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Effect of Solvent Type on PAN–Based Nonwoven Nanofibers Membranes Characterizations

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Abstract

Electrospun nanofiber membranes are employed in a variety of applications due to its unique features. the nanofibers' characterizations are effected by the polymer solution. The used solvent for dissolving the polymer powder is critical in preparing the precursor solution. In this paper, the Polyacrylonitrile (PAN)-based nanofibers were prepared in a concentration of 10 wt.% using various solvents (NMP, DMF, and DMSO). The surface morphology, porosity, and the mechanical strength of the three prepared 10 wt.% PAN-based nanofibers membranes (PAN/NMP, PAN/DMF, and PAN/DMSO) were characterized using the Scanning Electron Microscopy (SEM), Dry-wet Weights method, and Dynamic Mechanical Analyzer (DMA). Using DMF as a solvent resulted in a long, beaded, homogeneous, and smooth surface fibrous structure with an average diameter of 260 nm, which was the best among the solvents tested in this study in terms of porosity and mechanical strength.

Keywords: nanofibers, electrospinning, solvent, mechanical strength.

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1- Introduction

According to reports, polymer fibers have several applications, especially in functional textiles and composite reinforcements [1]. Melt, dry, and wet spinning, in which mechanical forces are employed to extrude polymer fluids, are traditional techniques for manufacturing polymeric fibers. According to Vasanthan [2], these procedures permit the fabrication of fibers with a diameter of roughly 10 to 500nm. Recently, the researchers disclosed the electrospinning technology, which offers good prospects for the production of submicron polymer nanofibers. Electrospinning has grabbed the attention of both the scientific and corporate communities because it eliminates the limits of current fiber production processes [3]. Electrospinning is a versatile method that utilises electrostatic forces to generate polymer nanofibers in a simple manner. The anode of a high voltage power source is briefly linked to a syringe holding polymer solution, while the cathode is connected to the fiber collector (rotating drum). During electrospinning, an electric field is generated between the capillary tip of the needle and the collector. When the applied voltage reaches a specific level, the surface tension of the polymer solution is overcome, and a single jet emits from a Taylor cone. Then, as a single jet passes from the capillary tip to the collector, whipping instability ensues. In the end, a single jet is split, the solvent evaporates, and nanofibers are collected on a collector [4, 5]. It is well known that the characterizations of electrospun fibrous membranes are affected by several factors, including solution properties, process parameters, and the environment [6]. The electrical conductivity, viscosity, and evaporation rate of the solvent are polymer solution properties that could determine the nanofiber's final characteristics. For the production of smooth and bead-free electrospun nanofibers, the selection of the polymer-dissolving solvent is crucial [7].

Before selecting a solvent for the electrospinning process, two parameters are normally considered: the solubility of the polymer and the boiling point of the solvent. The boiling point of a solvent approximates its volatility. In general, volatile solvents are utilised due to their high evaporation rates, which allow for the straightforward evaporation of the solvent from the nanofibers as they travel from the needle tip to the collector. However, particularly volatile solvents are normally avoided because their high evaporation rates cause the jet at the needle tip to dry out and clog. Similarly, less volatile solvents are avoided because their low evaporation rate prevents nanofiber jets from drying out during flight. The deposition of nanofibers containing a solvent on the collector will result in the creation of nanofiber beads [8, 9]. Thus, the volatility of the solvent must fall within a particular range; a highly volatile solvent may result in ribbon/flat fibers or intermittent spinning due to polymer solidification at the spinneret tip. Extremely low volatility, on the other hand, may result in the collection of wet, fused, or no fibers [5, 10].

Polyacrylonitrile (PAN) is one of the most prevalent polymers utilized in filtration membranes. It is soluble in numerous organic solvents, including N-methyl-2-

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pyrrolidone (NMP), N,N-dimethylformamide (DMF), and Dimethyl sulfone (DMSO) [11, 12]. Due to their inexpensive cost of raw materials, ease of synthesis, and good heat resistance, polyacrylonitrile (PAN)-based precursors are widely utilized in industrial and medical applications. The manufacturing of carbon fibers, medication delivery, wound dressing, sensor materials, and composite reinforcement are a few uses of PAN-based membranes [13, 14].

In this investigation, three types of PAN-based precursor solutions were employed in the electrospinning technique to produce nanofiber membranes. PAN polymer was dissolved in NMP, DMF, and DMSO to form precursor solutions PAN/NMP, PAN/DMF, and PAN/DMSO. To examine the effect of the solvent type on the surface morphology, porosity, and mechanical strength of three types of nanofiber membranes, Scanning Electron Microscopy (SEM), the Dry-wet Weights technique, and the Dynamic Mechanical Analyzer (DMA) was used.

2- Materials and Methods

2.1. Electrospinning of Nanofibers Membranes

Polyacrylonitrile (PAN) (molecular weight: 150,000 g/mol). Aldrich and Alfa Aesar supplied the solvents N-methyl-2-pyrrolidone (NMP) (density: 1.03 g/cm³), N,N-Dimethylformamide (DMF) (density: 0.948 g/cm³), and Dimethyl sulfoxide (DMSO) (density: 1.1 g/cm³). In order to prepare the precursor solutions of 10 wt. % PAN/NMP, 10 wt. % PAN/DMF, and 10 wt. % PAN/DMSO, a specific amount of PAN was dissolved for 5 hours at room temperature in NMP, DMF, and DMSO, respectively. All of the nanofiber membranes in this study were produced by the showed electrospinning method in Fig. **1**. This system consists of a pulling motion of polymer droplets in a high-voltage electrostatic field. The electrospinning apparatus consists of four primary components: a syringe containing the precursor solution, a metallic needle with an inner diameter of 0.6 mm, a voltage power supply, and a collector drum [15, 16].

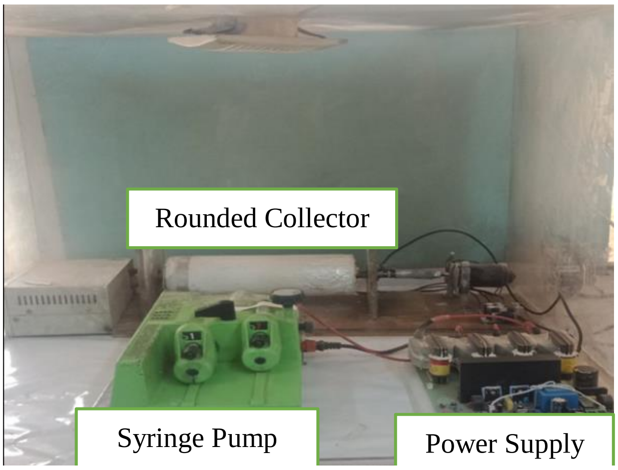


Fig. 1. The Digital Image Diagram of the Used Electrospinning System

The electrospinning conditions were 1 mL/h of solution flow, 70 rpm of collector rotation, and 15 cm of needle-to-collector distance. Voltages of 19, 22, and 27 kV were applied to 10 % PAN/NMP, 10 % PAN/DMF, and 10 % PAN/DMSO, respectively. All nanofiber membranes were fabricated at 20 % relative humidity and 25 degrees Celsius.

2.2. Membrane Characterizations

2.2.1. Morphology of Membrane surface

The scanning electron microscopy (SEM) method was utilized to characterize the surface characteristics of nanofiber membranes, such as the structure and diameter of the fibers. The average fiber diameters were calculated by analyzing the fiber sizes of thirty fibers of each membrane sample using Image J software and the obtained images (National Institutes of Health, USA).

2.2.2. Porosity

The porosity of a membrane is a fundamental criterion for many membrane applications, particularly membrane separation performance. Each membrane sample was weighed and then submerged in distilled water for one hour to determine its porosity. The sample's dry and wet weights were recorded before and after immersion in water, respectively. The nanofiber membranes' porosity was then calculated using Equation 1:

$$Porosity\ (\%) = (W_1 - W_2)/A * t * \rho \qquad (1)$$

Where: W_1 and W_2 are wet and dry membrane mass (g), A is membrane area (cm^2), t is membrane thickness (cm), and ρ: water density at room temperature g/cm^3.

2.2.3. Mechanical Properties

The mechanical property of the membrane is an important aspect of the membrane's practical applications like reusability, handling, and anti-deformation capacity [17]. Mechanical properties of the membranes were evaluated using the breaking strength and Young's modulus of the membrane samples using a Dynamic Mechanical Analyzer (DMA) (AG-A10T, Shimadzu, Japan). The specimen size of 10 cm in length and 1 cm in width was used for the tests, all performed at 25 °C and ambient humidity. Young's modulus quantifies the elasticity of a material; it is defined as the ratio of stress to strain [18, 19]. Young's modulus of the flexible materials is low.

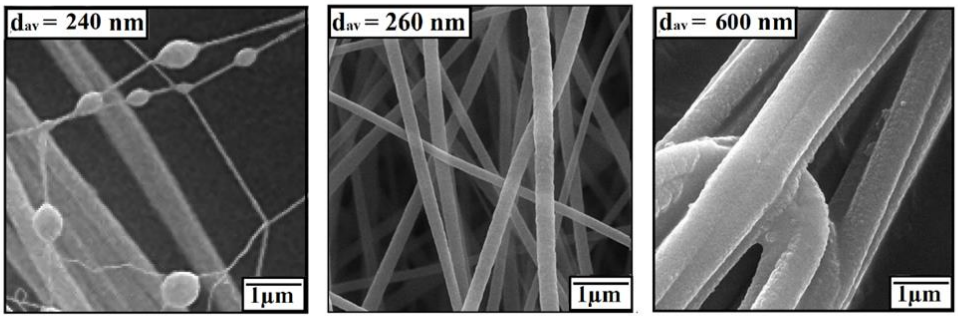
2.2.4. Water Contact Angle

Water contact angle is a convenient way to assess the hydrophilic/hydrophobic properties of the membrane surfaces and the interaction energy between the surface and water drop. The contact angle of the membrane surface can be defined as the intersection angle between water droplet and the membrane interfaces. Membranes of a water contact angle greater than or equal to 90° is counted as hydrophobic membranes, while the contact angle lower than 90o correspond to hydrophilic surfaces [12]. One of the easiest ways to measure the water contact angle is using a goniometer. This device contains a syringe of a liquid that is directed perpendicularly down onto the membrane surface, launching the droplet, and a digital camera of high accuracy.

3- Results and Discussions

It is well documented in the scientific literature [11] that solvent parameters, such as dielectric properties, surface tension, density, conductivity, and volatility, strongly affect the morphology of electrospun nanofibers. Fig. **2** depicts the surface morphology of 10% PAN-based nanofiber membranes treated with various solvents (NMP, DMF, DMSO). The SEM images in Figs. 2a and c demonstrated that spinning with NMP and DMSO solutions produced fibers that were nonwoven and stuck, respectively. With an average fiber diameter of 240 nm, the PAN/NMP nanofibers comprised several beads joined by microscopic fibers along with some stuck fibers. In addition, the PAN/DMSO nanofibers were big, uneven, and had an average diameter of 600 nm. Nevertheless, Fig. 2b demonstrated that employing the DMF solvent as a solvent for PAN resulted in the production of beadless, uniform, smooth, long fibers that were randomly distributed in a nonwoven structure and had an average diameter of 260 nm.

Due to its low boiling point (154 ºC), it was discovered that DMF evaporated swiftly, leaving the nanofibers dry. Due to their high boiling points (189 and 202 ºC, respectively), DMSO and NMP have low evaporation rates, resulting in moist nanofiber webs after electrospinning. Thus, the late evaporation of the solvents (NMP and DMSO) and the relaxing of the fibers during a lengthy drying period may account for the small and large diameters of the nanofibers formed from NMP and DMSO, respectively [12].



(a) (b) (c)

Fig. 2. The SEM Images of 10 wt.% PAN-based Electrospun Nanofibers Membrane Using Different Solvents (a) NMP, (b) DMF, (c) DMSO

Fig. **3** showed that the porosities of the different prepared membranes increased with average diameters increase. The porosities of PAN/NMP, PAN/DMF, and PAN/DMSO were (82%, 95%, and 96%). These results of porosities contributed to the fiber diameters of the fabricated membranes, the porosity of NMP is low because of the beads and small fibers, while the porosity of DMSO is large due to the large welded fibers. The porosity of DMF is high because of the nonwoven structure of the regular and continuous long fibers.

Fig. **4** indicated that using the DMF as a solvent produced fibers of higher strength due to their morphology; continuous polymeric fiber with no bead-like structure. The PAN/NMP showed a low strength due to the existence of the beads with the fibers. Although the large fibers of the PAN/DMSO membrane, the strength was low, contributing to the fibers' irregular formations [20]. The Young's modulus (stiffness) of PAN/NMP membranes showed the highest value due to the low number of fibers and the beads existence, as shown in the SEM image. In contrast, both PAN/DMF and PAN/DMSO membranes contained continuous fibers, resulting in a low value of Young's modulus. The flexibility of the PAN/DMSO is lower than that of PAN/DMF because of the larger fiber sizes and the sticky fibers' existence.

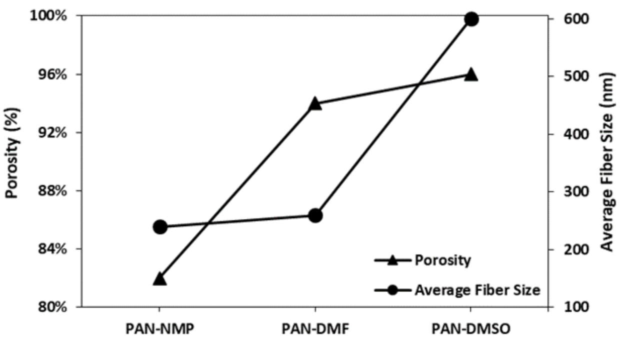
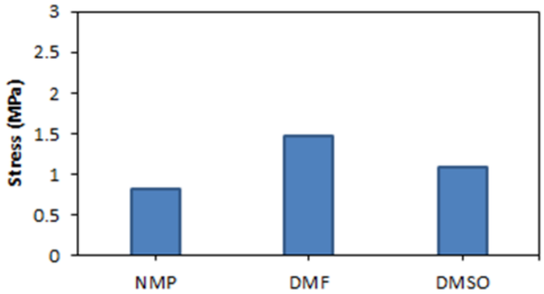


Fig. 3. The Porosity and Average Fibers Size of Fabricated 10 wt. % PAN-based Electrospun Nanofibers Membrane at Different Solvents

According to literature, the surface porosity is associated to the contact angle of a membrane by affecting the surface energy. The porosity has the opposite relationship with contact angle which means polyacrylonitrile nanofibers with the highest porosity showed the lowest water contact angle value [21]. Table **1** showed that the greater contact angle (110º) is for PAN/NMP nanofiber membranes in comparison with PAN/DMF nanofiber membranes (96º), and PAN/DMSO nanofiber membranes (73º). this result can be ascribed to the surface porosity in the case of NMP < DMF< DMSO, as shown previously in Fig. **3**. The solvent type showed obvious effect on the membrane porosity and contact angle due to the fibers morphology and the solvent evaporation rate during the nanofibers fabrication.



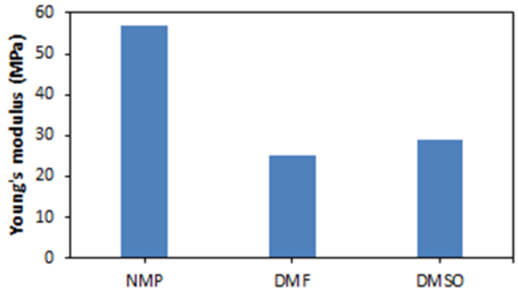


Fig. 4. Mechanical Properties (Breaking Strength and Young`s Modulus) of 10% PAN-based Electrospun Nanofibers Membrane Using Different Solvents

Table 1. The Contact Angel Values of the Various Fabricated 10 % PAN-based Electrospun Nanofibers Membranes Using Different Solvents (DMF, DMSO, and NMP)

The 10 % PAN-based electrospun nanofibers membranes	Contact Angle (º)
PAN/DMF	96
PAN/DMSO	73
PAN/NMP	110

4- Conclusions

This study has proven that solvent selection is one of the most important factors in defining the morphology of PAN nanofiber membranes produced by electrospinning. The features of the solution were influenced by the characteristics of the solvent (NMP, DMF, and DMSO); only DMF performed well in terms of electrospinnability. The nanofiber membranes electrospun from a DMF solvent-containing solution (10 % PAN/DMF) had the most desirable fiber shape and mechanical qualities; long, continuous, and beadless nanofibers. Also the solvent type showed an obcious effect on the water contact angle of the fabricated nanofibers. The NMP and DMSO solvents produced irregular fibers. Using the NMP as a solvent produced hydrophobic PAN-based nanofibers with the highest water contact angle (110º), while the DMSO produced the lowest water contact angle (73º). Due to the regular structure, high porosity, hydrophobicity, and high mechanical strength of 10% PAN/DMF nanofiber membranes, they could be useful for numerous prospective applications, such as biomedical, intelligent textiles, and nanofiltration.

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تأثير نوع المذيب على توصيف أغشية الألياف النانوية غير المنسوجة المصنعة من بوليمر البولي اكريلونايتريل

حنين صبيح الكعيدي و بسمة اسماعيل ويسي

قسم الهندسة الكيمياوية– كلية الهندسة –جامعة بغداد

الخلاصة

تستخدم أغشية الألياف النانوية المغزولة كهربائيا على نطاق واسع في العديد من التطبيقات بسبب خصائصها الفريدة، مثل المسامية العالية ومساحة السطح العالية لكل وحدة حجم. يعد محلول البوليمر أحد العوامل الحاسمة التي تؤثر على توصيفات الألياف النانوية. المذيب المستخدم لإذابة مسحوق البوليمر أمر بالغ الأهمية في تحضير محلول البوليمر. لا يوجد معيار واضح للحكم على ما إذا كان المذيب ذي القابلية العالية للذوبان للبوليمر سيكون جيدا للغزل الكهربائي مع خصائص قوة ميكانيكية جيدة. في هذا البحث، تم تحضير الألياف النانوية باستخدام بوليمر الاكريلونايتريل PAN بتركيز ١٠٪ .wt باستخدام مذيبات مختلفة NMP وDMF وDMSO. تم وصف مورفولوجيا السطح والمسامية والقوة الميكانيكية لأغشية الألياف النانوية الثلاثة المحضرة بنسبة ١٠٪ من الوزن PAN/NMP، PAN/DMF، و PAN/DMSO باستخدام المجهر الإلكتروني الماسح (SEM) ، وطريقة الأوزان الجافة الرطبة، والمحلل الميكانيكي الديناميكي (DMA) . أظهرت النتائج أن استخدام DMF كمذيب أنتج الياف طويلة، خالي من الخرزات، موحدة، وسطح أملس بمتوسط قطر ٢٦٠ نانومتر، وهو الأفضل بين المذيبات المستخدمة في هذا العمل مع مسامية مناسبة وقوة ميكانيكية.

الكلمات الدالة: الألياف النانوية، الغزل الكهربائي، المذيبات، القوة الميكانيكية.