ZnO NANOSTRUCTURE REINFORCED COMPOSITE FIBERS

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by

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DEDICATED TO MY FAMILY

CERTIFICATE

This is to certify that the thesis titled '**ZnO nanostructure reinforced composite fibers',** being submitted by **Ms. Ratyakshi** 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 her. She has worked under our guidance and supervision and fulfilled the requirements for the submission of thesis, which has attained the standard required for a PhD. 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

Polymer composites derived using nanomaterials has emerged as a fast growing research area for development of new materials with enhanced performance. Fibers are mechanically superior materials compared to films, moulds and casts for their use in various applications. Their properties principally depend on the orientation of the molecular chains in the direction of the fiber axis. Processing of composites in the form of fibers is expected to enhance the properties of these composites by coaligning nanostructures with molecular chains along the fiber axis. In order to achieve the benefit of nanostructures, it is essential to incorporate high aspect ratio nanostructures and ensure their homogeneous dispersion and uniform distribution in the polymer matrix. ZnO nanostructures are rigid hydrophilic entities that offer an alternate choice for reinforcement other than widely used CNTs.

In the first part of the study, the hydrothermal synthesis of ZnO nanostructures for tailoring of their aspect ratio was carried out. The ZnO nanostructures of same diameter of 50 nm and different aspect ratios of 1, 14 and 200 were selected and coded as ZnP, ZnR and ZnW, respectively, for further studies.

Further, the dispersion behavior was investigated in different solvents and polymer-solvent system in the second part of the study. The various polymer-solvent system selected were poly(vinyl alcohol)/water (PVA/H_2O), poly(vinyl alcohol)/water-N,N'-dimethylformamide (PVA/H_2O-DMF) and poly(acrylonitrile)/N,N'-dimethyl formamide (PAN/DMF) to make ZnO–polymer composite nanofibers. PVA/H_2O system was observed to be a poor dispersing medium for ZnRs. Large aggregates of ZnRs were observed on the surface of ZnO-PVA composite nanofibers. The use of DMF as a co-solvent resulted in a marginal improvement in

dispersion of ZnRs. However, with time ZnRs had a tendency to settle down, and again separate as aggregates in electrospun composite fibers. On the other hand, in PAN/DMF system, very stable and homogeneous dispersion of ZnRs was observed. The electrospinning was successfully carried out for samples upto 50 wt% of ZnRs on the weight of PAN. The ZnO-PAN composite nanofibers were observed to have uniformly dispersed ZnRs aligned along the axis of the nanofibers.

Composite PAN nanofibers using speciality grade PAN (special acrylic fiber, SAF) with well dispersed aligned ZnRs were also successfully electrospun. The incorporation of ZnRs was found to significantly improve the tensile strength (by 200%) as well as modulus (by 450%) of the nanowebs. The effect of the presence of ZnRs on structure development during carbonization process of PAN nanofibers has been investigated. On carbonization, all the samples with ZnRs were found to have significantly lower I_D/I_G ratios. The effect of carbonization temperature on the structural properties of carbon fibers was analyzed. The role of ZnO nanorods in carbonization was also investigated by performing carbonization of PAN and ZnO-PAN precursor nanofibers with and without oxidation step. The rigid ZnO nanostructures present in the fibers played crucial role by immobilizing the polymeric chains and keeping them oriented during the initial heating process with proper distribution of heat along the fiber. With the increase in the content of these rigid nanostructures, the fraction of polymer chains experiencing the above effect increased, and hence, results in overall better graphitic structure. The incorporation of ZnO rods allowed elimination of stabilization step and significantly faster carbonization with better graphitic content.

The melt spinning behavior of ZnO/nylon 6 composites was investigated in the third part of the study. The ZnO nanostructures of different aspect ratios (i.e. ZnP, ZnR and ZnW) having

similar diameter of ~50 nm were melt blended with nylon 6, and subsequently, melt spun and drawn to obtain composite fibers. The incorporation of ZnO nanostructures inside nylon 6 fibers resulted in significantly better mechanical properties. The maximum strength and modulus achieved were 2.28 and 10.8 GPa, respectively, with an improvement of 390 and 511%, respectively, over the control nylon 6 fibers. The combination of high strength and extension resulted in extremely high values of toughness. The energy to break was very high at 165 J/g, which is comparable to that of dragline spider silk. Also, the thermal properties of the composite fibers were significantly improved.

The structure of control nylon 6 and composite fibers having 1 wt% of ZnP, ZnR and ZnW was analyzed using FE-SEM, XRD and Raman spectroscopy. The presence of different ZnO nanostructures was found to change the extent of the fibrillar structure formation. The presence of anisotropic ZnO nanostructures in nylon 6, during its melt spinning and drawing, are instrumental in higher conversion of amorphous to highly oriented α crystalline regions resulting in increased α/γ ratio and increased crystallinity as well as crystalline orientation. Further, the orientation of remaining amorphous region was also increased which facilitated the formation of fibrillar structure. The significantly higher enhancement in mechanical properties of ZnW/nylon 6 fibers was attributed to much better alignment of polymeric chains, formation of higher extent of α crystals with highly fibrillar morphology in the presence of ZnW. It was inferred that the rigid nature and long dimensions of the anisotropic ZnWs changed the morphology of the fibers by helping in regulating the relaxation behavior of polymer chains during the spinning and drawing processes. Interestingly, the use of rigid anisotropic nanostructures such as ZnR and ZnWs could yield high performance fibers using commodity grade nylon 6.

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LIST OF SYMBOLS AND ABBREVIATIONS

Symbols/Abbreviation	Term/Expanded Form
α	Alpha (%)
f_{ab}	Amorphous orientation
χ_c	Crystallinity (%)
f_c	Crystalline orientation factor
T_c	Crystallization temperature (°C)
T_g	Glass transition temperature (°C)
γ	Gamma (%)
T_m	Melting temperature (°C)
F_{oa}	Oriented fraction of amorphous content
q	Scattering vector (nm^{-1})
σ	Tensile strength (Pa)
φ_f	Volume fraction
APTMS	(3-aminopropyl) trimethoxysilane
AS	As-spun
CFs	Carbon fibers
CNTs	Carbon nanotubes
CNFs	Carbon nanofibers
CTAB	Cetyltrimethyl amoinium bromide
DMF	N,N-dimethylforamide
DSC	Differential scanning calorimetry
DTG	Derivative of the weight loss
DR	Drawn
EDX	Energy dispersive X-ray

FE-SEM	Field emission scanning electron microscope
HS	Drawn and heat-set
HTHP	High temperature high pressure
MBC	Minimum bactericidal concentration
MMT	Montmorillonite
MWNTs	Multi-walled nanotubes
NaOH	Sodium hydroxide
NP	Nanoparticles
PAN	Poly(acrylonitrile)
PA	Polyamide
PANi	Polyaniline
PBO	Poly(p-phenylene benzobisoxazole)
PC	Polycarbonate
PET	Poly(ethylene terphthalate)
PLA	Polylactide
PP	Polypropylene
PS	Polystyrene
PU	Polyurethane
PVA	Poly(vinyl alcohol)
PVP	Poly(vinylpyrrolidone)
PVDF	Poly (vinylidene fluoride)
SDS	Sodium dodecyl sulphate
Si_3N_4	Silicon nitride
SWNTs	Single-walled nanotubes
TEM	Transmission electron microscope

THF	Tetrahydrofuran
TGA	Thermo gravimetric analyzer
TSE	Twin screw extruder
UHMPE	Ultrahigh molecular weight polyethylene
XRD	X-ray diffraction
ZnO	Zinc oxide
ZnP	ZnO nanoparticles
ZnR	ZnO nanorods
ZnW	ZnO nanowires