ELECTROSPINNING OF NANOFIBRES AND THEIR SCALE-UP FOR FILTRATION APPLICATION

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by

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CERTIFICATE

This is to certify that the thesis titled **'Electrospinning of Nanofibres and Their Scale-up for Filtration Application'** being submitted by **Mr. Dhirendra Singh** to the **Indian Institute of Technology Delhi**, for the award of degree **Doctor of Philosophy**, is a record of bonafide research work carried out by him. He has worked under our guidance and supervision and fulfilled the requirements for the submission of thesis which has attained the standard required for a Ph.D. Degree of this Institute**.** The results contained in this thesis have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

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Abstract

Automotive filters need high filtration efficiency at low pressure drop required to remove smaller sized dispersed contaminants present in fuels. Such contaminants can cause not only poor performance of engines due to abrasive action by the impurities, and incomplete combustion of fuels. Filters based on nanofibres, can significantly improve the filtration performance without affecting the pressure drop. For this nanofibre webs are usually deposited on a filter media. Nanofibres may be readily produced using electrospinning process Performance of nanofibre filters depends on the morphology and quality of the deposited nanofibre web.

Morphology of the deposited nanofibre web is believed to depend upon electrospinning process parameters, ambient conditions and material properties. To understand the effect of these parameters, poly(vinyl alcohol) (PVA)-water system was selected. PVA solutions of concentration in the range of 7 to 14 wt% were studied.

It was found that a minimum electrospinning voltage (MEV) was required to completely convert polymer solutions to nanofibres. The effect of various electrospinning and material parameters on morphology of nanofibres was studied at MEV condition. When the spinning was carried out at MEV, there was no significant effect of voltage, flow rate and spinning distance on the nanofibre diameter. However the MEV value was found to be dependent on all the spinning parameters. It increased with increase in spinning distance, flow rate and the concentration of the polymer solution. Polymer concentration has strong effect on nanofibre diameter while ambient parameters also affect nanofibre diameter. Needle diameter did not affect the nanofibre diameter or the MEV values.

The rheological studies was carried out for PVA to study the effect of viscosity, storage modulus and relaxation time on the diameter of the electrospun nanofibre and behavior was compared with poly(acrylonitrile) (PAN).The diameter was found to be a strong function of relaxation time of the spinning solution. The derived relationship was found to be applicable to both PVA-water and PAN-DMF systems, which are widely different in nature. The understanding developed can be used to predict the morphology of electrospun nanofibres for industrial applications.

Based on the above concepts, a pilot electrospinning machine was developed for continuous deposition of nanofibre web over substrate. Uniform deposition of nanofibres is necessary for consistent performance of filter during its application. Uniform deposition of the nanowebs could be successfully achieved by modifying the electrical fields in two perpendicular directions around each spinning needle. Small deposition of about 0.1 gram per square meter (GSM) of nanofibres could improve the fuel filtration efficiency for 4 micron-sized particle contaminants from 87% to 97%.

Application of nanofibres in filtration is usually limited by their ability to adhere to a supporting substrate. A novel approach was used where nanofibres were anchored to electrosprayed microparticles of adhesive to substantially enhance the interfacial bonding. The delamination force and adhesion energy increased by 90-250% and 80-170%, respectively, which were found to be limited only by the intra-web strength of the nanofibres. The permeability values of the composites remained unchanged. PVA nanofibre webs deposited on cellulosic substrate were found to be stable during the filter manufacturing process and to the various fuel media during use such as gasoline, biodiesel and diesel.

For applications, where high stability towards aqueous medium or contaminants is a necessity, two approaches for improving the stability were investigated (i) crosslinking of PVA nanofibres using different crosslinkers/initiators such as maleic anhydride, glutaraldehyde and ammonium dichromate (ii) use of cellulose acetate (CA) as a water insoluble hydrophilic polymer instead of PVA. Ternary system of acetone- dimethyl sufoxide (DMSO) - N,N-dimethyl formamide (DMF) with ratio of 3:1:1was found to be suitable for achieving continuous electrospinning of defect free nanofibres which is important for mass production of CA nanofibres on cellulosic media.

The present study is able to develop and demonstrate a technology for mass production of nanofibres of controlled morphology, which can be used for continuous and uniform deposition of nanofibres on a substrate for fuel filter application. The results may be readily extended to other systems for different industrial applications.

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LIST OF SYMBOLS AND ABBREVIATIONS

Symbol/ Abbreviation	Meaning
CA	cellulose acetate
CFM	cellulosic filter media
CV	collector voltage
d_f	final diameter of dried & drawn fibre or mean fibre diameter
d_i	initial diameter of dried & un-drawn fibre
DMAc	N, N´-dimethylacetamide
DMF	N, N´-dimethylformamide
DMSO	dimethylsulfoxide
E	extension rate
F_E	electrical force
F_R	rheological force
F_{ST}	surface tension force
F_T	total cohesive force
Ǵ	storage modulus
GA	glutaraldehyde
GSM	gram per square meter
ID	inner diameter
τ	relaxation time of polymer
l_f	final length of dried & drawn fibre
l_i	initial length of dried & un-drawn fibre
MA	maleic anhydride
MEV	minimum electrospinning
Mod-CFM	modified cellulosic filter media
$\overline{M_w}$	weight average molecular weight
NV	needle voltage

PAN	poly(acrylonitrile)
P_E	electrical work per unit time
P_M	mechanical work per unit time
PVA	poly(vinyl alcohol)
PVAc	poly(vinyl acetate)
Q	polymer solution feed rate
R	resistance of electrospinning system
RH	relative humidity
S	surface formation rate
SEM	scanning electron microscope
THF	tetrahydrofuran
UV	ultra violate
wt%	(weight/weight) percent concentration
×-PVA	crosslinked PVA
η	efficiency of conversion of electrical to mechanical energy
η'	viscosity
ϕ_v	volume fraction
ω	angular frequency