Nanotechnology Science and Technology

Nanofibers and Nanotechnology Research Advances

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Editor

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NANOFIBERS AND NANOTECHNOLOGY RESEARCH ADVANCES

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PREFACE

Nanotechnology is revolutionizing the world of materials. The research and development of nanofibers has gained much prominence in recent years due to the heightened awareness of its potential applications in the medical, engineering and defense fields. Among the most successful methods for producing nanofibers is the electrospinning process. Electrospinning introduces a new level of versatility and broader range of materials into the micro/nanofiber range. An old technology, electrospinning has been rediscovered, refined, and expanded into non-textile applications. Electrospinning has the unique ability to produce ultrathin fibers from a rich variety of materials that include polymers, inorganic or organic compounds and blends. With the enormous increase of research interest in electrospun nanofibers, there is a strong need for a comprehensive review of electrospinning in a systematic fashion. With the emergence of nanotechnology, researchers become more interested in studying the unique properties of nanoscale materials. Electrospinning, an electrostatic fiber fabrication technique has evinced more interest and attention in recent years due to its versatility and potential for applications in diverse fields. The notable applications include in tissue engineering, biosensors, filtration, wound dressings, drug delivery, and enzyme immobilization. The nanoscale fibers are generated by the application of strong electric field on polymer solution or melt. The non-wovens nanofibrous mats produced by this technique mimics extracellular matrix components much closely as compared to the conventional techniques. The sub-micron range spun fibers produced by this process, offer various advantages like high surface area to volume ratio, tunable porosity and the ability to manipulate nanofiber composition in order to get desired properties and function. Over the years, more than 200 polymers have been electrospun for various applications and the number is still increasing gradually with time.

This book represents the results of a first step toward integration, by bringing together an impressive interdisciplinary cross-section of researchers to discuss the practical problems involved in developing nanotechnology, as well as to chart a course for future development. This volume is basically a transcription of the meeting with a significant amount of work by the editors and authors put into faithfully reproducing the figures and meeting discussion. Still, this book serves as a highly accessible introduction to an interesting and expanding field. This book presents some fascinating phenomena associated with the remarkable features of nanofibers in electrospinning processes and new progress in applications of electrospun nanofibers as well.

This new book offers an overview of structure–property relationships, synthesis and purification, and potential applications of electrospun nanofibers. The collection of topics in this book aims to reflect the diversity of recent advances in electrospun nanofibers with a broad perspective which may be useful for scientists as well as for graduate students and engineers.

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Chapter 1

MULTILAYER LAMINATED NANOFIBERS

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ABSTRACT

The use of fine fiber has become an important design tool for filter media. Nanofibers based filter media have some advantages as lower energy consumption, longer filter life, high filtration capacity, easier maintenance, low weight rather than other filter media. The nanofibers based filter media made up of fibers of diameter ranging from 100 to 1000 nm can be conveniently produce by electrospinning technique. Common filter media have been prepared with a layer of fine fiber on typically formed the upstream or intake side of the media structure. The fine fiber increases the efficiency of filtration by trapping small particles which increases the overall particulate filtration efficiency of the structure. Improved fine fiber structures have been developed in this study in which a controlled amount of fine fiber is placed on both sides of the media to result in an improvement in filter efficiency and a substantial improvement in lifetime. In the first part of this study, the production of electrospun nanofibers investigated. In the second part, a different case study presented to show how they can be laminated for application as filter media.

Response surface methodology (RSM) was used to obtain a quantitative relationship between selected electrospinning parameters and average fiber diameter and its distribution.

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1. Introduction

Polymeric nanofibers can be made using the electrospinning process, has already been described in the literature [1-10]. Electrospinning (Figure 1) uses a high electric field to draw a polymer solution from tip of a capillary toward a collector [16-20]. A voltage is applied to the polymer solution, which causes a jet of the solution to be drawn toward a grounded collector. The fine jets dry to form polymeric fibers, which can be collected as a web [11-17].

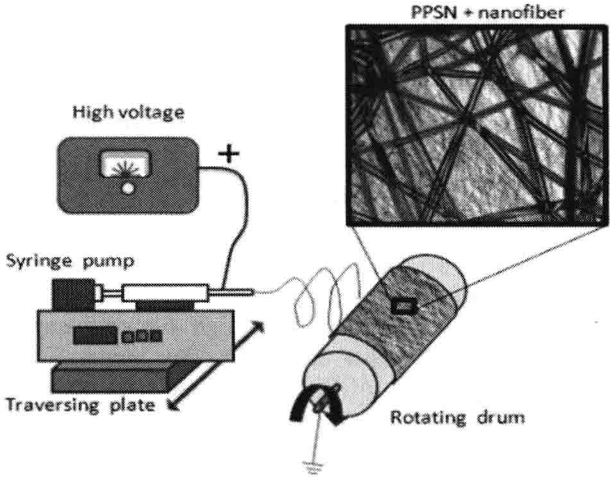

Figure 1. Electrospinning setup.

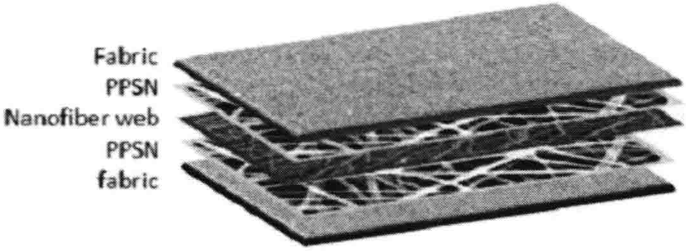

Figure 2. Multilayer fabric components.

In the non woven industry on of the fastest growing segments is in filtration applications. Traditionally wet-laid, melt blown and spun non woven articles, containing micron size fibers are most popular for these applications because of the low cost, easy process ability and good filtration efficiency. Their applications in filtration can be divided into two major areas: air filtration and liquid filtration (Figure 2).

Another type of electrospinning equipment (Figure 2) also used a variable high voltage power supply from Gamma High Voltage Research (USA). The applied voltage can be varied from 1- 30 kV. A 5-ml syringe was used and positive potential was applied to the polymer blend solution by attaching the electrode directly to the outside of the hypodermic needle with internal diameter of 0.3 mm. The collector screen was a 20×20 cm aluminum foil, which was placed 10 cm horizontally from the tip of the needle. The electrode of opposite polarity was attached to the collector. A metering syringe pump from New Era pump systems Inc. (USA) was used. It was responsible for supplying polymer solution with a constant rate of 20 μl/min.

Electrospinning was done in a temperature-controlled chamber and temperature of electrospinning environment was adjusted on variable temperatures. Schematic diagram of the electrospinning apparatus was shown in Figure 3.

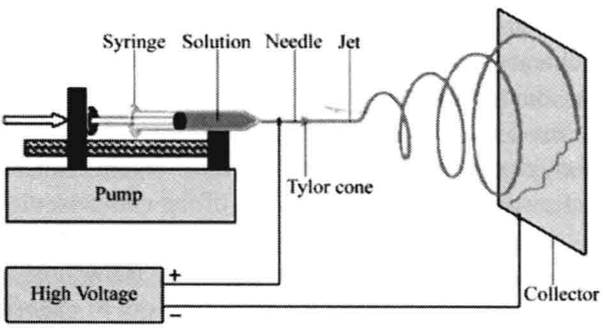

Figure 3. Schematic diagram of general type of electrospinning apparatus.

Elecrospinning is a process that produces continuous polymer fibers with diameter in the submicron range. In the electrospinnig process the electric body force act on element of charged fluid. Electrospinning has emerged as a specialized processing technique for the formation of sub-micron fibers (typically between 100 nm and 1 μm in diameter), with high specific surface areas. Due to their high specific surface area, high porosity, and small pore size, the unique fibers have been suggested for excellent condidate for use in filtration [18-22].

Air and water are the bulk transportation medium for transmission of particulate contaminants. The contaminants during air filtration are complex mixture of particles. The most of them are usually smaller than 1000 μm in diameter chemical and biological aerosols are frequently in range of 1-10 μm. The particulate matters may carry some gaseous contaminants. In water filtration removal of particulate and biological contaminants is an important step. Nowadays, the filtration industry is looking for energy efficient high performance filters for filtration of particles smaller than 0.3 μm and adsorbed toxic gases [23-30].

Nanofibrous media have low basis weight, high permeability, and small pore size that make them appropriate for a wide range of filtration applications. In addition, nanofiber membrane offers unique properties like high specific surface area (ranging from 1to 35m2/g depending on the diameter of fibers), good interconnectivity of pores and potential to incorporate active chemistry or functionality on nanoscale. In our study, to prepare the filters, a flow rate 1 μl/h for solution was selected and the fibers were collected on an aluminum-covered rotating drum (with speed 9 m/min) which was previously covered with a polypropylene spun-bond nonwoven (PPSN) substrate of 28cm× 28cm dimensions; 0.19 mm thickness; 25 g/m2 weight; 824 $cm^3/s/cm^2$ air permeability and 140°C melting point (Figure 2).

Structure characteristics of nanofiberous filtering media such as layer thickness, fiber diameter, nano fiber orientation, representative pore size, porosity dictate the filter properties and quality.

Clearly, the properties of a nanofiberious media will depend on its structural charcteristics as well as the nature of the component fibers.thus it is desirable to understand and determine these charactristics. In this work tryed to identify the orientation distribution function (ODF) of nanofibers in nanofilter , the fiber thickness distribution and porosity of nanofiberious media by using image processing algoritms.

Effect of Systematic Parameters on Electrospun Nanofibers

It has been found that morphology such as fiber diameter and its uniformity of the electrospun nano fibers are dependent on many processing parameters. These parameters can be divided into three main groups: a) solution properties, b) processing conditions, c) ambient conditions. Each of the parameters has been found to affect the morphology of the electrospun fibers.

Solution Properties

Parameters such as viscosity of solution, solution concentration, molecular weight of solution, electrical conductivity, elasticity and surface tension, have important effect on morphology of nanofibers.

Viscosity

The viscosity range of a different nanofiber solution which is spinnable is different. One of the most significant parameters influencing the fiber diameter is the solution viscosity. A higher viscosity results in a large fiber diameter. Beads and beaded fibers are less likely to be formed for the more viscous solutions. The diameter of the beads become bigger and the average distance between beads on the fibers longer as the viscosity increases.

Solution Concentration

In electrospinning process, for fiber formation to occur, a minimum solution concentration is required. As the solution concentration increase, a mixture of beads and fibers is obtained. The shape of the beads changes from spherical to spindle-like when the solution concentration varies from low to high levels. It should be noted that the fiber diameter increases with increasing solution concentration because the higher viscosity resistance. Nevertheless, at higher concentration, viscoelastic force which usually resists rapid changes in fiber shape may result in uniform fiber formation. However, it is impossible to electrospin if the solution concentration or the corresponding viscosity become too high due to the difficulty in liquid jet formation.

Molecular Weight

Molecular weight also has a significant effect on the rheological and electrical properties such as viscosity, surface tension, conductivity and dielectric strength. It has been observed that too low molecular weight solution tend to form beads rather than fibers and high molecular weight nanofiber solution give fibers with larger average diameter.

Surface Tension

The surface tension of a liquid is often defined as the force acting at right angles to any line of unit length on the liquid surface. By reducing surface tension of a nanofiber solution, fibers could be obtained without beads. The surface tension seems more likely to be a function of solvent compositions, but is negligibly dependent on the solution concentration. Different solvents may contribute different surface tensions. However, not necessarily a lower surface tension of a solvent will always be more suitable for electrospinning. Generally, surface tension determines the upper and lower boundaries of electrospinning window if all other variables are held constant. The formation of droplets, bead and fibers can be driven by the surface tension of solution and lower surface tension of the spinning solution helps electrospinning to occur at lower electric field.

Solution Conductivity

There is a significant drop in the diameter of the electrospun nanofibers when the electrical conductivity of the solution increases. Beads may also be observed due to low conductivity of the solution, which results in insufficient elongation of a jet by electrical force to produce uniform fiber. In general, electrospun nanofibers with the smallest fiber diameter can be obtained with the highest electrical conductivity. This interprets that the drop in the size of the fibers is due to the increased electrical conductivity.

Applied Voltage

In the case of electrospinning, the electric current due to the ionic conduction of charge in the nanofiber solution is usually assumed small enough to be negligible. The only mechanism of charge transport is the flow of solution from the tip to the target. Thus, an increase in the electrospinning current generally reflects an increase in the mass flow rate from the capillary tip to the grounded target when all other variables (conductivity, dielectric constant, and flow rate of solution to the capillary tip) are held constant.Increasing the applied voltage (*i.e.,* increasing the electric field strength) will increase the electrostatic repulsive 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.

Feed Rate

The morphological structure can be slightly changed by changing the solution flow rate. When the flow rate exceeded a critical value, the delivery rate of the solution jet to the capillary tip exceeds 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 big beads formation.

In the first part of this study, the production of electrospun nanofibers investigated. In another part, a different case study presented to show how nanofibers can be laminated for application in filter media.

2. Experiments: Case 1-Production of Nanofibers

2.1. Preparation of Regenerated SF Solution

Raw silk fibers (B.mori cocoons were obtained from domestic producer, Abrisham Guilan Co., IRAN) were degummed with 2 gr/L Na_2CO_3 solution and 10 gr/L anionic detergent at 100 ° C for 1 h and then rinsed with warm distilled water. Degummed silk (SF) was dissolved in a ternary solvent system of $CaCl_2/CH_3CH_2OH/H_2O$ (1:2:8 in molar ratio) at 70 ° C for 6 h. After dialysis with cellulose tubular membrane (Bialysis Tubing D9527 Sigma) in H_2O for 3 days, the SF solution was filtered and lyophilized to obtain the regenerated SF sponges.

2.2. Preparation of the Spinning Solution

SF solutions were prepared by dissolving the regenerated SF sponges in 98% formic acid for 30 min. Concentrations of SF solutions for electrospinning was in the range from 8% to 14% by weight.

2.3. Electrospinning

In the electrospinning process, a high electric potential (Gamma High voltage) was applied to a droplet of SF solution at the tip (0.35 mm inner diameter) of a syringe needle, The electrospun nanofibers were collected on a target plate which was placed at a distance of 10 cm from the syringe tip. The syringe tip and the target plate were enclosed in a chamber for adjusting and controlling the temperature. Schematic diagram of the electrospinning apparatus is shown in Figure 2. The processing temperature was adjusted at 25, 50 and 75 °C. A high voltage in the range from 10 kV to 20 kV was applied to the droplet of SF solution.

2.4. Characterization

Optical microscope (Nikon Microphot-FXA) was used to investigate the macroscopic morphology of electrospun SF fibers. For better resolving power, morphology, surface texture and dimensions of the gold-sputtered electrospun nanofibers were determined using a Philips XL-30 scanning electron microscope. A measurement of about 100 random fibers was used to determine average fiber diameter and their distribution.

3. Experiment: Case 2-Production of Laminated Composites

Polyacrylonitrile (PAN) of 70,000 g/mol molecular weight from Polyacryl Co. (Isfehan, Iran) has been used with Dimethylformamide (DMF) from Merck, to form a polymer solution 12% w/w after stirring for 5 h and staying overnight under room temperature. The yellow and ripen solution was inserted into a plastic syringe with a stainless steel nozzle 0.4 mm in inner diameter