

Study of the influence of the parameters of preparation of polymeric solutions obtaining nanofibers by electrospinning

Estudo da influência dos parâmetros de preparo das soluções poliméricas na obtenção de nanofibras por eletrospinning

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Abstract

The technique of electrospinning polymeric nanofibers has been emerging in the academic environment due to its well-parias and low operational, but the production of these nanofibers finds challenges regarding homogeneity and reproduction of obtained results. As properties of polymeric solutions are important for the determination of electrospinning parameters, such as the applied electrical voltage and injection rate. Seeking rheological behavior of polymeric solutions; which may be affected by the concentration of the polymeric solution and the preparation temperature of these solutions. This way this work studied the effect of the production temperature of polyacrylonitrile and methyl acrylate copolymer solutions and related them to the nanofibers produced at the same injection rates and electrical stresses. It was observed the inversely proportional behavior between the temperature of preparation of the solutions and the viscosity of the solutions at room temperature, which reflects in the integrity and homogeneity of the fibers formed, with the formation of pearls in the nanofibers produced to more viscous solutions.

Keywords: Nanofibers. Polyacrylonitrile. Methyl acrylate. Electrospinning.

Resumo

A técnica de eletrospinning de nanofibras poliméricas vem emergindo no meio acadêmico devido a sua versatilidade e baixo custo operacional, porém a produção destas nanofibras encontra desafios

no que tange a homogeneidade e reprodutibilidade de resultados obtidos. As propriedades das soluções poliméricas são importantes para a determinação dos parâmetros de eletrofiação, tais como a tensão elétrica aplicada e a taxa de injeção. Buscando comportamento reológico de soluções poliméricas; estas últimas que podem ser afetadas pela concentração da solução polimérica e pela temperatura de preparo destas soluções. Deste modo este trabalho estudou o efeito da temperatura de produção das soluções de copolímero de poliácrlonitrila e acrilato de metila e relacioná-las com as nanofibras produzidas nas mesmas taxas de injeção e tensões elétricas. Observou-se o comportamento inversamente proporcional entre a temperatura de preparo das soluções e a viscosidade desta em temperatura ambiente o que reflete diretamente na integridade e homogeneidade das fibras formadas, havendo formação de pérolas nas nanofibras produzidas a partir de soluções mais viscosas.

Palavras-chave: Nanofibras. Poliácrlonitrila. Acrilato de Metila. Eletrofiação.

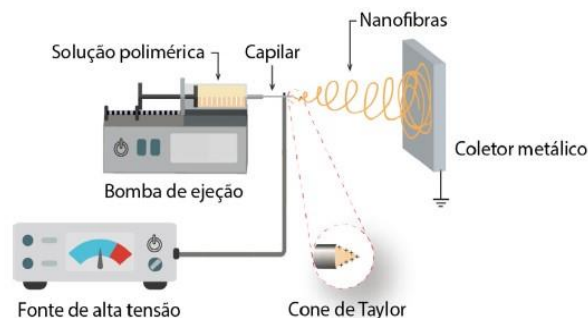
1. Introduction

The electrospinning method has applied several in today's society, mainly in the areas of materials sciences, chemistry and textiles, where the formation of nanofibers is sought through this technique, as they present in the nanometer range, thus satisfying the following relationship: $d \leq d^* \approx 100 \text{ nm}$.

These fibers can be produced from assisted polymerization by applying a potential difference in polymeric solutions. These materials are promissory materials for application in the most diverse areas of science and have been extensively studied in recent decades (Mercante, et al., 2021). The electrospinning technique comes from studies in the 19th century by Lord Rayleigh, who analyzed the behavior of useless droplets that when subjected to a potential difference (DDP) were expelled in the form of jets (Sahay, Thavasi and Ramakrishna, 2011).

Since then, much has been developed and basically for the composition of an electrospinning system are required at least one high voltage source, a controlled injection system and a grounded collector. The high voltage source with direct current provides a polarized electrical charge in the constant polymer solution in the injection system, with this as formed droplets are accelerated to the collected with opposite polarity, through the interference of the electromagnetic field formed in the system (Costa et al., 2012a; Rosell-Llompart, Grifoll and Loscertales, 2018; Lee et al., 2019).

Figure 1: Schematic design of a simple electrospinning system



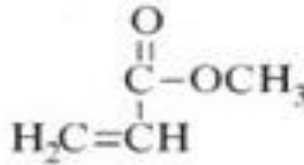
Source: (Mercante, Andre, Macedo, Pavinatto and Correa, 2021).

With the advance of the techniques and applicability of nanofibers, this configuration of material ended up being important for technological development, and from this, for several other areas, such as aeronautics. As research for aviation has become increasingly frequent, causing several researchers to change their field of study and apply their efforts to introduce nanofibers in the manufacturing process of aeronautical structures and components. Among the classes of materials that can be produced on the nanometric scale in the form of fibers, the most attractive for

the aeronautical industry are polymers (Costa et al., 2012b; Loukopoulos, Katsiropoulos and Pantelakis, 2019).

Polyacrylonitrile, in particular, gains visibility in this field, because in addition to being one of the precursors in the production of carbon fibers still presents characteristics of nitrile nitrogen cyclization and the large exotherm, theoretically lower than its fusion, it can be said that polyacrylonitrile is infuse (Fleming, Pardini and Granado, 2019). It is believed that the expected behavior of polyacrylonitrile homopolymer is influenced by copolymerization with other polymers such as methyl acrylate, figure 2.

Figure 2: Methyl Acrylate Structural Formula



Source: The Authors

In this context that the present work aims to identify the optimal parameters of preparation of polyacrylonitrile-co-Methyl Acrylate solutions, for the purpose of obtaining polymeric nanofibers by electrospinning.

2. Materials and Methods

Polymeric solutions of Polyacrylonitrile-co-Methyl Acrylate (PAN-MA) (Quimlab) in N,N-dimethylformamide (Neon) are prepared. For solubilization, the solvent was previously heated at the temperatures predicted in Figure 3 under agitation, after stabilization of the solvent temperature, the PAN-MA mass was slowly added. The mixture was kept heated and under magnetic agitation for 90 minutes and then submitted to ultrasound for 60 minutes. Stabilization of the solution is performed and, refrigerate for 12 hours. To perform the electrospinning step, parameters shown in Table 1 were followed.

Table 1: Parameter Comparisons

1st Parameter	X	2nd Parameter
10%	Concentration	10%
50°C	Temperature	80 °C
12,5 kV	DDP	12,5 kV
1,0 mL.h ⁻¹	Injection rate	1,0 mL.h ⁻¹
10 cm	Distance	10 cm

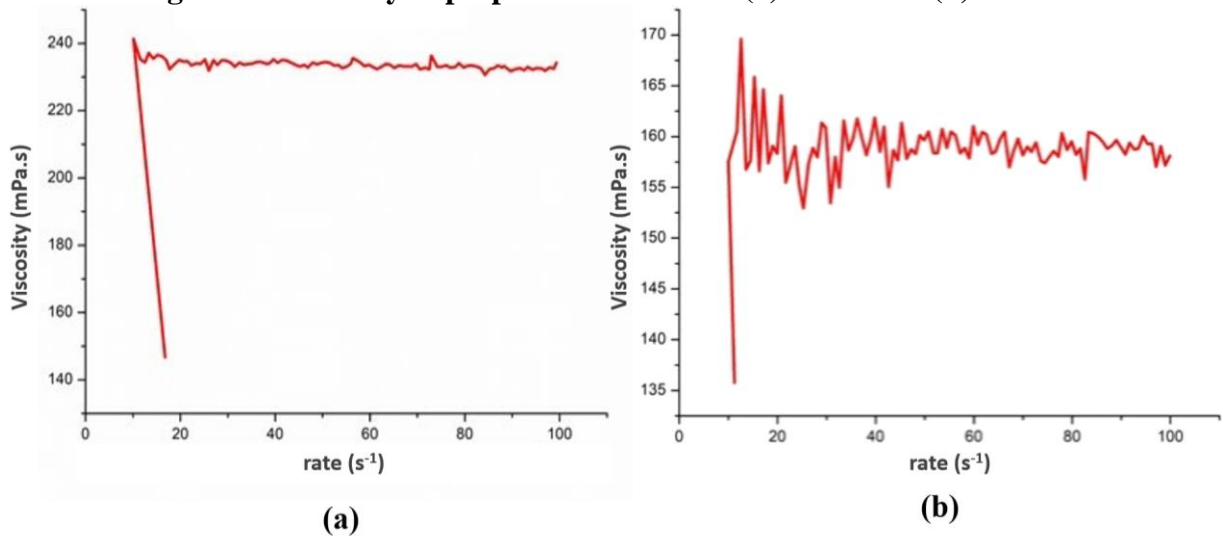
Source: The Authors

As polymeric solutions studied were evaluated by rheometric techniques at 24 °C in Thermo Scientific HAAKE MARS rheometer, 100 complete cycles with total duration of 300 seconds were applied. The morphology of the nanofibers obtained were evaluated by a scanning electron microscopy (SEM) in microscope Zeiss model EVO MA10.

3. Results and Discussion

During the preparation of the solutions, it was observed that with the increase of the temperature the solubilization was facilitated, reducing the time of dissolution of the solute in the solvent. The rheological assays of the prepared solutions show that both solutions are characteristic of Newtonian fluids and I the temperature of preparation of the solutions influencing inversely the viscosity of the solution forms. Figure 3 shows the rheological behavior of the solutions studied, it is observed that the solution obtained at 80 °C, figure 3(b), presents about 30% reduction in the viscosity of the solution. This reduction of viscosity as a function of the deformation rate is interesting for the gate of the solutions during the electrospinning process (Mercante et al., 2021).

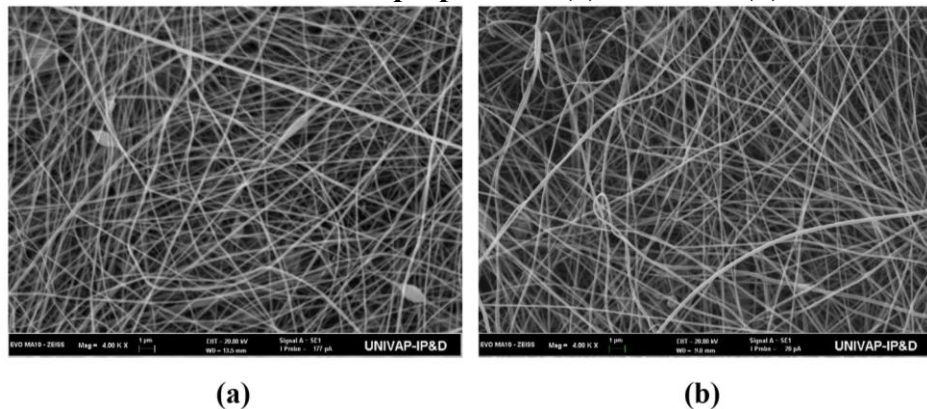
Figure 3 - Viscosity of prepared solutions at (a) 50 °C and (b) 80 °C.



Source: The authors

This characteristic reduces the occurrence of drip, which occurred during the process, this behavior is related to the formation of pearls during the deposition process. I use because there is insufficient cohesion in the solution capable of stabilizing the electrospinning jet, so when the solution is sprayed towards the collector, fibers with pearls are formed due to the instability of the solution.

Figure 4 - Photomicrograph obtained from polyacrylonitrile-co-Acrylate Methyl nanofibers obtained from solution prepared at (a) 50°C and (b) 80 °C



Source: The authors

As analyses performed by SEM, Figure 4, present nanofibers with homogeneous characteristics in their spatial distribution, but it is observed that in the image of the nanofibers obtained from the solution prepared at 50 °C present the pearl formation, resulting in drip, caused by higher viscosity, when compared to the solution obtained at 80 °C, figure 3(b), and consequently the most turbulent flow inside the injector. These morphological defects cannot be identified in the samples of nanofibers produced with solutions prepared at 80 °C, figure 4(b), being observed linear nanofibers and with apparently more homogeneous calibers.

4. Conclusions

The present study proved that to obtain polymeric nanofibers by integrative electrospinning and with morphological homogeneity, it is necessary to control the stages of the process, including the procedure of production of precursor solutions. It can be observed that the dissolution temperature of the solvent in the solute influences the morphological properties of the fibers, and at the temperature of 80 °C was observed the reduction in the viscosity of the solution resulting in the production of nanofibers with absence of pearls. Further studies are conducted by the research group to verify other parameters that can influence the characteristics of polyacrylonitrile-based polymeric nanofibers.

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