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Production and Characterization of Rechargeable Composite Nanofiber Membranes

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Research and development activities on rechargeable lithium-ion batteries are demanded day by day with the increasing demand for portable electrical and electronic devices, as well as the increasing importance of electric cars in the transportation sector. Lithium-ion batteries are preferred by environmentally conscious designers and consumers due to their high energy density and non-toxicity in mobile phones, laptops and small household appliances and due to the low level of CO_2 gas they emit. Ultra capacitors, such as lithium-ion batteries, have high capacity and offer extra fast charging. These ultra capacitors provide weight savings as well as their unique efficiency feature. It has been determined as a result of research that new types of capacitors offer up to 1000 times faster charging compared to ordinary batteries. In this study, polycaprolactone (PCL) and carbon nanotube (CNT) rechargeable composite nanofiber membranes were obtained by nanotechnological electrospinning technique. Material properties were determined by performing morphological (Scanning Electron Microscope-SEM) and mechanical (Tensile) analyzes on the produced composite nanofiber membranes.

Keywords: *Recharging, electrospinning, membrane, composite, nanofiber*

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1. Introduction

Most of the electrical appliances we use at home are becoming wireless. The main condition for all these portable electronic products to maintain their developed functions for a long time and effectively is to have an energy source with high energy density, safe, long-lasting, easy-to-maintain, rechargeable in a short time and does not harm the environment. Rechargeable / secondary (lithium-ion (Li-ion)) batteries are widely used today in portable electronic and electrical equipment due to their superior features. Literature studies have revealed that lithium-ion batteries will be used to store the energy required for many vehicles (cars, heaters, etc.) operating with energy from petroleum resources expected to be depleted in the near future. In addition to lithium-ion batteries, carbon nanotube (CNT) ultra capacitors have been developed that can significantly increase the range of electric vehicles. With the

increased range and efficiency, ultra capacitors have the capacity to be used in a wide area. Since there is no chemical reaction, only the physical separation of protons and electrons does not cause the battery to heat or swell. It also provides an extraordinary charge cycle of up to 1 million.

Capacitors using only carbon (C) and aluminum (Al) offer significant advantages by using natural and sustainable resources. With both the material strength and charging advantages of the capacitor, it is possible to fill the battery of an electric vehicle in just seconds. In regenerative braking systems, as much as 80% of the energy is lost as heat, 20% of it is used in batteries. However, thanks to the unique charging feature of ultra capacitors, 90 percent energy conversion is possible in regenerative braking. New generation batteries also offer significant efficiency in the field of transportation. For example; electric trucks can have a longer range. When braking downhill, the energy can be converted by 90 percent and the range can be increased [1,2].

Nanomaterials, the word "nano" derived from the Greek word "nanos" means little old man or dwarf. Today, the word nano is used as a technical unit of measurement. Mathematically, a nanometer is equivalent to one billionth of a meter.

The concept of nanofibers is defined as fibers with a fineness of approximately one-thousandth of a human hair with an average diameter of nanometers. Considering the fiber concept in general, the term "nano" refers to the size of the fiber diameter. One of the most important techniques developed to create fibers is the electrospinning method. With this production method, it is possible to obtain nano-sized, low weight and high mechanical strength, biocompatible materials.

Nanofiber production methods, conventional techniques used in fibers produced from solution or melt, are based on the principle of passing the melt or solution through a nozzle and solidifying it. However, it is not possible to produce nanofibers with these methods. The reason for this is that it is impossible to reduce the diameter of the spinneret used in conventional fiber production methods so that it can produce nanofibers. Today, nanofiber production can be carried out using fibrillation, meltblowing, bicomponent, spunbond and electrospinning methods [3,4].

Electrospinning is the process of transforming fluid into nano-sized fibers by applying kilovolt-sized voltage to viscous liquids at very small flow rates. In these applications, polymer solution or melt is used as viscous liquid. The solution arriving at the tip of the medical syringe at uniform flow forms a spherical droplet under the influence of surface tensions, and here, under the effect of electrical forces, it is tapered and transferred to the grounded collector at a certain distance as nanofibers. While electrospinning systems from solution can be set up simply in this way, the system to obtain nanofibers from the melt cannot be simplified as much. Because the polymer granules have to be melted at certain temperatures in order to fluidize at the appropriate viscosity.

The basic principle of the electrospinning process is to form very thin fibril structures from the solution by overcoming the viscoelastic and surface tension forces on the polymer solution by using electrostatic forces. These structures are reticulate structures formed by fibers with nanosized diameters. In the electrospinning method, the polymer that we will shoot is dissolved in a suitable solvent or heated and melted and placed in a pipette or syringe with a small hole at one end. An electric field is created by applying sufficient tension between this pipette / syringe and the metal collector plate used to collect the fibers at a certain distance.

Electrostatic forces are expected to overcome the surface tension and viscoelastic forces in the polymer droplet by gradually increasing the applied tension. As soon as the applied voltage reaches a critical value, the jet formation begins, the jet collector rapidly extends towards the plate and thinning out. Thus, nanoscale fiber production begins. The evaporation of solvent molecules by flying is also effective in decreasing the fiber diameter.

Electrospinning process is not a new technology. This process emerged in the 1600s when William Gilbert, while continuing his studies on magnetism, coincidentally observed the effect of electro-magnetism on liquids. In his work, he pointed out that a water droplet was pulled electrically in the form of a cone at a distance from a dry surface. This is where the history of electrospray and electrospinning began.

A wide variety of materials such as rechargeable materials, solar cell material production, biosensors, wearable technology products can be produced with the electrospinning technique. With the electrospinning technique, it is possible to obtain products for many sectors such as textile, food, defense, agriculture, filtration, especially the health sector [5-7].

In this study, polycaprolactone (PCL) and carbon nanotube (CNT) rechargeable composite nanofiber membranes were obtained by nanotechnological electrospinning technique. Material properties were determined by performing morphological (Scanning Electron Microscope-SEM) and mechanical (Tensile) analyzes on the produced composite nanofiber membranes.

2. Experimental Studies

2.1 Materials

In rechargeable nanofiber membrane production, CNT (50-90 nm of 95% carbon-based Sigma-Aldrich / Turkey) and molecular weight of 80,000 g / mol PCL (97% purity from Sigma-Aldrich / Turkey) is preferred. dimethylformamide to solve the polymer (DMF-$HCON(OH_3)_2$) (Sigma-Aldrich / Turkey), chloroform ($CHCl_3$) (Sigma-Aldrich / Turkey) were used as organic solvents. In the electrospinning method, greaseproof paper was preferred as the base material.

2.2 Preparation of composite solutions

10 gr of PCL polymer by weight was made into solution in DMF / chloroform (50-50) solvent with a heated magnetic stirrer at 60 °C mixing temperature and 50 minutes mixing time. By adding 1%, 5%, 8% CNT to the formed PCL solution, a solution in four different compositions was obtained. Table 2.1 shows the preparation values of composite solutions.

Table 2.1: Preparation values of composite solutions

Sample Name	Solution Mixing Time (min.)	Solution Mixing Temperature (°C)
10% PCL	50	30
10% PCL-1% CNT	50	30
10% PCL-5% CNT	55	45
10% PCL-8% CNT	55	45

2.3 Production of rechargeable nanofiber membranes by electrospinning method

Rechargeable composite nanofiber membranes were produced by applying the electrospinning operating parameters in Table 2.2 to the solutions obtained. Electrospinning operating parameters are shown in Table 2.2. The device image of FYTRONIX ELECTROSPINNING SYSTEM is given in Figure 2.1. Rechargeable membrane production steps are shown in Figure 2.2.

Table 2.2: Electrospinning parameters applied for composite nanofiber membrane production

Sample Name	Flow Rate (ml/hr.)	High Voltage (kV)	Working Distance (cm)
10% PCL	1.5	27.0	15
10% PCL-1% CNT	1.5	27.0	15
10% PCL-5% CNT	1.5	35	15
10% PCL-8% CNT	1.5	35	15

Figure 2.1. *Device image of FYTRONIX ELECTROSPINNING SYSTEM*

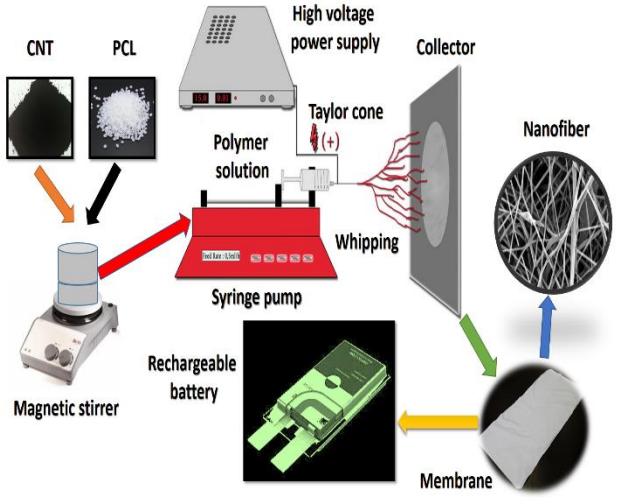

Figure 2.2. *The realization stages of rechargeable nanofiber membrane production*

2.4 Characterization of composites membrane

Refillable nanofiber membranes placed in the holders were examined and photographed with a Thermoscientific Phenom XL G2 Desktop microscope. For SEM analysis of the produced rechargeable nanofiber membranes, x12000 times magnified images at 15 kV potential were examined. The fiber sizes of the nanofibers were determined by measuring an average of 200 nanofibers with the device software on the images obtained.

In order to carry out mechanical characterization studies of rechargeable nanofiber membranes, samples were prepared in 1x4 cm dimensions. Digital micrometer (795.1 MEXFL-25, Starrett, USA) device was used for thickness measurements of rechargeable nanofiber membranes cut in appropriate size. The resulting thickness values were entered into the analysis program before mechanical analysis and used in determining the elastic modulus. The mechanical properties of the nanofibers formed were determined with a Zwickline (Zwick / Roell Ltd., Germany) analyzer. Studies have been done in room conditions. The samples are separated from the litter material and attached to the device clamps. The device is 5 mm / min under 500 N load. Mechanical properties were determined by adjusting the drawing speed and 10 mm jaw range.

3. Result and Discussion

3.1 Morphological (SEM) analysis

Nanofiber formation was observed in all observations. The nanofibers of the PCL membrane have a random distribution of homogeneous life distribution. A shifts and changes have occurred in the CNT change. Partly clumping occurred on the PCL fibers with 1% CNT contribution. The reason for this is due to the CNT contribution. When the 5% layer is taken, the clumping in the nanofibers has disappeared, but the diameters of the PCL nanofibers have expanded. It has been determined that the nanofibers with 8% CNT additive are oriented and the diameters of the nanofibers are examined against all observations. The main reason for this is that the CNT additive added to the PCL solution increases its conductivity. A better electrical conductivity is achieved in nanofiber [3,4]. The Thermoscientific Phenom XL G2 Benchtop microscope image is shown in Figure 3.1. SEM images of nanofiber membranes are shown in Figure 3.2., Figure 3.3., Figure 3.4., Figure 3.5. Nanofiber size distribution range of nanofiber membranes is shown in Table 3.1.

Figure 3.1. *Thermoscientific Phenom XL G2 Benchtop microscope image*

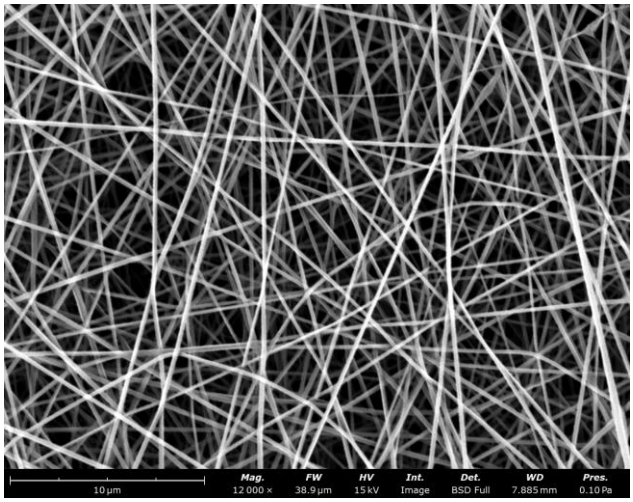

Figure 3.2. *Image of 10% PCL x12000 SEM*

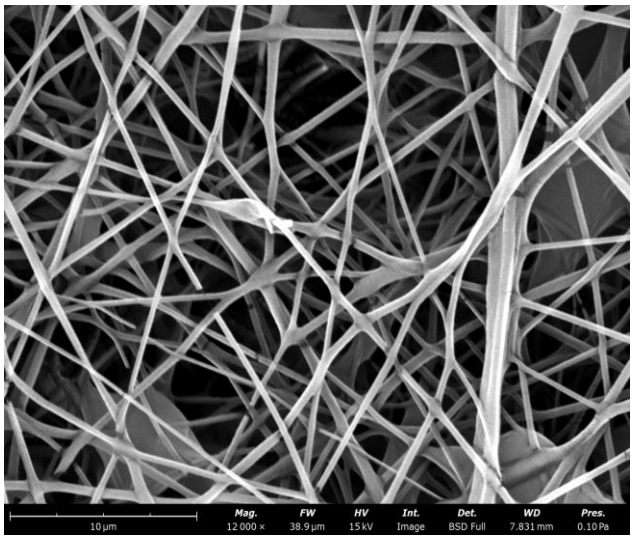

Figure 3.3. *Image of 10% PCL-1% CNT x12000 SEM*

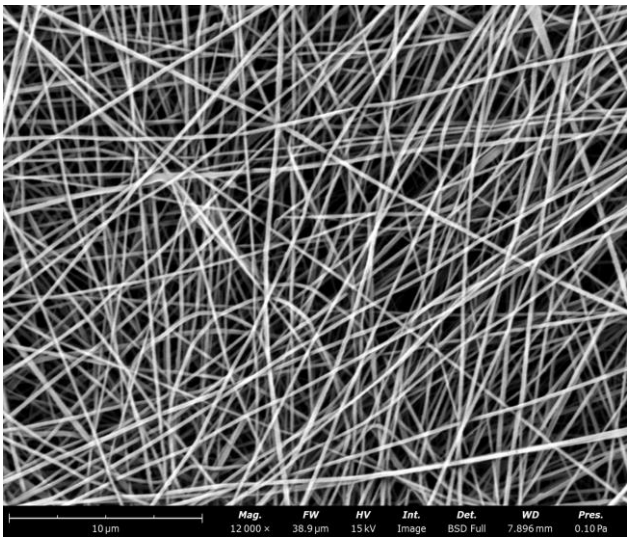

Figure 3.4. *Image of 10% PCL-5% CNT x12000 SEM*

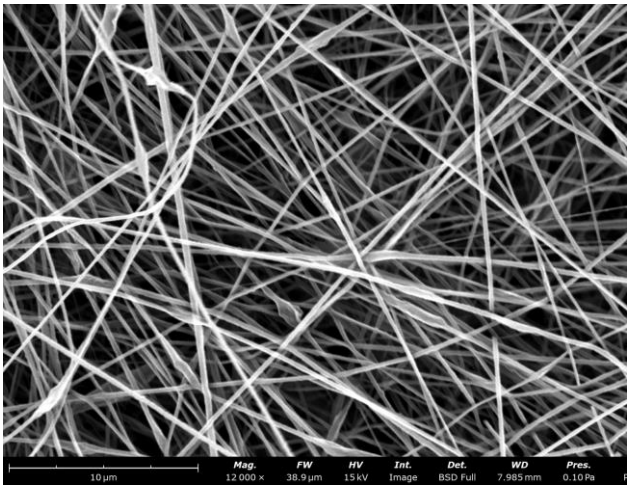

Figure 3.5. *Image of 10% PCL-8% CNT x12000 SEM*

Table 3.1: Nanofiber size distribution range of nanofiber membranes

Sample Name	Nanofiber avarage size (nm)
10% PCL	180-350
10% PCL-1% CNT	240-460
10% PCL-5% CNT	220-430
10% PCL-8% CNT	170-300

3.3. Mechanical (Tensile) analysis

Figure 3.6. shows the mechanical properties of rechargeable nanofiber membranes. The mechanical properties of the produced membranes were repeated in three centers. The average tensile strength value of the PCL membrane was 16.42 MPa. As a result of the addition of CNT to PCL, a linear tensile strength has been achieved. When the tensile strength values of all samples are examined, 10% PCL-8% CNT membrane has the highest value with a tensile strength value of 45.03 MPa. The reason for this is that the reinforced CNT additive wraps around the PCL membranes homogeneously, thinning the PCL nanofibers and making them a more tightly packed structure [3,8]. The tensile strength values of composite membranes are given in Table 3.2.

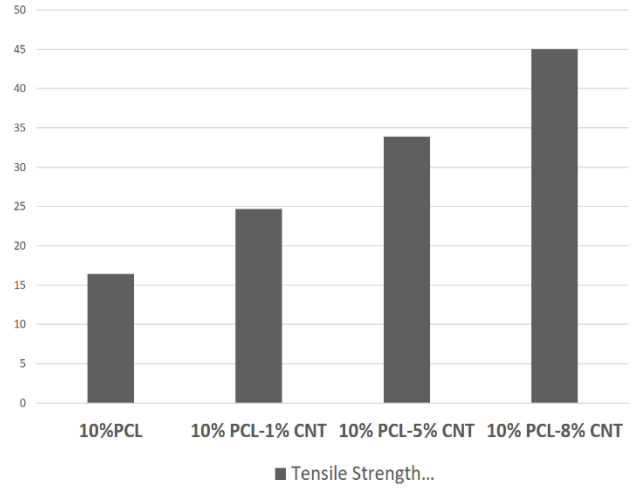

Figure 3.6. *Nanofiber membranes tensile test graphic*

Table 3.2: Tensile strength values of composite mats

Sample Name	Mat Thickness (mm)	Tensile Strength (MPa)
10% PCL	0.18	16.42
10% PCL-1% CNT	0.19	24.67
10% PCL-5% CNT	0.24	33.89
10% PCL-8% CNT	0.28	45.03

4. Conclusion

In our study, the production of PCL and CNT composite nanofiber membranes was successfully carried out using the electrospinning technique. When the morphological images of composite nanofiber membranes were examined, a homogeneous and regular structure of the nanofibers in the PCL membrane was observed. It has been determined that as the % CNT additive rate increases, the nanofibers become thinner and the nanofibers are directed. According to the mechanical analysis results, as the CNT contribution increased compared to PCL membrane, the mechanical

properties increased linearly. The CNT additive made the PCL fibers thinner by wrapping them homogeneously and provided a tighter structure form. This had a linear effect on the strength increase. Our nanofiber membrane can be an ideal rechargeable material. As a continuation of the study, different production methods such as dip coating will be tried in the production of conductive composite films. Since these conductive composite surfaces, which have multifunctional properties, display wearable sensor properties, the sensor behavior can be investigated in more detail. In addition, the nanofiber membranes we produce can be used as batteries that can be charged in seconds.

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