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Research Article

Morphology investigation of porous carbon nanofibers

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Abstract

Carbon nanofibers (CNFs) have been used in many applications such as sensors, energy storage and biomedical applications owing to high electronic conductivity and chemical stability of CNFs. Performance of carbon nanofibers are influenced by the physical and chemical properties of nanofibers. Furthermore, morphology, porosity and specific surface area are important properties for several applications including energy storage and sensors. There are several techniques to produce nanofibers including chemical vapor deposition, catalytic synthesis, arc discharge and electrospinning. Controlling surface area and porosity is vital considering the performance of CNFs. In this study, polyacrylonitrile (PAN) nanofibers were produced via two commonly used nanofiber production techniques; electrospinning and centrifugal spinning. The morphology of the polymeric nanofibers was studied by using SEM. Moreover, heat treatment was applied in air and the inert atmosphere to fabricate carbon nanofibers and porous carbon nanofibers. The effect of production technique on the morphology and chemical structure was investigated via SEM and XRD studies. Electrospun PAN/PS nanofibers showed beads on string morphology due to low viscosity of the spinning solution while uniform fibers without defects were obtained by using centrifugal spinning technique. Centrifugally spun PAN nanofibers have rough surface while PAN nanofibers with smooth surface was obtained by using electrospinning technique. PCNFs derived from centrifugally spun PAN/PMMA nanofibers had rough surface with porous structure and XRD analysis proved the amorphous structure of PCNFs.

Keywords: Nanofibers, Electrospinning, Porosity, Surface area

Gözenekli Karbon Nanoliflerin Yüzey Özelliklerinin İncelenmesi

Öz

Karbon nanofiberler (KNF'ler), KNF'lerin yüksek elektronik iletkenliği ve kimyasal stabilitesi nedeniyle sensörler, enerji depolama ve biyomedikal uygulamalar gibi birçok uygulamada kullanılmıştır. Karbon nanoliflerin performansı, nanoliflerin fiziksel ve kimyasal özelliklerinden etkilenir. Ayrıca, morfoloji, gözeneklilik ve spesifik yüzey alanı, enerji depolama ve sensörler dahil olmak üzere çeşitli uygulamalar için önemli özelliklerdir. Kimyasal buhar biriktirme, katalitik sentez, ark deşarjı ve elektro eğirme dahil olmak üzere nanolifler üretmek için çeşitli teknikler vardır. Yüzey alanını ve gözenekliliği kontrol etmek, KNF'lerin performansı göz önüne alındığında hayati önem taşır. Bu çalışmada, yaygın olarak kullanılan iki nanolif üretim tekniği ile poliakrilonitril (PAN) nanolifleri üretilmiştir; elektro eğirme ve santrifüj eğirme. Polimerik nanoliflerin morfolojisi SEM kullanılarak incelenmiştir. Ayrıca, karbon nanofiberleri ve gözenekli karbon nanofiberleri üretmek için havada ve azot atmosferde ısıl işlem uygulandı. Üretim tekniğinin morfoloji ve kimyasal yapıya etkisi SEM ve XRD çalışmaları ile araştırılmıştır. Elektrospun PAN/PS nanolifleri, eğirme çözeltisinin düşük viskozitesi nedeniyle sicim morfolojisi üzerinde boncuklar gösterirken, santrifüj eğirme tekniği kullanılarak hatasız homojen lifler elde edildi. Santrifüjle eğrilmiş PAN nanolifler pürüzlü bir yüzeye sahipken, elektroeğirme tekniği kullanılarak pürüzsüz yüzeyli PAN nanolifler elde edilmiştir. Santrifüjleüretilmiş PAN/PMMA nanoliflerinden türetilen PCNF'ler, gözenekli yapıya sahip pürüzlü bir yüzeye sahipti ve XRD analizi, PCNF'lerin amorf yapısını kanıtladı.

Anahtar Kelimeler: Nanolifler, Elektroeğirme, Gözeneklilik, Yüzey alanı

1. Introduction

Carbon nanofibers (CNFs) have been used in many areas such as selective adsorption, reinforcement, electrochemical catalysis, sensing, and energy storage owing to their high electronic conductivity, high specific surface area and high chemical stability. CNFs are composed of sp2-based filaments, with typical high aspect ratio. The direction of layers affects the mechanical properties [1]. Porous carbon nanofibers also gained tremendous attention owing to the surface properties and investigated for many applications including catalyst supports, adsorption agents, gas storage and sensing, and energy storage [2].PCNFs could be produced by combining electrospinning of PAN/PS, PAN/PMMA, PAN/Silica nanoparticles and heat treatment [3]. For example, Ming-xi Wang et al. oxidized NO into NO2 on PCNFs with unique properties of high length-to-diameter ratio and high specific surface area [4].

Chemical vapor deposition (CVD) and electrospinning techniques are commonly used to fabricate nanofibers. In CVD technique, high temperature is required to produce CNFs in the presence of gaseous hydrocarbon precursors and metal catalysts. In electrospinning technique, polymeric nanofibers with high carbon content such as polyacrylonitrile nanofibers are produced under the action of electrical field and heat treatment is applied to fabricate CNFs. In electrospinning technique, high voltage is applied on polymer solution. Polymer solution stretches and solvent evaporates under electric field [5]. In this technique, in order to achieve stable Taylor cone, voltage of around 15-20 kV is applied to homogenous solution fed with flow rate constant of around 0.5-1 mL/h. Fibers are collected on an aluminum foil collector which is around 10-20 cm far from the capillary tip. Fibers morphologies are affected by many parameters including solution properties, processing conditions and ambient parameters. Solution concentration is one of the most important parameters that affect the morphology. In the study of Ming-xi Wang et al., they found flexibity and diameter of fibers produced mainly dominated by PAN concentration in solution [4]. However, production rate is low in electrospinning and centrifugal technique is a fast and safe technique to produce nanofibers. Moreover, the morphology, porosity, surface texture, and specific surface areas could be tuned easily to improve properties of CNFs with this technique.

Considering large applications and superior properties of highly porous carbon nanofibers, it is vital to evaluate the morphology and structure of these materials produced via centrifugal spinning that produce nanostructures with the merits of not only high safety and high production rate but also variable morphologies and pore structures. In this study, carbon nanofibers and porous carbon nanofibers were produced via two commonly used techniques; electrospinning and centrifugal spinning for the first time to investigate the difference in the morphology and the chemical structure. The morphology of the polymeric nanofibers was studied by using SEM. Heat treatment was applied in the inert atmosphere to fabricate carbon and porous carbon nanofibers. The morphology and structure of the obtained nanostructured carbons were investigated via SEM and XRD. Results showed that highly porous structure, which is beneficial for many applications could be fabricated via centrifugal spinning and similar crystal structure was observed from centrifugally spun and electrospun carbon structures.

2. Material and Method

Polyacrylonitrile (PAN, 150000), polymethylmetacrylate (PMMA 120000), polystyrene (PS, 192000) were dissolved in dimethylformamide (DMF) and 10 wt.% polymer solution was used for electrospinning and centrifugal spinning. The feeding rate was 1 ml/h, the tip to collector distance was 15 cm and applied voltage was 15 kV during electrospinning. Distance was 15 cm and rotational speed was 4000 rpm in centrifugal spinning. After stabilization at 280 ºC for 5h and carbonization at 800 ºC for 2h, porous carbon nanofibers were obtained. Scanning electron microscope (SEM) was used for morphology study. X-ray diffraction (XRD) were used for structural characterization.3. Results and Discussion

In order to evaluate the effect of production technique on the structure and morphology of nanofibers, centrifugal and electrospinning techniques were used. Figure 1 shows SEM images of centrifugally spun (C-spun) and electrospun (E-spun) PAN nanofiber mats. Fibrous structure without defects were observed from both images.

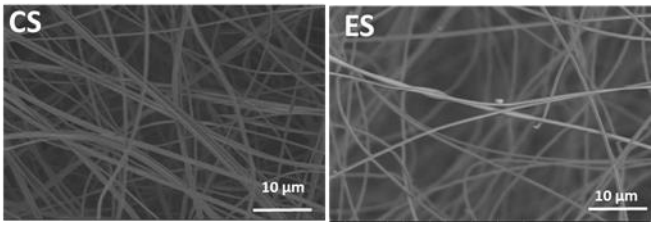

Fig. 1 SEM images of C-spun and E-spun PAN nanofibers

In order to create porous carbon nanofibers, PMMA and PS were added in PAN solution. Figure 2 and 3 shows the SEM images of PAN/PMMA and PAN/PS nanofibers. C-spun and E-spun PAN/PMMA nanofibers have similar morphology and average fiber diameters which is around 800 nm. The average fiber diameters are larger compared to PAN which could be explained by higher viscosity of PAN/PMMA solution (1430 cP) compared to that of PAN solution (610 cP). Rihova et al [6] also studied centrifugally spun PVA and PVP fibers and larger fiber diameters were reported with increasing velocities. Ming-xi Wang et al. reported relation between viscosity and fiber diameters. Solutions with different PAN concentrations (10, 12, 15, 16 wt%) were used to form fibers with diameters ranging from 175 to 1206 nm. As the PAN concentration becomes higher, fiber diameter becomes wider due to increased viscosity [4].SEM images of C-spun PAN/PS nanofibers show defect free fibrous structure whereas PAN/PS nanofibers have beads on string morphology.

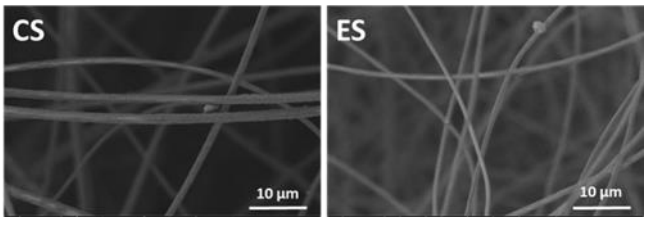

Fig. 2 SEM images of C-spun and E-spun PAN/PMMA nanofibers

In electrospinning, fiber formation relies on electrostatic forces whereas centrifugal force is applied on polymer solution in centrifugal spinning technique. In both electrospinning and

centrifugal spinning, surface tension and viscosity are the most important factors that affect the fiber formation. Besides, in electrospinning, solution conductivity is also effective. Table 1 shows the solution properties that are used for fiber formation in both techniques. As seen in the table, the viscosity of PAN/PS is 140 cP which is much lower than PAN and PAN/PMMA solutions.

Table 1 Solution properties

	Viscosity, cP	Surface tension mN/m	Conductivity, µS/cm
PAN	610	37	144
PAN/PMMA	1430	37	125
PAN/PS	140	37	116

SEM images of CNFs derived from C-spun and E spun nanofibers are seen in Figure 4. Fibrous structure was seen from both images however roughness of C-spun nanofibers is higher which is beneficial for many applications such as electrodes. Rough surface could improve the amount of active sites and thus improve kinetics of batteries and supercapacitor. For example, Geunsung Lee et al. studied surface roughness of CNT on CNFs with BET surface areas of 0.9522 m^2/g, 1.3280 m^2/g, 3.0758 m^2/g, 4.8636 m^2/g respectively. They found that roughness is essential property to cultivate CNTs on CNFs uniformly [7].

Fig. 5 show SEM images of porous carbon nanofibers. C-spun PAN-PMMA derived PCNFs have rougher surface compared to E-spun PCNFs. In Fig. 6, SEM images of PCNFs derived from PAN/PS are seen. Highly porous fibrous structure are seen from the images of PCNFs derived from C spun PAN/PS while SEM images of PCNFs derived from E-spun nanofibers shows fused short fibers. This morphology could be the result of beads on string morphology of E-spun PAN/PS.

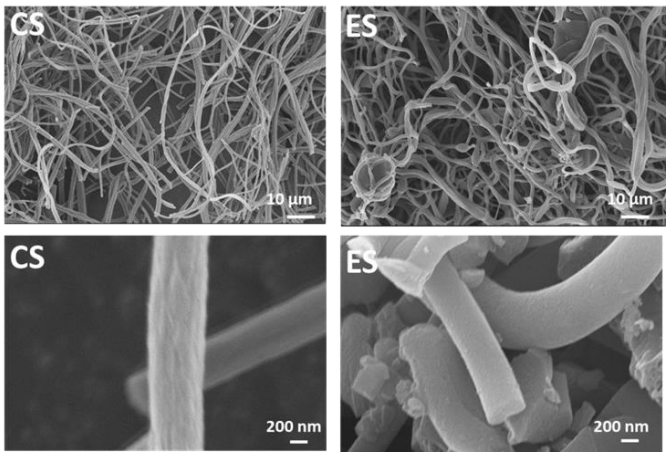

Fig. 4 SEM images of carbon nanofibers

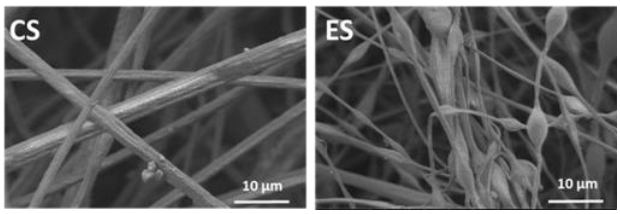

Fig. 3 SEM images of C-spun and E-spun PAN/PS nanofibers

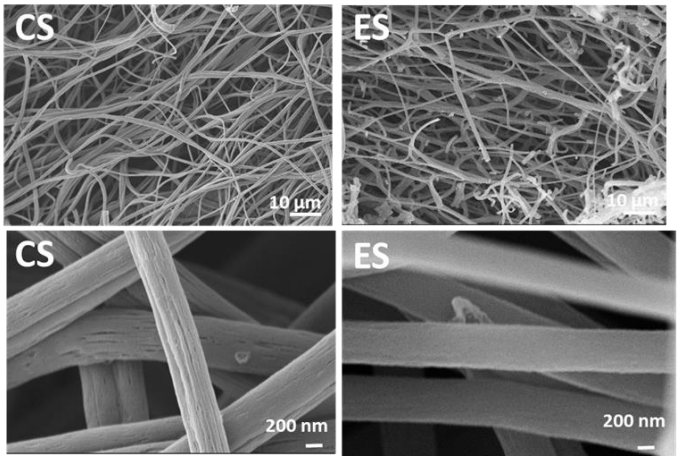

Fig. 5 SEM images of porous carbon nanofibers from PAN/PMMA precursor.

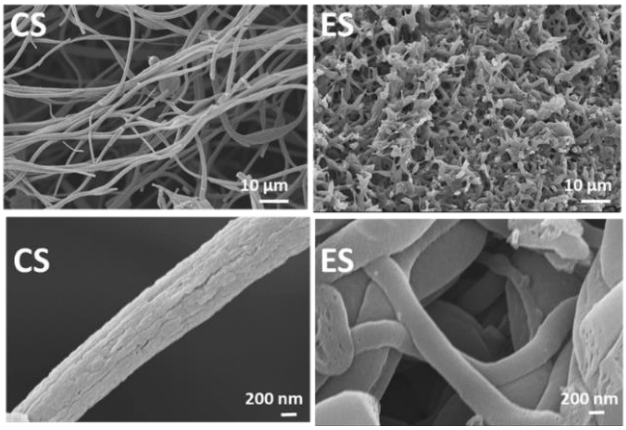

Fig. 6 SEM images of porous carbon nanofibers from PAN/PS precursor.

XRD spectra are seen in Fig.7. XRD technique could be used to determine whether a material has crystalline phases. Wider or broader intensities, as seen in Fig.7, indicates amorphous structures while sharp pattern is a sign of crystallinity. All studies samples show similar large peak at around 28º corresponding to amorphous carbons. XRD spectra proves that CNFs and PCNFs derived from both C-spun and E-spun nanofibers are amorphous.

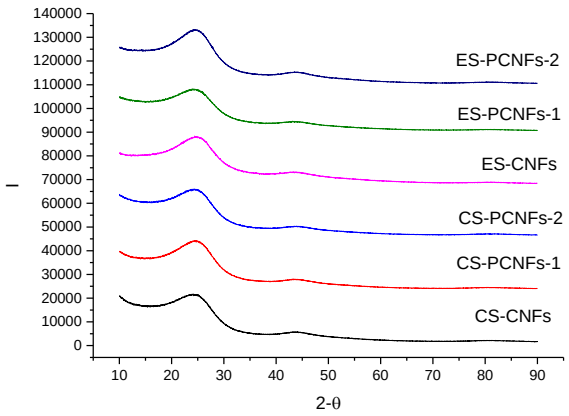

Fig. 7 XRD spectra

4. Conclusions and Recommendations

CNFs and PCNFs are fabricated via electrospinning and centrifugal spinning. The effect of production technique on the morphology and chemical structure was studied by using SEM and XRD. CNFs and PCNFs derived from C-spun PAN, PAN/PMMA and PAN/PS nanofibers have rougher surface with higher porosity compared to those obtained from E-spun nanofibers. Results prove that centrifugal spinning could be used to fabricate nanostructured carbons with tunable morphology and roughness.

5. Acknowledge

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