

CHAPTER III EXPERIMENTAL

3.1 Electrospinning

3.1.1 Materials

Commercial grade PAN fibers with molecular weight of 55,500 g mol⁻¹ and composition of 90% acrylonitrile monomer (CH₂=CHCN), 10% methylacrylate monomer (MA, CH₂=CHCOOHCH₃) were used to produce nanofibers of polyacrylonitrile. These PAN nanofibers were later used as precursors for producing carbon nanofibers. 99.98%wt. of dimethylformamide (DMF) was used as a solvent.

3.1.2 High Voltage Power Supply

A high voltage power supply (Gammar High Voltage Research model no. D-ES30PN/M692, Ormond Beach, Florida) was used to supply the electrical field between a needle tip and a collection screen.

3.1.3 Sample Preparation

PAN solution in DMF was prepared at the concentration of 2.1 to 17.4 percentage by weight (wt%).

3.1.4 Electrospinning Process

3.1.4.1 Effect of Concentration

The typical experimental set up for the study of the effect of concentration on electrospun fiber morphology was as follows. Polyacrylonitrile solution that has concentration of 9.5 wt% was placed in a 50-mL glass syringe. The syringe was clamped horizontally (-10° to the ground) to a PVC stand. It was placed at 15 cm from the grounded stationary collection screen (an aluminum foil sheet). The polymer solution was subjected to external electrical field by attaching a positive electrode to the nozzle. The constant pressure of nitrogen gas was applied into the

syringe to suspend the polymer drop at the tip of the nozzle. The pressure was increased when polymer concentration increased to achieve similar suspending polymer drop. The electrospun fiber was kept in vacuum for 24 h prior to characterization to ensure a complete drying of the sample. Similar technique was used to study the effects of other parameters on nanofiber preparation.

3.1.4.2 Effect of Collection Distance

Distance from 10-25 cm between the tip of the nozzle and screen were varied. A 9.5%wt PAN solution was used and the pressure was kept constant (5Psi).

3.1.4.3 Effect of Applied Voltage

The voltage of 10-30 kV was varied while the pressure for feeding 9.5%wt polymer solution is constant.

3.1.4.4 Effect of Electrode Polarity

For comparing the fiber morphology obtained from different polarity using 2.1-17.4%wt PAN solution, 20 kV, and the distance between the tip of nozzle and the collection screen of 15 cm were used.

3.1.4.5 Effect of Nozzle Radius

The electrospinning of 9.5%wt PAN solution was achieved by using the gauge 0.47, 0.51, 0.56, 0.64, 0.71 and 0.81 mm of needle tip. The distance between the tip of nozzle and the collector was kept constant at 15 cm. The applied voltage of 20 kV was used.

3.1.4.6 Effect of Take-up Speed

In this case, an adjustable speeds rotating drum was used as a collector. Electrospun fibers were collected by varying the take-up speed from 0 to 2,500 rpm.

3.2 Continuous Stabilization and Carbonization

A Carbolite furnace (type STF 15/75/450, maximum temperature of 1500°C) was used to convert precursors into carbon fiber. The electrospun PAN fibers were subjected to heat treatment at the temperature of 230°C, heating rate of 1°C/min. and 4L/min of purified air under tension for 5 h. Consequently, the stabilized fibers were treated at 1000°C at the same heating rate and gas flow rate under high purity nitrogen atmosphere.

3.3 Characterization

3.3.1 Viscometry

The viscosity of polymer solution was determined by using a Brookfield digital viscometer (model LVTDCP) at 30°C.

3.3.2 Tensiometer

A tensiometer (Krüss model KS10T) was used to measure the surface tension of the PAN solutions at the temperature of 30.0±0.1°C.

3.3.3 Conductivity Meter

The conductivity of PAN solutions were measured at 30.0±0.1°C by using conductivity meter.

3.3.4 Fourier-transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy was performed on commercial PAN precursor fibers to verify their composition (particularly comonomer types) and study the changes of chemical structure of stabilized and carbonized PAN fibers. FTIR measurements were made on a Bruker model 106/S FTIR using resolution of ±4 cm⁻¹ and 16 scans per sample. Infrared spectra were recorded in the wavenumber ranging from 400-4000 cm⁻¹.

Thin films of PAN were prepared by casting from an 18 wt% solution

of PAN precursor fibers in DMSO onto clean glass substrates followed by drying at 30°C. Heat treated PAN fibers were analyzed in the original non-woven form.

3.3.5 Scanning Electron Microscopy (SEM)

The surface morphology and diameter of the resulting electrospun PAN fiber, its stabilized and carbonized form, were observed by SEM (JEOL LS002). They were coated with thin film of gold for 5 min prior to analysis. The average fiber diameter and diameter distribution were obtained from the diameter of 100 fibers taken from a number of SEM micrographs. Fiber diameter was measured by using SemAfore program.

3.3.6 Wide-angle X-ray Diffraction Spectroscopy

An X-ray diffraction spectrometer (Rigaku RINT DMAX/2002H, 40 kV, 30 mA) with a $\text{CuK}\alpha$ ($\lambda=1.54 \text{ \AA}$) was used to observe the crystal size and crystallinity of PAN precursor fibers, electrospun PAN, and pyrolysed electrospun fibers. For the sample of PAN precursors and electrospun PAN, the spectra were taken between 5°-40°, while for the pyrolysed electrospun fibers, the spectra were taken between 5°-90° 2θ at a scanning rate of 1° $2\theta/\text{min}$ in 0.02° 2θ increment.

3.3.7 Differential Scanning Calorimetry (DSC)

To investigate the effect of electrospinning on the crystallinity, a Perkin-Elmer DSC7 was used. The fiber specimens were heated from 30 to 400°C in nitrogen at a heating rate of 10°C min^{-1} . The PAN precursor fibers and electrospun PAN fibers were cut into small pieces prior to weighing and capsulating in flat-bottom aluminum pan of 45 μL volume with crimped-on lids. Evolved heat was determined following calibration with indium (28.4 J g^{-1}) using the integration of the area under the endothermic peak and corrected baseline.

3.3.8 Thermogravimetric Analysis

Thermogravimetric and derivative thermogravimetric tests were carried out using a Dupont 2950 thermogravimetric analyzer. The percent weight

changes were monitored as a function of temperature. A sample weight of 10 ± 0.5 mg, and temperature range between 25-800°C at heating rate of 10°C/min in nitrogen atmosphere were used.