ELASTIC ELECTROSPUN NANOSTRUCTURES BASED ON POLYURETHANE/MWNT

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Abstract: Electrically conductive nanofibers were fabricated from elastic polyurethane (PU) and PU/multiwalled carbon nanotubes (MWCNTs) nanocomposite by electrospinning method. The nanocomposites were electrospun at various MWCNTs loading. Electron microscopy was used to investigate nanofibers morphology and dispersion of MWCNTs in the electrospun nanofibers. The results showed that the presence of the MWCNTs promoted the creation of fibrous structures in comparison with the PU without MWCNTs. On the other hand, increasing the MWCNTs content resulted in a slight increase in the average fiber diameter. Electrical behavior of the conductive mats was also studied, in view of possible sensor applications. Cyclic experiments were conducted to establish whether the electrical properties were reversible, which is an important requirement for sensor materials.

Keywords: Polyurethanes, Carbon Nanotube, Nanofiber, Mechanical properties, Sensors, TEM, SEM

1. Introduction

Electrospinning process has gained much attention due to being an effective method in producing ultra fine fibres or fibrous structures from many polymers with a diameter in a range from several micrometers down to a few nanometers. This method appears to be the most straightforward way to prepare nanofibres via transferring a polymer melt or solution through a spinneret using a high-voltage electrostatic field. The produced fibres often have a diameter in the range of nanometers. Several authors have explained this process; for the sake of brevity only a few are mentioned in the list of references [1-5]. The distinguished characteristic of these nanofibres is unexpected high surface area to volume ratios so that it makes them highly attractive for many applications ranging from textile to nanocomposites, sensors, biomaterials and membrane technology.

Polyurethanes (PU) represent a class of polymers that possess a range of very desirable properties: they are elastomeric, resistant to microorganisms and abrasion, and have excellent hydrolytic stability. Many commercially available PU's can be used to make good electrospinning solutions. There are various articles regarding electrospinning of PU [6, 7]. Electrospinning of PU/MWCNTs has briefly been explained by Kimmer and coworkers [8]. They have characterized the composite nanofibers morphology using FESEM and TEM. Hunley *et al.* [9] have studied melt dispersion and electrospinning of MWCNTs/PU and characterized morphology and electrical conductivity of the nanofibers.

Some authors have reported the application of the polypyrrole-coated fabrics as the sensing fabrics for detection of strain to enable the measurement and control of various movement of human body, which may be used as an intelligent material for preparation of wearable devices for training, fitting, rehabilitation, etc [10]. Ciselli and coworkers [11] fabricated elastomeric composites based on EPDM filled with multiwalled carbon nanotubes (MWCNTs). The main focus of their study was on the electrical behavior of these conductive polymer composites (CPCs), in view of possible sensor applications.

2. Materials and methods

2.1. Materials

Polyether/Polyester based thermoplastic polyurethane TPU Desmopan 5377A with melting point 191-210 ºC was obtained from Bayer GmbH, Germany. The MWCNTs were obtained as a powder from Neutrino (Neunano, Iran). The Solvent *N*, *N*-dimethylformamide (DMF) (99.9%, Aldrich Co. Ltd) was used as received.

2.2. Solution preparation and electrospinning

0.9 g of PU granules was dissolved in DMF to obtain 15%wt solution that is suitable for electrospinning process. For the fabrication of PU/MWCNTs solution, the following procedure was used. The necessary weight fractions of MWCNTs (0.018–0.45 g) were first dispersed in 6 ml DMF and then sonicated for 15 min. at room temperature using a sonicator (BANDELIN). Then, the PU solution was added and the mixture was stirred for 1 h and further sonicated for 15 min.

For electrospinning, about 3 ml of each PU/MWCNTs solution was put into a 5 ml syringe with a stainless steel needle (inner diameter: 0.7 mm) attached at the open end. The needle was connected to the emitting electrode of a high-voltage supply (Gamma High Voltage Research, USA), which is capable of generating DC voltage in the range of 0-30 kV. The electrospun nanofibers were collected on a target plate (aluminum foil) located at a distance of 10 cm from the syringe tip. A syringe pump (New Eva Pump System Inc., USA) was used to feed a constant amount of solution onto the tip. The output of the injection pump was 1 µl/min. The applied electrical potential was 10 kV at normal laboratory condition (about 22 °C). Details of the used electrospinning apparatus were explained in previous work [12].

2.3. Characterization

2.3.1. Scanning Electron Microscopy (SEM)

Morphology, surface texture and dimensions of the gold-sputtered electrospun PU and PU/MWCNTs nanofibres were determined using a Zeiss (LEO) 1455 VP scanning electron microscope, Angstrom Scientific Inc., England. Measurements of about 100 random points on the fibers were used for determining fiber diameter distribution and the average fiber diameter.

2.3.2. Electrical Properties

Electrical resistance of the PU/MWCNTs electrospun nanofiber mats was measured by the standard two point probe method using Digital Multimeter (DT9201A). In another set of experiment, electrical conductivity of PU/MWCNTs electrospun nanofiber mats was measured during stretching at a Shirley Micro 50 fiber tester with elongation rate of 10 mm/min up to 20% elongation. This measurement was also performed in cyclic elongations.

3. Results and discussion

3.1. Scanning Electron Microscopy (SEM)

Electrospun nanofibers were produced using neat and nanocomposite PU with a MWCNTs content that ranged between 2 and 12 wt.%. In order to study the effect of the MWCNTs on the final fibrous structure, all the electrospinning processing variables were kept constant. A series of experiments were performed, at 10 kV, while the PU concentration was equal to 15 wt.%.

SEM micrographs of the PU and PU/MWCNTs nanofibers are shown in figure 2. It is clearly visible that, the introduction of MWCNTs into PU solution resulted in the formation of a web with a more pronounced fibrous structure.

For pure PU solution, large spherical defects in combination with thin fibers (beads-on-string membrane structure) were observed (Figure 1a). Fewer defects and more uniform fibrous structures were observed as the MWCNTs content of the nanocomposite material increased to 2, 4 and 6 wt.% (Figures 1b–d, respectively). No beads and membranes with a more uniform fibrous structures were observed for 8 and 12 wt.% MWCNTs content (Figures. 1e and f). In other words, the presence of the MWCNTs promoted the creation of fibrous structures in comparison with the PU nanofibers without MWCNTs which is in agreements with the finding of kimmer and coworkers [8]. This observation could be attributed to the increase in electric conductivity and viscosity of the solution caused by the addition of MWCNTs. The formation of solution droplets that are transformed into polymer beads as the solvent evaporates is thermodynamically favored (over fiber formation) due to the interface reduction. However, as mutual charge repulsion causes a force directly opposite to the surface tension, the higher charge density on the surface of the solution jet favors the formation of fine fibers with fewer defects [13]. The latter is

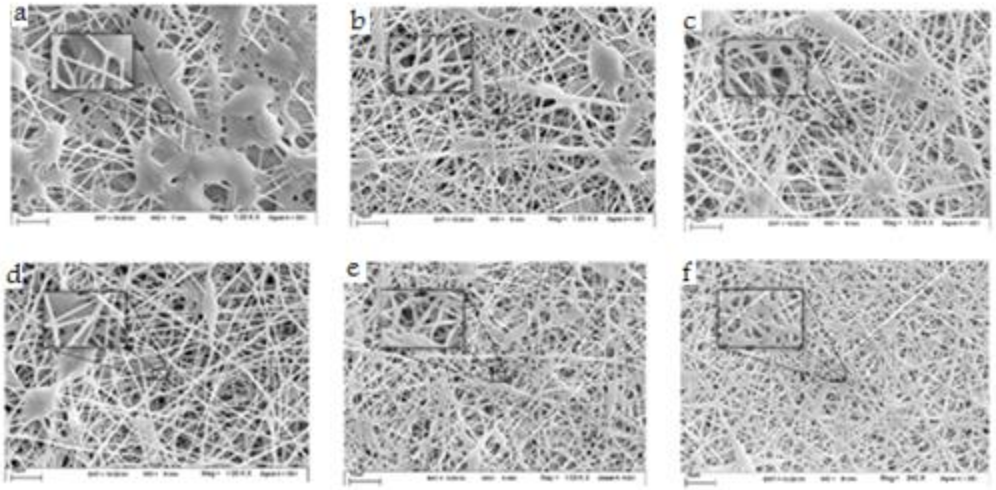

Figure 1. *Scanning electron micrographs of neat PU and PU/MWCNTs electrospun nanofibers at applied voltage of 10 kV . MWCNTs content was (a) 0% wt.%, (neat PU) (b) 2% wt.%, (c) 4% wt.%, (d) 6% wt.%, (e) 8% wt.% and (f) 12%.*

consistent with the observation of Zong et al. [14], who reported that the addition of small amounts of salt led to the production of nanofibers free of beads. Simultaneously increase in solution viscosity hinders the formation of droplets, resulting in the formation of fewer bead defects.

Furthermore, as summarized in table 1, increasing the MWCNTs content resulted in a slight increase in the average fiber diameter. This may be attributed to the increase in shear viscosity of the electrospinning solution (table 1). It has been reported that higher solution viscosity results in larger fiber diameters [1-5]. The solution viscosity mainly depends on the MWCNTs content in the solution. Thus, the higher MWCNTs content results in fibers with a larger diameter.

Table 1.*Summary of fibers diameter of PU and PU/MWCNTs electrospun at 10kV*

MWCNTs content (%)	Viscosity of electrospinning solution (cp)	Electrical conductivity of electrospinning solution (mS/cm)	Fiber Diameter Range (nm)	Average of Fiber Diameter (nm)
0	279.9	0.210	68.29-437.26	227.59
2	339	27	141.58-614.65	279.45
4	459.9	83	87.8-620.8	285.16
6	539.9	132	114.4-782.42	297.1
8	720.6	196	117.84-695.84	302.89
12	1300	429	138.83-639.24	330.59

3.2. Electrical properties during uniaxial stretching

Figure 2 shows electrical conductivity of the electrospun mats at various MWCNTs content. As expected, electrical conductivity of the mats was found to increase with an increase in MWCNTs content in the nanofibers. Figure 3 shows that the electrical conductivity of the mats increases sharply when the MWCNTs content is less than 4%, after which it will gradually reach to 10^{-7} S/cm at higher MWCNTs content. This result is in agreement with the observations of Ciselli and co workers [11] who studied electrical properties of polymer composites based on EPDM and MWCNTs.

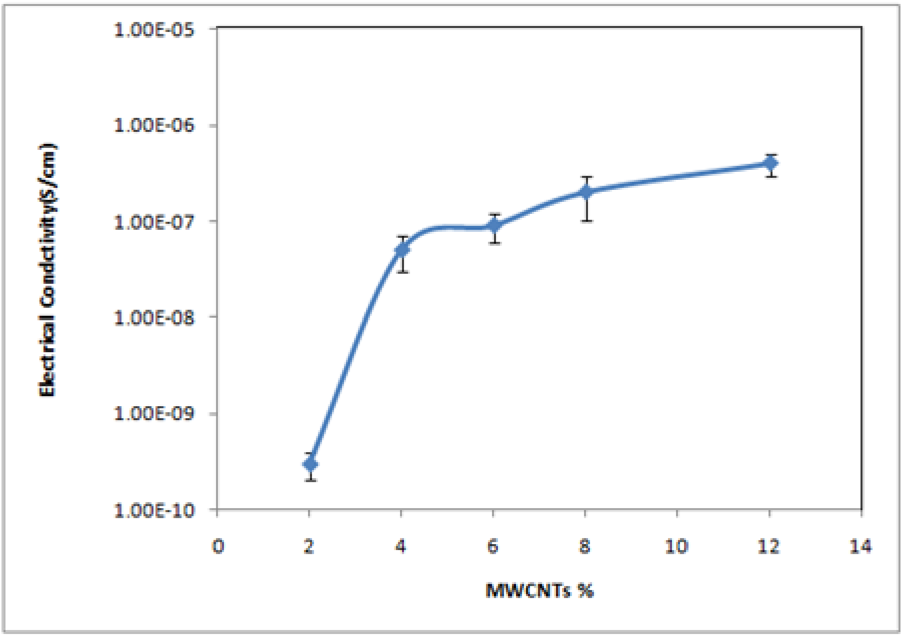

Figure 2. *Electrical conductivity of PU/MWCNTs electrospun nanofiber mats as a function of MWCNT content.*

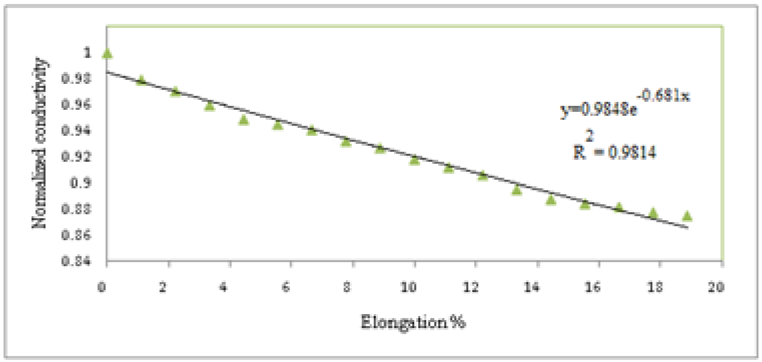

Figure 3. *Decrease in electrical conductivity of electrospun mat containing 8% MWCNTs during uniaxial stretching*

The conductivity of nanofiber mat containing 8 wt.% MWCNTs as a function of strain is displayed in Figure 4. This figure shows a gradual decrease in electrical conductivity during stretching of the nanofiber mat. The decrease of conductivity with increasing strain is similar to the results shown by MWCNTs filled EPDM [11]. The change in conductivity upon straining is generally explained by this fact that elongation of the web causes breakage of the existing continuous conducting network by increasing the gap between particles, which results in a reduction of the total number of possible conduction paths.

For application as sensor materials, electrical conductivity of nanofiber mat under repeated cyclic loading was examined. The typical curves of normalized conductivity change with strain of the PU/MWCNTs nanofiber mat during 4 cycles of elongation and relaxation measurements are illustrated in figure 4. This figures show that the normalized conductivity decreases and increase during cyclic loading. This observation reveals that due to the existence of elastic properties of PU matrix, the prepared mat shows good reversibility under large-strain deformation of up to 20%.

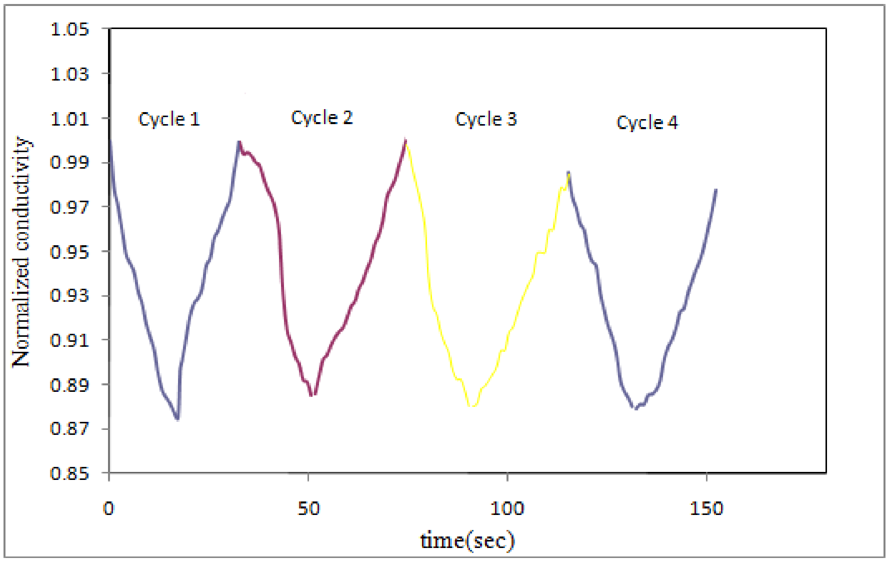

Figure 4. *Normalized electrical conductivity of PU/MWCNTs nanofiber mats in 4 cycles of elongation. Elongation rate was 10 mm/min and MWCNTs content was 8%.*

4. Conclusion

Nanofibers were fabricated from PU and PU/MWCNTs nanocomposite by electrospinning method with diameters ranging from 227 to 330 nm depending on electrospinning conditions. The addition of MWCNTs resulted in the formation of more fine fibrous structure with fewer defects. However, the mean fiber diameter was slightly increased with an increase in MWCNTs content in the nanocomposites. These observations were attributed to the increase in solution's electric conductivity and viscosity that were caused by the addition of the MWCNTs. MWCNTs were present inside the PU/MWCNT nanofibers as individual tubes well aligned with nanofibers axes at low level MWCNTs loading. However, some aggregates were visible at the high content of nanotubes. Mechanical tests show that, compared with pure PU, the tensile modulus, tensile strength are improved significantly while without sacrificing high elongation at break by incorporating MWCNTs less than 8 wt%. Electrical conductivities of the fibrous mats were increased with MWCNTs content. Electrical conductivity of nanofiber mats under repeated cyclic loading was examined. Due to the existence of elastic properties of PU matrix, the prepared mats show good reversibility in electrical properties under large-strain deformation of up to 20%. The PU/MWCNTs nanofiber mats are expected to be a potential candidate for applications as strain gauge sensors.

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