RESEARCH ARTICLE
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Preparing a Composite Nanofiber Film Using Carbon Nanotubes and Polycaprolactone by Electrospinning Method

ABSTRACT

Background: Nanofibers produced from carbon nanotubes (CNT) have received greater attention in various scientific fields due to their unique properties. Electrospinning, a versatile and cost-effective nanofiber production technique, is a promising method for obtaining composite nanofibers by adding other components, such as carbon nanotubes.

Methods: In this study, a 10% polycaprolactone (PCL) solution and a 0.1% CNT-containing PCL solution were prepared. The prepared solutions were used to prepare nanofibers by changing various parameters (such as voltage, flow rate, and distance between the needle and the collector) in the electrospinning device. Then, the films were examined under an atomic force microscope and a Fourier transform infrared (FTIR) spectrophotometer to investigate their physical appearance and bonds in the structure of molecules. Surface topologies and properties of nanofibers were visualized under atomic force microscopy (AFM). Thus, the feasibility of a film layer preparation containing 0.1% CNT was tested. The technique is explained in detail and will be available for future drug adsorption/desorption studies to develop a drug delivery system.

Results: The feed rate was increased due to the increase in viscosity in the electrospinning of carbon nanotube-doped nanofibers. As a result of half an hour of electrospinning, a 20 μm thick nanofiber surface was obtained. The absence of new peaks on FTIR and minimal shifts indicates minimal molecular interactions. A smooth surface was observed with AFM. The film was successfully prepared.

Conclusion: This novel approach was the first study and successful preparation technique can easily adopted and used in future studies.

Keywords: Carbon nanotubes, electrospinning method, pharmaceutical technology

What is already known on this topic?

- *The technique of electrospinning is well-known but adding carbon nanotubes to polycaprolactone (PCL) is not well studied. We used multiwalled carbon nanotubes (CNTs) to enhance drug adsorption onto PCL fibers which is also new.*

What does this study add to this topic?

- *The electroconductivity of PCL was also enhanced by using CNTs. The system parameters were optimized and given to readers who like to perform similar studies. The physical appearance of developed PCL+ carbon nanotube fibers was visualized and evaluated.*
- *Although this study was an initial study, the potential of using it for many applications including cosmetical or cosmeceutical applications was mentioned,*
- *These kinds of pioneering studies and high-tech ideas/methods/settings unfortunately cannot be found in every journal. Therefore it can be also helpful for readers to get new and current ideas for their research.*

INTRODUCTION

Nanotechnology is a field of science that aims to process, measure, design, model, and organize substances at the atomic and molecular level and to provide new physical, chemical, and biological properties.[1] It is possible to reduce the amount of materials using nanofibers, and it is possible to improve mechanical strength and electrical conductance by increasing the conductive material ratio or its surface area/volume ratio. Research on nanofibers and nanotechnology has been rapidly increasing in recent years.[2]

Electrospinning is an important technique that provides high control and variety in nanofiber production. This method makes it possible to produce nano-sized fibers from polymers or other materials using a high electric field.[3] There are 4 main elements in the electrospinning method: a high-voltage power supply, a feed unit, a grounded collector, and a viscous polymer in liquid form.[4,5] The liquid polymer is fed through a capillary tube. A high-voltage power supply applies a high voltage to the polymer solution. A high voltage is applied to the polymer solution via a high-voltage power supply. As a result of this process, the surface of the solution droplet suspended on the tip of the needle is electrically charged. As the voltage value increases, the polymer droplet takes on the shape of a cone, and this shape is called a "Taylor cone."[6] When the voltage reaches the threshold value, the repulsive forces of the charges in the droplet

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overcome the surface tension forces, and a thin jet is seen at the tip of the Taylor cone. This jet elongates and thins due to the repulsion of the electrical charges on its surface and moves toward the grounded collector. During this movement, the polymer jet first follows a stable and then an unstable path.[7] As a result of the evaporation of the solvent in this process, an electrically charged polymeric fiber with nano-sized diameters is formed. The nanofibers formed are randomly positioned on the collector plate and form a surface.[8]

The electrospinning method allows the production of nanofibers and nanotubes with diameters ranging from 10 to 100 nm and provides the ability to control the pore size. In addition, it is possible to produce nanofibers with different structures by changing the method parameters.[9]

The success of the electrospinning process is directly dependent on the properties of the solution used. These properties include viscosity, surface tension, conductivity of the solution, and dielectric constant.[10] The molecular weight of the polymers in the solution affects the viscosity of the solution. Polymers with high molecular weights form high-viscosity solutions; therefore, solutions must have the appropriate molecular weight for the electrospinning process.

Too high a solution viscosity can cause the needle tip to clog, while too low a viscosity can cause the solution to drip from the needle tip due to gravity.[11] Low-viscosity solutions form a bead-like structure on the fibers. As viscosity increases, this bead-like structure disappears; this structure is undesirable. In addition, viscosity also affects the fiber diameter; as viscosity increases, the fiber diameter also increases.[12] For fiber production to take place with electrospinning, electrostatic forces must overcome surface tension forces. In regions where the solvent density is high, molecules come together under the effect of surface tension and cause bead formation. In high-viscosity solutions, the interaction between solvent molecules and polymer molecules prevents beading.[13] During electrospinning, the charges on the jet repel each other, causing elongation of the jet. Increasing the solution conductivity allows more charge to be carried on the jet.[14] A high dielectric constant of the solution prevents the formation of a beaded structure and allows the production of fibers with smaller diameters. The increase in the dielectric constant of the solvent also increases the instability of jet.[7] Rapid evaporation of the solvent and rapid phase separation of the jet as it becomes thinner are important factors. Experimental studies have shown that denser fibers are formed from solutions with high volatility.[15]

The electrospinning method allows the production of nanofibers containing other additives with diameters ranging from 10 to 100 nm by changing the properties of solution.[9] In this method, the properties of the solution, such as viscosity, surface tension, conductivity, and dielectric constant, determine the properties of the fibers obtained.[7] The use of high molecular weight polymers increases the viscosity of the solution, while solutions with low viscosity can cause the formation of bead-like structures.[12] The high voltage application during electrospinning processes allows electrostatic forces to overcome the surface tension, causing elongation on the jet.[16] When the dielectric constant of the solution is too high, beading decreases and thinner fibers can be obtained.[17] Other important parameters in the electrospinning process include solution flow rate, temperature, needle diameter, and the distance between the needle tip and the collector. Control of these parameters is critical in the production of nanofibers with the desired properties.[17] Carbon is one of the most important conductive materials found widely in nature. The arrangement of carbon atoms provides for the emergence of carbon forms with different physical properties, and these structures are known as carbon allotropes.[18] Carbon nanotubes (CNTs), which are versatile nanomaterials, are formed by wrapping graphene in a cylindrical shape and have properties superior to the hardness of diamond and the conductivity of graphite.[19] Carbon nanotubes have high mechanical strength and can return to their original form after applying forces. While the electrical conductivity of CNTs varies depending on their diameter, their thermal conductivity also shows an anisotropic character, meaning they have high thermal conductivity.[20] Their unique structural and physicochemical properties make them strong candidates for various biomedical applications. Especially in drug delivery systems, they enable the adsorption of drugs onto the surfaces or hollow cores of CNTs, thus protecting drugs from degradation, and the system provides controlled release.[21] Their large surface area allows the adsorption of therapeutic molecules and facilitates targeted drug delivery to specific cells or tissues. Furthermore, the ability of CNTs to penetrate cell membranes simplifies the delivery of drugs, genes, or imaging agents into cells and is particularly useful for treating diseases at the molecular and cellular levels.[22]

This study aims to demonstrate the feasibility of preparing composite nanofibers with carbon nanotubes by electrospinning and to provide a setting of the system parameters. One problem in electrospinning is the material's electroconductance; this study also aimed to enhance and optimize it by preparing a composite polycaprolactone (PCL) with CNTs. Carbon nanotubes are conductive materials, and preparing composite material allows changing or optimizing it using different ratios of materials. Carbon nanotubes are also adsorptive in nature and the loading capacity can be augmented according to the need.

MATERIAL AND METHODS

Dimethylformamide (DMF) was purchased from Merck Millipore. Polycaprolactone) was obtained from Sigma Aldrich Company. Carbon nanotube was purchased from Nanocyl (MWCNT). The nanofiber structure was prepared with the Inovenso brand Nanospinner Electrospinning

Device (NP24) (by Inovenso Ltd. Co., Cambridge, USA). Nicolet FT-IR Spectrometer 6700 (Thermo Fisher Scientific) was used to obtain information about the chemical bonds and functional groups of the nanofibers and materials.

Preparation of Electrospinning Solutions

Preparation of Polymer Solution: Polycaprolactone polymer and dimethylformamide were used as solvents to produce nanofibers. One gram PCL polymer was prepared by stirring in 10 g DMF solvent at 80°C for 2 hours at 1200 rpm speed on a magnetic stirrer. The mixing process was carried out until the polymer was completely dissolved in the solvent and a homogeneous solution was obtained.

Preparation of Carbon Nanotube Added Solution

After the prepared solution was completely mixed and cooled, 0.1% (w/v) CNT was added (PCL-CNT), and the mixing process was continued at room temperature for half an hour on a magnetic stirrer.

Production of Nanofibers by Electrospinning Method

Nanofiber production of the prepared PCL solution and PCL-CNT mixture was carried out with an electrospinning device of the brand Inovenso in the Laboratories of Inovenso Ltd. The electrospinning device consists of 3 main components: a feeding pump, a high-voltage source, and a collector plate on which the nanofibers are deposited. A rotating cylinder was used as the collecting surface, and a 20 mL syringe was used as the feeding unit (Figure 1).

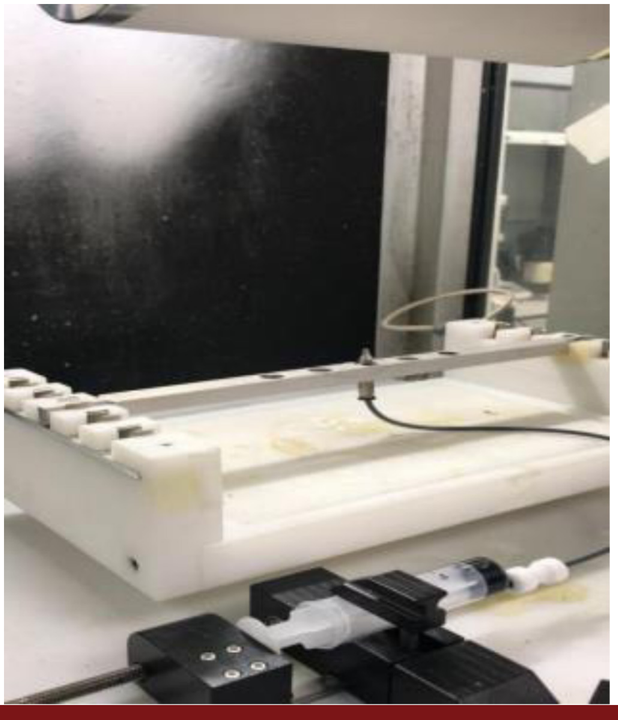

Figure 1. Electrospinning device used in the study.

Table 1. Electrospin Device Parameters of the Prepared Solutions

Sample	Feed Rate (mL/h)	Voltage (kV)	Distance (mm)	Nanofiber Formation
PCL/DMF	4	40	225	+
PCL/DMF/CNT (%0.1)	6	40	226	+

The CNT-added solution (PCL-CNT) was placed in an ultrasonic bath before spinning. Electrospinning parameters are given in Table 1. During production, the operation continued with voltage values that provided uninterrupted and optimum conditions.

In the study, a homogeneous solution was obtained after dissolving 10% PCL in DMF (PCL). This solution was used for comparison. The electrospinning device was set with a feed rate of 4 mL/h and a voltage of 40 kV for half an hour from a distance of 225 mm, resulting in a 4 µm thick whitish-colored nanofibrous surface (Figure 2).

Similarly, a 10% PCL-CNT solution with a 0.1% CNT additive was successfully prepared homogeneously, and a black-colored 4 µm thick nanofibrous surface was obtained as a result of spinning for half an hour from a distance of 226 mm under 40 kV voltage with a feed rate of 6 mL/h (Figure 3).

Atomic force microscope imaging was performed at Yeditepe Biocidal Laboratory (YUBAL) to determine the

Figure 2. Nanofibrous surface formed by spinning 10% PCL solution in DMF. Abbreviations: PCL, polycaprolactone; DMF, dimethylformamide.

Figure 3. CNT added nanofibrous surface.

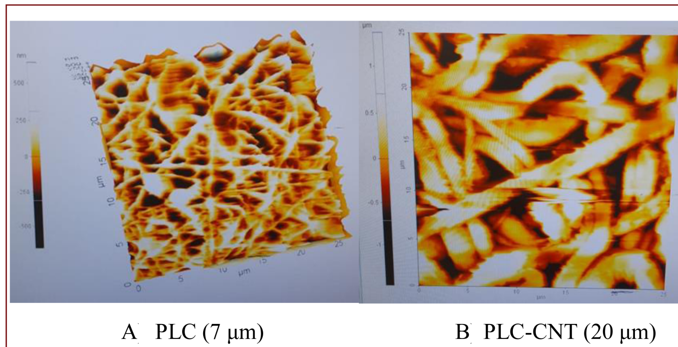

Figure 4. Three-dimensional AFM image of PCL and PCL-CNTs prepared by electrospinning. (A) PLC (7 µm). (B) PLC-CNT (20 µm).

surface topography of the prepared samples (Figure 4). Fourier transform infrared spectrophotometer measurements were performed (Figure 5).

DISCUSSION

In the study, nanofibers were obtained from carbon nanotubes. The feed rate was increased due to the increase in viscosity in the electrospinning of carbon nanotube-doped nanofibers. As a result of half an hour of electrospinning, a 20 µm thick nanofiber surface was obtained. Since nanofibers have a very high surface-to-weight ratio and exhibit properties that open up a wide range of special potential applications, interest in nanofibers has increased greatly in recent years.[23]

Fourier transform infrared spectrophotometer (FTIR) spectroscopy is a spectral method based on the vibrational and rotational motions of atoms and is widely used to detect internal molecular structures. Figure 5 presents the FTIR spectra of nanofibers composed of PCL polymer, DMF solvent, PCL-DMF, and PCL-CNT. The blue spectrum corresponds to DMF, with a prominent peak at 1650 cm^{-1} due to the C=O stretching vibration of the carbonyl group. The orange and gray spectra represent PCL polymer and PCL-DMF, respectively. These spectra exhibit characteristic PCL peaks: C=O stretching at 1720-1740 cm^{-1}, C–O stretching at 1240-1160 cm^{-1}, and C–H stretching at 2850-2960 cm^{-1}. The yellow spectrum represents PCL-CNT nanofibers. In addition to PCL peaks, a weak peak around 1580-1600 cm^{-1} suggests C=C bonds in CNTs. The coexistence of both PCL and CNT peaks in the PCL-CNT spectrum confirms the successful integration of these 2 materials. The

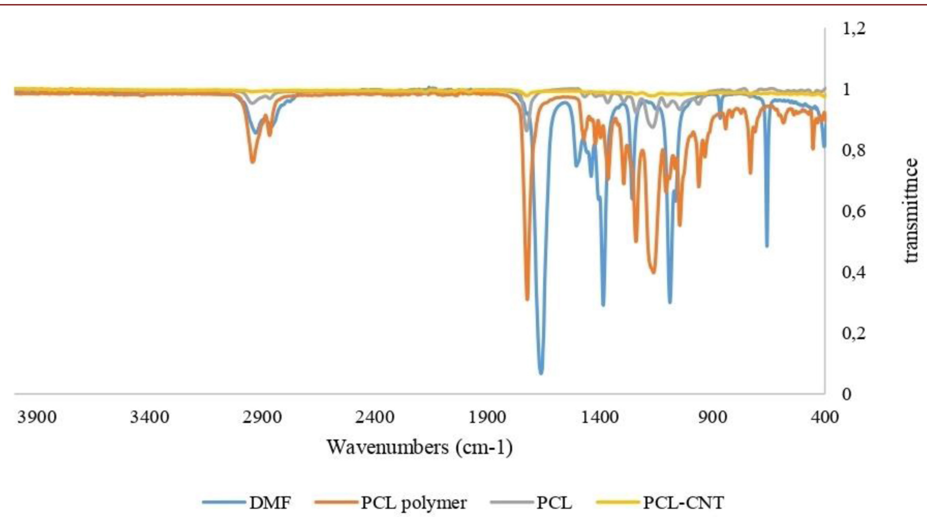

Figure 5. FTIR spectra of the PCL (polymer), PCL, and PCL-CNTs prepared by electrospinning.

absence of new peaks or shifts indicates minimal molecular interactions.

In polymer solution preparation, PCL polymer has been frequently used in the electrospinning method due to its unique mechanical properties, miscibility, biodegradability, biocompatibility, etc.[24] However, modified solvents or cosolvents can also be also used.[25]

In our study, DMF was used as a cosolvent, and a 1%-50% PCL solution was prepared in DMF (PCL) as reported in the literature.[26] However, in our study, it was decided to use the ratio of 10% of the PCL solution as it gave good results. Then, the CNTs of this content were added. Mixing modified structures with PCL solution is a frequently used method in the literature.[27] Boron nitride nanotubes (BNTs) can be given as another example for the preparation of composite film.[28] In addition, when BNTs or CNTs are also used for preparing a composite film, some problems can occur, such as dispersibility in water/most organic solvents or low crystallization.[29] In the literature, PCL-CNT ratios vary between 0.25% and 1%.[30,31]

CONCLUSION

In this study, PCL was prepared with CNTs (PCL-CNT), and various ratios were tried. No study is found in the literature that uses multiwall CNTs at a 0.1% concentration. Although there are some studies in the literature in which nanofibers are produced with various polymers using CNTs and their properties are examined, no study was found with PCL-CNT. Therefore, all findings support the novelty of the present study. This study is the first to be conducted, will contribute to the literature, and will guide future studies.

Availability of Data and Materials: The data that support the findings of this study are available on request from the corresponding author.

Ethics Committee Approval: No ethics committee approval is required as the study did not use any human or animal material.

Informed Consent: No informed consent is required as the study did not use any human or animal material.

Peer-review: Externally peer-reviewed.

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