

ELECTROSPINNING OF POLYACRYLONITRILE NANOFIBERS

by

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CERTIFICATE

This is to certify that the thesis titled, “**Electrospinning of Polyacrylonitrile Nanofibers**”, being submitted by **Sandip Basu**, to the Indian Institute of Technology Delhi, for the award of the degree of Doctor of Philosophy is a record of original bonafide research work carried out by him under our guidance and supervision and that the results contained in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma. This is also to certify that he has fulfilled the requirements of submission of thesis.

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ABSTRACT

The process of electrospinning is complex due to the involvement of a large number of interrelated process parameters all of which have not been independently studied. Poly(acrylonitrile) (PAN) solution in N,N-dimethylformamide (DMF) was taken as a model system to study and correlate the electrospinning process parameters, environmental parameters and material parameters with the morphology of the nanowebs.

PAN solutions in DMF were electrospun into nanofibers by charging the polymer fluid in an electric field. Controlled experiments were performed using a needle type spinneret to investigate the effect of various electrospinning parameters on the percentage conversion of polymeric fluid into fibers and on fiber diameter obtained. It was found that when the polymeric fluid was fed at a constant rate, application of a Minimum Electrospinning Voltage (MEV) was necessary to achieve maximum conversion of the ejected fluid into nanofibers. Also, that the maximum amount of splitting or elongation that a polymeric fluid could undergo was primarily dependent on the number of entanglements per chain in the fluid. This resulted in obtaining nanofibers with a particular diameter irrespective of the values of important electrospinning variables such as applied voltage, flow rates, and distance between the electrodes. On the other hand, MEV was found to be strongly dependent on the spinning parameters and was unique for a given set of parameters. The significance of the MEV was evident from the fact that the square of MEV, which is a measure of the electrical energy utilized by the system, is directly proportional to the surface formation rate (S) during the electrospinning process.

However, the slope of the plot between $(MEV)^2$ and surface formation rate was found to increase with increasing needle to collector distance signifying that the resistance in electrospinning increases linearly with the distance.

The effect of parameters on the area of deposition of nanofiber web was also studied. In contrast to the behavior seen for the diameter of the nanofibers, the area of deposition on collector was found to vary significantly with all electrospinning parameters such as dope concentration, flow rate, needle to collector distance and the collector voltage. Among these parameters, the needle to collector distance and collector voltage had the greatest effect. The electrospinning parameters appear to determine the cone angle made by the spinning jets, which has been defined as “ultimate cone angle (UCA)”. This in turn influences the area of deposition. A simple model has been proposed to explain the deposition behavior of the spinning jets with changing parameters. The effect environmental process parameters in the process of fiber formation by electrospinning have been studied by maintaining the MEV. Electrospinning of PAN in DMF was carried out by varying the temperature under constant relative humidity (RH). Nanofiber diameter was found to decrease with increase in temperature and then attain a constant value at higher temperatures. The diameter of PAN was found to increase with increase in RH. It was suggested that the moisture absorbed by the solvent reduced the solvating power of solvent causing changes in polymer chain conformations. Increase in entanglement of the PAN result in higher diameter. The proportionality of surface formation rate with square of MEV was found to remain unaffected by changing either the temperature or the RH%, and the slope of the trend lines was found to be similar to other PAN-DMF trend lines at varying concentrations.

A series of poly(acrylonitrile-co-methylacrylate) copolymers (PAN) with varying molecular weight were synthesized. These solutions were electrospun at Minimum electrospinning voltage (MEV) to correlate electrical energy required to perform the mechanical work during the spinning of the fibers. It was seen that at MEV, electrical power required by the spinning system, was directly proportional to the rate of surface formation irrespective of the molecular weight or concentrations of copolymer used in the study.

It was observed that number of entanglements per chain, which represents the capacity of the polymer system to store elastic energy, could correlate better with the ultimate diameter of the fiber than Berry number, which is a measure of resistance of the polymer solution to flow. Interestingly, the diameters of the nanofibers were found to increase linearly with increase in number of entanglements per chain with two distinct regions having transition of the slope at number of entanglement value of 3.5. This transition in slope corresponds to the onset of formation of highly entangled network structure in the solution, which appears to make the polymer exhibit significantly higher tendency to store elastic energy resulting in higher diameter of nanofibers.

The good solubility of PAN in three organic polar solvents DMF, DMAc and DMSO was utilized in studying the effect of solvents on electrospinning of PAN. The effect of density, saturated vapour pressure, dielectric constant and dipole moment, in electrospinning was studied by changing the solvents of PAN. From the experimental data it may be concluded that there is no difference between the solvents of PAN in terms of conversion efficiency of the dope into nanofibers and the fiber diameter obtained.

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