

Green Processing of PS/Nanoparticle Fibers and Studying Morphology and Properties

M. Kheirandish, S. Borhani

Abstract—In this experiment Polystyrene/Zinc-oxide (PS/ZnO) nanocomposite fibers were produced by electrospinning technique using limonene as a green solvent. First, the morphology of electrospun pure polystyrene (PS) and PS/ZnO nanocomposite fibers investigated by SEM. Results showed the PS fiber diameter decreased by increasing concentration of Zinc Oxide nanoparticles (ZnO NPs). Thermo Gravimetric Analysis (TGA) results showed thermal stability of nanocomposites increased by increasing ZnO NPs in PS electrospun fibers. Considering Differential Scanning Calorimeter (DSC) thermograms for electrospun PS fibers indicated that introduction of ZnO NPs into fibers affects the glass transition temperature (T_g) by reducing it. Also, UV protection properties of nanocomposite fibers were increased by increasing ZnO concentration. Evaluating the effect of metal oxide NPs amount on mechanical properties of electrospun layer showed that tensile strength and elasticity modulus of the electrospun layer of PS increased by addition of ZnO NPs. X-ray diffraction (XRD) pattern of nanocomposite fibers confirmed the presence of NPs in the samples.

Keywords—Electrospinning, nanoparticle, polystyrene, ZnO.

I. INTRODUCTION

POLYSTYRENE is one of the transparent and most common plastics. This material indicates very high electrical resistance polymer. It is also a hard and brittle material with a low dielectric loss [1], [2].

Electrospinning of polystyrene fibers have brought great interest because of its varied applications such as ion exchanger [3], sensors [4] and etc. Some researchers embedded various types of nanoparticles (NPs) dispersed in polymer solutions and studied properties of electrospun fibers prepared from this solutions.

D-limonene is a hydrocarbon classified as a terpene. This compound has a colossal class of natural vegetable oil extracted from the rinds of citrus fruits. D-limonene has spacious and various usage including perfume, medicine, flavoring and use up as cleaner, pesticide, heat transfer fluid, and solvent [5].

In this work, safe and biodegradable limonene was used as solvent of PS in electrospinning process. PS Solutions including various concentrations of zinc oxide nanoparticles

(ZnO NPs) are electrospun. In this experiment we studied effect of ZnO NPs on thermal and mechanical properties and morphology of nanocomposite fibers.

II. MATERIALS AND METHOD

PS pellets with a average molecular weight of 280,000 g/mol and ZnO NPs with a particle size of about 50nm and a specific surface area about 60 m²/g, were received from the Aldrich Co. dl-Limonene were purchased from Merck Co.

PS has been dissolved in predetermined amount of D-limonene. Then ZnO NPs dispersed in limonene by ultrasonic vibration for 10min (the concentration of NPs were 0, 2, 4, 6 and 8 percent by weight). Dispersed NPs were mixed in polymer solution for 12h with vigorous stirring. The final concentration of PS in limonene was 35 weight percent (wt%).

Scanning Electron Microscopy (SEM) of Seron Technology was employed to characterize morphologies of fibers. The thermal stability of PS/ZnO electrospun fibers were investigated by Thermo Gravimetric Analysis (TGA) using a simultaneous thermal analysis. The effects of the NPs on polymer's glass transition temperature, (T_g) in nanocomposite fibers were measured using Differential Scanning Calorimeter 2010 (DSC). The absorbance spectra were recorded for fibers contained different concentration of ZnO by means of UV-vis spectrophotometer. The mechanical properties were carried out in a material prufung model 1446-60 with a 10 N load cell. The confirmation for presence of NPs in the structure of fibers was performed by X-Ray Diffraction (XRD) of Philips Xpert-MPD.

III. RESULTS AND DISCUSSION

SEM images of electrospun fibers produced with different percentages of ZnO NPs that shown in Fig. 1. The average diameters are listed in Table I. As shown in this table the fiber diameter distribution ranged from 1.69 to 2.09 micrometer.

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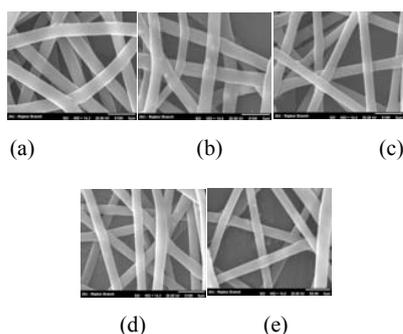


Fig. 1 SEM images of electrospun PS NPs at different concentration. a) pure PS; b) 2% ZnO; c) 4% ZnO; d) 6% ZnO; e) 8% ZnO

Those images as you see in Fig. 1 confirmed that the higher ZnO NPs percentages produced thinner microfibrs, and the lower concentration produced thicker microfibrs. Because the variation of fiber diameter for the resulting electrospun fibers is owing to differences in conductivity of the solutions; therefore, we can conclude ZnO NPs are increasing electrical conductivity of polymer solution and cause decreasing in microfibr diameter.

TABLE I
DIAMETER OF ELECTROSPUN PS NANOCOMPOSITE AT DIFFERENT NANOPARTICLE CONCENTRATION

Sample	ZnO content (wt%)	Diameter (μm)
PS-0	0	2.09
PS-2	2	2.07
PS-4	4	1.83
PS-6	6	1.72
PS-8	8	1.69

TABLE II
TGA DATA OF PS/ZnO ELECTROSPUN FIBERS

Sample	T_{10} ($^{\circ}\text{C}$)	T_{50} ($^{\circ}\text{C}$)
PS-0	374.4	472.9
PS-2	380.8	429.9
PS-4	382.7	430.6
PS-6	391.5	431.3
PS-8	394.3	432.2

The results of thermal decomposition behavior of polystyrene nanocomposite fibers are shown in Table II. It is obvious that as ZnO NPs were incorporated in structure of polystyrene fibers, the temperature required for 10% and 50% degradation (T_{10} ($^{\circ}\text{C}$) and T_{50} ($^{\circ}\text{C}$)) were slightly shifted.

Fig. 2 shows TGA curve of electrospun polystyrene nanocomposite fibers. In this figure residual tar increased by increasing ZnO NPs in PS electrospun fibers. This increment of thermal stability could be attached to restriction of nanoparticles on out-diffusion for volatile decomposition products.

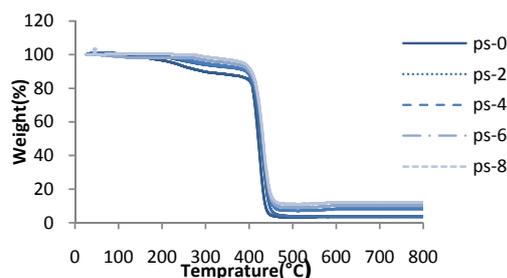


Fig. 2 The TGA curves of pure PS and PS/ZnO nanocomposites fibers with different concentration of NPs

Fig. 3 shows DSC analyses of electrospun PS/ZnO nanocomposites for 0, 4 and 8 wt% of NPs. The results of glass transition behavior for pristine PS microfibrs and microfibrs included 4 and 8 wt% of NPs are presented in Table III. The results showed T_g of microfibrs decreased by increasing the concentration of ZnO NPs. The observation can be explained by the effect of the NPs as plasticizers.

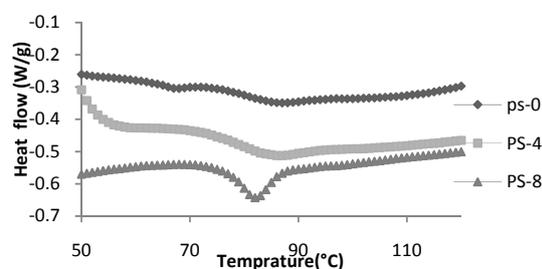


Fig. 3 DSC curve of electrospun microfibrs with different concentration of NPs

TABLE III
GLASS TRANSITION TEMPERATURE VALUE OF PURE PS AND PS/ZnO NPS ELECTROSPUN FIBERS

Sample	T_g ($^{\circ}\text{C}$)
PS-0	87
PS-4	86
PS-8	82

Fig. 4 shows absorbance spectra of PS/ZnO microfibrs. The absorbance patterns of the microfibrs with various concentrations of NPs are obviously different. In the UV region, the absorbance of electrospun PS/ZnO fibers is much lower than pure PS microfibrs due to UV absorption of ZnO NPs.

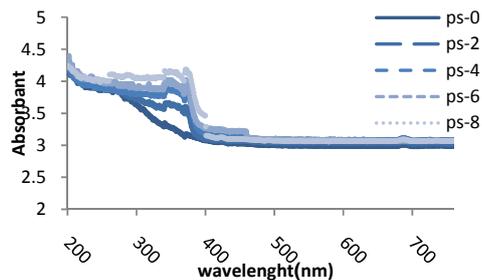


Fig. 4 UV-vis absorption spectra of pure PS and PS/ZnO electrospun fibers

The difference in the UV region from 300-400nm is correlation to excitations of donor level electrons to the conduction band. In order to jump an electron from a valence band to a conduction band, it requires a specific minimum energy for the transition- the band gap energy. So, the usage of ZnO NPs in electrospun fibers can be applied to inhibit the UV radiation.

The relationship between ZnO NPs concentration and tensile strength of electrospun PS/ZnO nanocomposite fibers is shown in Fig. 5. As you see; all the microfibers included ZnO content showed higher tensile strength than pure microfibers. Tensile strength of nanocomposite has been enhanced when interfacial adhesion was improved. This result can be correlated to the interaction of the filler with the matrix. Therefore, well-adhering nano-ZnO can bear on part of the load applied to the matrix and contribute to the tensile strength of the nanocomposites [6]. Modulus for all compositions of PS/ZnO fibers reported in Fig. 6. The modulus of the microfibers contain 2-8% of ZnO NPs are higher than pure PS microfibers.

Several parameters are influencing the increase in composite modulus such as the aspect ratio of the filler, interfacial interaction, dispersion of the fillers, etc. The particle size of filler-ZnO used in this work was 50nm. NPs with great amount of surface area caused enhancement interaction between filler and polymer matrix.

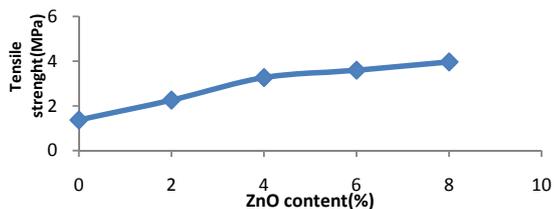


Fig. 5 Tensile strength of PS/ZnO microfibers

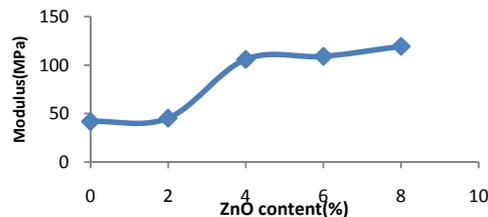
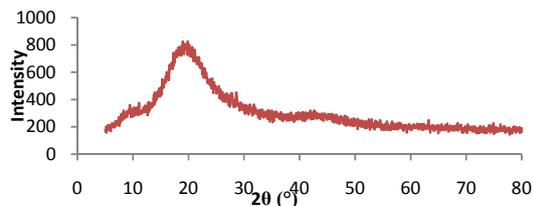
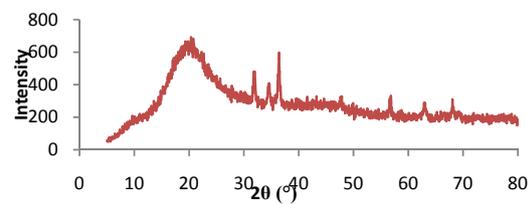


Fig. 6 Modulus of PS/ZnO microfibers

The results of X-ray diffraction for pure PS and PS microfiber included 8% NPs are shown in Figs. 7 (a), and (b).



(a)



(b)

Fig. 7 The XRD pattern for (a) PS microfibers, (b) 8 wt% ZnO nanoparticle filled PS microfibers

In these figures a wide noncrystalline peak from 10 to 30 belonged to PS. The XRD pattern of pristine PS is specified by one peak at $2\theta = 19.06^\circ$. Sharp diffraction peaks of ZnO can be observed in Fig. 7 (b). These peaks at scattering angles (2θ) value of 31.89, 34.57, 36.39, 47.87, 56.82, 62.97, 68.07, and 69.37 correspond to crystal planes of 100, 002, 101, 102, 110, 103, 200, and 112 crystal planes, respectively. The XRD characteristic was presented the hexagonal phase with Wurtzite structure of ZnO NPs. So, ZnO NPs conjunction did not make a new peak neither shifted the peak with respect to PS which illustrate that PS/ZnO microfibers made from these two phase structures of polymer and NPs.

IV. CONCLUSION

The electrospun PS/ZnO fibers were characterized by SEM, TGA, DSC and XRD. Mechanical and amount of UV absorption also investigated. SEM images showed that PS fiber diameter decreased by increasing ZnO NPs concentration. TGA results showed that adding zinc oxide NPs in electrospinning fibers would increase thermal stability of product. Considering Differential Scanning Calorimeter of polystyrene fibers showed that with increasing the amount of zinc oxide or NPs, the glass transition temperature was

decreased. Evaluating the effect of amount of metal oxide NPs on mechanical properties of electrospinning layer showed that NPs of zinc oxide increased the stability and elasticity module of electrospinning layer of polystyrene. Results from X-ray diffraction of electrospinning fibers bearing NPs confirmed the presence of NPs in the samples.

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