

POLYACRYLONITRILE-BASED CARBON NANOFIBERS PREPARED BY ELECTROSPINNING

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ABSTRACT

Electrospinning is a cost effective method to produce novel fibers whose diameters range from few nanometers to several microns. The high specific surface area of ultrafine fibers can be used as high performance filters, scaffolds in tissue engineering, sensors, composites and in radiation shielding. Polyacrylonitrile (PAN) nanofibers were produced using electrospinning by dissolving polyacrylonitrile in N,N-dimethylformamide (DMF) solution. The spinning was carried out for 10, 15 & 20% (by weight) concentrations at different voltages, flow rates, varying distance between needle and collector and at different needle diameters. The electrospun fiber was collected by attaching it to stainless steel foil wrapped on a drum of diameter 4.5 inch rotating at various speeds. The electrospun fiber web was stabilized by heating at 280°C for 1 hour in air. The stabilized nanofiber webs were carbonized at 700°C in an inert atmosphere. The spun fibers were characterized using scanning electron microscope. The aligned fibers (around 80%) were formed by rotating drum at ~1000 rpm. At lower speeds the fibers were not aligned. The diameter of the fiber decreased with increase in stabilized and carbonization temperatures. The char yield was found to be around 63%.

KEYWORDS: Electrospinning, polyacrylonitrile, nanofiber

1. INTRODUCTION

Electrospun nanofibers have broad application in composite nonwoven structure in traditional markets. Electrospun nanofibers are being considered for a variety of applications where their unique properties contribute to product functionality. Those properties include high surface area, small fiber diameter, potential to incorporate active chemistry, filtration properties, layer thicknesses, high permeability, and low basis weight

As the fiber themselves have a small diameter, the thickness of the nanofiber web can likewise be quite small, under one micron. The thin web has limited mechanical properties that preclude the use of conventional web handling techniques and instead require the formation of a nanofiber web on a substrate. The substrate could be incorporated into the product to be used to deposit the nanofiber web on a product and the supporting substrate will be removed. Substrate materials are selected to provide appropriate mechanical properties and complementary functionality to the nanofiber web.

2. ELECTROSPINNING METHODOLOGY

Electrospinning uses the electrostatic force to spin fibers from a polymeric solution or melt. In 1934 Formhals [1-3] patented the electrospinning process for the production of the polymer filaments. Polymers are dissolved into a proper solvent before being subjected to spinning. The polymeric solution is initially ejected from the tip of a fine orifice or nozzle maintained at a potential up to several tens of kilovolts by a DC power supply. When the electrostatic repelling force of the charges overcomes the surface tension force of a polymer solution droplet at the tip of the liquid stream, the charges leave the droplet and drag the polymer to form fiber streams. The fiber streams will become unstable to a whip-like motion that further elongates them and reduces their diameter. This process continues until a large number of fine polymer filaments (nanofibers) are formed by evaporation of the carrier solvent. These filaments or nanofibers are deposited on a grounded target, where they bond together to form a nanofiber fabric. Depending on the polymeric material and the operating conditions, the

fine fibers can range from ten to several thousand nanometers in diameter. An important feature of the electrospinning process is that electrospun fibers are produced in atmospheric air and at room temperature, rather than at temperatures high enough to keep the polymeric materials in a molten state.

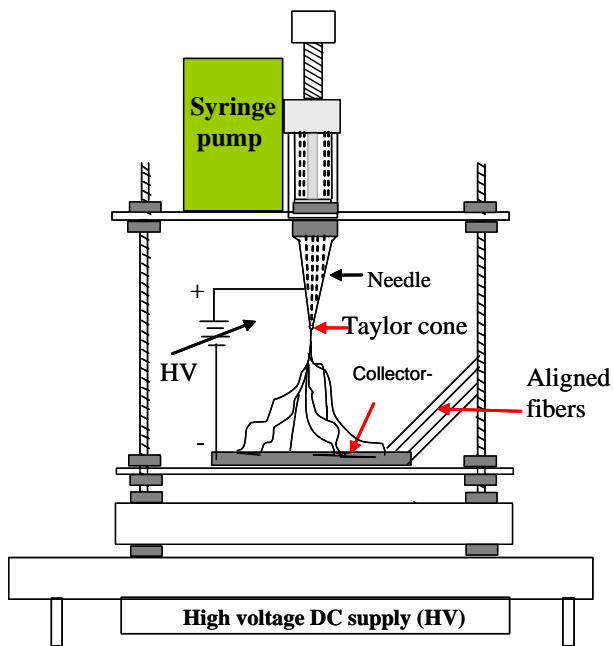
The polymer solution or melt is contained in a glass tube, usually a pipette that is connected to syringe like apparatus. A metering pump attached to the plunger of the syringe generates a constant pressure and flow of the fluid through the pipette. The driving force is provided by a high voltage source through a wire immersed in the solution. The high voltage source can generate upto 30 kV, and the setup can be run on either positive or negative polarity. Adjusting the flow of the fluid and the magnitude of the electric field controls the spinning rate. The following parameters affect the electrospinning process.

- **System parameters:** Molecular weight, molecular weight distribution and architecture (branched, linear etc.) of the polymer
- **Process parameters:** Electric potential, flow rate, concentration, distance between capillary and collection screen, ambient parameters (temperature, humidity and air velocity in the chamber) and motion of target screen.

An important characteristic of electrospinning is the ability to make fibers with diameters in the range of few nanometers to a few microns. Consequently these fibers have a large surface area per unit mass so that nonwoven fabrics of these nanofibers collected on a screen can be used medical application [4], advanced aerodynamic applications [5,23]and also in advanced composites to improve crack resistance.

3. EXPERIMENTAL DETAILS

The electrospinning equipment was designed and assembled. The schematic of the component layout and the fabricated experimental setup for stationary target is shown below.



a. Layout of electrospinning system



b. Spin down



c. Spin up

Figure 1: Electrospinning setup

The electrospinning process parameters are given below:

- Voltage: 10 -30 kV
- Flow rate: 0.5 – 5 ml/hr
- Distance between target and nozzle: 15 – 30 cms
- Nozzle diameter: 0.4 – 1.2 mm
- Current: 1 - 20 μ A

4. PREPARATION OF POLYACRYLONITRILE POLYMERS

The electrospinning system developed at Center for Composite Materials Research was optimized by spinning polymethylmethacrylate (PMMA), polybenzimidazole (PBI) and polyacrylonitrile (PAN) polymers.

Polyacrylonitrile was purchased from Aldrich Corporation. The PAN polymer was dissolved in dimethylformamide (DMF) solvent. This mixture was vigorously stirred by an electromagnetically driven magnet at 60°C until it becomes a homogeneous polymer solution. Different concentrations of PAN solution (10, 15 and 20% by weight) was made using the same process. The advantage of choosing polyacrylonitrile is due to the following reasons: (i) it is used for the production of carbon fibers and (ii) polymer can be oxidized to make it thermoset.

5. ELECTROSPINNING OF POLYACRYLONITRILE ON STATIONARY TARGET

The electrospinning equipment for stationary target (spin down and spin up configurations) is shown in the above figure 1.

PAN and PBI polymers are the precursor materials for the formation of carbon nanofibers [6-10, 15]. The PAN polymers were electrospun on a stationary target. Fibers were formed by varying the solution concentration, voltage, solution flow rate and distance between needle and collector. The morphology of the PAN fibers for 10, 15 and 20% concentrations were studied using SEM and is shown in figure 2 (a-c) respectively. As the concentration of the solution was increases, the diameter of the fiber was also increases.

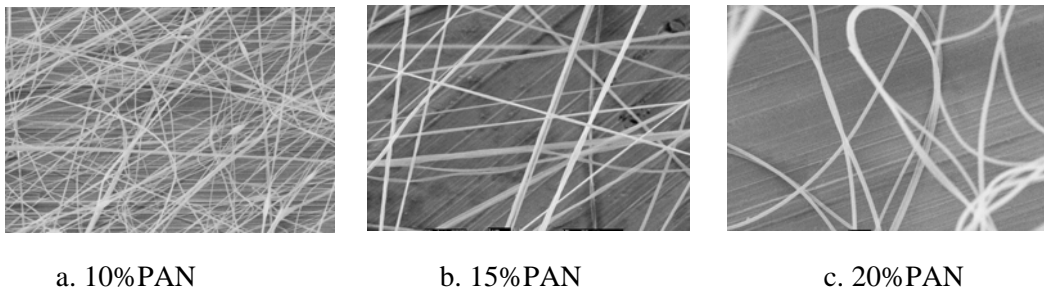


Figure 2: SEM analysis of PAN fibers for 10, 15 & 20% concentration

The electrospun PAN fabrics were stabilized at 280°C for 1 hour duration under air flow. The stabilized fabrics were carbonized at 900°C (by maintaining the ramping rate at 5°C/min) in nitrogen atmosphere for 1 hour duration.

The morphology of as spun, stabilized and carbonized electrospun 15%PAN fibers are studied using scanning electron microscopy [Figure 3 (a-c)]. All these figures show the

rpm and type I collagen fibers at 4500 rpm [19]. A significant advancement in collecting aligned fibers has been recently made by Zussman and co-workers. They modified the design of a drum and used a tapered, wheel-like disk as the collector [20]. It was found that most of the fibers could be collected on the sharp edge. The collector fibers were oriented parallel to each other along the edge. Because of the strong electrostatic attraction, the charged fibers were continuously wound on the edge when the disk was rotating at a relatively high speed. It has been demonstrated that with this approach polyethylene oxide nanofibers with diameters ranging from 100 to 400nm were in alignment with a pitch (the distance between two fibers) varies from 1 to 2 μ m. Lee et al [21] electrospun nano-structured poly(caprolactone) (PCL) nonwoven mats by varying the linear velocity of the drum from 1.3 to 4.5 m/min. They found that the mechanical properties of these fabrics decreased when the linear velocity of drum was higher than 3.2 m/min. Sian et al [22] electrospun PAN nanofibers nonwoven mats by varying linear velocity of the drum from 3.5 m/sec to 12.5 m/sec. They found the failure of aligned fibers when the linear velocity of drum increases above 8.6 m/sec. The molecular orientation measurement was carried out using dichroism and the WAXD techniques.

The aligned fiber mechanism behind the rotating drum technique is as follows: When a linear speed of the rotating drum surface, which serves as a fiber take-up device, matches that of evaporated jet depositions, the fibers are taken up on the surface of the drum tightly in a circumferential manner, resulting in a fair alignment. Such a speed can be called as an alignment speed. If the surface speed of the cylinder is slower than the alignment speed, randomly deposited fibers will be collected, as it is the fast chaos motions of jets determine the final deposition manner. On the other hand, there must be a limit rotating speed above which continuous fibers cannot be collected since the over fast take-up speed will break the fiber jet. The reason why a perfect alignment is difficult to achieve can be attributed to the fact that the chaos motions of polymer jets are not likely to be consistent and are less controllable.

7. ELECTROSPINNING OF POLYACRYLONITRILE ON ROTATING DRUM TARGET

The schematic of electrospinning with rotating drum target is shown below.

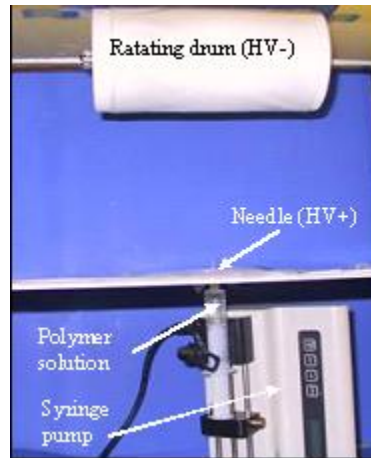
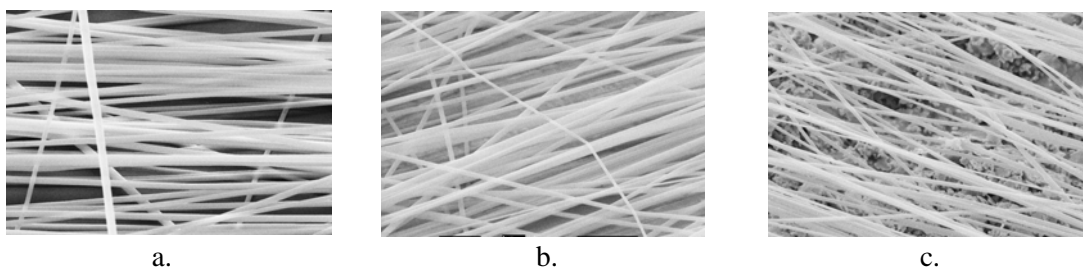


Figure 4: Schematic of rotating drum target assembly

The rotating drum is electro charged so that the nanofibers are deposited on the circumference of the drum. The drum is rotated using a suitable DC motor. The drum can also be moved in transverse direction to cover the uniform fabric mat over the entire area. Provision is made to carryout the spinning by tilting the syringe at 45° which further enhances the alignment of fibers [14]. The advantages of spinning at 45° angle is further reduction of diameter of fibers compared to normal spinning because of long travel path of the fiber. The other advantage is, in low viscous polymers tilting will avoid the droplets from the nozzle. In the present study, the spinning is carried out in normal position. By varying the process parameters and the linear velocity of drum, aligned fabrics are prepared. Fibers are prepared by rotating the drum at 1000 rpm. The fibers are deposited on a porous teflon sheet so that the fabric can be removed from the supporting sheet. Provision is made to adjust the rotational speed of the drum up to 2500 rpm. The speed of the drum can be varied depending on the evaporation rate of the polymer which in turn depends on the concentration of polymer solution, flow rate, voltage and the distance between the needle and rotating drum. Experiments were carried out by varying

the linear speed of the drum and spinning parameters. At lower speed of the drum collector, random fibers were formed. At higher speed of the drum collector (around 1000 rpm), aligned fibers were formed.

Figure 5 (a-c) shows the morphology of as spun, stabilized and carbonized electrospun 15% PAN fibers studied using scanning electron microscopy. All these figures show the formation of aligned fibers in the winding direction. The diameter of the fiber decreases with increase in stabilization and carbonization temperatures.



a. As spun (1-1.3 μ) b. Stabilized @ 280°C (0.9-1.1 μ) c. Carbonized @ 900°C (0.4-1 μ)

Figure 5: SEM analysis of as spun, stabilized and carbonized aligned PAN fibers

The char yield of the PAN fibers were found to be around 63%. Experiments will be conducted to characterize the fibers using Raman micro spectrometry. Measurement of electrical conductivity of carbonized PAN nanofibers and mechanical properties of the fabrics are under progress.

8. CONCLUSIONS

Polyacrylonitrile based nanofibers were prepared using electrospinning techniques and subsequently oxidatively stabilized and carbonized. The nanofibers were prepared on stationary and rotating target collectors. Nanofibers were characterized using scanning electron microscopy. Aligned fibers were formed by rotating the target at specified speed. The char yield of the PAN fibers were found to be around 63%.

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