable development of ionic liquids which fits in the context of

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lignocellulosic biomass refining, and with usefulness in others science fields as Pharmaceuticals, Nuclear Fuel Reprocessing, Solar Thermal Energy, Waste Recycling, Catalysis, Carbon Capture, Batteries, etc [13-17].

Electrospinning is a method for generating fibers through the formation of a jet from a charged polymer or non-polymeric system under an electrical field technique as showed in the Figure 1 and consists essentially of the spinning system formed by a needle connected to a syringe with a polymer solution, a collector screen, and a high voltage power supply which is connected to the needle. When the applied electric field overcomes the surface tension of the liquid, a continuous jet is ejected from the needle to the collector direction. During the ejection, solvent evaporation takes place, producing fibers on the collector surface. Many process parameters affect fiber size and morphology as solution viscosity, solution conductivity, applied voltage, polymer solution feeding rate, capillary size, and the distance between the capillary (needle) and the collector [18-29].



Figure 1. Scheme of the electrospinning apparatus with their different elements.

As a result of the electrospinning process, fibrillar structures like porous mats of fibers (non-woven) with high specific surface area and better pore distribution are produced. The technique is relatively simple, has good cost effectiveness, can be used to produce 2D and 3D nanostructures, and can be easily scalable to produce nanostructures at an industrial level, i.e., the upscalability of this technology opens the pathway for the facile fabrication of macroscopic 3D structure with microfibrous features on a commercial scale [30-40].

Electrospinning has been one of the most widely used techniques for nanofiber preparation between the late 20th (1990) and early 21st (2000) centuries. Since it was first used in the early 20th (1900) century, significant improvements have been made in the instrument design, the material used, and the nanomaterials produced. Now-adays, scientific, and governmental institutions have a special interest in this research area, with differences applications as Medicine, Biomedical, Tissue Engineering, Filtration, Material Science, Textiles, Agriculture, Cosmetics, Food and Defense. Polymer nanofibers, nanofiber mats, and their applications has seen a remarkable growth over the last few years resulting in the number of publications tremendously increasing in the last ten years. The reason for this special interest is obvious because the enormous application fields as commented before yet [41-47].

Concentration of the polymer solution dictates the structures of the resulting materials. Spherical particles are observed at lower solution concentrations. As the concentration approaches a critical value, bead-on-string morphologies are typically generated i.e., electrospun fibers with particulates. Above the critical solution concentration, uniform fibers can be produced. The Figure 2 show the different type of morphology depending on the concentration of polymeric material present in solution {48].

We have used this technique to produce proton conductive membranes for application as Polymer Electrolyte Membrane Fuel Cell (PEMFC) aiming as an alternative for Nafion, which is the best material for this application [48]. The work proposed a new strategy for proton conductive membranes that consists in preparing a composite dense membrane in which a mat of proton conducting polymer nanofibers obtained from electrospinning generates a network of channels capable to conduct protons

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Increasing of polymer solution concentration



. These nonwoven formed by nanofibers were immobilized inside a mechanically resistant polymer matrix, forming the composite. The membranes were based on a matrix of poly(methyl methacrylate) (PMMA) and nanofibers of a blend of poly(styrene sulfonic acid-co-maleic acid) (PSSAMA) and poly(vinyl alcohol) (PVA). Such polymers were chosen for this study for two reasons: (1) in addition to the inherent proton conductivity of PSSAMA, which contains sulfonic acid groups, PSSAMA and PVA can react with each other, producing a crosslinked system with low solubility in water; and (2) PMMA matrix is soluble in apolar organic solvents, and cannot attack the PSSAMA/ PVA fibers during the casting/evaporation process.

We have continued the research, and, in this work, the morphology and thermal stability of another polymer system are reported.

### 2 EXPERIMENTAL

### 2.1 Materials

The materials used in this work were: PVA (Mn = 30,000 g/mol), PSSAMA (Mn = 20,000 g/mol), and the ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIM TfO), all supplied by Sigma-Aldrich. A mass ratio PSSAMA/PVA = 2/3 was employed and BMIM TfO was used as an ionic liquid at 10, 30, and 50 wt% about the polymers.

### 2.2 Equipments

The electrospinning apparatus was constituted by KD Scientific syringe pump KDS Model 100 and a High Voltage DC Power Supply PS/FC60P02.0-22 Glassman High Voltage. SEM analyses were carried out in a Scanning Electron Microscopy Model QUANTA 200/ FEI with samples metalized with Au for 2 minutes. A Thermo Analyzer TA Instruments Model Universal VA 5 was used for thermal analysis investigation.

### 2.3 Nanofiber preparation

The reference system was PSSAMA/PVA. Using the standard electrospinning apparatus, mats of PSSAMA/PVA and PSSAMA/PVA/BMIM-TfO nanofibers were prepared. Polymers solutions were prepared by dissolving PVA in deionized water near 80°C, then PSSAMA was added in order to attain the proportion PSSAMA/PVA = 2/3. In other cases, BMIM-TfO was added to PSSAMA/PVA too. The solution was stirred for mixing homogenization. The polymer solutions were then electrospun by using the electrospinning equipment, producing the mats of fibers which were collected on an aluminum plate target.



## 3. RESULTS AND DISCUSSION

A screening of electrospinning conditions for the preparation of PSSAMA/PVA nanofibers without and with the ionic liquid BMIM TfO was first investigated. The better conditions for the preparation of mats of PSSA-MA/PVA/BMIM TfO fibers considering the characteristics of molecular weight of the polymers used in this work were: distance between the needle and the collector (aluminum plate) = 17 cm, applied voltage = 15 kV, solution flow rate = 0.25 mL/h. We showed in our previous work that the system PSSAMA/PVA exhibits remarkable ionic conductivity [49].

Table 1 shows the influence of the IL content on the average diameter of PSSAMA/PVA fibers obtained at the needle-collector distance, flow rate and applied voltage used. The average diameter was obtained with the programs: Size Meter and Photo Filter Studio X.

 Table 1. Effect of IL addition in the average diameter of PSSAMA/PVA fibers prepared using electrospinning (volt-age =

IL content	Fiber Average diameter			
(%)	(nm)			
0	123			
10	76			
30	113			
50	97			

15 kV, needle-collector distance = 17 cm, flow rate = 0.25 mL/h).

The addition of 1-butyl-3-methylimidazolium trifluoromethane-sulfonate (BMIM TfO) as the ionic liquid in the polymer solution used in the electrospinning process results in fibers with smaller diameters, as can be seen comparing the SEM images of the control mat (PSSAMA/PVA) compared with mats of PSSAMA/PVA/BMIM TfO. This smaller diameter of the fibers suggests that this ionic organic compound acted as size reducing agent. In fact, it is known that ionic substances can change the dielectric constant of the polymer solution, modifying the polymer solution jet which reduces the diameter of the fibers, also observed in this work. It is expected that due to this decrease in the fiber diameter, an increase in the proton conductivity with the addition of the ionic liquid could occur, due to the presence of this charge conducting components.

The addition of 10 and 50 wt% of BMIM TfO in the PSSAMA/PVA blend resulted in fibers with diameters smaller than 100 nm. The average diameter was 76 and 97 nm, respectively, as compared with 123 nm of fibers prepared without the ionic liquid. In both cases, these diameters are considered as in the nanometer scale. In the case of the fibers containing 30 wt% of BMIM TfO, a reduction of fiber average diameter was also observed, but not in the nanometer scale, considering the classical definition for nanomaterial which is below 100 nm.

Based on SEM results, we believe that the fibers containing 10 wt% of BMIM TfO may have the best proton conductivity behavior for future fuel cell membrane preparation due to the smaller diameter (76 nm) since for the same volume of membrane it is expected a larger content of the proton conducting material. This smaller diameter may allow

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the proton to travel through the membrane in a more effective and controlled way. The global effect of this addition of IL is the reduction of the average diameter of the fibers of the PSSAM/PVA mixture.



Figure 2. SEM images of mats of PSSAMA/PVA fibers a) without BMIM TfO and b) with the addition of 10%, c) 30%, and d) 50% of BMIM TfO.

The stability of PSSAMA/PVA and PSSAMA/PVA/BMIM-TfO fibers was investigated by using thermogravimetric analysis (TGA). Table 2 shows the data obtained for these fibers as well as for the individual components of the materials. TGA analyses of the mats showed basically 4 weight loss events that can be associated with the components of the fibers and attributed to loss of water/moisture, chain dehydration, desulfonation, and chain scission and decomposition. All the components (PSSAMA, PVA, and BMIM TfO) absorb water and the first event of weight loss (T<sub>1</sub>) can be attributed to the loss in moisture of the components. The fibers showed to have about 10 wt% of retained water after the electrospinning process. The second weight loss ( $T_2$ ) seems to be due to dehydration of the PVA chains which generates water molecules [45]. Desulfonation processes of PSSAMA are the probable cause of the third weight loss event ( $T_3$ ), and the fourth and last event of weight loss can be attributed to chain scission and decomposition of the components.

As PSSAMA presents a very high content of residue at 700°C (47.6%), all the PSSAMA/PVA fibers showed also a high content of residue at that temperature, which is between 21 to 28 wt%.

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Sample	%IL BMIM TfO	%H₂O lost up to 175°C (T₁)	T₂ (°C)	T₃ (°C)	T₄ (°C)	(%) Residue *
			004		400	
PVA		6.3	304		422	6.2
PSSAMA		16.9	420	508	688	47.6
BMIM TfO		2.7	424	441		4.9
PSSAMA/ PVA		11.0	289	422	560	23.5
PSSAMA/ PVA/						
BMIM TfO	10	10.6	288	420		26.5
	30	6.5	295			28.0
	50	10.0	260	423	670	21.7

 Table 2. Weight loss, temperatures of mass lost, and residue at 700°C for PSAMMA/PVA and PSAM-MA/PVA/BMIM-TfO fibers and individual components.

T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub> and T<sub>4</sub> are the temperatures of maximum weight loss rate of steps 1, 2, 3 and 4; Residue \* at 700°C.

## 4. CONCLUSIONS

The addition of the ionic liquid 1-butyl-3-methylimidazolium trifluoromethane- sulfonate (BMIM TfO) in the polymer solution used for the preparation of electrospun fibers has a significant effect on the morphology, reducing the diameter of the final fiber. When 10 and 50 wt% of the IL were used in the formulations, nanofibers could be obtained, 76 nm and 97 nm, respectively. The global effect of this addition of IL is the reduction of the average diameter of the fibers of the PSSAM/PVA mixture. It seems that the ideal concentration of LI for the preparation of proton conducting composite membranes for fuel cell application is 10% since a smaller fiber diameter is obtained. From TGA analyses, these IL containing PSSAMA/PVA fibers showed to present about 10% of water and an initial degradation temperature around 280 °C which is attributed to PVA component.

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