The Effects of Dopant and Solvent on Morphology, Conductivity and Mechanical Properties of Polyacrylonitrile / Polyaniline Composite Nanofibers

Dopant ve Solventlerin Poliakrilonitril / Polianilin Kompozit Nanoliflerinin Morfolojisi, İletkenliği ve Mekanik Özellikleri Üzerine Etkileri

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THE EFFECTS OF DOPANT AND SOLVENT ON MORPHOLOGY, CONDUCTIVITY AND MECHANICAL PROPERTIES OF POLYACRYLONITRILE / POLYANILINE COMPOSITE NANOFIBERS

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ABSTRACT: In this study, the effects of different dopants such as camphorsulfonic acid (CSA), dodecylbenzene sulfonic acid sodium salt (DBSANa+), different solvents such as N,N'-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) and different mixing processes such as magnetic mixing and mechanical mixing on the morphology, conductivity and mechanical properties of PAN/PANi composite nanofibers are investigated. It has been seen that composite nanofibers had the smallest fiber diameter, lowest conductivity and lowest mechanical properties when CSA (dopant) and DMF (solvent) are used. However, the composite nanofibers in which the polyaniline is doped with CSA in DMSO (solvent) had better conductivity and mechanical properties, besides having thicker diameters. When the mixing effects compared, mechanical mixing process resulted in higher mechanical properties of nanofibers compared to magnetic mixing process, while there was not much difference between fiber diameter and conductivity values.

Keywords: Composite, conductive, electrospinning, nanofiber, polyacrylonitrile, polyaniline.
elde edilen nanoliflerin en düşük nanolif çapına, en düşük mekanik özelliklere ve en düşük iletkenlik değerine sahip olduğu görülmüştür. Kamforsulfonik asitin dopant olarak ve dimetilsulfoksitin solvet olarak kullanılan durumunda elde edilen nanoliflerin daha kalın olduklarını göstermektedir, bu lifler daha yüksek iletkenlik ve mekanik özelliklere sahiptir. Manyetik karışıma ve mekanik homojenizasyon işlemlerinin etkileri kıyasladığında, lif çapı ve mekanik belirgin şekilde etkilenmektedir, mekanik homojenizasyon daha iyi mekanik özellik gösteren liflerin üretilmesini sağlar.

**Anahtar Kelimeler:** Elektroeğirme, iletken, kompozit, nanolif, poliakrilonitril, polianilin.

1. INTRODUCTION

Inherently conductive polymers (ICP) such as doped polyacetylene, polyaniline and polythiophene, which offer a special combination of properties (processability, electrical conductivity), have drawn great attention since 1970s [1]. Among all conducting polymers, polyaniline (PANi) is the most intensively investigated due to its high environmental stability, low cost of raw material, ease of synthesis and good compatibility with other polymer supports and its wide application potential such as sensors, energy device etc. [2-7]. The conductive emeraldine salt (ES) form of polyaniline is obtained by adding protons into the insulating emeraldine base (EB) form through treatment with an acid (dopant) [8]. The type of the acid (dopant), and the solvent used, have important effects on the conductivity of the polyanilines since the interactions between the dopant, solvent and the polymer define the charge transport properties. Besides, the homogeneous distribution of doped polyaniline becomes important when it is used in polymer composites. When a literature survey is conducted, no studies related with the effects of different dopants, different solvents, different types of mixing processes (dispersion of PANi in the polymer matrix) on the morphology, conductivity and mechanical properties of PAN/PANi composite nanofibers were seen. Thus, in this study, the effects of different dopants such as camphorsulfonic acid (CSA), dodecylbenzene sulphonylic acid sodium salt (DBSANA\(^+\)), polyacrylonitrile (PAN) (Sigma Aldrich, 181315, average Mw: 150.000g/mol), dimethylsulfoxide (DMSO), and \(N, N'-\) Dimethylformamide (DMF) were used as received. PANi solutions were filtered using Sartorius Stedim filter paper (No.389).

2. MATERIALS AND METHOD

2.1 Materials

Polyaniline (PANi) (emeraldine base form, Sigma Aldrich, 530689, average Mw: 65.000g/mol), camphorsulfonic acid (HCSA), dodecylbenzene sulfonylic acid sodium salt (DBSANA\(^+\)), polyacrylonitrile (PAN) (Sigma Aldrich, 181315, average Mw: 150.000g/mol), dimethylsulfoxide (DMSO), and \(N, N'\)- Dimethylformamide (DMF) were used as received.

2.2 Methods

**Preparation of the solutions.** Required amount of sulfonic acid (dopant) was added to the solvent (DMSO or DMF) and after its dissolution PANi was added. The amount of PANi was 10 w% of the amount of PAN. The molar ratio of EB (tetramer unit) to sulfonic acid was 1: 2. The mixture was stirred with a magnetic at 40°C for 2 days and then filtered using Sartorius Stedim filter paper (No.389). 7 w% PAN was added to the doped PANi solution. To be able to compare the effects of magnetic stirring and mechanical homogenization another solution was prepared. For this, 10w% PANi.CSA/PAN solution in DMSO was prepared and then 7w% PAN was added to this solution. The solution was then mechanically mixed at 7000 rpm for 15 minutes with WiseTis HG 15D mechanical homogenizer.

**Electrospinning.** Nanoweb production was performed on an horizontal electrospinning setup consisting of a high voltage power supply (0–50 kV), syringe pump and a grounded rotating collector. The electrospinning solution was fed through a capillary tip with a
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The diameter of 1.25 mm from 10mL syringe. The feeding rate was adjusted as 1mL/h. A high voltage of 15 kV was applied and the distance between the tip and the collector was set as 10 cm. The list of the samples produced are presented in Table 1.

Table 1. List of the PAN/PANi composite nanowebs produced.

| Samples                        | Codes                |
|--------------------------------|----------------------|
| 10w% PANi.CSA/PAN (DMF)        | CSA-DMF              |
| 10w% PANi.CSA/PAN (DMSO)       | CSA-DMSO             |
| 10w% PANi.DBSANa+/PAN (DMSO)   | DBSANa+-DMSO         |
| 10w% PANi.CSA/PAN (DMSO) - mech| CSA-DMSO-mech        |

Characterization. Scanning electron microscopy (SEM), tensile tester and conductivity tester were used for the characterization of the nanowebs. Images of PAN/PANi composite nanowebs were taken with scanning electron microscope (SEM; EVO MA 10). The diameters of at least 50 randomly selected nanofibers were measured on SEM photomicrographs and the average nanofiber diameters were calculated using Image Analysis Software. Mechanical properties of the nanowebs were measured using a tensile tester with a 100N load cell at a crosshead speed of 20 mm/min. The length and width of the specimens were 35 mm and 5 mm, respectively. The gage length was set as 15 mm. Resistance measurements were performed using a two-probe system connected to Microtest 6370 LCR meter with four-wire system. Using the resistance measurement results and geometric dimensions of the nanowebs, conductivity in S/cm was calculated.

3. RESULTS AND DISCUSSION

3.1 Morphology

The SEM images of the PAN/PANi composite nanowebs are presented in Figure 1 while information regarding their mean diameters are presented in Table 2.

Figure 1. SEM images of (a) PAN/PANi.CSA (DMF), (b) PAN/PANi.CSA (DMSO) (c) PAN/PANi. DBSANa+ (DMSO), (d) PAN/PANi.CSA (DMSO)-mech nanowebs.
As can be seen from SEM images, the nanofibers were uniform in diameter. Besides, it is seen that the nanowebs except CSA-DMF were in highly aligned form which might have been due to the increased net charge density resulting in higher drawing during electrospinning.

Table 2. Mean diameters of PAN/PANi composite nanowebs.

| Samples                      | Nanofiber Diameter (nm) |
|------------------------------|-------------------------|
| 10w% PANi.CSA/PAN (DMF)      | 276.01±42.93            |
| 10w% PANi.CSA/PAN (DMSO)     | 465.20±81.69            |
| 10w% PANi.DBSANa+/PAN (DMSO) | 1137.43±150.41          |
| 10w% PANi.CSA/PAN (DMSO) - mech | 438.49±82.75         |

When the diameters of the nanofibers were compared, the most outstanding difference was the larger diameters observed for the nanofibers produced with use of DBSANa+ as the dopant. This was attributed to the higher viscosity of the electrospinning solutions and the larger molecular size of DBSANa+ preventing the closer packing of the macromolecules. The nanowebs produced with the dopant CSA using different solvents also had different diameters. Use of DMSO resulted in the formation of larger diameters. This is considered to be the result of the late evaporation of DMSO allowing the relaxation of the nanofibers after being collected on the collector. Application of the mechanical homogenization process resulted in a slight decrease in mean nanofiber diameter.

3.2 Mechanical Properties

Table 3 shows the mechanical properties of the composite nanowebs. Comparing the mechanical properties of the nanowebs produced using different solvents, the breaking strength of CSA-DMSO nanoweb was higher than the CSA-DMF nanoweb most probably due to the better alignment of the nanofibers as a result of the increased conductivity. Besides the breaking elongation was much higher for the nanowebs of CSA-DMSO. This was also attributed to the better alignment of nanofibers in the web of CSA-DMSO. When the nanoweb is uniaxially strained, the fibers that lying in the direction of the axis of the strain start to slip over each other which results in higher breaking elongations.

On using DBSANa+ as the dopant in DMSO, decrease was observed in the breaking strength and the breaking elongation values which might have been due to the structural differences between the nanowebs. CSA-DMSO contained thinner nanofibers which might have resulted in the more compact structure. Also the thinner fibers might have behaved more elastically than the thicker nanofibers which led to the higher breaking elongation value of CSA-DMSO. Application of mechanical homogenization resulted in higher tensile breaking stress which is considered to be the result of the more homogeneous solution obtained by mechanical dispersion process applied as an additional process to magnetic mixing. The breaking elongation was not very much affected by the application of the mechanical homogenization process.

3.3 Conductivity

Table 4 shows the conductivity values of PAN/PANI composite nanowebs.

Table 3. Mechanical properties of PAN/PANI composite nanowebs.

| Samples                      | Breaking strength (MPa) | Breaking elongation (%) | E-Modulus (MPa) |
|------------------------------|-------------------------|-------------------------|----------------|
| 10w% PANi.CSA/PAN (DMF)      | 0.48±0.13               | 3.18±0.67               | 9.54±2.09      |
| 10w% PANi.CSA/PAN (DMSO)     | 3.94±0.72               | 50.23±11.96             | 16.60±4.42     |
| 10w% PANi.DBSANa+/PAN (DMSO) | 3.65±0.55               | 20.81±3.33              | 18.97±4.85     |
| 10w% PANi.CSA/PAN (DMSO) - mech | 6.36±1.02              | 58.13±11.75             | 28.32±5.34     |

Table 4. Conductivity values of PAN/PANI composite nanowebs.

| Samples                      | Conductivity (S/cm) |
|------------------------------|---------------------|
| 10w% PANi.CSA/PAN (DMF)      | 5.38E-09±2.06E-09   |
| 10w% PANi.CSA/PAN (DMSO)     | 4.82E-06±1.10E-06   |
| 10w% PANi.DBSANa+/PAN (DMSO) | 3.70E-09±1.06E-09   |
| 10w% PANi.CSA/PAN (DMSO) - mech | 3.17E-06±8.36E-07   |
Pure PAN nanofibers have a conductivity of $10^{-12}$ S/cm and they are insulators [9]. The addition of doped PANi resulted in an increase in conductivity. With the conductivities around $10^{-6}$ and $10^{-9}$ S/cm, PAN/PANI composite nanowebs are expected to be effective in antistatic applications [10].

Comparison of the nanowebs produced with CSA as the dopant in different solvents shows that the use of DMSO resulted in higher conductivity which might have been due to the better solvating ability of DMSO. Besides it is reported that the sulfonic groups in the structure of DMSO keeps/maintains the conductivity of doped PANi.

In parallel with the literature [11], the nanowebs doped with CSA showed higher conductivity values than the nanowebs doped with DBSANA$^+$ in DMSO. The effect of dopant on conductivity of doped PANi is strong and affected by many factors. For example, the pH value (acidity) of the dopant affects the conductivity. The smaller the pH (the stronger the acidity), more H$^+$ will dope into PANi chains and form polarons, which will lead to increase in the conductivity. Since CSA is more acidic than DBSA, PANi doped by CSA had a greater conjugation length and higher conductivity [11]. Besides the pH value, molecular size of the dopant will also influence the conductivity of doped PANi. CSA doped PANi is more conductive than DBSANA doped PANi because of its smaller counter-ion size and therefore stronger interchain interactions [12-14]. Another factor may be the differences in molecular weight. Molecular weight of CSA is 232.20 g/mol while that of DBSANA$^+$ is 348.48 g/mol [15]. The smaller molecular weight of CSA might have provided higher mobility and solubility, and therefore higher doping ability.

The effect of the mechanical homogenization process on the conductivity was negligible.

### 4. CONCLUSIONS

Polyacrylonitrile nanofibers with 10w% polyaniline content using different dopants and solvents were produced successfully. It has been seen that composite nanofibers had the smallest fiber diameter, lowest conductivity and lowest mechanical properties when CSA (dopant) and DMF (solvent) are used. However, the composite nanofibers in which the polyaniline is doped with CSA in DMSO (solvent) had better conductivity and mechanical properties, besides having thicker diameters. When the mixing effects compared, mechanical mixing process resulted in higher mechanical properties of nanofibers compared to magnetic mixing process, while there was not much difference between fiber diameter and conductivity values.

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