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Preparation of Cellulose-based Nanofibers Using Electrospinning

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1. Introduction

Eelctrospinning is a straightforward method to prepare fibers with diameters as small as several tens of nanometers (Doshi & Reneker, 1995). In eclectrospinning, a high electrostatic voltage is imposed on a drop of polymer solution held by its surface tension at the end of a capillary. The surface of the liquid is distorted into a conical shape known as the Taylor cone. Once the voltage exceeds a critical value, the electrostatic force overcomes the solution surface tension and a stable liquid jet is ejected from the cone tip. Solvent evaporates as the jet travels through the air, leaving behind ultrafine polymeric fibers collected on an electrically grounded target (Fong et al., 1999, 2002; Shin et al., 2001). Electrospun mats have a larger specific surface area and small pore size compared to commercial non-woven fabrics. They are of interest in a wide variety of applications including semi-permeable membranes, tissue engineering scaffolds and drug delivery systems (Tsai et al., 2002; Gibson et al., 2001; Kenawy et al., 2002; Luu et al., 2003).

Recently, electrospun nanofibers (NFs) based on cellulose and its derivatives have been studied as potential candidates for applications within the field of pharmaceuticals. For instance, several reports deal with the investigation of electrospun fiber mats as delivery vehicles, showing dosage forms with useful and controllable dissolution properties. This interest in cellulose-based NFs is primarily driven by its environmental value as a biomaterial. The cellulose is an abundant and renewable resource found in most parts of the world, which makes it a cheap raw material for various applications (Zeng et al., 2003; Jiang et al., 2004; Verreck et al., 2003; Liu & Hsieh, 2002). However, little research has been done on the use of cellulose and cellulose derivatives as a raw material within electrospinning. The complications involved in electrospinning of cellulose are mainly due to the many difficulties ascribed to the material, one being its reluctance to interact with conventional solvents. Therefore, the choice of solvent systems is very important.

Ethyl-cellulose (EC) is a kind of cellulose ether, and it shows a non-biodegradable and biocompatible polymer. EC is one of the extensively studied encapsulating materials for the controlled release of pharmaceuticals (Prasertmanakit et al., 2009). The film made from EC has quite good permeability, it has been widely used industrial air filter (Park et al., 2007).

Hydroxypropyl methylcellulose (HPMC) is frequently used as the basis for sustained release hydrophilic matrix tablets (Ford, 1999). HPMC backbone is composed of glucose

units linked by β-1,4-glycosidic bonds (Zhao et al., 2009; Péreza et al., 2008). The hydrophobic (methyl) and hydrophilic (hydropropyl) groups are distributed along the cellulose backbone. It can be lower the surface tension when adsorbed at fluid interface (Zhao et al., 2009; Kulicke et al., 1998). The HPMC molecule is rod-like and has many hydroxyl groups to participate in intermolecular hydrogen bonds, which allows the cellulose chains to form bundles or fibrils (Zhao et al., 2009; Péreza et al., 2008).

However, this chapter deals with the electrospinning of cellulose derivatives such as EC and HPMC. The fiber morphology and influence of experimental parameters including the solution concentration, flow rate and electric voltage and pattern of the derivatives on the eclectrospinning process were discussed.
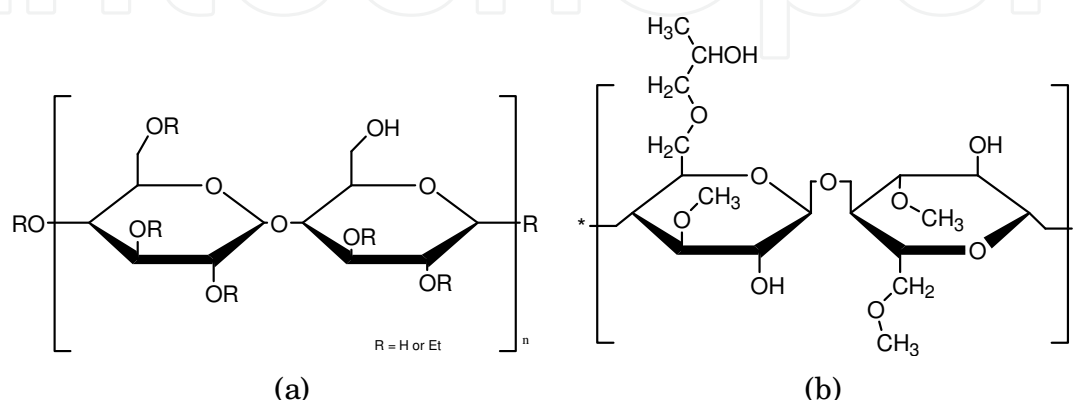

Fig. 1. The structure of (a) ethylcellulose (EC) and (b) hydroxypropyl methylcellulose (HPMC).

2. Experimental

2.1 Materials

EC (ethoxy content, 48%; viscosity, 46 cps) and HPMC (M_n, 120000; D.S. (methoxy), 1.10-1.60; M.S. (propylene oxide), 0.10-0.30; viscosity, 100000cps 2wt% in H_2O at 20ºC) were obtained from Aldrich Chemical and used without further purification. 2,2,2-Trifluoroethanol (Aldrich, USA) was used as a solvent and used as received from commercial supplier.

2.2 Preparation and characterization of cellulose derivatives solutions

EC and HPMC solutions were prepared by dissolving a measured amount of EC and HPMC at room temperature. Four concentrations were prepared about EC: 6, 8, 10 and 12 wt%. Two concentrations were prepared about HPMC: 0.5, 1.0 wt%. These solutions were characterized for their viscosity using a Brookfield DV-II viscometer.

2.3 Electrospinning of cellulose derivatives solutions

In the electrospinning process, a high electric potential was applied to a droplet of EC solution at the tip (ID 0.15 mm) of a syringe needle. The electrospun EC NFs were collected on a target drum which was placed at a distance of 5 cm from the syringe tip. A voltage of 5-28 keV was applied to the collecting target by a high voltage power supply. The flow rate of polymer solution was 0.001-0.01 ml/ min. The HPMC NFs were collected on a target plate which was placed at a distance of 5-15 cm from the syringe tip. A voltage of 10, 15 keV was

applied to the collecting target by a high voltage power supply. The flow rate of polymer solution was 0.05 ml/ min. Fig. 2 shows the photograph of electrospinning apparatus.

Fig. 2. The photograph of electrospinning apparatus.

2.4 Characterization of cellulose NFs

The morphological changes of the samples were observed using a scanning electron microscope (SEM, JMS6390 JEOL Company). Specimen surfaces were coated with a thin layer of gold palladium alloy by sputtering to provide a conductive surface. The fiber diameter of the electrospun fibers was measured by Adobe Photoshop 5.0 software from the SEM pictures in original magnification of 10k X.

Polymers	Concentration [wt%]	Electric voltage [keV]	Flow rate [ml/ min]	Tip-target distance [cm]	Note
EC	6	10	0.001	5	
	8	15	0.003	7	
	10	20	0.005	9	
	12	25	0.01	11	
HPMC	0.5	10	0.05	5	
	1.0	15		10	
	-	-		15	

Table 1. Electrospinning condition of the cellulose solutions

3. Result and discussion

3.1 Effect of the solution concentration

The viscosity of the polymer solutions are summarized in Table 1. Increasing the concentration of the cellulose solution increased. Viscosity plays an important role in determining the rage of concentrations from which continuous fibers can be obtained by electrospinning. At low viscosity, surface tension is the dominant effect on fiber morphology. Below a certain concentration, drops will form instead of fibers. At high

concentrations, processing will be prohibited by an inability to control and maintain the flow of a polymer solution to the tip of the needle and by the cohesive nature of the high viscosity. As shown in Fig. 3, with increasing concentration, the morphology was changed from beaded fiber to uniform fiber structure and the fiber diameter was also increased gradually. At 6wt%, a large amount of smooth fibers and beaded fibers were obtained. (With increasing the concentration of the solution to 8 wt%, very small amount of beads was present.) With further increasing concentration of the solution to 10 wt%, only smooth, bead-less fibers were obtained. At 12 wt%, the average fiber diameter was much larger than those of fibers spun at lower concentrations.

Polymers	Concentration [wt%]	Viscosity [cP]	note
EC	6	461	
	8	1245	
	10	2918	
	12	6347	
HPMC	0.5	1284	
	1.0	8614	

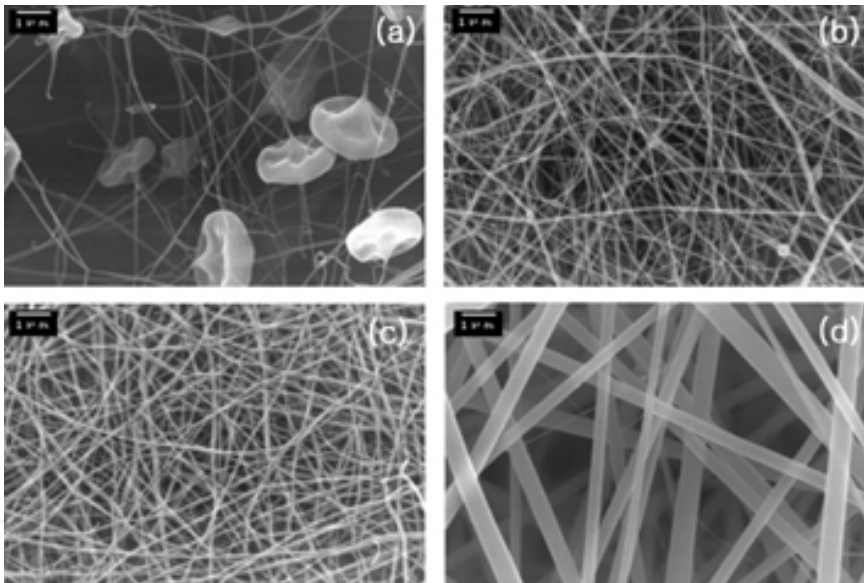Table 2. Viscosity of polymer solutions as a function of concentration.

Fig. 3. SEM micrographs of electrospun fibers from EC solution with different solution concentration (voltage=10 keV, flow rate=0.005 ml/ min). EC concentration; (a) 6 wt%; (b) 8 wt%; (c) 10 wt%; (d) 12 wt%.

The morphologies of HPMC NFs in Fig. 4. (??) No big change in the morphology of fibers as a function of concentration. At 0.5wt%, a large amount of smooth fibers and thick fibers was obtained. Increasing the concentration of the solution to 1.0 wt%, only smooth, bead-less fibers were obtained. The average fiber diameter was investigated 155 and 162nm, respectively.

In electrospinning, the coiled macromolecules in solution were transformed by the elongational flow of the jet into oriented entangled networks that persist with fiber solidification. Below this concentration, chain entanglements were insufficient to stabilize the jet and the contraction of the diameter of the jet driven by surface tension caused the

solution to form beads or beaded fibers. At high concentration, viscoelastic force which resisted rapid changes in fiber shape resulted in uniform fiber formation. However, it was impossible to electrospin if the solution concentration or the corresponding viscosity was too high due to the difficulty in liquid jet formation.
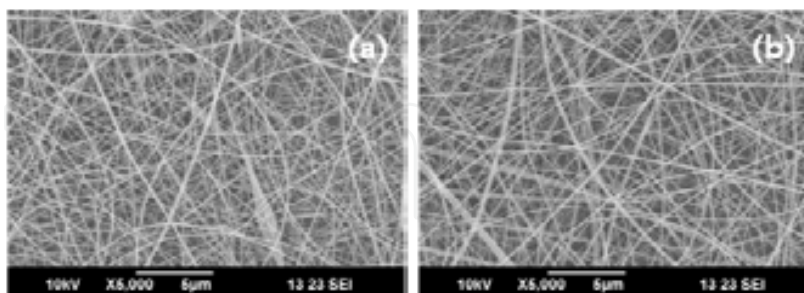

Fig. 4. SEM micrographs of electrospun fibers from HPMC solution with different solution concentration (voltage=15 keV, flow rate=0.05 ml/ min). HPMC concentration; (a) 0.5 wt%; (b) 1.0 wt%.

3.2 Effect of the electrospinning flow rate

The morphological structure can be changed by changing the solution flow rate as shown in Fig. 5. At the flow rate of 0.001 ml/ min, uniform fiber structure was observed. But increasing flow rate, the average fiber diameter was much larger than those of fibers spun at lower flow rate. At the flow rate of 0.01 ml/ min, a considerable amount of thick fibers with diameters above 1mm were found. When the flow rate exceeded a critical value, the delivery rate of the solution jet to the capillary tip exceeded the rate at which the solution was removed from the tip by the electric forces. This shift in the mass-balance resulted in sustained but unstable jet and fibers with broad distribution in the fiber diameter were formed.
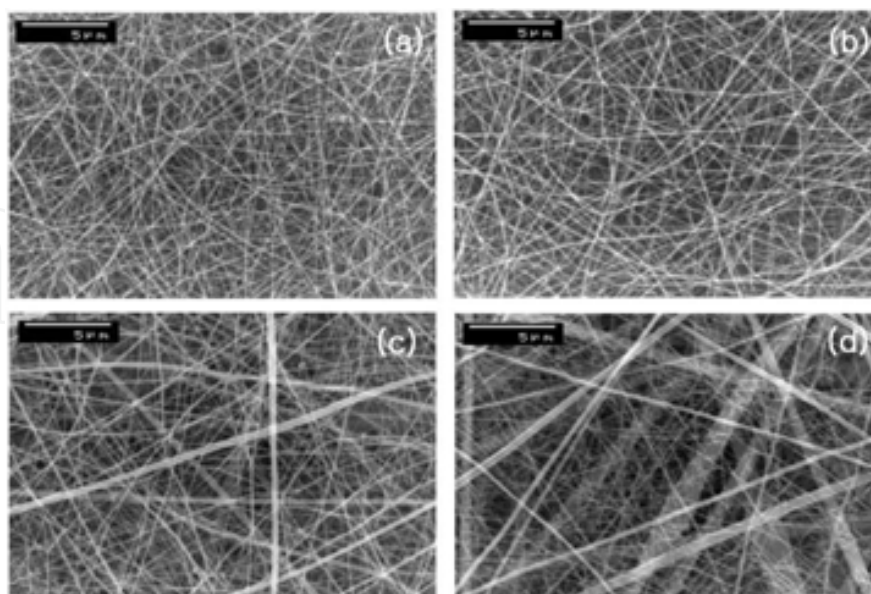

Fig. 5. Effect of flow rate of 10 wt% EC solution on fiber morphology (voltage=15 kV). Flow rate: (a) 0.001 ml/ min; (b) 0.003 ml/ min; (c) 0.005 ml/ min; (d) 0.01 ml/ min.

3.3 Effect of the electric voltage

A series of experiments were carried out when the applied voltage was varied from 5 to 28 keV. The results are shown in Fig. 6 and Fig. 7. Weaker voltage, such as 5 keV, was not strong enough to overcome the surface tension and viscoelastic forces of the polymer solution, but at higher voltages at this distance, electrical discharge would occur. There was a slight decrease in average fiber diameter with increasing applied electric field. A considerable amount of thin fibers with diameters below 100 nm were found when the applied voltage above 20 keV. Increasing the applied voltage, i.e., increasing field strength will increase the electrostatic repulsion force on the fluid jet which favors the thinner fiber formation. On the other hand, the solution will be removed from the capillary tip more quickly as jet is ejected from Taylor cone. This results in the increase of the fiber diameter. Corona discharge was observed at voltage above 28 keV, making electrospinning impossible.
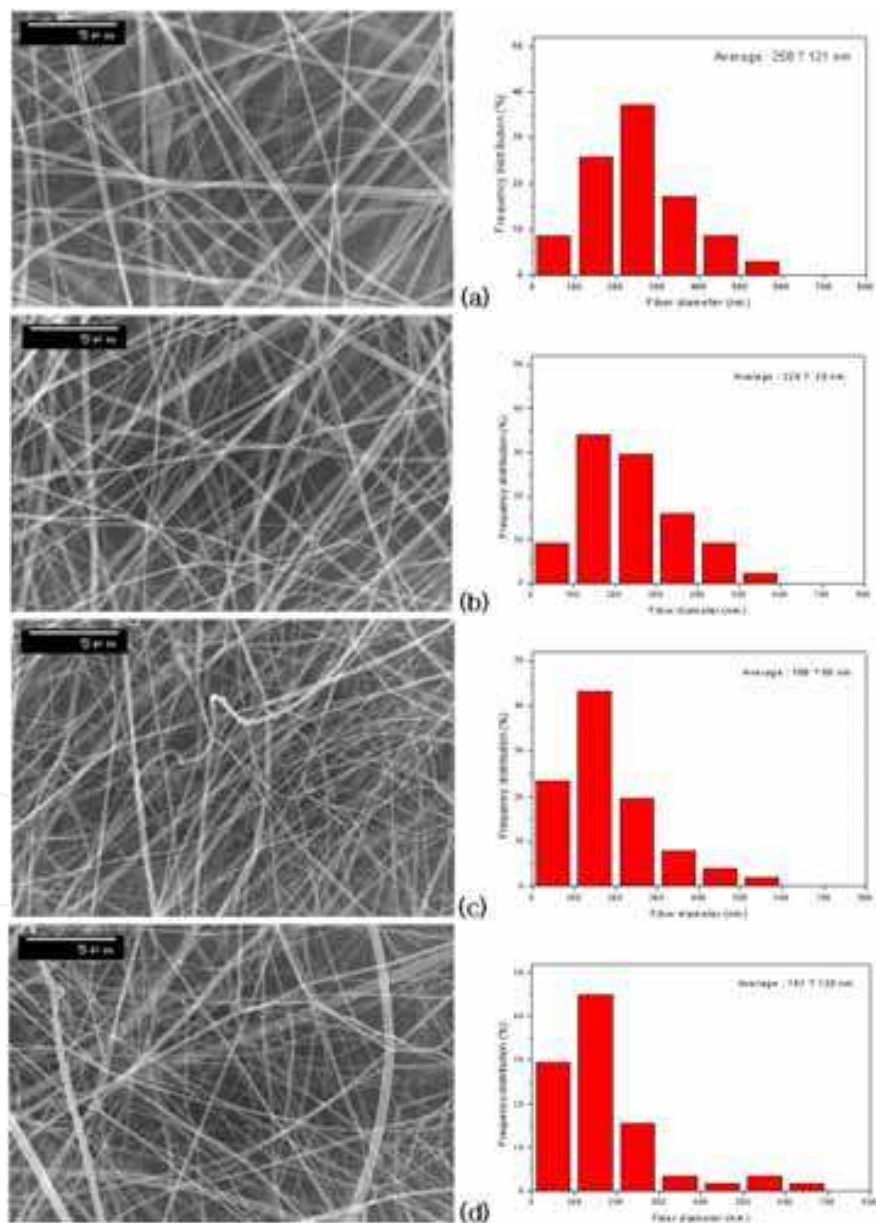

Fig. 6. Effect of electric voltage on EC fiber morphology (solution concentration=10 wt%, flow rate=0.005 ml/ min). Voltage: (a) 10 keV; (b) 15 keV; (c) 20 keV; (d) 25 keV.

The diameter of HPMC NFs was measured (??) a narrow distribution when the electric voltage decreased. It was found that the fibers had an average diameter of 129nm at a voltage of 10keV and an average diameter of 140nm at a voltage of 15keV. Electrospun NFs of HPMC showed similar results to EC NFs
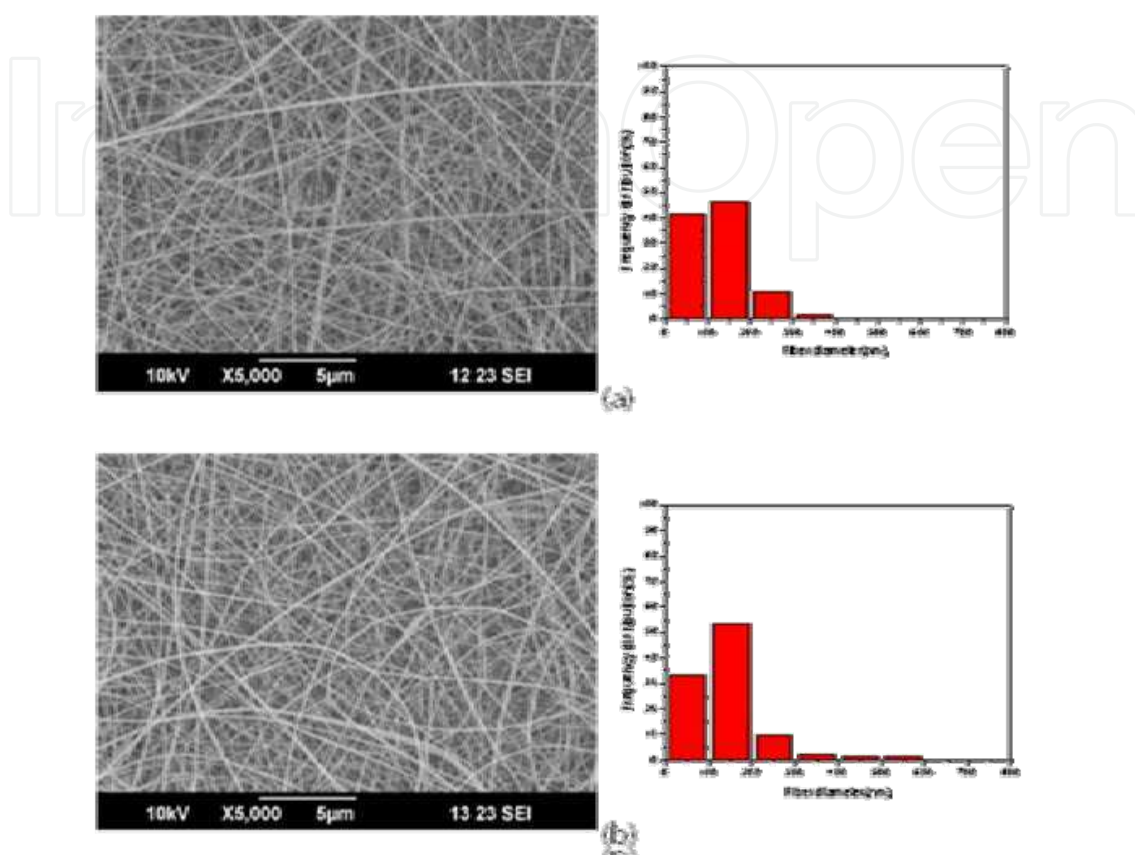

Fig. 7. Effect of electric voltage on HPMC fiber morphology (solution concentration=1.0 wt%, flow rate=0.05 ml/ min). Voltage: (a) 10 keV; (b) 15 keV.

3.4 Effect of the needle tip-target distance

Fig. 8 shows that NFs formed with decreasing tip-target distance of EC. As tip-target distance of NFs was increased, the diameter of NFs. The NFs had non-uniform diameters. It may be assumed that the lower electric strength solvent from evaporating. However, (??we were observed that formation of HPMC NFs regardless of tip-target distance. ??) The most uniform NFs derived with our experimental conditions were afforded at 5cm of tip-target distance. Increasing diameter of NFs at 10cm and decreasing diameter of NFs at 15cm (??).

4. Conclusions

Submicron EC and HPMC fibers have been successfully prepared by electrospinning of polymer solutions. The morphology of the fibers was strongly affected by the parameters such as polymer concentration, tip-target distance, solution flow rate, and applied voltage. At below 6 wt% EC solutions, electrospinning was not enhanced due to the low viscosity. (the concentration of EC solution,) the morphology was changed from beaded fiber
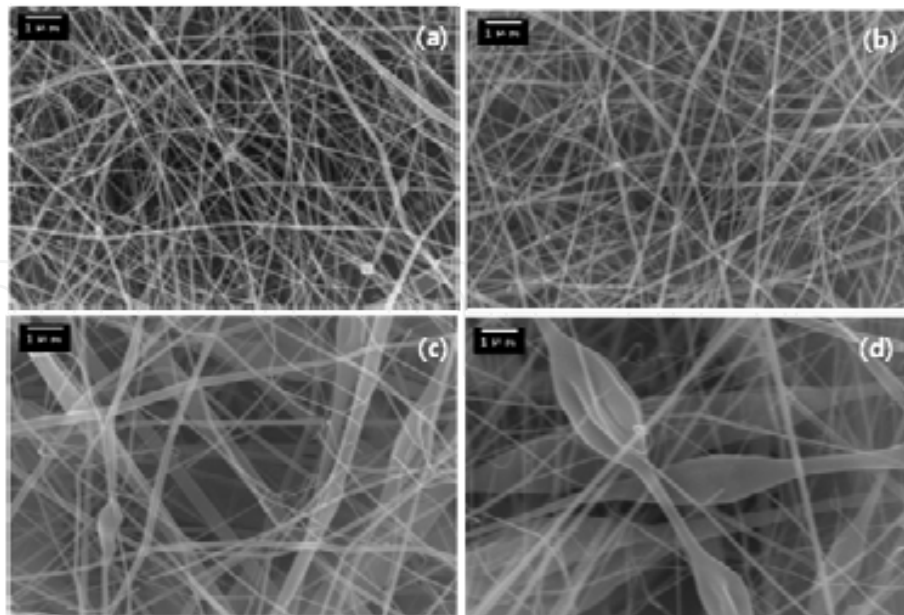
Fig. 8. Effect of needle tip-target distance of EC NFs (solution concentration, 10wt%; electric voltage, 15 keV; flow rate, 0.005 ml/ min). (a) 5 cm, (b) 7 cm, (c) 9 cm, (d) 11 cm.
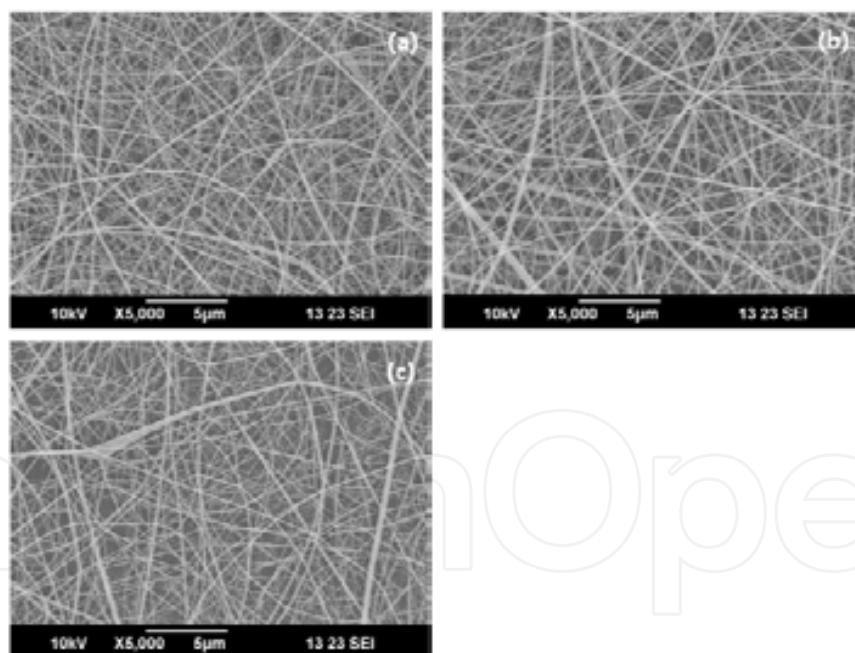

Fig. 9. Effect of needle tip-target distance of HPMC NFs (solution concentration, 1.0wt%; electric voltage, 15 keV; flow rate, 0.05 ml/ min). (a) 5 cm, (b) 10 cm, (c) 15 cm.

to uniform fiber structure and the fiber diameter was also increased. There was an increase in fiber diameter and fiber distribution with increasing solution flow rate, while there was a slightly decrease in average fiber diameter with increasing applied electric field. The HPMC NFs are feasible for use as wound healing and drug delivery systems for biomedical applications.

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Nanofibers

Edited by Ashok Kumar

"There's Plenty of Room at the Bottom" this was the title of the lecture Prof. Richard Feynman delivered at California Institute of Technology on December 29, 1959 at the American Physical Society meeting. He considered the possibility to manipulate matter on an atomic scale. Indeed, the design and controllable synthesis of nanomaterials have attracted much attention because of their distinctive geometries and novel physical and chemical properties. For the last two decades nano-scaled materials in the form of nanofibers, nanoparticles, nanotubes, nanoclays, nanorods, nanodisks, nanoribbons, nanowhiskers etc. have been investigated with increased interest due to their enormous advantages, such as large surface area and active surface sites. Among all nanostructures, nanofibers have attracted tremendous interest in nanotechnology and biomedical engineering owing to the ease of controllable production processes, low pore size and superior mechanical properties for a range of applications in diverse areas such as catalysis, sensors, medicine, pharmacy, drug delivery, tissue engineering, filtration, textile, adhesive, aerospace, capacitors, transistors, battery separators, energy storage, fuel cells, information technology, photonic structures and flat panel displays, just to mention a few. Nanofibers are continuous filaments of generally less than about 1000 nm diameters. Nanofibers of a variety of cellulose and non-cellulose based materials can be produced by a variety of techniques such as phase separation, self assembly, drawing, melt fibrillation, template synthesis, electro-spinning, and solution spinning. They reduce the handling problems mostly associated with the nanoparticles. Nanoparticles can agglomerate and form clusters, whereas nanofibers form a mesh that stays intact even after regeneration. The present book is a result of contributions of experts from international scientific community working in different areas and types of nanofibers. The book thoroughly covers latest topics on different varieties of nanofibers. It provides an up-to-date insightful coverage to the synthesis, characterization, functional properties and potential device applications of nanofibers in specialized areas. We hope that this book will prove to be timely and thought provoking and will serve as a valuable reference for researchers working in different areas of nanofibers. Special thanks goes to the authors for their valuable contributions.

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