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Carbonized Copolymers Nonwoven Nanofibers Composite: Surface Morphology and Fibers Orientation

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Abstract

Carbonized nonwoven nanofibers composite were fabricated using the electrospinning method of a polymeric solution composite followed by heat treatment including stabilization and calcination steps. The spun polymeric solution was a binary polymer mixture/organic solvent. In this study, two types of polymers (Polymethylmethacrylate (PMMA) and Polyethylene glycol (PEG)) were used separately as a copolymer with the base polymer (Polyacrylonitrile (PAN)) to prepare a binary polymer mixture in a mixing ratio of 50:50. The prepared precursor solutions were used to prepare the precursor nanofibers composite (PAN: PMMA) and (PAN: PEG). The fabricated precursors nonwoven fibers composite were stabilized and carbonized to produce carbon nonwoven nanofibers composite. The effect of the combined polymer type on the fiber size, fiber size distribution, and surface morphology of the prepared nonwoven nanofibers was studied. The nonwoven fibers orientation and surface morphology were characterized using field emission scanning electron microscope (FESEM). In addition, ImageJ software has been used to calculate the fiber size and fiber size distribution. Here, the obvious effect of the copolymer type on the surface morphology, fiber size, and fiber orientation has been demonstrated. Using a copolymer with PAN polymer led to increasing the fiber size. The carbonized nanofibers composite prepared using PEG polymer as a copolymer was more ordered fibers in comparison with the fiber orientation of carbon nanofibers based on pure PAN. In contrast of that, using PMMA as a copolymer resulted curly carbonized nonwoven nanofiber composite.

Keywords: Copolymers, Nanofibers, Orientation, Surface morphology, Fiber

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1- Introduction

Polymeric membranes have wide applications in various fields including water treatment [1],[2]. Recently, electrospinning technique has been widely used to fabricate nonwoven polymeric nanofiber membranes using an electrically forced fluid jet [3], [4]. The electrospun nanofiber membranes are considered good candidates for many applications, specifically, water filtration due to high permeability, high porosity, fully interconnected pore structures, low hydraulic resistance, and tunable wettability [5], [6]. In addition, polymeric membranes, based on specific types of polymers, can be converted into carbon nonwoven nanofibers through post-thermal treatment steps including stabilization and carbonization steps [7], [8]. Carbon nanofibers are considered as one of the typical one-dimensional nanomaterials and they are commonly fabricated using polyacrylonitrile (PAN) as a precursor due to the high carbon yield, high melting point, and low cost of this type of polymer [9]. This type of carbon material has unique features such as high specific area, high permeability, high aspect ratio, good conductivity and mechanical properties [5], [6], [8], [10]. There are several applications for carbon fibers such as energy storage in lithium-ion batteries, sensors, fuel cells, and catalysts [7], [9], [11],[12].

The precursor solution properties have a significant effect on surface morphology of electrospun fibers [13]. The surface morphology and fibers properties of electrospun nonwoven fibers can be tuned through various approaches including embedding nanoparticles [14],[15], using some chemicals to impart functionalities [16], [17], and using combined polymers [18].

The combined polymers can have a significant effect on the fabricated spanned fibers according to the introduced polymer properties [19]. For an instance, a novel anode material in rechargeable lithium-ion batteries (LIB) was made using modified carbon nanofibers based on copolymer precursor (Polyacrylonitrile (PAN): Polypyrrole (PPy)/ Dimethylformamide (DMF) solvent) [18]. The copolymer PPy was used as a conductive polymer to improve the conductivity of the fabricated carbon fibers composite.

This study is mainly concerned with fabrication electrospun carbon nonwoven nanofibers using pure PAN/DMF, composite (PAN: PMMA)/DMF, and composite (PAN: PEG)/DMF using a copolymer mixing ratio of 50:50. The obtained results of the composite carbon nonwoven nanofiber membranes have been compared with carbon nanofiber based on pure PAN to investigate the effect of the copolymer type on the surface morphology of the fabricated carbon membrane.

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Scanning electron microscopy (SEM) and ImageJ software have been used to study the surface and fibers characterization.

2- Materials and Methods

2.1. Preparation of Carbonized Nonwoven Nanofibers

Polyacrylonitrile (PAN) (Mwt. 150,000 $g.mol^{-1}$), Polyethylene glycol (PEG) (Mwt. 20,000 $g.mol^{-1}$), and Polymethylmethacrylate (PMMA) (Mwt. 996,000 $g.mol^{-1}$) were purchased from Sigma-Aldrich. Dimethylformamide (DMF) solvent was provided by Fisher as an appropriate solvent for the used polymers.

The base polymer was PAN, while PMMA and PEG were the copolymer with PAN to prepare the composite nonwoven. The blend ratio of base polymer (PAN)/co-polymer (PEG or PMMA) was 50:50 weight ratio in DMF and the final polymer concentration was kept constant as 12 wt. %.

The precursor solutions were prepared by constant stirring for 12 hr at 50 ℃. The precursor solution was then fed through a 20 gauge end needle using a syringe (30 ml) to be dispensed onto a collector rotating at 70 rpm using a syringe pump (KD Scientific) as shown in Fig. **1**. During electrospinning, the flow rate of the charged solution (pure PAN, PAN: PMMA and PAN: PEG) was constant at 1ml/hr and the applied voltage was 15, 18, and 21 kV, respectively.

Then, the fabricated precursor nonwoven fibers was stabilized in a muffle furnace (Carbolite) at 270 °C for 1 h in air atmosphere followed by carbonization in a tube furnace (Lindberg Blue M, Thermo Scientific) at 650 ^{o}C for 1 hr in a nitrogen atmosphere.

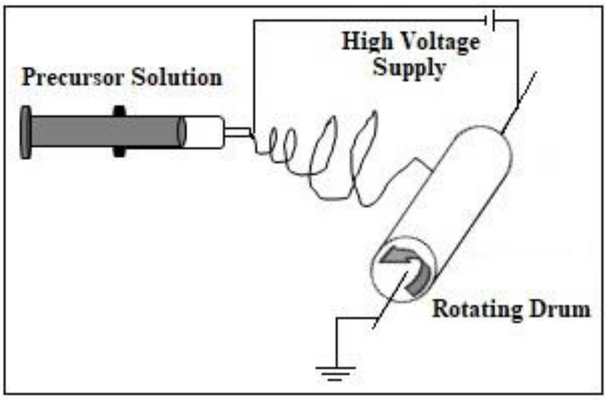

Fig. 1. Schematic diagram of the electrospinning machine

2.2. Fabricated nonwovens characterizations

To explore the possible changes in nonwoven fibers structure and surface morphology, the carbonized nonwovens were analyzed using a JSM-5610 scanning electron microscope (SEM, Japan) after coating with platinum to minimize the charging effect. In addition, the average fiber diameter and fiber size distribution were characterized using ImageJ software (National Institutes of Health).

3- Results and discussion

3.1. Nanofibers Morphology

During electrospinning, the molecular chains in the precursor nanofibers collected on the rotating drum and relax to some extent resulting in a certain orientation depending on the used precursor polymer properties.

After carbonization step, many structural imperfections in the precursor fibers are likely to be retained carbon fibers.

Fig. **2** shows the SEM image of the carbonized nonwoven fibers based on pure PAN, the fibers have curvature structure with presence of some beads within the mat structure.

The SEM images presented in Fig. **3** a and b are for the carbonized nonwoven fibers composite based on PAN: PMMA and PAN: PEG with a mixing ratio of 50:50.

Regarding to the precursor polymer type, introducing the copolymer with PAN resulted in an obvious change in the nonwoven structure and fibers size of the fabricated carbonized composite mats.

According to the precursor solution recipe, the overall surface morphology was changes comparing to the carbonized nanofibers based on pure PAN. The fibers of the carbonized nonwoven composite based on PAN: PMMA were spaghetti-like fibers and with some stacked fibers with each other. While the carbonized composite fibers based on PAN: PEG were straight and structurally ordered fibers.

This can be explained by the difference in glass transition (T_g) and melting temperatures (T_m) for the used polymers (PAN, PMMA, and PEG) as listed in Table **1**.

During the carbonization step, PAN pyrolyzed to carbon while PMMA and PEG were thermally degraded to small molecules or even evaporated due to the low glass and melting temperatures comparing with those of PAN.

Some intermolecular interactions between PAN and the copolymer phases occurred in the composite precursor nanofibers, which influenced the stabilization and carbonization of nonwoven composite precursor.

In addition, the loss of macromolecular orientation in final carbonized nanofibers composite may be the reason behind inferior fibers properties of the resulting carbon nanofibers composite.

Table 1. The glass transition and melting temperatures for the used polymers [20]

Polymer type	Glass transition temperature T_g (^{o}C)	Melting temperature T_m (^{o}C)
Polyacrylonitrile (PAN)	109	321
Polymethylmethacrylate (PMMA)	105	144
Polyethylene glycol (PEG)	-67	66

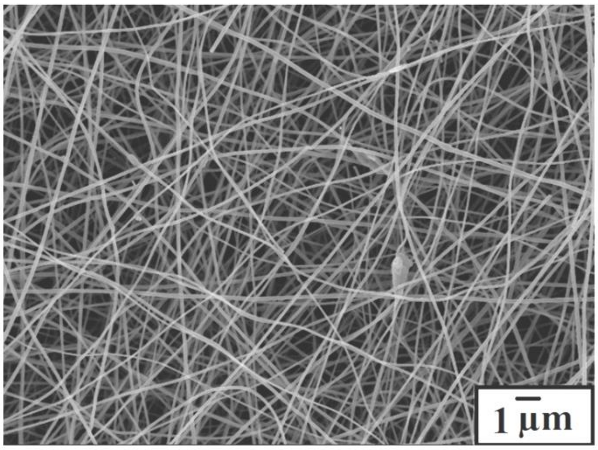

Fig. 2. The SEM images of carbonized 12 % PAN/DMF nonwoven nanofibers

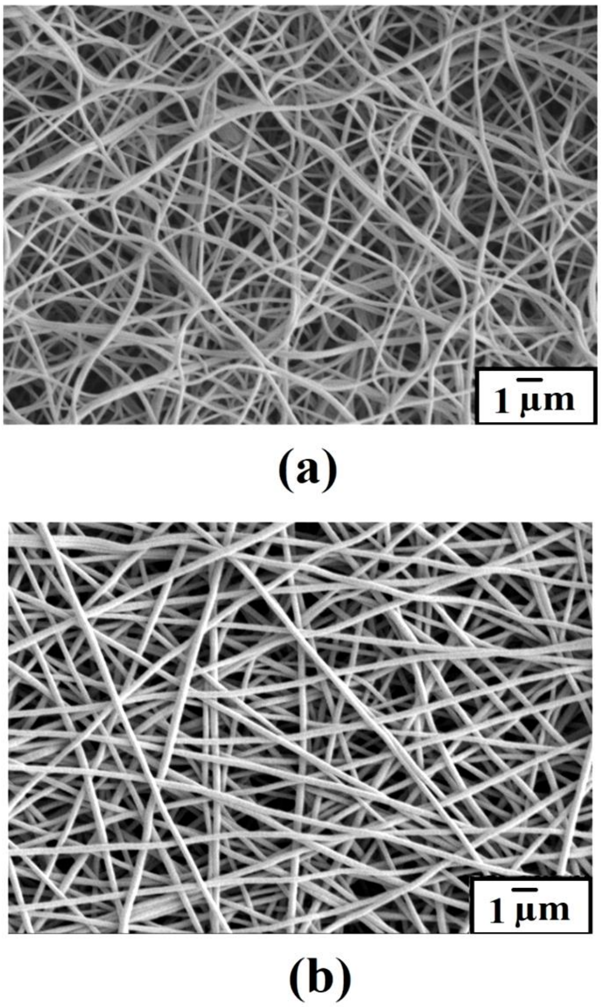

Fig. 3. The SEM images of carbonized nonwoven nanofiber composite: (a) (PAN: PMMA)/DMF and (b) (PAN: PEG)/DMF

3.2. Nanofibers size distribution

Fig. **4** shows carbon nanofiber based on 12% PAN/DMF has nanosized fibers with 140 nm average fiber diameter which lays within the range of 80 - 200 nm. Introducing a copolymer with PAN resulted larger fiber size of the carbonized nonwoven nanofibers composite: 170 nm for (PAN: PMMA) and to 260 nm for (PAN: PEG) as shown in Fig. **5** a and b. Most of the fibers of PAN: PMMA was in the size range of 140-220 nm, while the fiber size of PAN: PEG nonwoven was distributed almost equally between 200-320 nm.

Increasing the average fiber size can be likely attributed to increasing the precursor solution viscosity (cP) resulted from introducing the copolymer. For the same total polymer concentration in the prepared precursor solutions, the lowest viscosity amongst the various precursors was for pure PAN, while PAN: PEG had the largest viscosity. Increasing the solution viscosity decreased the extension during spinning because chain entanglements become more flexible chain resulting thicker fibers [21].

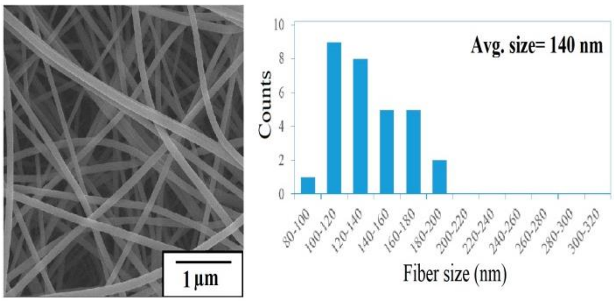

Fig. 4. Average fiber size and distribution of the fabricated carbon nonwoven based on 12% PAN/DMF

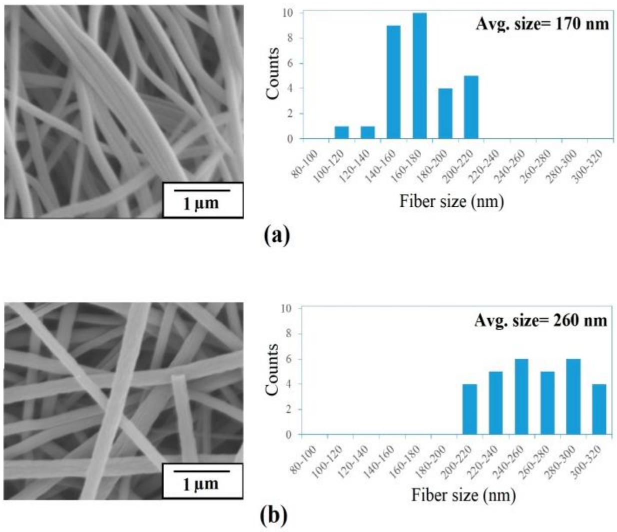

Fig. 5. Average fiber size and distribution of the fabricated carbon composite nonwoven nanofiber (a) (PAN: PMMA) /DMF(b) (PAN: PEG)/DMF

4- Conclusions

The surface morphology is a very important property to control the porosity of the required nonwoven membrane for various applications. Carbon nanofiber can be prepared with different surface morphology when it is prepared from different precursor polymer solutions using various types of copolymers.

The nonwovens structure of the carbonized mats based on pure PAN contained bend nanofibers with some beads. Introducing a copolymer with PAN produced larger fiber size with different surface morphology due to the difference in the glass and melting temperatures.

Using PMMA as a copolymer resulted in spaghetti-like nonwoven fibers while using PEG resulted in large fiber size with a straight structure.

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شبكة الالياف النانوية البوليميريه الكاربونية المركبة: طبيعة السطح واتجاه الالياف

الخلاصة

تم تصنيع نسيج ألياف نانوية كاربونية باستخدام طريقة البثق الكهربائي لمركب المحلول البوليمري متبوعًا بالمعالجة الحرارية بما في ذلك عملية التثبيت والتكلس. كان المحلول البوليمري عبارة عن مزيج ثنائي البوليمر / مذيب عضوي. في هذه الدراسة ، تم استخدام نوعين من البوليمرات (Polymethylmethacrylate (PMMA) و (Polyethylene glycol (PEG)) بشكل منفصل كبوليمر ثانوي مع البوليمر الأساسي (Polyacrylonitrile (PAN)) لتحضير خليط بوليمر ثنائي بنسبة خلط 50:50 .

تم استخدام المحاليل التي تم تحضيرها لإعداد ألياف نانويه بوليمرية مركبة (PAN: PMMA) و (PAN: PEG) والتي تم تحويلها الى ألياف كاربونية مركبة بواسطة عمليه الكلسنة. تمت دراسة تأثير نوع البوليمر المشترك على حجم الألياف وتوزيع حجم الألياف وطبيعة السطح للألياف النانوية. تم دراسة اتجاهات الألياف وطبيعة السطح باستخدام المجهر الإلكتروني الماسح (FESEM) بالإضافة إلى ذلك ، تم استخدام برنامج ImageJ لحساب حجم الألياف وتوزيع حجم الألياف. هنا ، تم اكتشاف التأثير الواضح لنوع البوليمر الثانوي على التشكل السطحي وحجم الألياف واتجاه الألياف. حيث أدى استخدام البوليمر الثانوي مع البوليمرالاساسي إلى زيادة حجم الألياف. كان ألياف الألياف النانوية الكربونية المحضرة باستخدام بوليمر PEG أكثر ترتيبًا من الألياف الكاربونية المنتجة من بثق PAN النقي. على النقيض من ذلك ، فإن استخدام PMMA كبوليمر ثانوي أدى إلى انتاج ألياف نانوية مركبة مجعدة.

الكلمات الدالة : بوليمر ثانوي, الياف نانوية , اتجاه, طبيعة السطح , حجم الالياف.