

ELECTROSPINNING OF NANOFABRICS

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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 ultra fine fibers can be used as high performance filters, scaffolds in tissue engineering, sensors, composites and in MHAV applications. Polyacrylonitrile (PAN), and polybenzimidazole (PBI) nanofibers were produced using electrospinning by dissolving PAN in N,N-dimethylformamide (DMF) and PBI in N,N-dimethylacetamide (DMAc) solutions. Nylon-66 nanofibers were produced by dissolving Nylon-66 polymer in formic acid and chloroform solutions. The electrospinning was carried out for 10, 15 & 20% (by weight) concentrations at different process conditions. The electrospun nanofiber was collected by attaching it to stainless steel foil wrapped on a drum of diameter 4.5 inch rotating at various speeds. The electrospun nanofibers were characterized using scanning electron microscope. The aligned fibers were formed by rotating drum at higher speeds (up to 2500 rpm). The diameter of the nanofibers range from 50 to 200nm. At lower speeds the nanofibers were random. The tensile modulus and strength of partially aligned Nylon-66 nanofabric was about 2.4GPa and 154MPa, respectively.

KEYWORDS: Electrospinning, PAN, PBI, Nylon-66, nanofiber, mechanical properties

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.

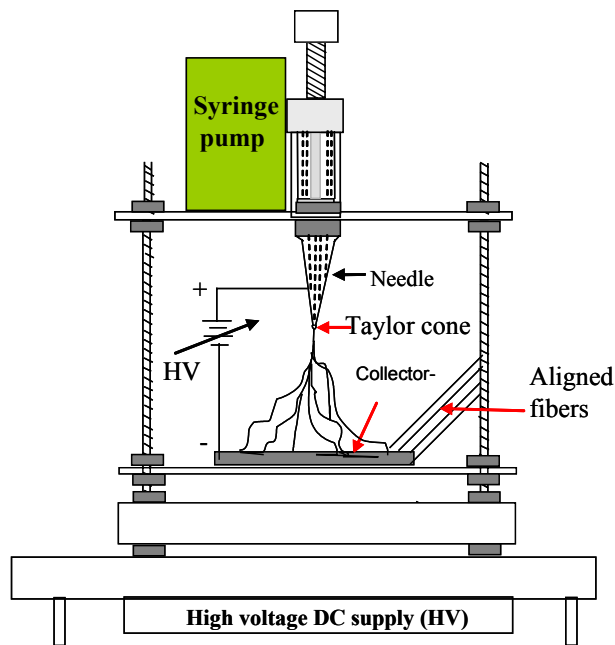
The polymer solution or melt is contained in a glass tube, usually a pipette that is connected to syringe like apparatus. A metering pump attached to the plunger of the syringe generates a constant pressure and flow of the fluid through the pipette. The driving force is provided by a high voltage source 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

3.1. Preparation of Different Polymers The electrospinning system developed at Center for Composite Materials Research was optimized by spinning polymethylmethacrylate (PMMA), polybenzimidazole (PBI) and polyacrylonitrile (PAN) polymers. The PMMA was purchased from Aldrich Corporation. The polymer was stirred in dimethylformamide (DMF) solvent and at 60°C until the solution becomes homogeneous in nature. The PMMA solution was prepared at 20 and 25% polymer concentration (by weight).

Polybenzimidazole was obtained from Hoechst Celanese Corporation in Charlotte, North Carolina. The PBI polymer was dissolved in N,N-dimethylacetamide (DMAc) with a lithium chloride (LiCl) (about 4% by weight). PBI polymer solution was prepared by dissolving dry PBI polymer and LiCl in DMAc under nitrogen gas at a bath temperature above the boiling point of DMAc for 4 hours with a refluxing condenser. LiCl was used to increase solution shelf life from days to several months. The PBI solutions were filtered to remove any residual polymer particles. The PBI solution was prepared at 20 and 25% concentration (by weight).

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) were prepared using the same process.

Nylon-66 was purchased from DuPont Company (Zytel 101, MW=20,000 g/mol). The different concentration (10-20% by weight) polymer solution for electrospinning were prepared by using a solvent mixture of formic acid and chloroform with a ratio of 75/25 (v/v). The mixture was vigorously stirred by an electromagnetically driven magnet at ambient temperature until it becomes a homogeneous polymer solution. The importance of these polymers are given in the table 1.

Polymer	Rationale	Concentration used
Polymethylmethacrylate (PMMA)	1. Widely used in Electrospinning 2. Applications include Filtration devices membranes & protective clothing	20-30%
Polyacrylonitrile (PAN)	1. Used in production of carbon fibers 2. Polymer can be oxidized to make it thermoset	10, 15 & 20%
Polybenzimidazole (PBI)	1. Polymer can be oxidized to make it thermoset 2. Has high char yield	20 & 25%
Nylon-66	1. Used as an interply to toughen epoxy/carbon fiber composites 2. Used as a skin for simulated dragonfly wings	10 to 20%

Table 1: Polymers chosen and rationale

3.2. Electrospinning of Polymers on Stationary Target The electrospinning equipment for stationary target (spin down and spin up configurations) is shown in the above figure 1.

The PMMA polymer was electrospun on stationary target for 20 and 30% concentrations by varying voltage, polymer flow rate and distance between needle and collector. The morphology of the PMMA fibers were studied using scanning electron microscopy and is shown in figure 2(a-b). The diameter of the fibers varied from 300 to 500 nm.

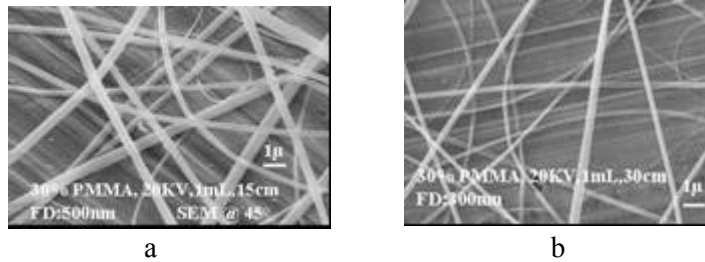


Figure 2: SEM analysis of PMMA fibers for 30% concentration

PBI and PAN polymers are the precursor materials for the formation of carbon nanofibers. The advantages of these polymers are summarized in the above table1. The PBI and PAN polymers were also electrospun on a stationary target. Fibers were formed by varying the solution concentration, voltage, solution flow rate and distance between needle and collector. The PBI nanofibers were washed with, methanol, to remove residual solvent and LiCl. The fabric was also washed with 2% phosphoric acid to provide stabilization against shrinkage during heat treatment and to increase the strength of the fabric. Following the wash, the fabric was dried at 80°C. The morphology of the PAN fibers for 10, 15 and 20% concentrations were studied using SEM and are shown in figure 3(a-c) respectively. As the concentration of the solution was increases, the diameter of the fiber was also increases. At 10% concentration, the diameter of fibers was around 300 nm and increased to 500 nm at 15% and 1μ at 20% PAN concentration.

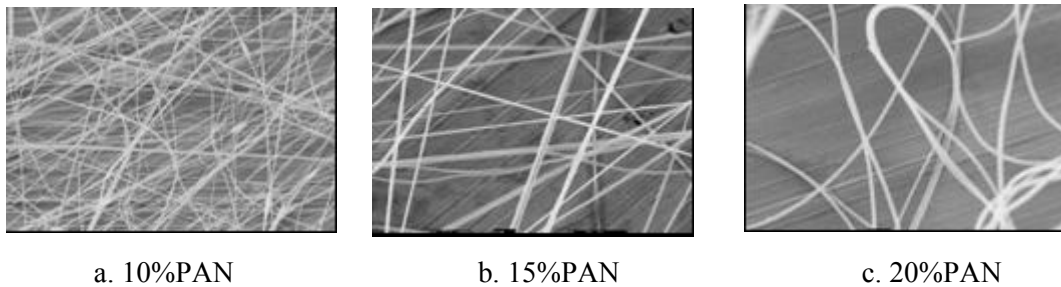


Figure 3: SEM analysis of PAN fibers for 10, 15 & 20% concentration

3.3. Development of Rotating Drum Target For many applications, it is necessary to control the spatial orientation of 1D nanostructures. In the fabrication of electronic and photonic devices, for example, well-aligned and highly ordered architectures are often required [5]. Even for application as fiber-based reinforcement, it is also critical to control the alignment of fibers. Because of the bending instability associated with a spinning jet, electrospun fibers are often deposited on the surface of collector as randomly oriented, nonwoven mats. The whipping instability is mainly caused by the electrostatic interactions between the external electric field and the surface charges on the jet. The formation of fibers with fine diameters is mainly achieved by the stretching and acceleration of the fluid filament in the instability region. In the past several years, a number of approaches have been demonstrated to directly collect electrospun nanofibers as uniaxially aligned arrays [11-14]. The most popular method of obtaining aligned fibers is by using rotating drum target.

Alignment of electrospun fibers was observed by several groups by rotating drum at high rotating speed [15,16]. Air flow may also favor the orientation of fibers along the winding directions [17]. Researchers from Virginia Commonwealth University [18] have used this technique to obtain aligned electrospun poly(glycolic acid) (PGA) fibers at 1000 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.

3.3.1 Electrospinning of Polymers on Rotating Drum Target The schematic of electrospinning with rotating drum target is shown in figure 4.

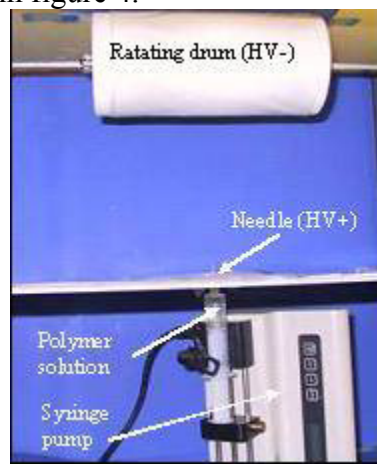


Figure 4: Schematic of Rotating drum target assembly

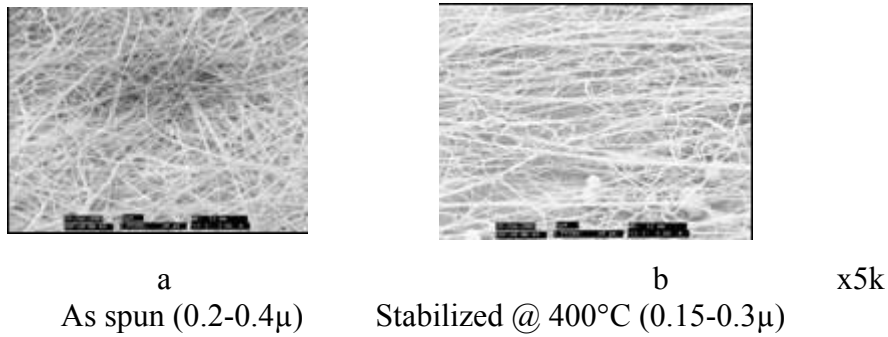


Fig.6: SEM analysis of as spun and stabilized random PBI fibers

3.3.3 Preparation of Aligned Nanofabrics of PAN & PBI Polymers on Rotating Drum Target

Aligned nanofabrics of PAN and PBI polymers are prepared by rotating the drum at speeds approximately 1000 rpm. Figure 7(a-c) shows the morphology of as spun, stabilized and carbonized electrospun 15% aligned PAN fibers studied using scanning electron microscopy. Figure 8 (a-c) shows the morphology of as spun, stabilized and carbonized PBI nanofabrics. Figures 7 and 8 shows the formation of aligned fibers. The diameter of the fiber decreases with increase in stabilization and carbonization temperatures.

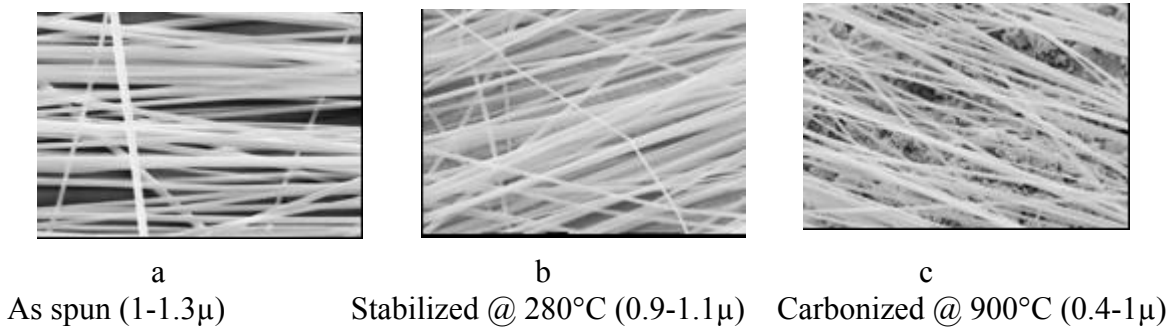


Figure 7: SEM analysis of as spun, stabilized and carbonized aligned PAN fibers

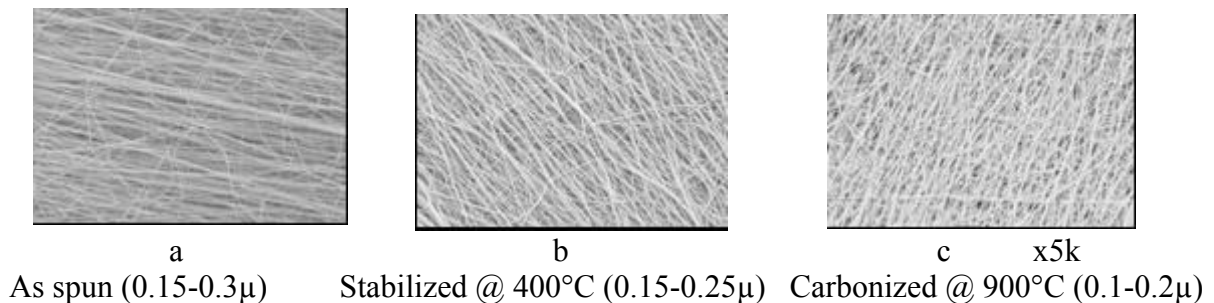
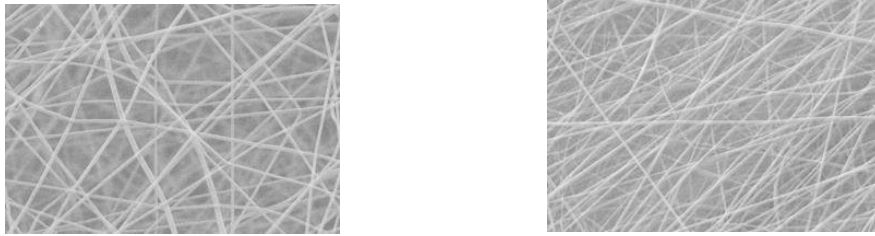


Figure 8: SEM analysis of as spun, stabilized and carbonized aligned PBI fibers

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.

3.3.4 Preparation of Random & Aligned Nanofabrics of Nylon-66 Polymer on Rotating Drum
Target Random and aligned nanofabrics of Nylon-66 polymer are prepared by rotating the drum at 1000 and 2500rpm speeds respectively. Figure 8 (a-b) shows the morphology of random and aligned 20% Nylon-66 nanofabrics studied using scanning electron microscopy.



(a) Nylon-66 random fabric(150-300nm) (b)Nylon-66 aligned fabric (50-200nm)

Figure 8: SEM analysis of as spun random and aligned Nylon-66 nanofabrics

3.4 Mechanical Testing of Nylon-66 Nanofabrics The mechanical behaviour of electrospun Nylon-66 fabrics was tested using an Instron 4204 (Figure 9) with a crosshead speed of 1.27mm/min in tension at room temperature. Samples were mounted and had a 5cm gage length with 6.2mm width. The thickness of the fabric was calculated from the areal density of the nanofabrics. Table 2 shows the initial modulus and ultimate strength of the nanofabrics measured along longitudinal and transverse directions. The areal densities of aligned and random Nylon-66 nanofabrics was around 4.1and 5.3gm/m² respectively and the average thickness of the fabric was 3.5 and 4.7µm respectively.

Speed RPM		Average Modulus GPa	Strength MPa
1000*	Longitudinal	1.1 (.04) ¹	62
	Transverse	0.8 ²	34
2500*	Longitudinal	2.4 (.27) ¹	154
	Transverse	0.3 (.02) ¹	17

¹ standard deviation

* spinning duration= 4 hrs.

² samples



Table 2: Mechanical testing of Nylon-66 fabrics Fig.9.Mechanical testing of Nylon-66

The average modulus and strength of random nanofabrics were 1.1GPa, 62 MPa respectively in longitudinal direction; 0.8GPa and 34MPa respectively in transverse direction. For aligned fabrics they were 2.4GPa, 154MPa respectively in longitudinal direction; 0.3GPa and 17MPa respectively in transverse directions.

4. CONCLUSIONS

Polyacrylonitrile, polybenzimidazole and Nylon-66 based nanofabrics were prepared using electrospinning technique. The nanofibers were prepared on stationary and rotating target collectors. Random nanofabrics were formed on stationary target as well as rotating target at lower rotational speeds. Aligned fibers were formed by rotating the target at specified speed. Nanofabrics were characterized using scanning electron microscopy. The diameter of Nylon-66 nanofabrics varied from 50 to 200nm. The tension modulus and strength of partially aligned Nylon-66 nanofabric was about 2.4GPa and 154MPa respectively in the longitudinal direction.. The char yield of the PAN fibers were found to be around 63%.

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