FABRICATION OF PCL/SEPIOLITE COMPOSITE NANOFIBERS

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ABSTRACT: *In this study, it was aimed to produce and characterize PCL-based composite nanofibrous material containing various concentrations of sepiolite (SEP). The PCL polymer concentration was kept constant at 10 wt% in consideration. Sepiolite was added to the PCL solution at concentrations of 0, 0.5, 1.0, 1.5, 2.0, and 2.5 wt % respectively. Firstly, the properties of the prepared solutions such as viscosity, surface tension and conductivity were determined. The results of the solution properties indicated that the addition of SEP resulted in an increase in the viscosity, conductivity, and surface tension values of the solutions. Then, the nanofiber production was carried out via electrospinning method. Subsequently, the nanofibers were characterized morphologically by the SEM-EDS analysis. The results of the analysis demonstrated that all nanofibers exhibited smooth, bead-free, and uniform structures. Additionally, the fiber diameter was observed to decrease as the SEP concentration increased. The EDS analysis revealed the presence of magnesium (Mg) and silicon (Si) in nanofibers containing SEP. Considering the excellent features of sepiolit such as being biocompatible and non-toxic along with those of nanofibers, it is thought that the nanofibrous material produced can be used in medical applications such as wound dressing, medicine, bone regeneration.*

Keywords: *Sepiolite, Polycaprolactone, Nanofibers, Electrospinning.*

IZRADA PCL/SEPIOLIT KOMPOZITNIH NANOVLAKNA

SAŽETAK: *Cilj ovog rada bio je da se proizvede i karakteriše kompozitni nanovlaknasti materijal na bazi PCL-a koji sadrži različite koncentracije sepiolita (SEP). Koncentracija PCL polimera je održavana konstantnom na 10 tež%. Sepiolit je dodat u PCL rastvor u koncentracijama od 0, 0,5, 1,0, 1,5, 2,0 i 2,5 tež. % respektivno. Prvo su određena svojstva pripremljenih rastvora kao što su viskozitet, površinski napon i provodljivost. Rezultati svojstva rastvora su pokazali da je dodavanje SEP-a dovelo do povećanja vrednosti viskoziteta, provodljivosti i površinskog napona rastvora. Zatim je proizvodnja nanovlakna sprovedena metodom elektropredenja. Nakon toga, nanovlakna su morfološki okarakterisana SEM-EDS analizom. Rezultati analize su pokazali da su sva nanovlakna pokazala glatke strukture bez perli i ujednačene strukture. Pored toga, primećeno je da se* *prečnik vlakana smanjuje kako se koncentracija SEP povećava. EDS analiza je otkrila prisustvo magnezijuma (Mg) i silicijuma (Si) u nanovlaknima koja sadrže SEP. Uzimajući u obzir odlične karakteristike sepiolita kao što je biokompatibilnost i netoksičnost zajedno sa onima nanovlakna, smatra se da se proizvedeni nanovlakni materijal može koristiti u medicinskim aplikacijama kao što su zavoji rana, medicina, regeneracija kostiju.*

Ključne reči: *sepiolit, polikaprolakton, nanovlakna, elektropredenje.*

1. INTRODUCTION

Sepiolite is a naturally occurring hydrated magnesium silicate clay mineral ($Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$) with a fibrous structure and unique physicochemical characteristics. It is used in many industrial applications, including adsorbents, catalysts, plastics and polymeric materials, animal feed additives, pharmaceuticals and cosmetics, soil amendments, ceramics and refractories, environmental remediation, and medical applications [1-2]. Sepiolite is generally considered to be biocompatible and non-toxic [3], which makes it a promising material for a wide variety of medical applications. Its unique properties make it stand out among other materials in the medical field [4]. Current studies indicate possible uses in wound dressings [5], drug delivery systems [6], tissue engineering [4], bone grafting, dental materials and diagnostic imaging. The use of sepiolite in medicine is relatively new compared to other industries.

Electrospinning is a versatile and scalable technique for the fabrication of nanofibers with diameters in the range of a few nanometers to several micrometers. Nanofibers have unique properties, such as high surface area-to-volume ratio, flexibility, low density, porosity, and tunable mechanical, electrical, and optical properties, making them suitable for various applications, including tissue engineering, filtration, drug delivery, and sensors. Electrospun nanofibers can be produced from a variety of materials, including synthetic polymers, natural polymers, biopolymers, ceramics, composites, minerals, and hybrid materials. Each material offers unique characteristics suitable for specific applications [7-9].

Polycaprolactone (PCL) is a biodegradable polyester, whose unique combination of properties and versatility have made it popular in a wide variety of industries. PCL is a valuable material with broad applications across multiple industries, including biomedical, packaging, and textiles. Its biodegradability, biocompatibility, mechanical properties, thermal stability, processability, and environmentally friendly characteristics make it highly sought after. PCL finds applications in various biomedical fields such as drug delivery systems, tissue engineering scaffolds, wound dressings, dental materials, and implantable biomaterials [10-11].

The objective of this study is to produce nanofibrous composite nanofibrous material through the electrospinning method using PCL polymer and sepiolite in different ratios (0, 0.5, 1.0, 1.5, 2.0, and 2.5 wt %). In literature, there is limited study with sepiolite and therefore this pre-experimental study will be useful for biomedical applications of nanofibers especially bone regeneration etc.

2. MATERIALS AND METHODS

2.1 Materials

In the study, PCL (Mn=80,000) was used as a polymer, chloroform and dimethylformamide (DMF) were used as solvents and sepiolite was used as a mineral additive to fabricate the nanofibrous materials. PCL, chloroform and DMF were purchased from Sigma-Aldrich Corporation (St. Louis, MO, USA). The sepiolite mineral was supplied from Eskişehir, Turkey.

2.2 Methods

In all solutions, the PCL polymer concentration was set at 10 wt%. Table 1 displays contents of the solutions along with their corresponding sample codes.

Table 1: The concentration of PCL and SEP with sample codes

Sample Codes	PCL Concentration (wt%)	SEP Concentration (wt%)
SEP-0	10	0
SEP-0.5	10	0.5
SEP-1	10	1.0
SEP-1.5	10	1.5
SEP-2	10	2.0
SEP-2.5	10	2.5

The first step in the production of nanofibers was the preparation of the PCL polymer solution. Various concentration of SEP was added into the PCL polymer solution. All of the solutions were prepared at room temperature for a period of 24 hours with constant stirring.

After preparing the polymer solutions, their properties including conductivity (measured using Selecta CD 2500), viscosity, and surface tension (measured using the Wilhelmy Plate technique with Biolin Scientific Sigma 702) were determined. The production of nanofibrous materials was subsequently carried out by electrospinning system under the optimized process parameters.

The electrospinning process was used to fabricate the nanofibers at laboratory scale. The process parameters identified Table 2, such as applied voltage, needle-to-collector distance, and solution flow rate, were optimized and maintained during spinning. The nanofibers were collected on an aluminum sheet for 15 min. The electrospinning process was performed under the same environmental conditions for all samples.

Table 2: Process parameters of electrospinning

Voltage (kV)	Distance Between Electrodes (cm)	Feed Rate (mL/h)	Humidity (%)	Temperature (°C)
23.5 (± 0.5)	22	0.450	47 (± 3)	23.5 (± 0.5)

The morphology of the produced nanofibers was characterized by Scanning Electron Microscope (SEM). Additionally, quantitative chemical analysis of the inorganic matter in the nanofibers was performed by Energy Dispersive Spectrometry (EDS). SEM-EDS analyses were conducted on an FEI Quanta 250 FEG instrument. The average fiber diameter was determined by measuring the diameter of 100 randomly selected fibers on SEM images. Moreover, the uniformity of the fiber diameter, and the surface structure of the nanoweb was assessed via SEM images. ImageJ program was used to measure fiber diameters and then statistical analysis of morphological parameters such as fiber diameter histogram was performed using SPSS analysis program. The average fiber diameter uniformity coefficient values were calculated using the following formula.

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

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

ni=fiber number *di=fiber diameter*

The fiber diameter uniformity coefficient was calculated by the ratio of Aw to An. An ideal optimum value for uniform fibers should be close to 1 [12].

3. RESULTS AND DISCUSSION

The results about solution properties of PCL/SEP are given in Table 3.

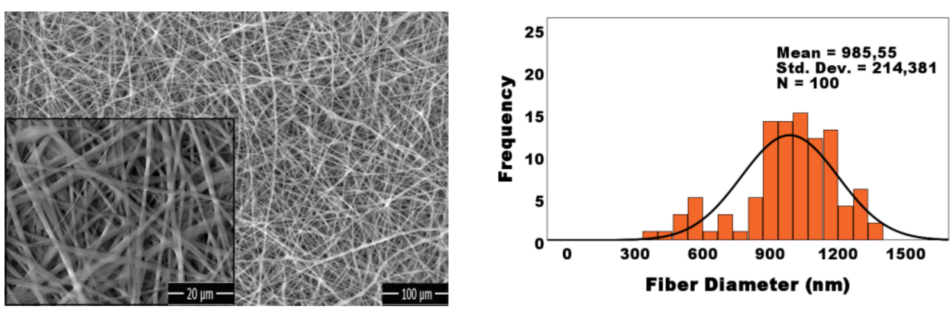
Table 3: Solution properties of PCL/SEP polymer solutions

Sample Codes	Conductivity (µS/cm)	Viscosity (Pa·s)	Surface Tension (mN/m)
SEP-0	0.43	0.709	27.07
SEP-0.5	0.99	0.734	30.20
SEP-1	1.32	0.991	30.05
SEP-1.5	1.49	1.044	30.07
SEP-2	1.73	1.818	30.46
SEP-2.5	1.85	2.461	35.23

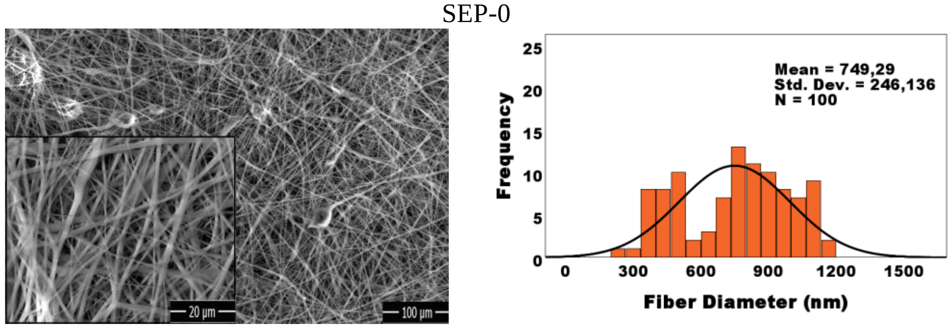
The results indicated that the conductivity and viscosity increased in direct relation to the SEP concentration in the solutions. While the viscosity of the first three samples (*SEP-0.5*, *SEP-1*, *SEP-1.5*) increased by minimal amounts, the viscosity values of the *SEP-2* and *SEP-2.5* samples exhibited a notable increase. The SEP mineral is known to be sensitive to pH [13]. It is postulated that the increase in viscosity is dependent on the pH value of the solution. The electrical conductivity exhibited a logarithmic increase with the concentration of SEP in the solutions. The conductivity of polymer solutions is related to the number of ions present [14]. The observed increase in conductivity indicated that SEP undergoes ionization in the polymer solution.

Upon analysis of surface tension values, it can be concluded that the addition of SEP results in a slight increase in surface tension within the solutions. This increase was particularly pronounced in the SEP-2.5 sample. While the surface tension of the sample without SEP (SEP-0) was 27.07 mN/m, the surface tension of the sample containing 2.5 wt% SEP (SEP-2.5) was 35.23 mN/m. This increase in surface tension resulted in a decline in electrospinning performance.

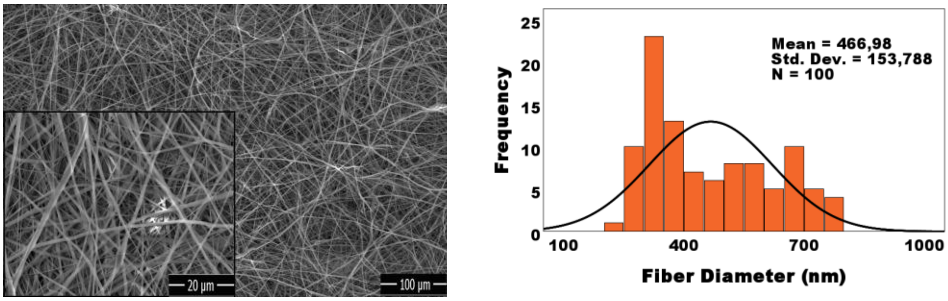
Figure 1 presents SEM images (1.000x and 10.000x) and fiber diameter histograms of PCL-based nanofiber samples produced with various concentrations of SEP



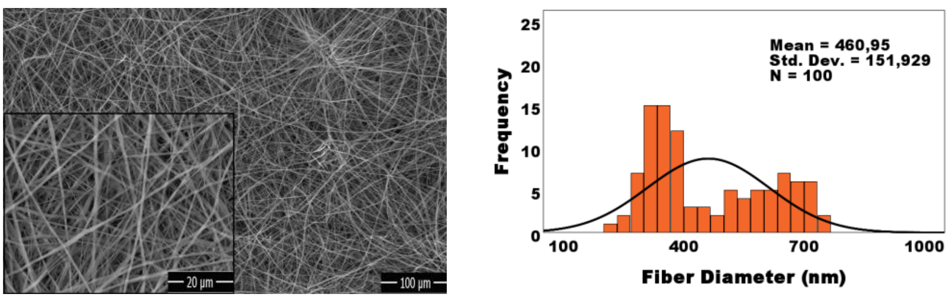
SEP-0



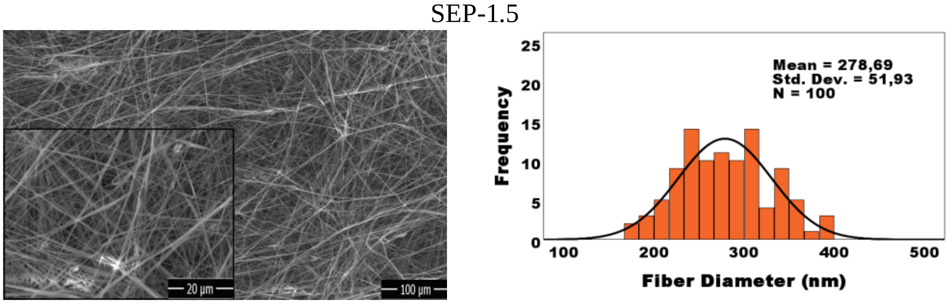
SEP-0.5



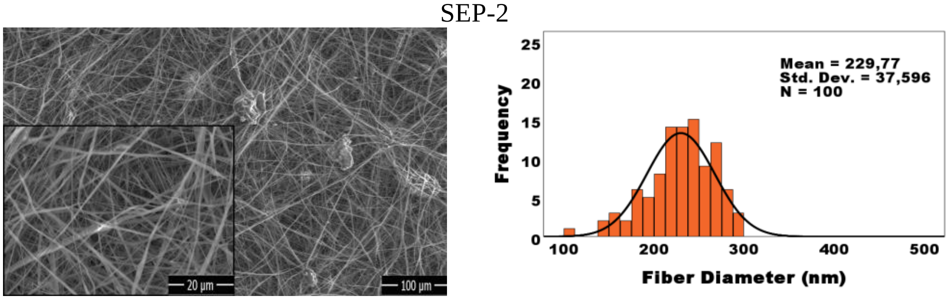
SEP-1



SEP-1.5



SEP-2



SEP-2.5

Figure 1: SEM images (1.000x, 10.000x) and fiber diameter histograms of PCL-based nanofiber samples produced with various SEP concentrations

Upon examination of the SEM images of the nanofibers produced, it was determined that only those produced with PCL polymer resulted in the formation of very thick fibers. Despite this, the fibers were found to be smooth, beadless, and uniform. When the SEM images of the nanofibers obtained by adding SEP to the PCL solution were examined, it was understood that the fibers gradually became thinner. All nanofibers obtained from solutions with different SEP concentrations were found to be smooth, beadless, and uniform. When the histograms obtained by measuring the diameters of 100 randomly selected fibers from SEM images are examined, it is evident that all histograms are single-peaked and have a flattened frequency distribution curve.

In Figure 2, the impact of varying concentrations of the SEP on the average fiber diameter and the fiber diameter uniformity coefficient is presented.

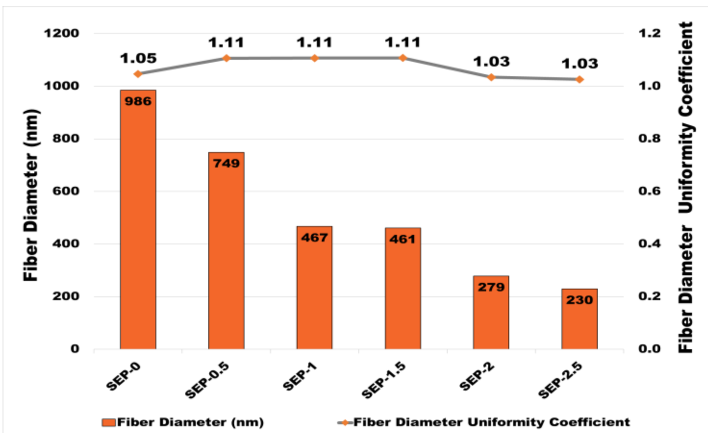


Figure 2: The effect of SEP concentration on the average fiber diameter and fiber diameter uniformity coefficient of PCL-based nanofibers

Figure 2 clearly demonstrated that the incorporation of SEP resulted in a reduction in the average fiber diameter. The most uniform fibers were observed in the SEP-2.5 sample. The average fiber diameter of this solution was determined to be 230 nm. The fiber diameter uniformity coefficient value for the SEP-0 sample without SEP was found to be 1.05. Upon the addition of SEP, the fiber diameter uniformity coefficient initially increased to 1.11 and subsequently decreased to 1.03 for the SEP-2 and SEP-2.5 samples. A value approaching 1 indicates a uniform fiber structure. This suggests that the SEP-2 and SEP-2.5 samples possess a more uniform fiber diameter than the others.

The results of the EDS analysis of nanofibers containing various concentrations of SEP particles are presented in Table 4.

Table 4: EDS results of the PCL nanofibers with various concentrations of SEP

Sample Codes	C (%)	O (%)	Mg (%)	Si (%)
SEP-0	70.76	29.24	-	-
SEP-0.5	71.00	28.90	0.09	-
SEP-1	69.85	29.52	0.38	0.25
SEP-1.5	70.41	29.10	0.21	0.27
SEP-2	69.34	29.59	0.43	0.63
SEP-2.5	72.67	25.86	0.51	0.96

The presence of SEP minerals on PLC-based nanofiber surfaces was confirmed by EDS analysis. The EDS results of all nanofibers exhibited Carbon (C) and Oxygen (O) values. No different elements were detected in the SEP-0 sample, which without SEP, as anticipated. However, the presence of Magnesium (Mg) and Silicon (Si) was revealed by the addition of SEP to the solutions. As the concentration of SEP in the solutions increased, the amounts of Mg and Si detected in the nanofibers also increased, in general.

4. CONCLUSION

In the study, PCL-based nanofibrous materials containing various concentrations of sepiolite were successfully electrospun and characterized via SEM-EDS. The concentration of PCL polymer was maintained at 10 wt %. Sepiolite was added to the PCL solution at concentrations ranging from 0 to 2.5 wt%. The effect of SEP concentration on the conductivity, viscosity, and surface tension of PCL solutions was determined. The results indicated that the addition of SEP to the solutions resulted in an increase in conductivity, viscosity, and surface tension. The findings of the SEM analysis indicated that all nanofibers exhibited smooth, bead-free, and uniform structures. Furthermore, the fiber diameter was observed to decrease as the concentration of SEP increased. The EDS analysis demonstrated the presence of Mg and Si elements in nanofibers containing SEP. In addition; the relations between SEP concentration, spinning performance, fiber morphology, average fiber diameter and fiber diameter uniformity were analyzed. The high surface tension and viscosity of the SEP-2.5 sample led to a reduction in electrospinning performance. The exceptional properties of sepiolite, such as biocompatibility and non-toxicity, and the superior properties of nanofibers suggest that the resulting nanofiber material can be used in various medical applications, such as bone regeneration.

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