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Karbon Nanotüp (KNT) İlave Edilmiş Poliakrilonitril (PAN) Nanoliflerin Elektroeğirme Yöntemi ile Üretilmesi ve Karakterizasyonu

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Anahtar Kelimeler
Karbon Nanotüp (KNT);
Poliakrilonitril (PAN);
Elektroeğirme;
Nanolif;
Polimer Kompozit.

Öz

Bu çalışmada elektroeğirme yöntemi ile karbon nanotüp (KNT) ilave edilmiş poliakrilonitril (PAN) nanolif üretimi rapor edilmiştir. Boncuksuz ve düzenli PAN/KNT elektroeğirme yöntemi ile elde edilmiş nanofiberler elde etmek için beş farklı KNT konsantrasyonu (0.05, 0.1, 0.2, 0.5 ve %1 ağırlık) denenmiş ve nanolifleri karakterize etmek için Taramalı Elektron Mikroskobu (SEM), Raman ve X-Işını Difraksiyonu (XRD) analizleri kullanılmıştır. Sonuçlar, artan KNT konsantrasyonu ile PAN/KNT nanoliflerinin çapının arttığını ve optimum bir konsantrasyondan sonra nanolifler üzerinde bazı düzensiz bölgeler ve boncuklanmaların oluştuğunu göstermiştir. Bununla birlikte, KNT'lerin eklenmesi, PAN nanoliflerinin grafitizasyonunu ve kristalliğini arttırmıştır. Boncuksuz ve kristalizasyon seviyesi yüksek PAN/KNT nanolifler için optimum KNT konsantrasyonu ağırlıkça %0.1 olarak bulunmuştur.

Carbon Nanotube (CNT) Embedded Polyacrylonitrile (PAN) Electrospun Nanofibers Production and Characterizations

Keywords
Carbon Nanotube (CNT);
Polyacrilonitrile (PAN);
Electrospinning;
Nanofiber;
Polymer composite.

Abstract

Carbon nanotube (CNT) embedded polyacrylonitrile (PAN) nanofibers production by electrospinning method was reported in this study. Five different CNT concentrations (0.05, 0.1, 0.2, 0.5, and 1wt%) were tried to obtain beadless and regular PAN/CNT electrospun nanofibers. Scanning Electron Microscopy (SEM), Raman and X-Ray Diffaraction (XRD) analyses were utilized to characterize nanofibers. The results indicated that with increasing CNT concentration, the diameter of PAN/CNT nanofibers increased, and after an optimum concentration some disordered sites and beads were observed on the nanofibers. However, the addition of CNTs enhanced the graphitization and crystallinity of PAN nanofibers. The optimum CNT concentration for beadless and high crystalline PAN/CNT nanofibers was found as 0.1 wt%.

1. Introduction

For the fabrication of long organic fibers, electrospinning is a suitable electrostatic technique (Bhardwaj and Kundu 2010). In the electrospinning process, a sufficiently high voltage is needed to be applied to a liquid droplet in order to charge the body of the liquid (Li, Laurencin et al. 2002). This method could be utilized for the generation of porous, hollow and core-shell structures and allows for functionalization of the surface of nanofibers with various molecules and nanoparticles during or after the electrospinning process, as well. Nanofibers obtained with the electrospinning method with their excellent properties such as large surface area, small pore size, elasticity, high mechanical strength and biocompatibility are well-suited for many applications including actuators (Park, Gu et al. 2016), catalysts (Guerrero-Pérez 2021), air filtration (Yardimci, Kayhan et al. 2022), water purification (Ramakrishna, Jose et al. 2010, Chinnappan, Baskar et al. 2017), energy storage (Zhang, Kang et al. 2016), food applications (YARDIMCI and TARHAN , Kumar, Kumar et al. 2019), protective clothing (Gorji, Bagherzadeh et al. 2017), drug delivery (Son, Kim et al. 2014), tissue engineering (Ince Yardimci, Aypek et al. 2019, Ince Yardimci, Baskan et al. 2019), biosensors (Kivrak, Ince-Yardimci et al. 2020), and chemical sensors (Ince Yardimci, Yagmurcukardes et al. 2022).

Carbon nanotubes (CNTs) with the carbon-carbon sp^2 bonds they have display high stiffness and axial strength, and large Young modulus in their axial direction (Popov 2004). At the same time, they show extraordinary electrical conductivity and heat conductivity (Spitalsky, Tasis et al. 2010). They are appropriate nanomaterials to utilize for polymer composites. By adding CNTs to the polymer, their electrical and mechanical properties could be enhanced, the strength of the material could be increased and problematic creep could be decreased (Spinks, Mottaghitalab et al. 2006). By aligning CNTs to one direction, anisotropic mechanical and electrical properties could be obtained and especially along the alignment direction these properties improve dramatically (Zheng, Razal et al. 2011). In literature, CNTs were used with different polymers some of these polymers are epoxy (Kim, Seong et al. 2006), gel-coat (Yardimci, Tanoglu et al. 2013), polydimethylsiloxane (PDMS) (Jang, Yoon et al. 2021), polyvinylidene difluoride (PVDF) (Zhang and Vecitis 2014), poly(methyl methacrylate) (PMMA) (Yao, Wu et al. 2007), poly(vinyl alcohol) PVA (Jung, Cha et al. 2011) are some polymers utilized with CNTs.

In this study, we report the preparation of CNT embedded PAN nanofibers. Different CNT concentrations were investigated to obtain regular and beadless nanofibers and the results indicated that the generation of beadless PAN/CNT electrospun nanofibers with high crystallinity was achieved with the CNT concentration of 0.1 wt%.

2. Materials and Method

2.1. Materials

To produce PAN/CNT nanofibers PAN (MW=150000) was utilized as a polymer and N,N-dimethylformamide (DMF) was utilized as a solvent and they were purchased from Aldrich and used without further purification.

2.2 Preparation of PAN/CNT Solutions and Electrospinning Process

The process of CNT growth was presented in our previous work (Yardimci, Yılmaz et al. 2015). For PAN/CNT nanofibers production, the electrospinning method was used. To enhance the crystallinity of PAN, CNTs were inserted into the electrospinning solution in different amounts.

The applied voltage was changed between 15-25 kV and the flow rate of the solution was changed between 1.5 and 2.5 ml/h depending on solution viscosity and conductivity. The schematic of the electrospinning process is given in Fig. 1.

2.3 Characterization of PAN/CNT Electrospun Nanofibers

The morphology and diameter of PAN/CNT electrospun nanofibers were analysed by SEM. X-ray diffraction (XRD) studies using Cu Kα radiation source were utilized to understand the crystal phase of synthesized fibers and Raman spectroscopy was used with 514 nm Ar laser excitation to characterize the graphitic nature of pure PAN nanofibers and its CNT embedded forms.

3 Results and Discussions

SEM was utilized to characterize the surface morphology and diameter of pure PAN and PAN/CNT nanofibers. Fig. 2 displays the SEM micrographs of PAN nanofibers including the different amounts of CNT.

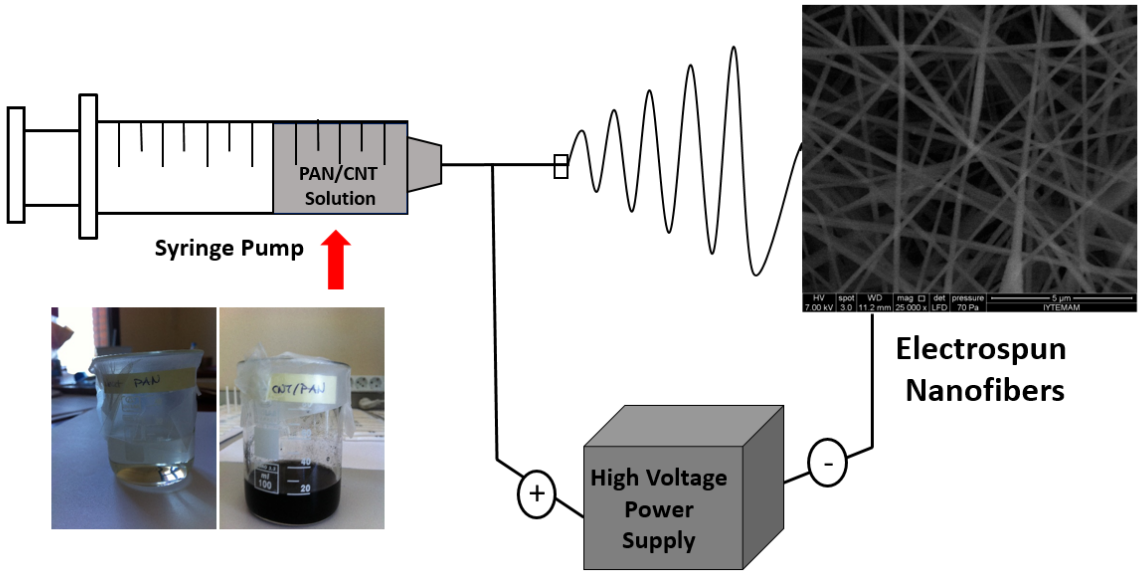

Figure 1 Schematic representation of electrospinning process.

It was observed that the fibers showed a smooth surface at low concentrations of CNTs, however with the increasing amount of CNT, especially at concentrations higher than 0.2 wt%, roughness increased dramatically. The reason for this roughness is CNT agglomeration and not embedded CNTs into the PAN nanofibers. Another effect of the increase in CNT concentration was observed on the diameter of nanofibers. The diameter of PAN nanofibers increased with increasing CNT concentration.

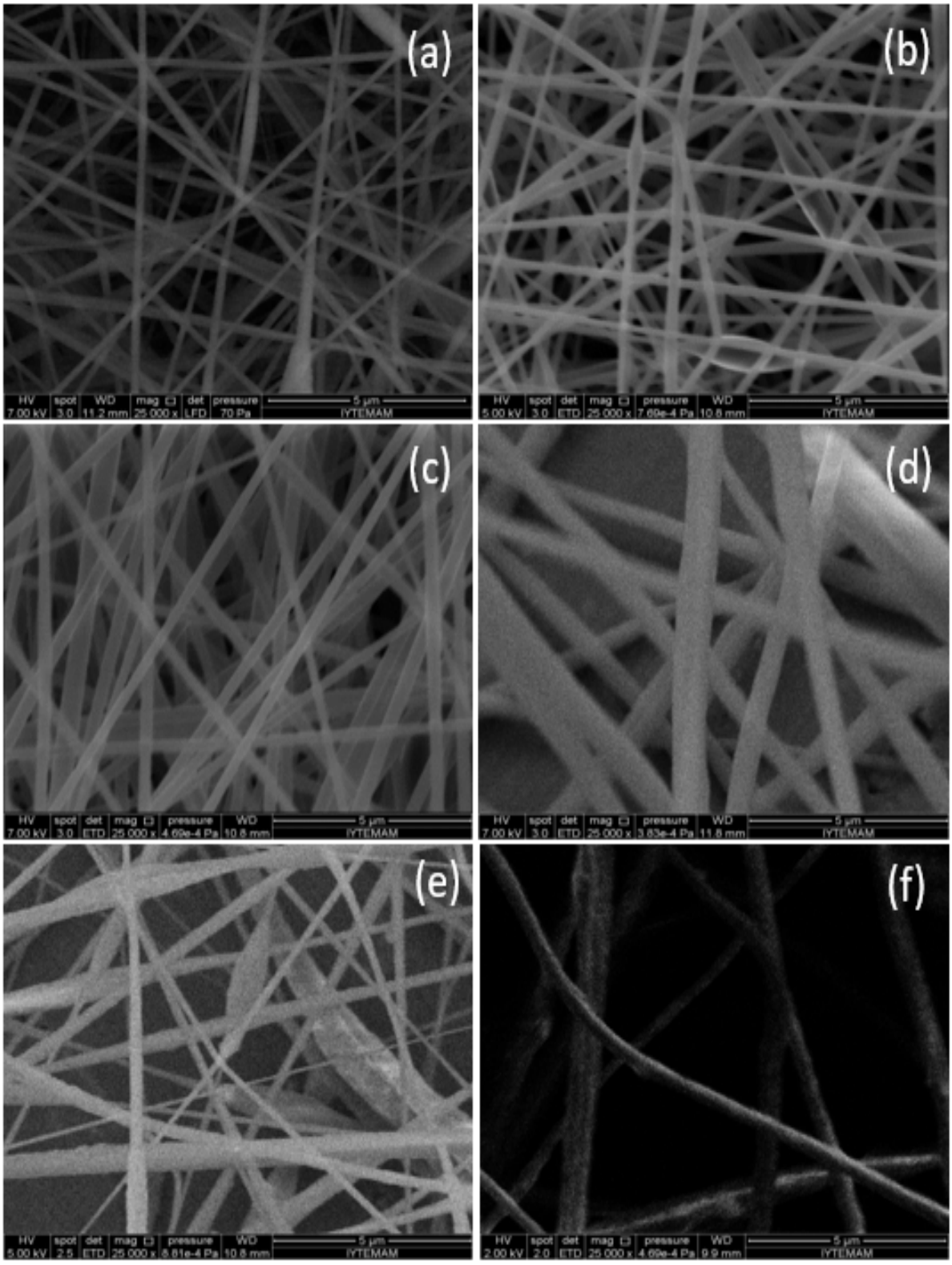

Figure 2 PAN/CNT nanofibers SEM images

While the average CNT diameter was about 83 nm for pure PAN nanofibers, this value increased to 405 nm for the sample including 1wt.% CNT as seen in Fig. 3. Diameters increased up to 0.5 wt% CNT loading, however at 0.5 wt% CNT amount, the average diameter decreased significantly. The reason for this change was probably because of the existence of beads on nanofibers. As expected, at 1 wt% CNT concentration the average diameter increased again.

XRD analysis was carried out in order to determine the improvement in graphitization in electrospun PAN nanofibers by adding CNT. XRD spectra obtained from PAN/CNT nanofiber are presented in Fig. 4. For the neat PAN nanofiber sheet, there was a strong peak at 29.95° which is relating to (020) crystal plane of PAN and a weak peak at 17.19° assigned to (200) crystal plane of PAN. The intensity of the peak of (200) crystal plane increased with increasing CNT concentration. CNT (002) at 27.2° and (004) at 54.4 ° crystal plane peaks (Kaur, Kumar et al. 2016) began to appear at 0.1 wt% CNT concentration and 0.5 wt% CNT concentrations, respectively. These CNT peaks appearance indicates better crystallinity than neat PAN nanofibers.

Fig. 5 displays Raman spectra of the electrospun PAN nanofibers. For neat PAN nanofibers, it was observed only the Raman scattering peak of the nitrile group (-CN) at 2240 cm^{-1} (Matsuno, Takagaki et al. 2020). With CNT addition, this peak intensity began to decrease and at high CNT concentrations, this peak disappeared. D-band at ~1370 cm^{-1} and G-band at ~1590 cm^{-1} of CNTs were observed at 0.2 and 0.5 wt% of CNT concentrations (Dresselhaus, Dresselhaus et al. 2005). With increasing CNT concentrations I_G/I_D value of electrospun nanofibers also increased. This Raman data support XRD results; graphitization increased with increasing CNT concentration.

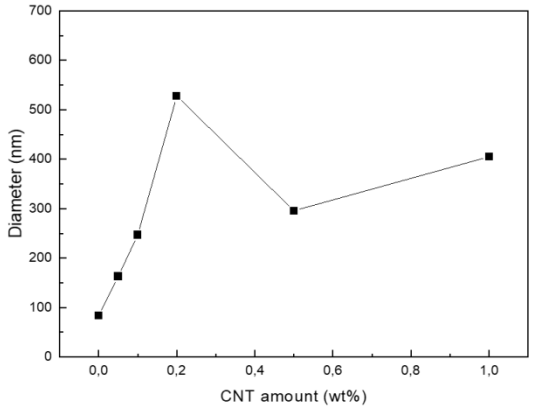

Figure 3 Average diameter distribution of PAN/CNT electrospun nanofibers.

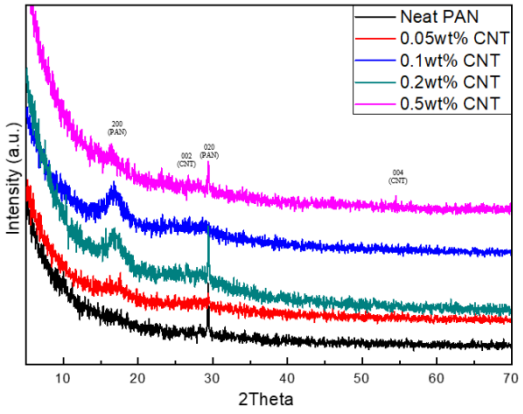

Figure 4 XRD scans of CNT embedded PAN electrospun nanofibers.

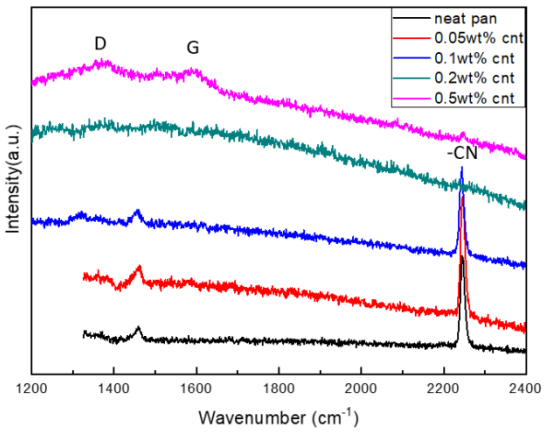

Figure 5 Raman spectra of CNT embedded PAN electrospun nanofibers.

4. Conclusions

In conclusion, PAN/CNT nanofibers containing different amounts of CNT were prepared through the electrospinning method. The results indicated that CNT addition enhanced the crystallinity and graphitization of PAN nanofibers. However, SEM pictures showed that the size of electrospun nanofibers was firstly became thicker and then their morphology and shape began to deteriorate with increasing CNT concentration. Bead formation on nanofibers and some irregulars in the nanofiber morphology were observed at high CNT concentrations. Overall, the optimum CNT concentration was found as 1 wt% and the average diameter of nanofibers obtained by using this concentration of CNT was measured as 248 nm.

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