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Improved mechanical and electrical properties in electrospun polyimide/multiwalled carbon nanotubes nanofibrous composites

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Highly aligned polyimide (PI) and PI/multi-walled carbon nanotubes (PI/MWCNTs) nanofibrous composites by incorporating poly(ethylene oxide) as the dispersing medium were fabricated using electrospinning technique. The morphology, mechanical, and electrical properties of the electrospun nanofibrous composites were investigated. Scanning electron microscope showed that the functionalized MWCNTs (f-MWCNTs) were well dispersed and oriented along the nanofiber axis. Analysis of electrical properties indicated a remarkable improvement on the alternating current conductivity by introduction of the aligned f-MWCNTs. Besides, with addition of 3 vol. % f-MWCNTs, the obvious enhancement of tensile modulus and strength was achieved. Thus, the electrospun PI/MWCNTs nanofibrous composites have great potential applications in multifunctional engineering materials. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4897230>]

I. INTRODUCTION

Conductive composite films have been attracted a lot of attention in recent years.¹ However, they have a poor flexibility, usually exhibiting fragile mechanically at a high loading of fillers. It is considered that the nanofibrous composites can endow excellent electrical and mechanical properties, because the nanofiber structure can provide flexibility to otherwise stiff materials and simultaneously the nanofibers network can provide structural strength.^{2,3} Electrospinning is regarded as an efficient technique for continuously fabricating polymer nanofibers with diameter ranging from a few to several hundred nanometers. In recent years, the polymers, such as polyurethanes, polycarbonate, polyacrylonitrile, polyvinyl alcohol, and polylactic acid, have been successfully electrospun into nanofibers.⁴⁻⁶ Owing to their outstanding performance, the electrospun polymer fibers can be fulfilled the practical application in many fields including sensors, filtration, tissue engineering scaffolds, supercapacitors, and so on.⁷⁻¹²

Due to its high modulus and strength, excellent thermal stability, and dielectric properties, polyimide (PI) has been considered to be a high performance engineering material and used as adhesives, dielectrics, and membrane materials.¹³⁻¹⁷ The electrospun PI nanofibers have been investigated in terms of their microstructure and intrinsic properties. In order to improve its mechanical properties, PI has also been electrospun with inorganic fillers to prepare nanofiber composites.^{15,18-21} However, the investigation on electrospun PI nanofibrous composites with excellent electrical properties is still lacking.

The combination of outstanding mechanical and electrical properties as well as high aspect ratios of carbon nanotubes (CNTs) makes them realistic alternatives to be widely used in many fields such as electrodes, nanometer electron device, and composites. Recently, the polymer nanofibers by incorporating of CNTs have been focused on. With the development of electrospinning technique, some attempts have been made to fabricate the electrospun polymer/CNTs nanofiber composites, and some satisfactory results have been achieved.²²⁻²⁶ However, the dispersion of CNTs in the polymer matrix is still a challenge. Many methods have been discussed to well disperse CNTs including sonication, shear mixing, and chemical functionalization. Among them, the chemical functionalization with functional groups introduced on CNT surface could be achieved by acid or silane treatment. It is worth noting that electrospinning is one approach to realize homogenous CNT dispersion.²⁷⁻³⁰ During this process, we usually focus on controlling and optimizing the diameter and orientation of nanofibers. Besides, the distribution and alignment of CNTs in the nanofibers are also important issues. The related mechanisms behind this method need to be further studied.

In this work, the electrically conductive PI nanofibrous composites with a certain amount of multi-walled carbon nanotubes (MWCNTs) were prepared by electrospinning technique. In order to realize uniform MWCNT dispersion in the PI nanofibers, the functional groups were introduced on the surface of MWCNTs by chemical functionalization. The poly(ethylene oxide) (PEO) was used as a dispersing medium, and it was finally removed by imidization process. Up to now, there have been few reports on the fabrication of electrospun PI/MWCNTs nanofibrous composites by introducing PEO during the electrospinning process. The dispersion and alignment of MWCNTs in the electrospun

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nanofibers, as well as the electrical and mechanical properties of the nanofibrous composites, were investigated. The relationship between the microstructure and mechanical and electrical properties of the composites were discussed.

II. EXPERIMENTAL

A. Materials

The MWCNTs with a diameter of about 10–30 nm, length of 2 μm , and purity of 95% were supplied by Shenzhen Nanotech Port Co. Ltd., China. Commercial pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) used as received were obtained from Sinopharm Chemical Reagent Co. Ltd. and Shanghai Sanaisi Reagent Co., China, respectively. N,N-dimethylformamide (DMF) was purchased from Beijing Chemical Reagent Co., China, and it was refluxed with CaH_2 for 3 h and distilled to remove adsorbed water prior to use. PEO with a weight-average molecular weight of 10^5 was provided by Guangzhou Lihou Trade Co. Ltd., China.

B. Acid modification of MWCNTs

The MWCNTs were treated in concentrated HNO_3 solution for 12 h in a refluxing apparatus to produce carboxyl on the MWCNTs surface. The resulted MWCNTs were washed by deionized water until $\text{pH}=7$. Then, they were dried at 70°C under atmospheric condition.

C. Preparation of the electrospun solution

The electrospun solution of polyamic acid (PAA), namely, the precursor of polyimide, was synthesized from PMDA and ODA at room temperature for 5 h. The mole ratio of PMDA to ODA was set as 1:1, and the solid content in the solution was 20 wt.%. The electrospun solution of PEO/MWCNTs was obtained as follows. First, the MWCNTs were well dispersed into the DMF solution using ultrasonic for 2 h. Second, PEO was added into the MWCNTs solution and stirred for 4 h at 60°C .

D. Fabrication of the electrospun nanofibrous composites

The electrospinning setup employed in this work consisted of a spinning jet, a syringe pump, a collection unit, and a high-voltage supply unit. All the electrospinning processes were carried out at room temperature. The distance between the needle tip and rotating collector was set as 10.0 cm. An adjustable feeding rate was provided by the syringe pump. In order to form the aligned nanofibers, the linear speed of rotating collector was set as 6 ms^{-1} . The electrospun nanofibrous composites were collected on one aluminum foil attached to the collector. To obtain the MWCNTs/PEO-PAA multilayer nanofibers, the PEO/MWCNTs solution was first electrospun on the aluminum foil, and then the PAA solution was electrospun on the surface of PEO/MWCNTs nanofiber membranes. The above two processes were duplicated in turn. After that, the nanofibrous mat was carefully peeled off from the aluminum foils.

Then, the MWCNTs/PEO-PAA multilayer nanofiber mats were compressed at 20 MPa for 30 min. The PEO was removed from the multilayer nanofibrous composite by imidization. The imidization process includes three steps: (1) The film was heated up to 100°C at a rate of 5°C min^{-1} and annealed for 1 h; (2) heated up to 200°C at a rate of 5°C min^{-1} and annealed for 1 h; and (3) heated up to 300°C at a rate of 5°C min^{-1} and annealed for 1 h. Finally, the PI/MWCNTs nanofibrous composites were achieved. For comparison, the electrospun pure PI films were also prepared.

E. Characterization

Surface morphologies of the electrospun nanofibrous composites were observed by scanning electron microscope (SEM, JSM-7500F Hitachi, Japan). MWCNT dispersion in the PEO nanofibers was evaluated by transmission electron microscope (TEM, H-7650B Hitachi, Japan). Tensile tests of the electrospun pure PI and PI nanofibrous composites were performed on a machine (Shimadzu, Model AG-IC, Japan) at room temperature. Five samples with dimensions of $50.0 \times 10.0 \times 0.2\text{ mm}$ were measured at a speed of 2 mm min^{-1} under the same condition. Alternating current (AC) conductivity of the samples was measured using an impedance analyzer (Agilent 4294A, USA) in the frequency range of 10^2 to 10^7 Hz at room temperature. Prior to measurement, silver paste was applied on both sides of the specimens to ensure good electrical contact.

III. RESULTS AND DISCUSSIONS

Fig. 1 shows the FT-IR spectra of pristine MWCNTs (p-MWCNTs) and functionalized MWCNTs (f-MWCNTs). The peak at 1720 cm^{-1} and 1210 cm^{-1} was assigned to the C=O and C–O stretch of –COOH, respectively. Features at wavenumber of 1400 cm^{-1} are the absorption peaks of O–H bending of –COOH in the f-MWCNTs, indicating that they have been acidized by HNO_3 .

For comparing the dispersion of p-MWCNTs and f-MWCNTs, they were, respectively, dispersed into DMF solution and placed for 1 month. It can be clearly seen from

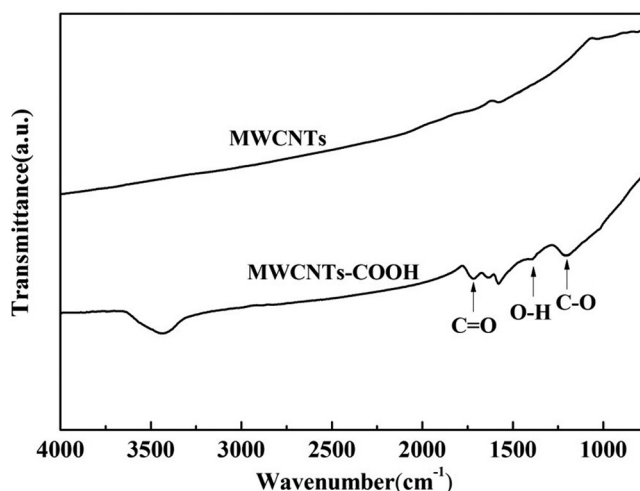


FIG. 1. FT-IR spectra of the p-MWCNTs and f-MWCNTs.

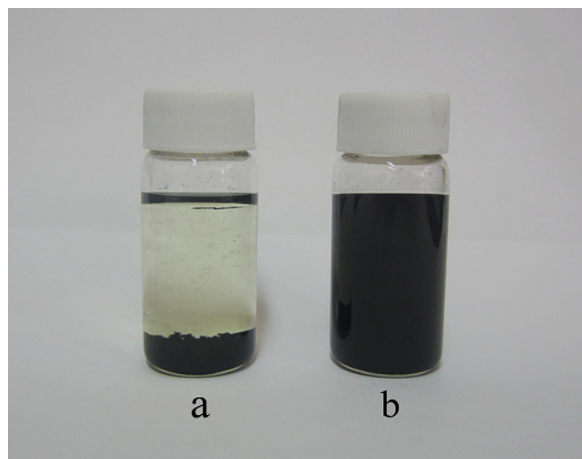


FIG. 2. Photographs of the dispersion of the (a) p-MWCNTs and (b) f-MWCNTs in DMF solution.

Fig. 2(a) that most of the p-MWCNTs are deposited at the bottom of the bottle, indicating their poor dispersion. However, the f-MWCNTs still remain uniform dispersion state (see Fig. 2(b)). It is because that the carboxyl groups are introduced onto MWCNT surfaces, which are helpful for MWCNT dispersion in the DMF solution.

Figs. 3(a) and 3(b) show SEM images of the fresh and fractured surfaces of neat PI nanofibrous films. We can see that the nanofibers are highly aligned, and their diameters display uniform distribution. Besides, their surfaces are smooth and almost free of other defects. It is known that the diameter uniformity and the absence of defects in the electrospun nanofiber are important for high strength and toughness. Figs. 3(c) and 3(d) show the morphologies of electrospun neat PEO and PEO/f-MWCNTs nanofibers. It can be seen that the diameter of PEO/f-MWCNTs was not as uniform as that of neat PEO, because the incorporation of MWCNTs results in the fluctuation of diameter distribution. Figs. 3(e) and 3(f) present TEM images of the PEO/p-MWCNTs and PEO/f-MWCNTs nanofibers, respectively. As shown in Fig. 3(e), the aggregations of p-MWCNTs can be clearly seen in the matrix. However, the f-MWCNTs are well dispersed and highly aligned, due to the chemical functionalization effect (see Fig. 3(f)). In addition, the f-MWCNTs are well encapsulated within the nanofibers. Thus, the functionalization of MWCNTs greatly improves their dispersion and orientation in the PEO matrix. In this case, during the imidization process, when PEO was totally removed at about 120 °C, MWCNTs could be uniformly dispersed rather than agglomerated on the PI nanofibers.

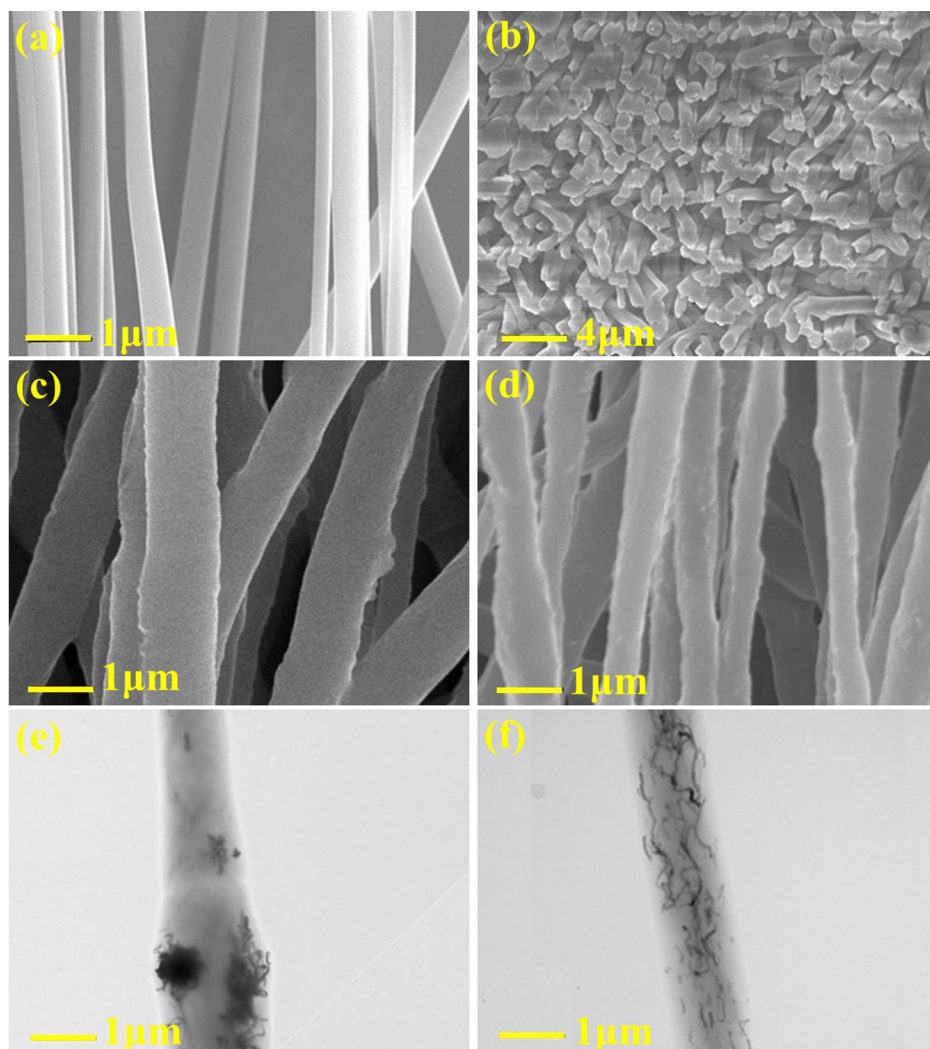


FIG. 3. (a)–(d) SEM images of the electrospun nanofibers. (a) and (b) The fresh and fractured surfaces of neat pure PI films; (c) and (d) neat PEO and PEO/f-MWCNTs; and (e) and (f) TEM images of PEO/p-MWCNTs (10 vol. %) and PEO/f-MWCNTs (10 vol. %).

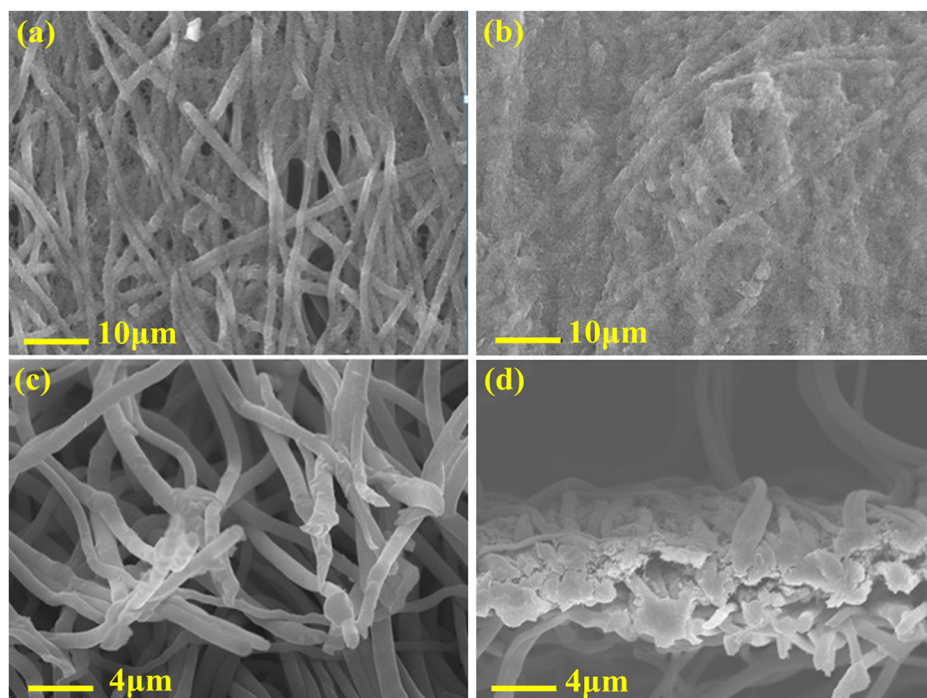


FIG. 4. SEM images of PI/MWCNTs nanofibrous composites with 3 vol.% and 9 vol.% f-MWCNTs.

SEM morphologies of the fresh surface of PI/MWCNTs nanofiber composites with 3 vol.% and 9 vol.% f-MWCNTs are shown in Figs. 4(a) and 4(b). It can be obvious to see that MWCNTs are evenly dispersed on the surface of PI nanofibers. Figs. 4(c) and 4(d) demonstrate the fractured surfaces of the PI/MWCNTs nanofibrous composites with 3 vol.% and 9 vol.% f-MWCNTs. MWCNTs almost connect with each other and the MWCNT networks are formed.

The stress-strain curves of the electrospun pure PI and PI/f-MWCNTs nanofibrous composites with 3 vol.%, 9 vol.%, and 14 vol.% f-MWCNTs are shown in Fig. 5(a). The obtained values of tensile strength and break elongation are demonstrated in Fig. 5(b). With increasing the loading, the tensile strength, and the break elongation of the PI/f-MWCNTs nanofibrous composites with 3 vol.%, f-MWCNTs reach the maximum value and then decrease distinctively. Compared to the tensile strength value of 72.3 ± 2.0 MPa for the electrospun pure PI films, the addition of 3 vol.% f-MWCNTs leads to an obvious improvement (49.7%) of tensile strength. The improvement of mechanical properties can be explained as follows. The functional groups on MWCNT surface can improve the interfacial adhesion between MWCNTs and the surrounding matrix, giving rise to effective stress transfer between the matrix and MWCNTs interface. However, the tensile strength of the nanofibrous composites decreases to 88.7 MPa with 9 vol.% f-MWCNTs loading, and as further increasing MWCNT content, tensile strength is continuously reduced. The initial increase of the mechanical properties is due to the uniform dispersion of MWCNTs in the matrix. However, the following deterioration of mechanical properties is attributed to the gradual aggregation of MWCNTs at higher loadings, easily resulting in stress concentration and micro-crack propagation in the matrix. Besides, the tensile modulus of the PI/f-MWCNTs nanofibrous composites is

evidently higher with respect to the pristine PI. It can be seen that the tensile modulus increases with the increase of f-MWCNTs content.

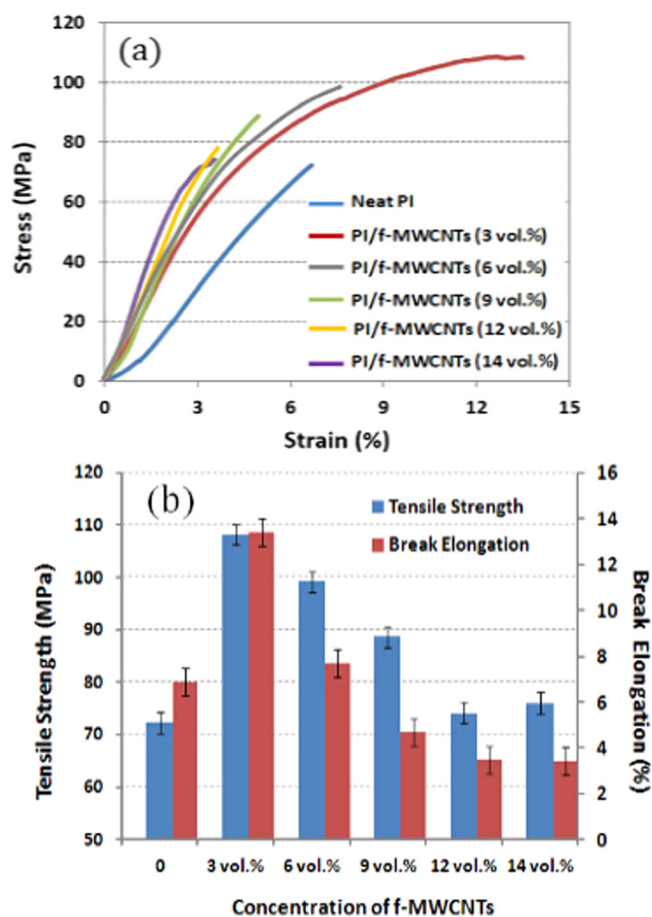


FIG. 5. Mechanical properties of the nanofibrous composites. (a) Typical stress-strain curves; and (b) tensile strength and break elongation vs. f-MWCNT concentration.

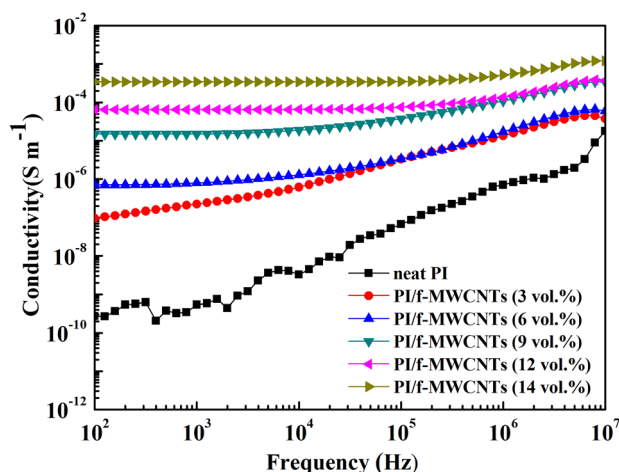


FIG. 6. Dependences of AC conductivity of the PI/MWCNTs nanofibrous composites on frequency.

Fig. 6 shows the variation of AC conductivities of the PI/f-MWCNTs nanofibrous composites as a function of frequency ranging from 10^2 to 10^7 Hz at room temperature. When the f-MWCNTs concentration is lower than 6 vol. %, the conductivity increases significantly with the frequency. When f-MWCNTs concentration reaches to 12 vol. %, there is a notable frequency-independence of conductivity at low frequency ranges, indicating that the conducting networks are well formed. In this case, the frequency has weak effect on conductivity at low frequency. AC conductivity of the electrospun neat pure PI films at 10^2 Hz is about 10^{-10} S cm $^{-1}$. A sharp increase (about 7 orders of magnitude) of the conductivity at 10^2 Hz is observed in the composites with 14 vol. % f-MWCNTs loading, which well satisfies the requirements of conductive polymer composites. In this case, the aligned MWCNTs in the nanofibrous composites could connect with each other within the PI nanofibers, thus resulting in the formation of conductive networks.

IV. CONCLUSION

This work focused on the fabrication of PI/MWCNTs nanofibrous composites employing electrospinning technique. The morphologies, mechanical, and electrical properties of the electrospun nanofibrous composites were investigated. From the SEM images, it can be seen that the functionalized MWCNTs are well dispersed and highly aligned within the PI matrix. With the addition of f-MWCNTs, tensile modulus and strength of the nanofibrous composite are evidently improved with respect to that of the electrospun neat pure PI films. Besides, the PI/f-MWCNTs nanofibrous composite with 14 vol. % orientated f-MWCNTs possesses a high conductivity of about 10^{-3} S cm $^{-1}$ at 10^2 Hz. As a result, the electrospun PI/MWCNTs nanofibrous composites can be used as high performance materials in many applications.

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