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Production and Characterization of PAN/Zeolite Based Nanofibers

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Abstract: In this study, it was aimed to achieve production and characterization of polyacrylonitrile (PAN)/zeolite nanofibers via electrospinning technique. Firstly, polymer solutions were prepared with various concentrations of zeolite. Then, solution properties were determined such as; viscosity, conductivity and surface tension. Nanofiber production was carried out with electrospinning under the optimum process parameters (voltage, the distance between the electrodes, feed rate, and atmospheric conditions). Lastly, nanofibers were morphologically characterized by SEM-EDS. According to the results; solution viscosity and surface tension increased while conductivity decreased with zeolite concentration increment. Also, during the spinning process, it was observed that spinning performance decreased and average fiber diameter increased dramatically with zeolite concentration especially for 10 wt % PAN/10 wt % zeolite. Moreover, zeolite particles held on to the nanofibrous structure successfully even at the minimum and maximum concentrations.

Key words: Polyacrylonitrile, Zeolite, Inorganic, Nanofiber, Electrospinning

PAN/Zeolit Esaslı Nanoliflerin Üretimi ve Karakterizasyonu

Öz: Bu çalışmada, poliakrilonitril (PAN)/zeolit nanoliflerin elektro lif çekim yöntemi ile üretimi ve karakterizasyonunun gerçekleştirilmesi amaçlanmıştır. İlk olarak, farklı zeolit konsantrasyonlarında polimer çözeltileri hazırlanmıştır. Daha sonra, viskozite, iletkenlik ve yüzey gerilimi gibi çözelti özellikleri belirlenmiştir. Nanolif üretimi optimum proses parametreleri (voltaj, elektrotlar arası mesafe, besleme hızı ve atmosferik koşullar) altında elektro lif çekim yöntemi ile gerçekleştirilmiştir. Son olarak, nanolifler SEM-EDS ile morfolojik olarak karakterize edilmiştir. Sonuçlara göre; zeolit konsantrasyonu artışı ile iletkenlik azalırken çözelti viskozitesi ve yüzey gerilimi artmıştır. Ayrıca, lif çekim prosesi boyunca, zeolit konsantrasyonu artışı ile lif çekim performansının azaldığı ve ortalama lif çapının özellikle %10 PAN/%10 zeolit için önemli ölçüde arttığı gözlemlenmiştir. Dahası, zeolit partikülleri maksimum ve minimum konsantrasyonda bile nanolifli yapıya başarıyla tutunmuşlardır.

Anahtar Kelimeler: Poliakrilonitril, Zeolit, İnorganik, Nanolif, Elektro lif çekimi

1. Introduction

Zeolite is a natural raw material which has superior functional properties such as environmental pollution control, filtration, energy applications (storage of solar energy, purification of natural gas, deodorizing of malodor), antibacterial property, absorption of radioactive waste, drug delivery, gas sensing, and gas separations [1-7]. It has a natural distinctive microporous and three-dimensional structure. This structure enables to high surface area and excellent stability. Besides, zeolites are cost-effective and non-toxic raw materials [8].

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Electrospun nanofibers have superior properties than conventional fibers such as; high specific surface area (m^2/g), high porosity, small and controllable pore size, and very small fiber diameter [9–11]. Similarly, polyacrylonitrile (PAN) which is used widely for the electrospinning technique was chosen as a polymer in terms of high spinning performance, absorbent properties, excellent thermal stability, and insoluble to most solvents. Due to these properties, PAN nanofibers are used widely in filtration, dialysis, and water treatment applications [3, 12-13].

In literature, there are limited studies about electrospinning of nanofibers with zeolite while, fiber form of zeolite is very attractive recently [1, 3, 5-7]. Kang and Kang (2016) studied PVDF/zeolite nanofibers and their surface energy characteristics. For this aim, they analyzed morphology, contact angle and hygroscopic properties, wettability. They found that surface energy can be controlled with zeolite concentration and the composite nanofibrous structure has potential for dust filtration application [14]. Rad et al (2014) investigated PVA/zeolite nanofibers and their Ni^{2+} and Cd^{2+} adsorption properties. They determined that these composite materials absorbed Cd^{2+} ions higher than Ni^{2+} and the nanowebs could be reused for more than one with high adsorption capacity [15]. For this aim, in this study, the effect of zeolite concentration on the solution properties and fiber morphology was investigated. It is thought that this nanofibrous composite material has an important end-use potential as a filtration application or adsorption material.

1. Experimental Methods

In this study, PAN (150.000 g mol^{-1}) was used as a polymer, dimethylformamide (DMF) was used as a solvent and zeolite was used as an inorganic additive. PAN and DMF were purchased from Sigma Aldrich Corporation (St. Louis, MO, USA), zeolite was supplied from Rota Mining Inc., Gördes, Manisa, Turkey (<40 µm particle size). All solutions were prepared with 10 wt % PAN polymer concentration in consider of our previous studies (in terms of high spinning performance and bead-free fiber structure). PAN/DMF polymer solutions were prepared with various zeolite concentrations (Table 1).

Table 1. PAN sample codes with various concentration of zeolite

Sample Codes	PAN Concentration (wt %)	Zeolite Concentration (wt %)
ZEO-0	10	0
ZEO-2	10	2
ZEO-4	10	4
ZEO-6	10	6
ZEO-8	10	8
ZEO-10	10	10

After polymer solutions prepared, solution properties were determined such as; conductivity (Selecta CD 2500), viscosity (shear rate 5 s^{-1}) (Lamy Rheology, B-One Touch Screen) and surface tension with Wilhelmy Plate technique (Biolin Scientific Sigma 702). Then, nanofiber production was carried out with electrospinning system under the optimum process parameters (Table 2, Figure 1).

Table 2. Process parameters of the electrospinning process

Voltage (kV)	Distance Between Electrodes (cm)	Feed Rate (mL/h)	Humidity (%)	Temperature (°C)
23.4	18.2	0.7	54	25.4

All nanofibers were produced for 20 minutes and collected on an aluminum foil. The nanofiber morphology and inorganic substance were analyzed with SEM-EDS on an FEI Quanta 250 FEG model instrument. Fiber diameters were measured by ImageJ software from 100 different fibers. And also, histogram curves were created with a statistical program to analyze fiber diameter distribution.

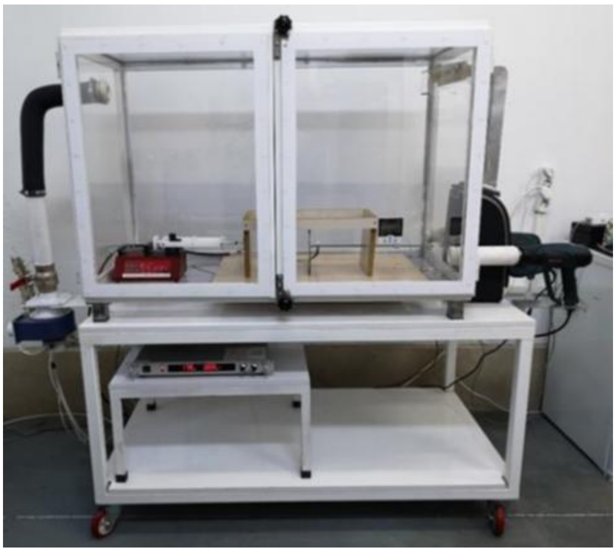


Figure 1. Images of the electrospinning apparatus

Lastly, the number average and weight average values were calculated using equation (1) and (2) given below.

$$A_n = \frac{\sum n_i d_i}{\sum n_i} \text{(number average)} \quad (1)$$

$$A_w = \frac{\sum n_i d_i^2}{\sum n_i d_i} \text{(weight average)} \quad (2)$$

where d_i is the fiber diameter, n_i is the: fiber number. The fiber uniformity coefficient was determined by ratio A_w/A_n. An ideal optimum value should be close to 1 for uniform fibers [16].

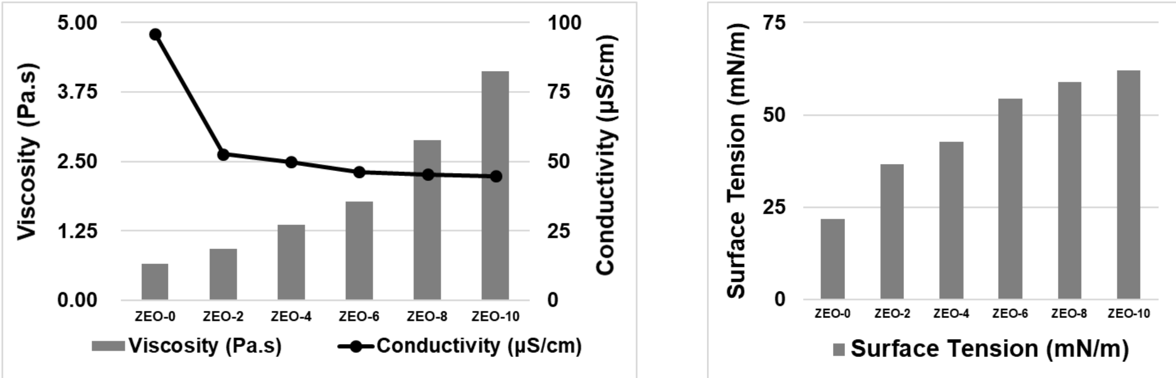
2. Results and Discussion

The results about solution properties of PAN/zeolite are given in Table 3 and Figure 2.

Table 3. Solution properties of PAN/zeolite polymer solutions

Solution Codes	Conductivity (µS/cm)	Viscosity(Pa.s) (shear rate 5s^{-1})	Surface Tension (mN/m)
ZEO-0	95.8	0.65	21.7
ZEO-2	52.6	0. 92	36.6
ZEO-4	49.8	1.35	42.8
ZEO-6	46.2	1.78	54.4
ZEO-8	45.4	2.88	58.8
ZEO-10	44.7	4.12	62.1

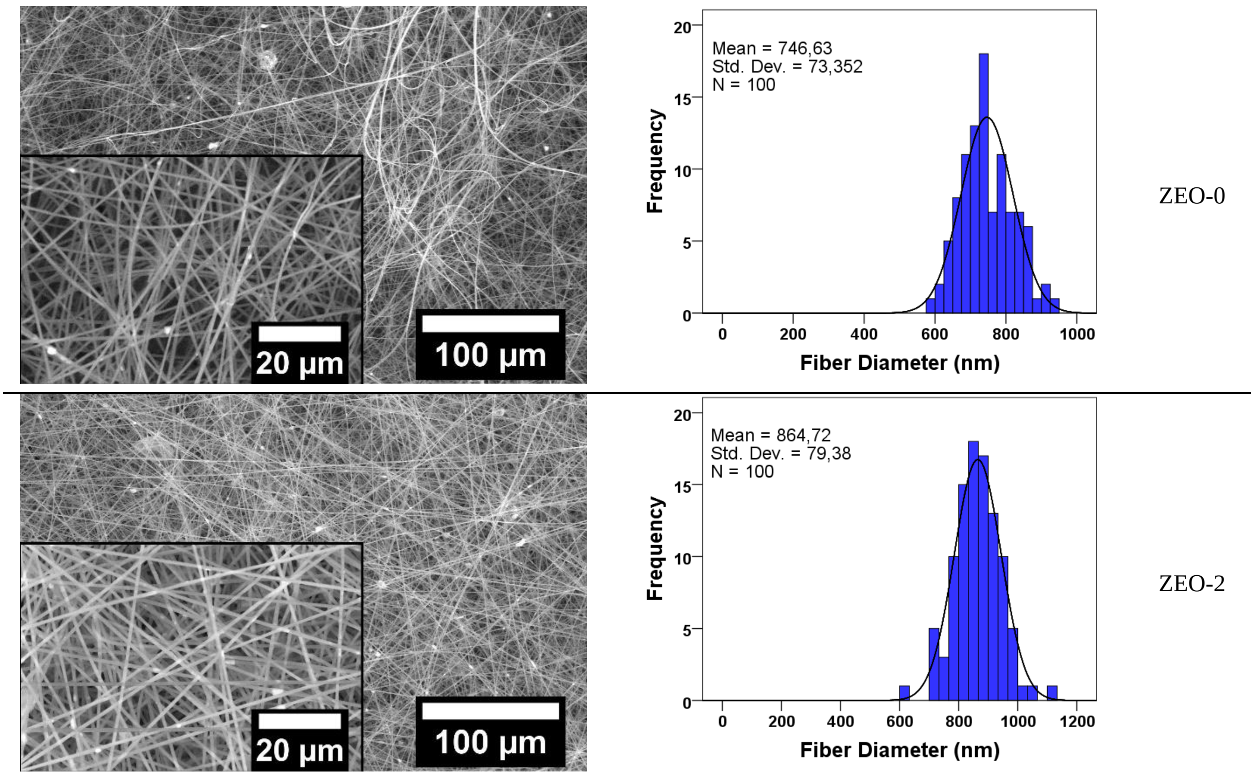
According to the solution properties results; viscosity and surface tension increase and conductivity decreases with zeolite concentration increment. It is seen clearly that from Table 3 and Figure 2; conductivity decreases with the addition of 2 % wt zeolite to the PAN solution dramatically while slightly for the addition of zeolite 4, 6, 8, 10 % wt to the PAN solution. As expecting result that viscosity increased with addition of zeolite. Conductivity is related to number of ions in the polymer solutions. Decreased conductivity indicates that the zeolite cannot ionize in the polymer solution [17]. There are relation between surface tension and cohesion force of polymer solution [18]. It is thought that the addition of zeolite increased the cohesion forces and therefore the surface tension.



(a) (b)

Figure 2. a) Viscosity and conductivity of PAN/zeolite solutions b) Surface tension of PAN/zeolite solutions

SEM images and fiber diameter histograms of PAN nanofibers with various concentrations of zeolite are given in Figure 3.



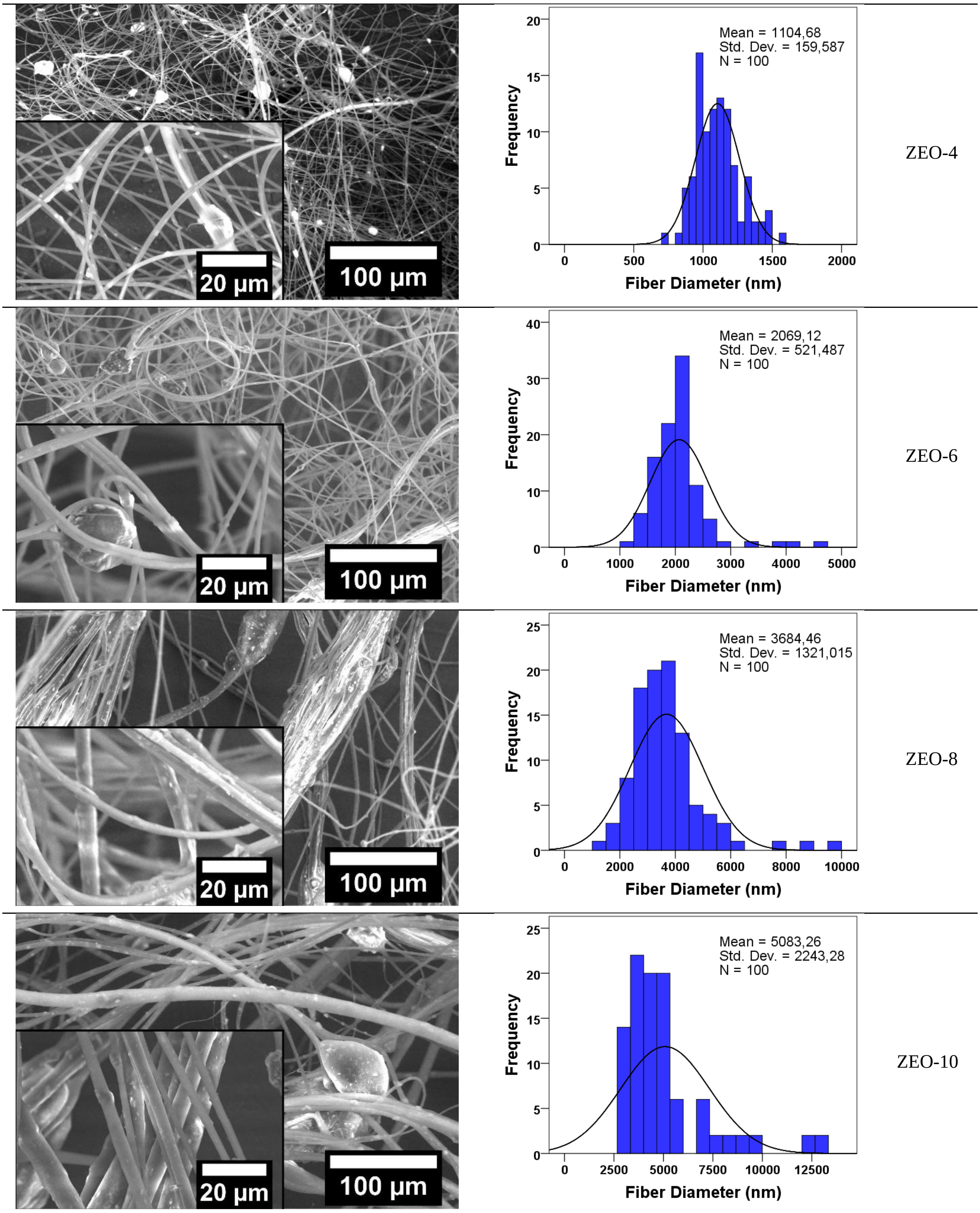


Figure 3. SEM images (1.000x and 5.000x) and histograms of PAN nanofibers samples with various concentrations of zeolite

According to the fiber morphology analysis, it is seen clearly that, average fiber diameter increased with zeolite concentration increment. It is possible to say that nanofibers were obtained with ZEO-0 and ZEO-2 while microfibers (higher than 1000 nm) were obtained with ZEO-4, 6, 8, 10.

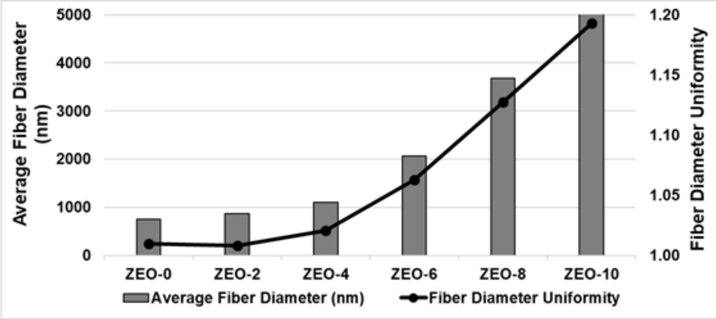
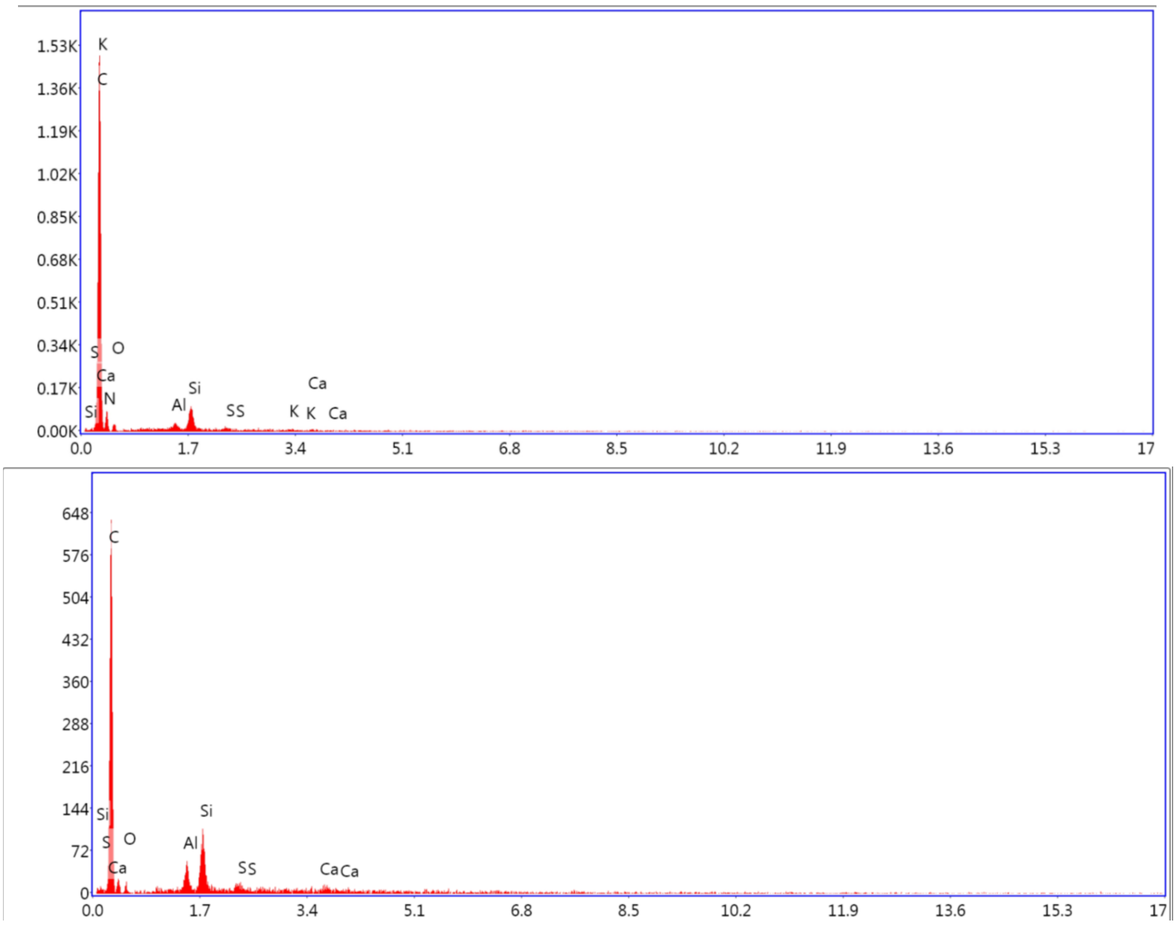


Figure 4. Average fiber diameter and diameter uniformity coefficient of PAN/zeolite nanofibers

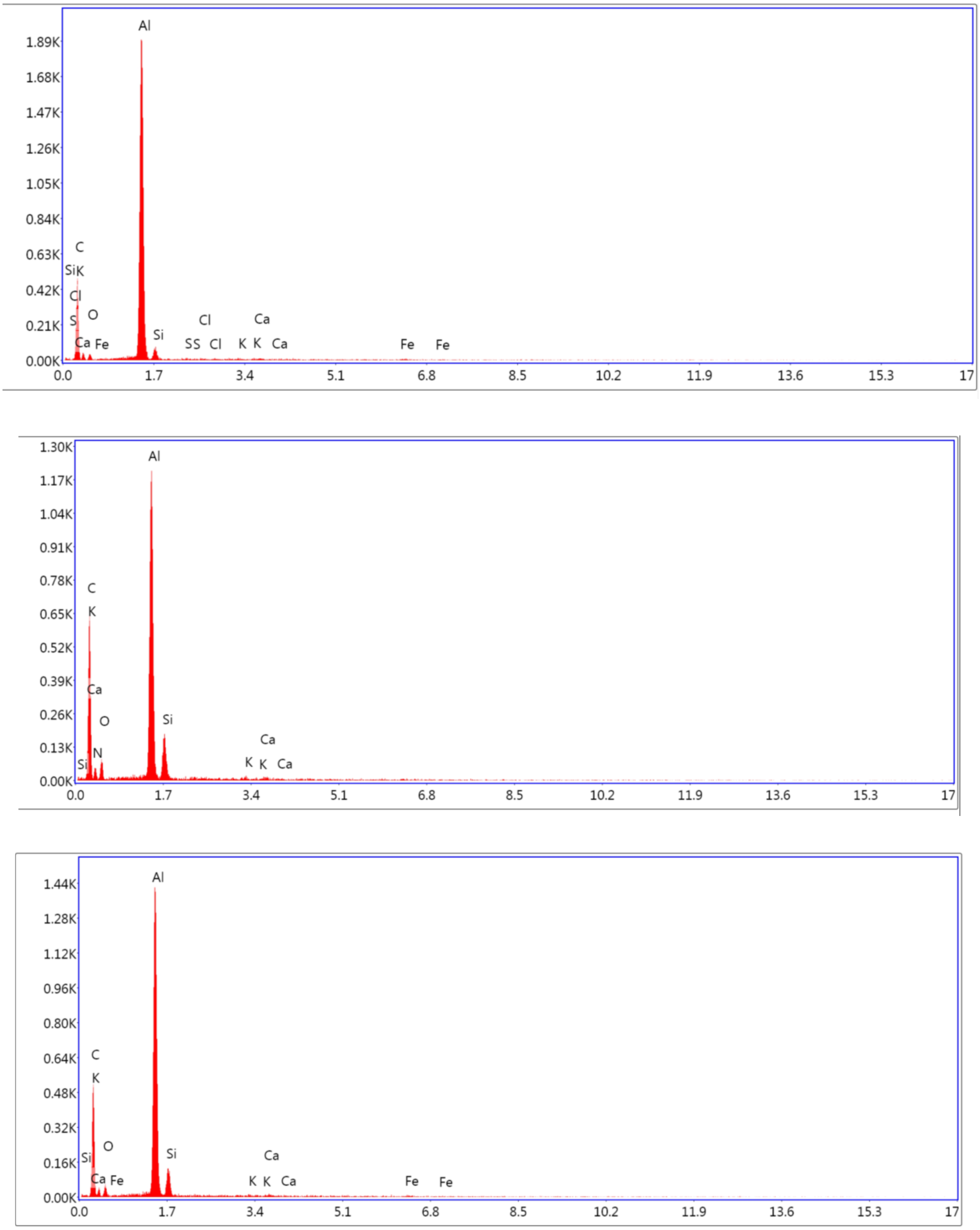
Moreover, spinnability reduced with zeolite concentration significantly. Also, solution properties and fiber morphology results are compatible with each other in terms of reduced spinnability, decreased conductivity, increased viscosity and increased surface tension with zeolite concentration increment. Generally, nanofiber samples had unimodal histogram curves. It has been seen clearly that from SEM images, zeolite particles hold on to the fiber surface successfully for each sample. The relationship between average fiber diameter and fiber diameter uniformity coefficient is given in Figure 4.

According to Figure 4, average fiber diameter and fiber diameter uniformity coefficient increase with zeolite concentration. And, the finest (864,72 nm) and most uniform (1.008) PAN nanofibers with zeolite were obtained with ZEO-2. SEM-EDS results are given in Figure 5 and Table 4.



ZEO-2

ZEO-4



ZEO-6

ZEO-8

ZEO-10

Figure 5. SEM-EDS Spectroscopy of PAN nanofibers with various concentrations of zeolite

Generally, zeolite inorganic raw material consists of Carbon (C), Oxygen (O), Aluminum (Al) and Silicium (Si). Elemental structure can be show difference from each other regionally due to natural structure of zeolite (Table 5). For this reason, elemental analysis results of zeolite nanofibers showed differences between each other.

Table 4. SEM-EDS results of PAN/zeolite nanofiber samples

Sample Codes	C (%)	N (%)	O (%)	Al (%)	Si (%)	S (%)	Cl (%)	K (%)	Ca (%)	Fe (%)
ZEO-2	66.55	28.11	4.56	0.32	1.24	0.10	-	0.06	0.06	-
ZEO-4	90.93	-	5.66	0.89	2.13	0.17	-	-	0.22	-
ZEO-6	64.70	-	3.94	28.98	1.34	0.08	0.07	0.16	0.22	0.52
ZEO-8	56.37	15.69	8.74	16.25	2.63	-	-	0.13	0.19	-
ZEO-10	66.92	-	6.72	22.91	2.56	-	-	0.18	0.24	0.45

Table 5. SEM-EDS results of pure zeolite raw material

Sample Codes	C (%)	N (%)	O (%)	Mg (%)	Al (%)	Si (%)	S (%)	Cl (%)	K (%)	Ca (%)	Fe (%)
Sample-1	13.65	-	40.96	0.42	6.32	30.73	-	-	2.69	3.62	1.62
Sample-2	7.07	-	57.16	0.98	6.10	25.03	-	-	1.23	1.71	0.71
Sample-3	8.59	-	45.38	2.06	14.00	20.49	-	-	2.96	-	1.52

3. Conclusions

This study was carried out the production and characterization of PAN nanofibers with various concentrations of zeolite. PAN concentration was adjusted at 10 wt % constantly and zeolite concentrations were applied 2, 4, 6, 8 and 10 wt %. Firstly, solution properties were determined and then nanofiber production was achieved using optimum process parameters. Lastly, PAN nanofibers including various zeolite concentrations were analyzed with SEM-EDS. According to the results; zeolite concentration has a significant effect on the solution properties. Viscosity and surface tension increase while conductivity decreases with zeolite concentration increment. It was observed from the SEM-EDS analyzes, average fiber diameter increased and spinnability decreased with zeolite concentrations. However, fiber diameter histograms showed that fiber diameter distributions were unimodal. In conclusion; it is possible to say that zeolite particles hold on to the surface of the fibers successfully. It is expected that the results of this study provide basic information for the application of the material and also the PAN/zeolite nanofibrous composite material generates significant end-use potential as a filtration or adsorption applications.

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