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Fabrication, characterization, and microscopic imaging of Fe_2O_3-modified electrospun nanofibers

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ABSTRACT

This study explored the fabrication, characterization, and microscopic imaging of highly porous electrospun nanofibers based on pure and Fe_2O_3 nanoparticle modified polyacrylonitrile (PAN) fibers. The desired electrospinning mixture comprising polymer and nanoparticles in dimethyleformamide, was prepared. During electrospinning, the precursor solution was injected using a syringe pump. The empirical parameter influences, including nanoparticles dose, polymer weight percentage, and thickness as applied polymer syringe, were studied on the product morphology and uniformity. The products were analyzed by Fourier transform infrared (FT-IR) spectrophotometer, scanning electron microscopy (SEM), and X-ray diffraction (XRD). The results demonstrate that changes in the investigated empirical parameters cause fiber morphology variations and uniformity. Therefore, a strong interaction exists between Fe_2O_3 and PAN. In general, addition of nanoparticles to PAN solution resulted in a decrease in the average fiber diameter compared to pure PAN.

Keywords: Electrospun, nanofibrous, PAN, Fe_2O_3

Introduction

In general, fibers are divided in three groups comprising microfibers, nanofibers, and moderate fibers. The nanofibers include three important types of polymeric, mineral, and carbon nanofibers.[1] This study used polymeric nanofibers due to their importance in fabricating the nanofibers. Several methods are reported to fabricate nanofibers, such as phase separation, drawing, templates, selfassembly, and electrospinning.[2] Electrospinning process has attracted immense attention since its first report in 1934.[3] The electrospinning of various polymers is an internationally highly recognized method used to fabricate the polymeric nanofibers of nanosized diameter and for a broad range of complex architectures of nanofibers.[4-9] This technology has several applications in the medical field, namely tissue engineering, equipment and medical implants, medical masks, and drug delivery, and also in other fields where composites reinforced with the layers of nanofibers are used in filtration, water and wastewater treatment, and ion-exchange membranes.[4-10] Moreover, it is used to magnificate a variety of hybrid nanofibers by incorporating the nanomaterials into several polymer matrices. The nanofibers produced by electrospinning method reveal several significant advantages: small diameter (50 nm–10 mm), high aspect ratio (the ratio of length to diameter), large specific area (surface area to volume ratio), variety in composition, unique physicochemical properties, and design flexibility for physical/chemical surface functionalization.[11-13] Long nanofiber with controllable morphology can produce continuously by electrospining technique.[14] During electrospining, a high voltage supply is applied for jet formation in the polymeric solution at the needle tip. The unwoven nanofibers gather on the collector.[15] Nanofiber

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membranes with several properties including small pore size, high permeability, high porosity, and interconnected pores form a good alternative for filtration purposes.[16-17] In this study, pure PAN fibers and PAN fibers modified with various percentages of Fe_2O_3[18] nanoparticle loadings have been fabricated via an electrospinning process. Optimum conditions (weight percentage of polymer and Fe_2O_3 nanoparticles dose) to achieve bead-free fibers with several characteristics, in particular nanoparticle loadings, are explored. The surface morphology of the PAN fiber and PAN fiber modified with various percentages of Fe_2O_3 nanoparticles are characterized by several techniques, including Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD).

Materials and Methods

Materials

Polyacronitrile (PAN, MW = 100,000) was purchased from Polyacryl Iran Corporation (Iran), *N,N*-dimethylformamide (DMF, 99.9%) was purchased from Merck (Iran), and for the synthesis of Fe_2O_3 nanoparticles by sol-gel method, salt ferric chloride ($FeCl_3$) and sodium hydroxide (NaOH) were used from Merck.

Fabrication of pure casting solution and nanosized fibers

Polymeric solution preparation

The casting solution involved PAN/DMF with polymer loading of 8.0, 10.0, 12.0, and 14 wt% was prepared. A specific amount of Fe_2O_3 nanoparticles (0.01, 0.1, and 1.0 wt%) was added into the casting solutions. Ultrasonication was performed for 45 min to disperse the Fe_2O_3 nanoparticles within the solutions at room temperature. Both the pure casting solutions and the nanoparticle modified solutions were used for electrospinning fibers and subsequent morphological investigation.

Fabrication of nanosized fibers

Both pure and PAN/Fe_2O_3 nanosized fibers were prepared using the electrospinning method. The viscous polymeric solutions were loaded in a 1 ml syringe equipped with a stainless steel gauge 25 needle. The needle was connected to the positive pole of a high voltage power supply, generating a DC voltage up to 20 kV. The formed polymeric fibers were collected on a rotating cylindrical collector after solvent evaporation. The solution was constantly and controllably supplied using a syringe pump (STC-527, Korea). The volume rate of the polymeric solution was controlled at 23 ml/min. In this study, the applied voltage was adjusted in the range of 16–18 kV. An external electric field with a high voltage applied to the polymer solution through the positive electrode can overcome the surface tension of the viscous polymer solution and form a polymer jet, which is accelerated toward the collector and forms the fibers.

Characterization

The surface morphology of the electrospun pure nanofiber and the one modified by Fe_2O_3 nanoparticles, was studied with the SEM (TSCAN, Czech). The intact samples were coated with gold for SEM observation. In the SEM photos, the nanofiber average diameters were evaluated using Digimizer.v4.1.1.0 software and the results were presented as the average diameter ± standard deviation. Fourier transform infrared spectroscopy (FT-IRTensor 27, Brucker Optics, Germany) was used between 1000 and 4000 cm^{-1}, in the absorbtion mode, with 4 cm^{-1} of resolution. The crystal structure of the pure PAN nanofiber and the nanofiber modified with Fe_2O_3 nanoparticles was characterized using an X-ray diffraction (Inel, France) with Cu Kα (λ = 1.5405 Å) radiation over the 2θ range of 0–80°.

Results and discussion

PAN concentration effect

The bead formation during electrospining process affects the properties of the electrospun fibers and results in several issues, such as a decreased specific surface area.[5,19] Hence, in this research, several PAN concentrations used to investigate the effect of the concentration on beads formation at the process include: 8, 10, 12, and 14 wt%. Figure 1 presents the SEM of

the pure PAN nanofibers with 8, 10, 12, and 14 wt% polymer in the casting solution, respectively. As observed in Figure 1, the beads may form on the surface of the fibers at low concentrations. Polymeric solutions involved 8 wt% polymer loading results in the fibers along with beads, (Fig. 1A); however, almost uniform PAN nanofibers with few beads were obtained at 10 wt% PAN casting solution, (Fig. 1B). On increasing the polymer concentration to 12 wt%, the fibers become more uniform, smooth, and lack nodes. Nevertheless, at 14 wt% concentration, a little nonuniformity is observed on the surface of the fibers. It could be a result of the increasing concentration of the polymer, which increases the mass and the diameter of the nanofibers in jet spinning. Thus, the polymer chains are strongly held due to the increase in viscosity. Therefore, the fibers stretch more. An optimum concentration exists to achieve uniform fibers without beads. It was observed that increasing the concentration of the polymer results in less beads formation. Hence, 12.0 wt% polymeric solution was chosen for this study. Moreover, the diameter distribution of the nanofibers is presented in Figure 2. In general, the diameter of the nanofibers varies from 190 to 211 nm. The average diameter of the nanofibers including 8, 10, 12, and 14 wt% PAN was 211.03, 205.82, 190.76, and 196.76 nm, respectively. A falling trend of the average diameter was observed from 8 to 12 wt% casting

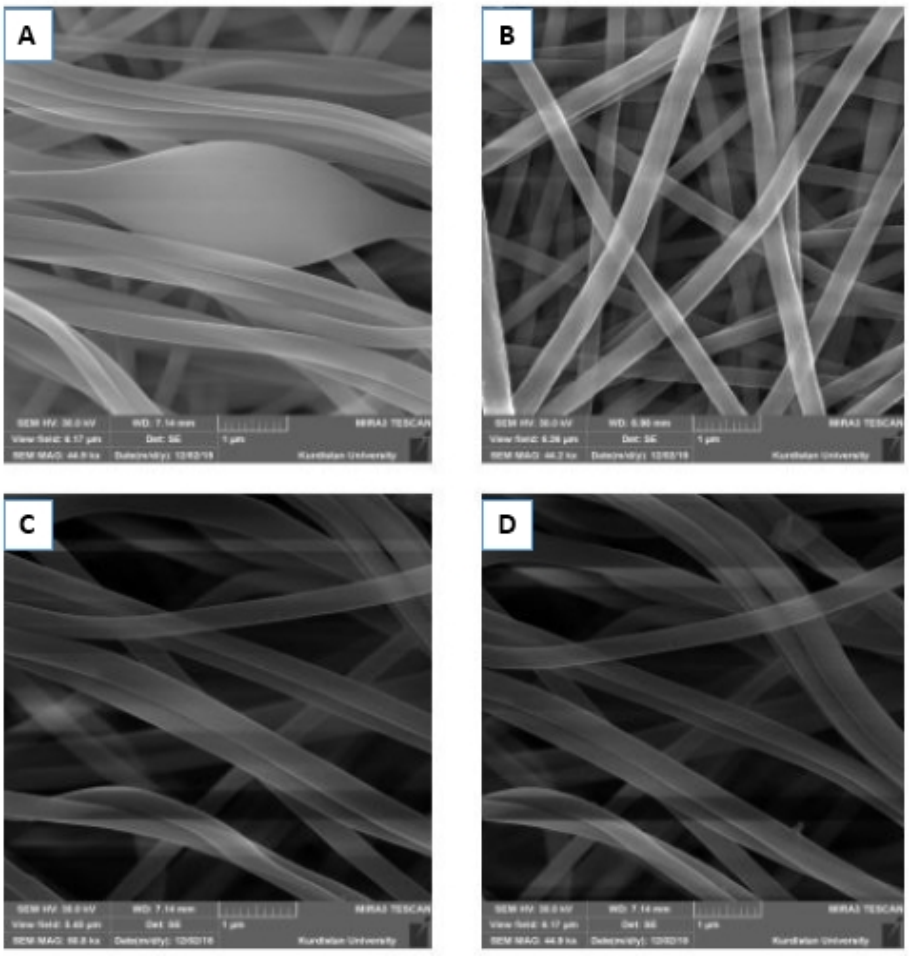

Fig. 1. SEM images of pure PAN nanofibers with a PAN loading (A) 8 wt%, (B) 10 wt%, (C) 12 wt%, zand (D) 14wt%.

solution, but after that the average diameter was increased. Uniform pure nanofibers (12.0 wt% PAN) were obtained with an average diameter of about 190.76 nm. The more concentrated

polymeric solution, the more viscosity and less evaporization. It could be expected that the nanofibers with more thickness were obtained due to higher concentration of the polymer.

Therefore, the diameter of the nanofibers could change due to the varying polymer concentration, as presented in Figure 2. Several parameters including electrostatic repulsion, surface tension, and viscoelastic force, are essential in controlling the fiber quality during electrospinning.[5,20,21]

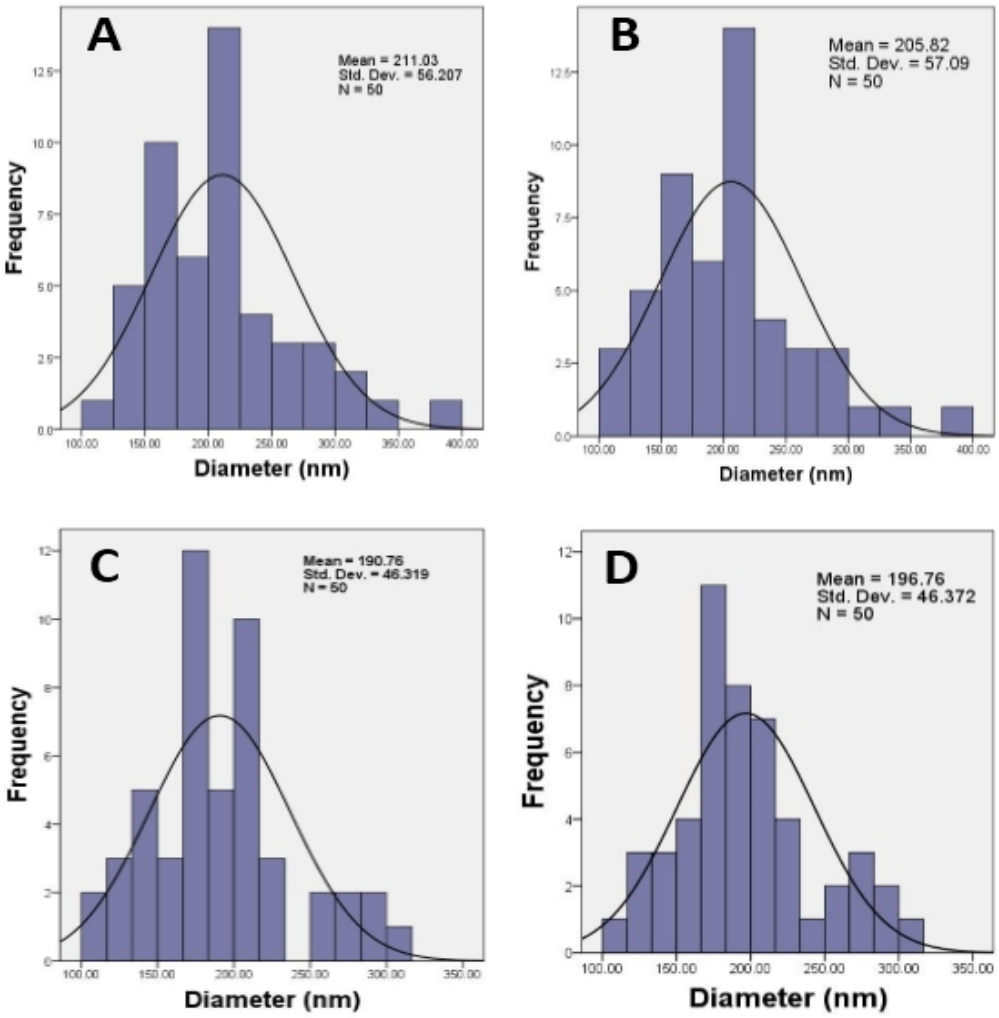

Fig. 2. Diameter distribution of pure PAN nanofibers with loadings (A) 8 wt%, (B) 10 wt%, (C) 12 wt%, and (D) 14 wt%.

Effect of Fe_2O_3 nanoparticles on the fiber morphology

Modified Fe_2O_3-nanofibers with distinct nanoparticle loadings (0.01, 0.1, 1 wt%) were fabricated (Fig. 3). The variation in the nanoparticle concentration due to weight affects the several features of the fibers; however, the of the agglomeration of Fe_2O_3 particles increased. This affects the physical characteristics of the nanofibers.

The morphological features of Fe_2O_3 nanoparticles are presented in Figure 4 challenges such as particles dispersion and agglomeration were encountered during electrospinning, when the loading of the Fe_2O_3 nanoparticle was increased. An efficient dispersion was achieved in lower loadings such as 0.01 and 0.1 wt%, whereas when Fe_2O_3 loading was raised up to 1 wt%, the possibility indicating porous nanosized particles with a little homogeneous and polygonal structure.

The addition of nanoparticles within the polymeric solution increases the mechanical strength of the fibers and creates nanopores

within the nanofibers.[21] Moreover, the structural modification with Fe_2O_3 nanoparticles enhances the strength and uniformity of the nanofibers.

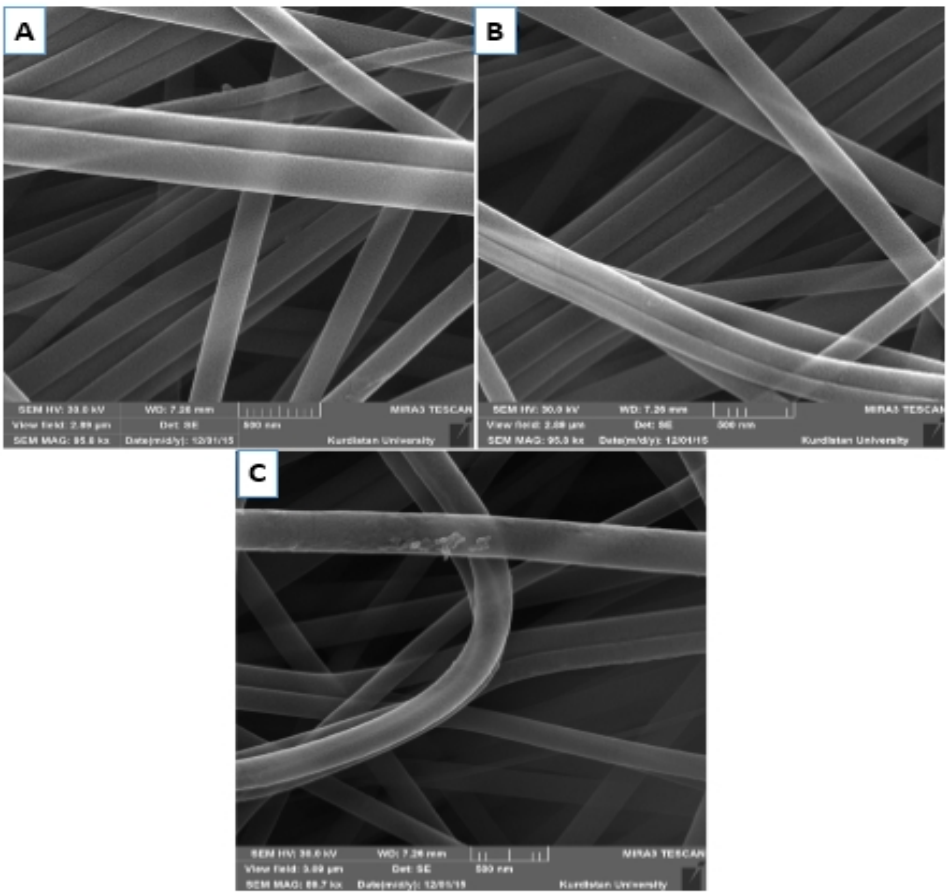

Fig. 3. The effect of nanoparticle loadings (A) 0.01 wt%, (B) 0.1 wt%, and (C) 1 wt% on the morphological features of the nanofibers

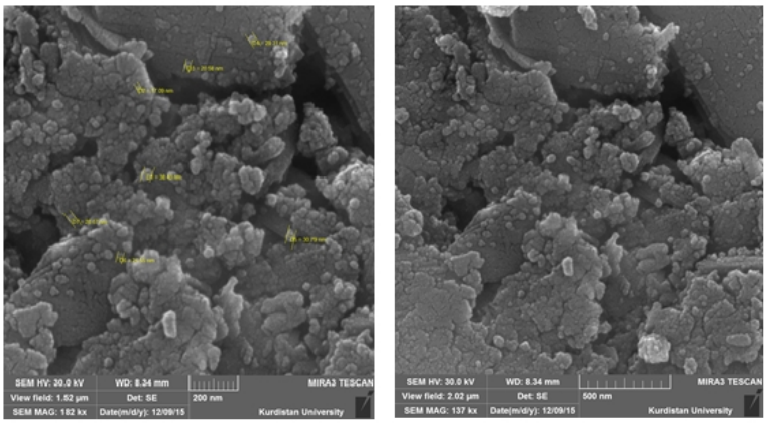

Fig. 4. SEM images of Fe_2O_3 nanoparticles

FT-IR spectra

Figure 5 presents the FT-IR spectra recorded in the spectral range of 1000–3500 cm^{-1} of the as-received PAN powder, pure PAN fibers, and nanofibers with 0.1 wt%, respectively. The peak at around 2931 cm^{-1} is assigned to the stretching vibration of the methylene (–CH_2–) group and at 2243 $cm^{-1}$and 1452 cm^{-1} is assigned to the stretching vibration of nitrile groups (–CN–) and the bending

vibration of methylene (–CH_2–), respectively.[21] The peaks at around 1235 $cm^{-1}$and 1094 cm^{-1} correspond to the stretching carbonyl group in the aliphatic amines.[21-22]

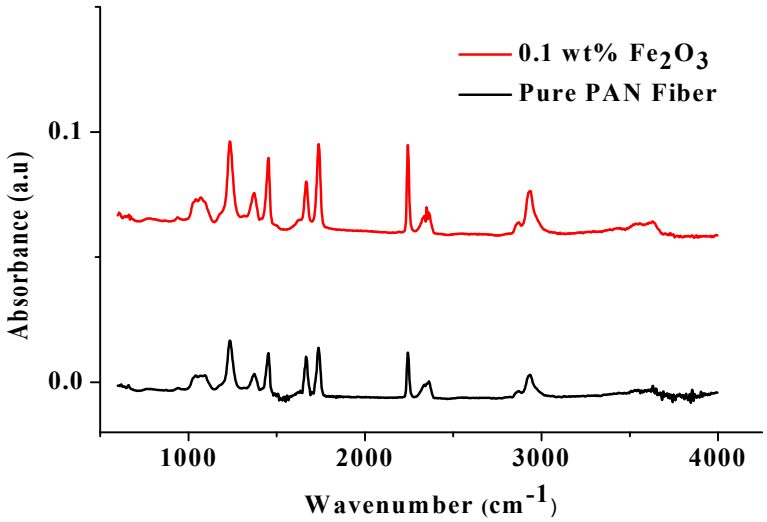

Fig. 5. FT-IR spectra of pure PAN fibers and PAN/Fe_2O_3 nanocomposite fibers with 1 wt% Fe_2O_3 nanoparticle

XRD

The crystalline properties of nanofibers in the electrospining processes are essential when the materials are designed and fabricated for commercial purposes.[23]In order to investigate the crystalline structure of the iron oxide modified nanofibers in electrospining, XRD measurements were performed.[21] Figure 6 presents the XRD patterns of the electrospun pure PAN fibers and the PAN/Fe_2O_3 nanofibers involved in 0.1 wt% Fe_2O_3 loading.

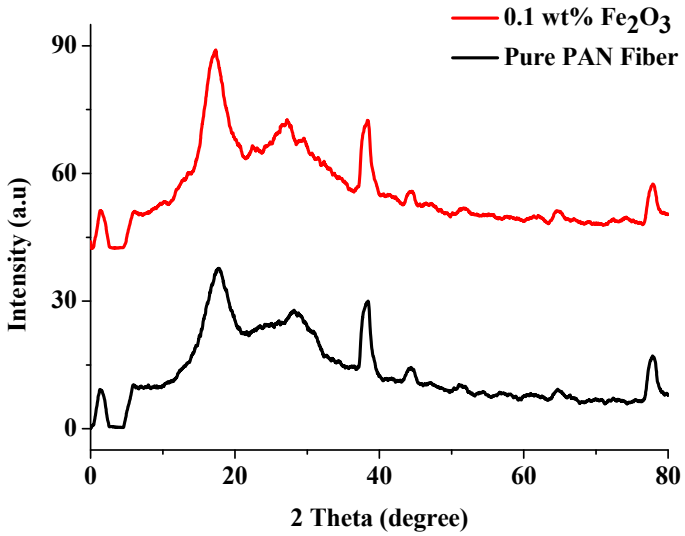

Fig. 6. XRD patterns of pure PAN fibers and PAN/Fe_2O_3 nanocomposite fibers with 1 wt% Fe_2O_3 nanoparticle

Conclusion

Pure and modified PAN fibers by Fe_2O_3 were prepared by the electrospinning process. The results indicated that both the polymer and nanoparticles concentration have significant effects on the fiber morphology. SEM analysis revealed that uniform bead-free nanofibers could be fabricated over 10 wt% PAN

concentration. The beads could be effectively minimized by increasing the polymer concentration. XRD and FT-IR results indicated that the addition of Fe_2O_3 nanoparticles reveals a significant impact on the PAN crystallization structure and the changing diameter of fibers. Hence, there is a strong interaction between Fe_2O_3 and PAN. In general, the addition of nanoparticles to PAN solution resulted in a decrease in the average diameter of modified fibers compared to the pure ones.

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