



TEKSTİL VE MÜHENDİS
(Journal of Textiles and Engineer)



<http://www.tekstilvemuhendis.org.tr>

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

Nuray KIZILDAG¹, Nuray UCAR¹, N. DEMİRSOY², Esmâ SEZER², Belkıs USTAMEHMETOĞLU², O. EREN², Ayşen ONEN², İsmail KARACAN³, Seniha GUNER⁴

¹Istanbul Technical University, Department of Textile Engineering, Istanbul, Turkey

²Istanbul Technical University, Department of Chemistry, Istanbul, Turkey

³Erciyes University, Department of Textile Engineering, Kayseri, Turkey

⁴Istanbul Technical University, Department of Chemical Engineering, Turkey

Online Erişime Açıldığı Tarih (Available online): 30 Mart 2015 (30 March 2015)

Bu makaleye atıf yapmak için (To cite this article):

Nuray KIZILDAG, Nuray UCAR, N. DEMİRSOY, Esmâ SEZER, Belkıs USTAMEHMETOĞLU, O. EREN, Ayşen ONEN, İsmail KARACAN, Seniha GUNER (2015): The Effects of Dopant and Solvent on Morphology, Conductivity and Mechanical Properties of Polyacrylonitrile / Polyaniline Composite Nanofibers , Tekstil ve Mühendis, 22: 97, 1-6.

For online version of the article: <http://dx.doi.org/10.7216/130075992015229701>



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

Nuray KIZILDAG^{1*}

Nuray UCAR¹

N. DEMİRSOY²

Esmâ SEZER²

Belkıs USTAMEHMETOĞLU²

O. EREN²

Ayşen ONEN²

İsmail KARACAN³

Seniha GUNER⁴

¹Istanbul Technical University, Department of Textile Engineering, Istanbul, Turkey.

²Istanbul Technical University, Department of Chemistry, Istanbul, Turkey.

³Erciyes University, Department of Textile Engineering, Kayseri, Turkey.

⁴Istanbul Technical University, Department of Chemical Engineering, Turkey.

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.

DOPANT VE SOLVENTLERİN POLİAKRİLONİTRİL / POLİANİLİN KOMPOZİT NANOLİFLERİNİN MORFOLOJİSİ, İLETKENLİĞİ VE MEKANİK ÖZELLİKLERİ ÜZERİNE ETKİLERİ

ÖZET: Bu çalışmada, kamforsulfonik asit (CSA), dodesilbensensulfonik asitin sodyum tuzu (DBSANA⁺) gibi farklı dopantların, dimetilformamid (DMF), dimetilsulfoksit (DMSO) gibi farklı solventlerin ve manyetik karıştırma, mekanik homojenizasyon gibi farklı çözelti karıştırma tekniklerinin poliakrilonitril (PAN)/polianilin (PANi) kompozit nanoliflerinin morfolojik özellikleri, mekanik özellikleri ve iletkenlik özellikleri üzerine etkileri incelenmiştir. Kamforsulfonik asitin dopant olarak ve dimetilformamidin solvent olarak kullanılmasıyla

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 solvent olarak kullanılmasıyla elde edilen nanoliflerin daha kalın oldukları görülürken, bu lifler daha yüksek iletkenlik ve mekanik özellikler göstermişlerdir. Manyetik karıştırma ve mekanik homojenizasyon işlemlerinin etkileri kıyaslandığında, lif çapı ve iletkenlik belirgin şekilde etkilenmezken, mekanik homojenizasyon daha iyi mekanik özellik gösteren liflerin üretilmesini sağlamıştır.

Anahtar Kelimeler: Elektroçirime, iletken, kompozit, nanolif, poliakrilonitril, polianilin.

* Sorumlu Yazar/Corresponding Author: kizildagn@itu.edu.tr

DOI: 10.7216/130075992015229701, www.tekstilvemuhendis.org.tr

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 sulphonic 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.

2. MATERIALS AND METHOD

2.1 Materials

Polyaniline (PANi) (emeraldine base form, Sigma Aldrich, 530689, average Mw: 65.000g/mol), camphorsulfonic acid (HCSA), dodecylbenzene sulfonic 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).

2.2 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 homogenizator.

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

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.DBSSANa ⁺ /PAN (DMSO)	DBSSANa ⁺ -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.

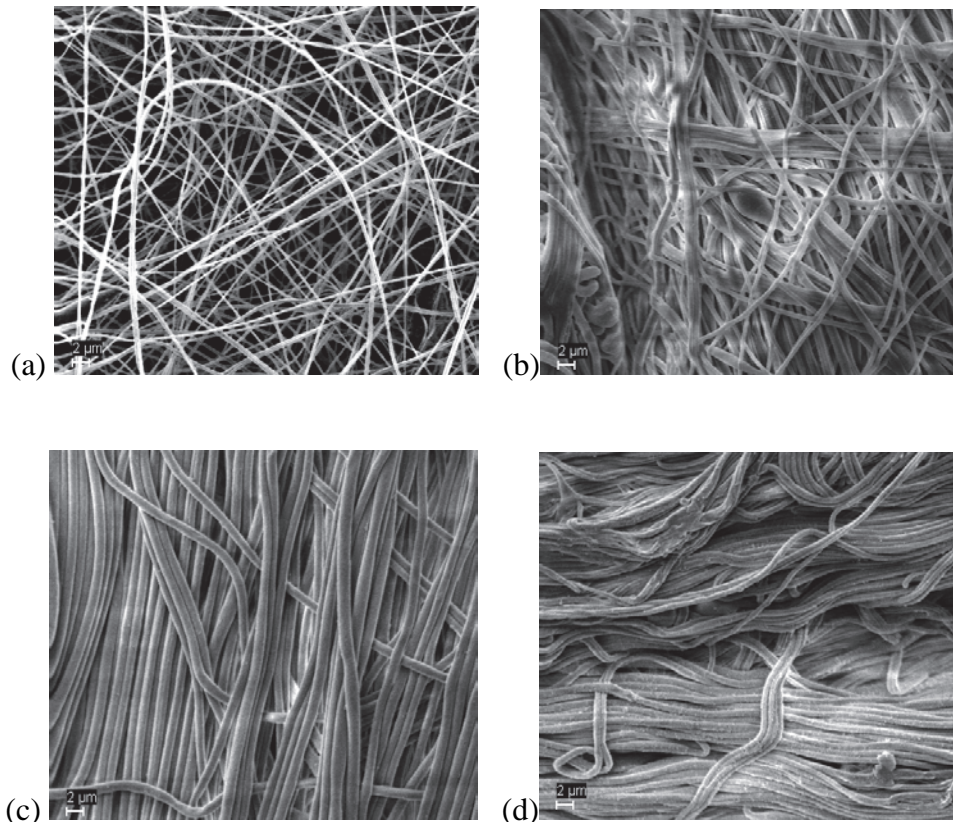


Figure 1. SEM images of (a) PAN/PANi.CSA (DMF), (b) PAN/PANi.CSA (DMSO) (c) PAN/PANi.DBSSANa⁺ (DMSO), (d) PAN/PANi.CSA (DMSO)-mech nanowebs.

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.DBSSANa ⁺ /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 DBSSANa⁺ as the dopant. This was attributed to the higher viscosity of the electrospinning solutions and the larger molecular size of DBSSANa⁺ 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

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.DBSSANa ⁺ /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.DBSSANa ⁺ /PAN (DMSO)	3.70E-09±1.06E-09
10w% PANi.CSA/PAN (DMSO) - mech	3.17E-06±8.36E-07

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 DBSSANa⁺ 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.

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 DBSA 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.

Acknowledgement

We would like to thank to TUBITAK for supporting this study with Project (112M877).

REFERENCES

- Jousseume V., Morsli M., and Bonnet A., (2000), *Aging of electrical conductivity in conducting polymer films based on polyaniline*, Journal of Applied Physics, 88(2), 960-966.
- Wei P., Sheng L.Y., Guang L., and Jian M.J., (2005), *Electrical and structural analysis of conductive polyaniline/polyacrylonitrile composites*, European Polymer Journal, 41, 2127-2133.
- Guangzhao Z., Qingqing F., Yue T., Yu Z., Ding P. and Zongyi Q., (2010), *Conductive composite films composed of polyaniline thin layers on microporous polyacrylonitrile surfaces*, Thin Solid Films, 519, 169-173.
- Stejskal J. and Sapurina I., (2005), *Polyaniline: Thin Films and Colloidal Dispersions*, Pure and Applied Chemistry, 77(5), 815-826.
- Jiang J., Pan W., Yang S. and Li G., (2005), *Electrically conductive PANI-DBSA/Co-PAN composite fibers prepared by wet spinning*, Synthetic Metals, 149, 181-186.
- Li M.Y., Guo Y., Wei Y., MacDiarmid A.G. and Lelkes P.I., (2006), *Electrospinning polyaniline contained gelatin nanofibers for tissue engineering applications*, Biomaterials, 27, 2705-2715.
- Cardenas J.R., De Franc M.G.O, De Vasconcelos E.A., and et al., (2007), *Growth of sub-micron fibres of pure polyaniline using the electrospinning technique*. J Phys D: Appl Phys, 40: 1068-1071.
- Joo J., Song H.G., Chung Y.C., Baeck J.S., (1997), *The effects of dopant and solvent on charge transport of doped polyanilines*, Journal of the Korean Physical Society, 30(2), 230-236.
- Almuhamed N., Khenoussi L., Schacher D., Adolphe H.B., (2012), *Measuring of Electrical Properties of MWNT-Reinforced PAN Nanocomposites*, Journal of Nanomaterials, 1-7, 2012.

10. Saini P., Choudhary V., (2013), *Electrostatic charge dissipation and electromagnetic interference shielding response of polyaniline based conducting fabrics*, Indian Journal of Pure Applied Physics, 51, 112-117.
11. Lee H.T., Yang S.J., (2010), *Synthesis and characterization of polyaniline/silica doped with camphorsulfonic acid and dodecylbenzylsulfonic acid*, Journal of Applied Polymer Science, 116(2), 934-945.
12. Li G., Zheng P., Wang N. L., Long Y. Z., and Chen Z. J., Li J. C. and Wan M. X., *Optical study on doped polyaniline composite films*, <http://arxiv.org/pdf/cond-mat/0404629.pdf>
13. Xuehong L., Hsiao Y.N., Jianwei X., Chaobin H., (2002), *Electrical conductivity of polyaniline-dodecylbenzene sulphonic acid complex: thermal degradation and its mechanism*, Synthetic Metals, 128, 167-178.
14. Long Y., Chen Z., Wang N., Zhang Z., Wan M., (2003), *Resistivity study of polyaniline doped with protonic acids*, Physica B 325, 208-213.
15. www.sigmaaldrich.com