

## **Dispersion and alignment of MWCNTs in polyurethane for making flexible and conductive nanofiber by electrospinning**

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### **ABSTRACT**

The electrospinning process was used successfully to fabricate nanofibers of polyurethane (PU) in which multiwalled carbon nanotubes (MWCNTs) are embedded. For improving dispersion of MWCNTs in PU solution, MWCNTs were first modified by 1-butyl-3-methylimidazolium chloride, an ionic liquid, which could be strongly adsorbed onto MWCNTs surface. These dispersions provided separation of the MWCNTs and their individual incorporation into the PU nanofibers by subsequent electrospinning. The focus of this work is on the development of the high conductive and flexible electrode. The characteristic of the nanofibers is the combination of conductive and flexible properties. The morphology and microstructure of the electrospun nanofibers were characterized using field emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results of the experiments showed the MWCNTs were well incorporated into the nanofibers and highly smooth surface without the occurrence of bead defects even at high MWCNTs content of 10 wt.%. Moreover, the prepared MWCNTs/PU nanofibers show the extraordinary conductivity of 1.8 S/cm when the concentration of MWCNTs is 10%. It can be concluded that such MWCNT/PU nanofibers could potentially be useful options for the fabrication of flexible electrodes and the integrated actuators.

**Keywords:** conducting nanofiber; multiwalled carbon nanotubes; electrospinning; flexible electrodes

### **1. INTRODUCTION**

It is well known that displays, supercapacitors, electrical artificial muscle, solar cells and integrated actuators are the typical examples of flexible photoelectronic apparatus which involve the flexible conducting material (Diao 2010, Ji 2012, Jiang 2011, Li 2011, Lin 2010, Liu 2012, Pan 2011, Peng 2012, Postma 2001, Shang 2009, Shang 2009, Shang 2010, Shang 2012, Wang 2010, Wei 2012, Xu 2011, Yang 2010, Yang 2010, Yang 2010, Yang 2011, Yang 2011, Yang 2011, Zhang 2011, Zhang 2012). Among these applications, the 1D nano-structure conducting materials have aroused huge

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attention and been further developed as the potential options for fabricating newly invented flexible electrode materials (e.g. nanowires, nanotubes, and nanorods ) because of their unique optical, electronic, and mechanical properties. Carbon nanotubes (CNTs) involving the characteristic of theoretically ballistic conductivity, good electromechanical properties and chemical inertness, have become the intensive focus of various studies during the last several decades. During the practical use of CNTs, the blending and twisting of them is inevitable, while the weak attractive forces (van der Waals forces) between the CNTs would hinder their applications under long-term running condition. The appearance of the CNTs based nanocomposites might to some extent overcome the above deficiencies as a vigorous candidate in making flexible electrodes, and even have been claimed the “the next-generation materials” (Han 2010, Liu 2012, Shang 2009, Xu 2010). As to the common approaches in manufacturing the CNTs based nanocomposites, melt processing, solution casting, plasma coating and layer-by-layer assembly technique are generally utilized (Deng 2011, Etika 2010, Rios 2011, Yang 2011). However, how to improve the dispersion and alignment of CNTs in a polymer matrix when processing these nanocomposites that still the main challenges for fabricating high-performance flexible electrodes to achieve their full potential. The employment of electrospinning technique could effectively disperse and align the CNTs in the polymer nanofiber. Recently, the poly (vinylpyrrolidone) nanofibers embedded with SWCNT have been successfully manufactured. Through the characterizing of the nanofibers, the SWCNTs arrange along the axial direction of the fibers since electrospinning technique offers high DC electric field, along with the high elongation of fiber. Hence, reliable electrodes with excellent conductivity and flexibility are expected to be fabricated by electrospinning technique, through making CNTs align in the polymer nanofiber.

In the present work, MWCNTs embedded PU nanofibers are attempted to be developed using electrospinning technique with the mass fraction of MWCNTs in the nanofibers is controlled from 1.0 wt.% to 10.0 wt.%. Then these nanofibers are tested for their availability to fabricate high conductive and flexible electrodes, and a feasible way to fabricate the electrodes is also discussed. Based on the outcome of other studies (Shang 2010, Shang 2011, Shang 2012, Weaver 2010), ionic liquid pretreated MWCNTs are more compatible with PU solution, MWCNTs are pretreated by 1-butyl-3-methylimidazolium chloride, an ionic liquid in an attempt obtain more homogeneously dispersion in the PU solution. Finally, the ultimate goal of this study is to fabricate the nanofibers of which MWCNTs align along the axial direction and scanning electron microscope (SEM) and transmission electron microscope (TEM) are applied to characterize the morphology and microstructure of the fabricated MWCNT/PU nanofibers, and their conductive properties were also examined in this study.

## **2. EXPERIMENTAL**

### *2.1 Preparation of the MWCNTs/PU solution*

A mixture of MWCNTs (0.25 g) and ionic liquid (0.05 g) was heated at 90 °C for 1

hour. Then, the pretreated MWCNTs (with the concentrations from 1.0 wt.% to 10.0 wt.%) were transferred to the PU solution (dissolved in dimethylformamide). These MWCNTs/PU composite solutions were stirred at 25°C for 72 hours and sonicated for another 1 hour to afford a black swollen gel with MWCNTs dispersed in it homogeneously.

### 2.2 Fabrication of the MWCNTs/PU nanofiber

The MWCNTs/PU nanofiber was fabricated by an electrospinning device (Kato Tech Co., Ltd., Japan) with a syringe, a ground electrode and high-voltage power supply. In the eletrospinning process, the PU and MWCNT/PU composite solution were poured in a syringe of 25 ml with a stainless steel nozzle of 1 mm in diameter. The rotating collector was covered by a piece of aluminum foil. The power supply through Cu electrode was inserted into the precursor solution. The voltage was 20 kV, and the tip-to-collector distance was 15 cm.

## 3. RESULTS AND DISCUSSION

It has been reported that the additive of ionic liquid will weaken the interactions between MWCNTs, and the hydrogen bonding between MWCNTs and polymer chains is much higher than the interactions between the MWCNTs themselves (Van der Waal force), which can stabilized the dispersion of MWCNTs in polymer solutions. To investigate the dispersion of MWCNTS in electrospun solution, Fig. 1 shows the photographs of the MWCNT/PU electrospun solution stored for two months. Compared to the non-pretreated MWCNTs/PU composite solution in which MWCNTs precipitates appeared at the bottom only after a few days, MWCNTs pretreated by ionic liquid can be stably dispersed in MWCNTs/PU electrospun solution due to strengthen interfacial bonding between the MWCNTs and PU polymer chain.. Therefore, a uniform dispersed MWCNTs/PU solution was formed and no obvious precipitation of the MWCNTs was observed.

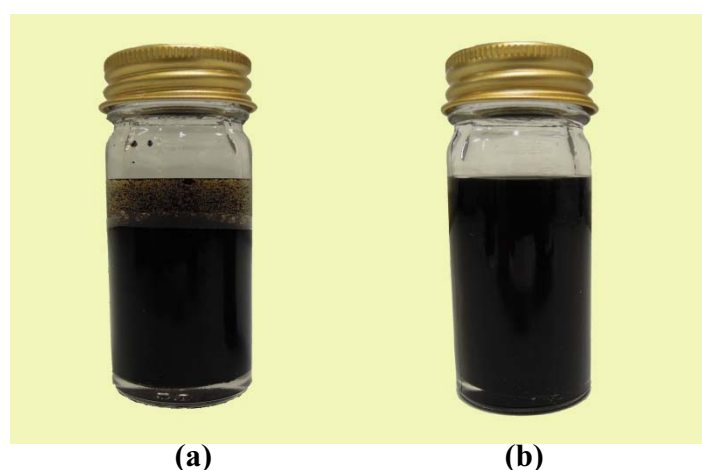


Fig. 1 Dispersion stability of (a) MWCNTs (b) ionic liquid pretreated MWCNTs in PU solution after two month (concentration: 10 wt.%)

Fig. 2 present the typical SEM micrographs of the conductive nanofiber samples which contained different MWCNTs ranging from 0 wt.% to 10.0 wt.%, respectively. It is evident that all nanofiber samples were formed uniformly with highly smooth surfaces and void of bead defects. Compared to the average diameter of pure PU nanofibers (800 nm), the addition of the MWCNTs increased the diameter of the formed electrospun nanofibers. Moreover, further increase of the MWCNTs content led to the increase of average diameter of PU/MWCNTs nanofibers with wider diameter distribution. More to the point, it was known from the previous study that increasing the MWCNTs content could bring up a few beads of at least 1 $\mu$ m along the fibers. Seriously, if the MWCNTs content was increased to more than 2 wt% in MWCNT/PU composite solution, the solution could not even been fabricated to nanofibers by electrospinning technique (Mazinani 2010). While it was shown from the result of this study that all MWCNTs/PU solutions (MWCNTs content from 1 wt% to 10 wt%) were able to be electrospun to nanofibers without any bead defects, which probably resulted from the high conductivity and flexibility owned by the MWCNTs/PU electrospun solution (Fukushima 2007).

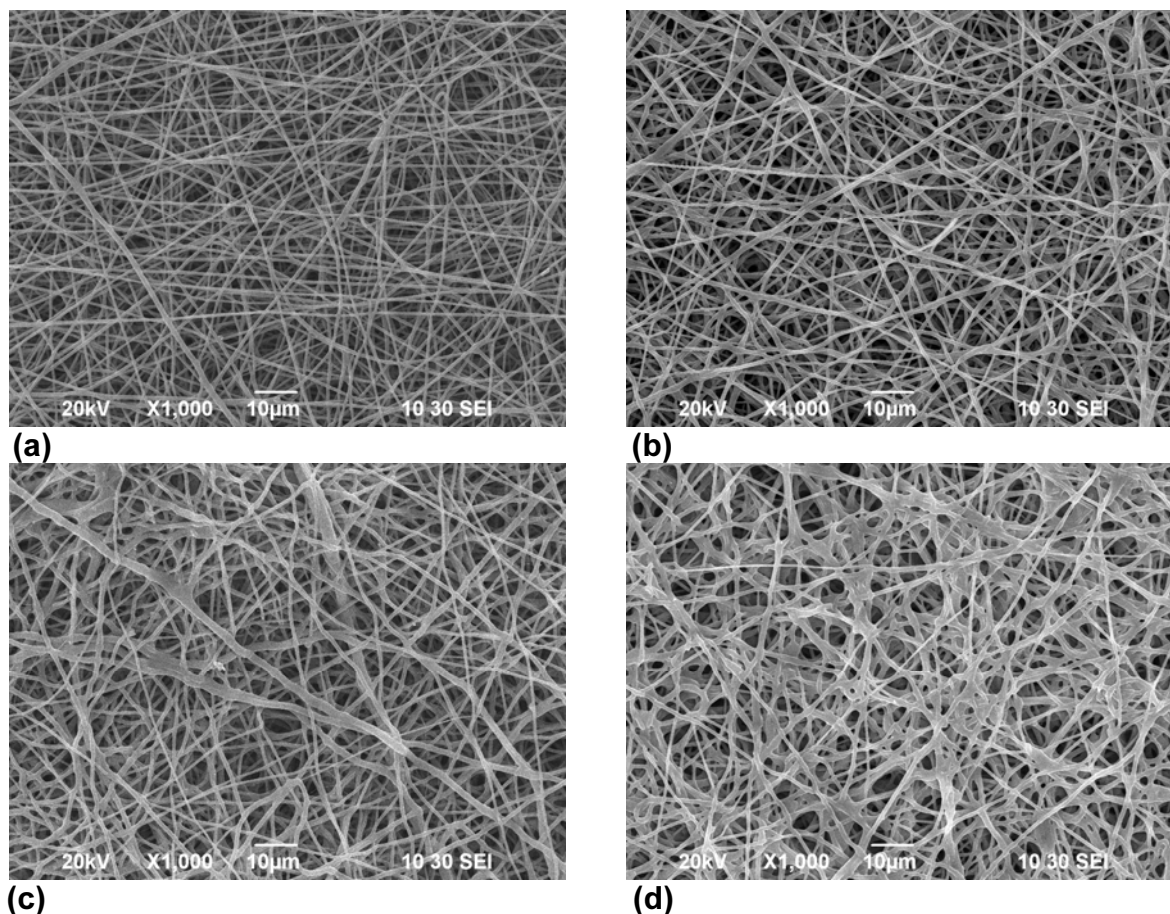


Fig. 2 SEM images of nanofibers (a) Pure PU, (b) PU-1.0 wt.% MWCNTs, (c)PU-5.0 wt.% MWCNTs, (d)PU-10.0 wt.% MWCNTs

The TEM micrographs (Fig. 3) of the MWCNTs/PU nanofibers were observed to investigate the distribution of the MWCNTs in them. Apparently, MWCNTs were well

dispersed in PU matrix. More importantly, contrast to the previous electrospun SWCNT/poly(lactic acid) composites within which CNT was chaotically dispersed with ball-shaped agglomerates (Ko 2003), MWCNTs tended to axially arranged along the fibers as revealed in Fig. 3. A uniformly dispersed MWCNTs/PU solution and an adequately adjusted process for electrospinning may lead to the high degree alignment of MWCNTs in the matrix of electrospun nanofibers. There might be three detailed contributions. The first is the strong electrostatic fields and the shear forces provided to the liquid jet in time of electrospinning. The second is the effect of what is called nanoscale confinement. The large aspect ratio of the MWCNTs and the nanoscale diameter of the nanofibers could result in the limited orientations in the electrospun nanofibers that restrict the alignment of the MWCNTs. The last one is the strengthened bonding between the pretreated MWCNTs and PU chains. As a result of this interaction, the alignment of the MWCNTs is benefited from the activity of the PU chains. The electrospun MWCNTs/PU nanofibers with ordered alignment of the MWCNTs in them were hence fabricated because of the coupling of the above contributions.

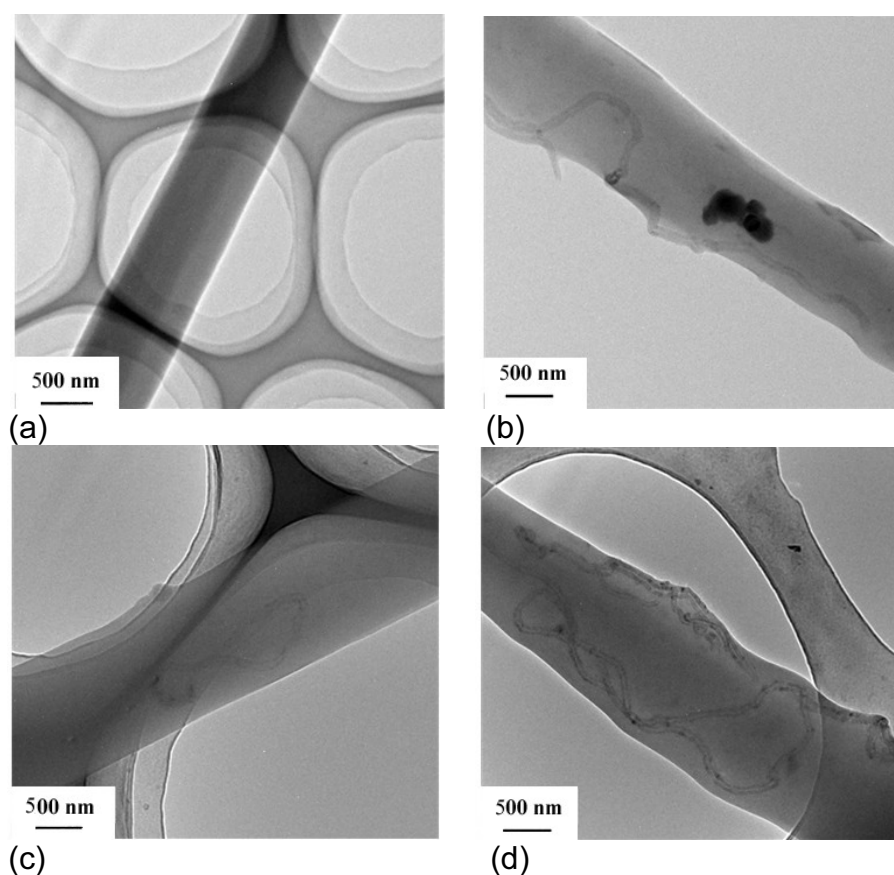


Fig. 3 TEM micrographs of nanofibers (a) Pure PU, (b) PU-1.0 wt.% MWCNTs, (c)PU-5.0 wt.% MWCNTs, (d)PU-10.0 wt.% MWCNTs

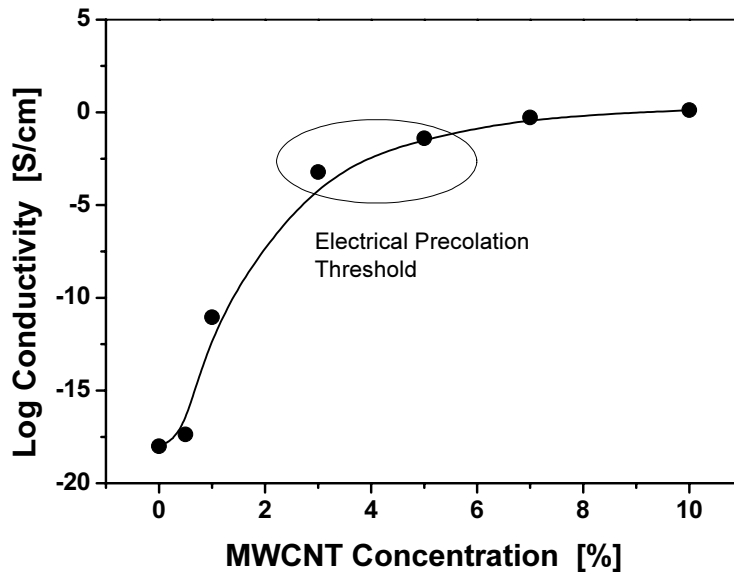


Fig. 4 Conductivity of nanofiber containing different MWCNTs ranging from 0 wt.% to 10 wt. %

Four-probe method was carried out to measure the conductivity of all nanofiber samples and the result is shown in Fig. 4. From the change of the conductivities, one can see that the conductivity was rather low in the nanofibers in which the weight percentages of MWCNTs were below 0.5%, since there was not enough amounts of MWCNTs to form conducting network in the MWCNTs/PU nanofibers. While as weight percentages of MWCNTs rose, a remarkably increase of the conductivity was noticed from the nanofibers and when the weight percentage of the MWCNTs was 3.0% or more, it was seen that the conductivity of the MWCNTs/PU nanofibers had a distinct change. But the electrical percolation threshold of the MWCNTs/PU nanofibers is still not obtained from the 3 wt% MWCNTs/PU nanofibers since the conducting network of the MWCNTs is not fully formed yet. Under such condition, all nanofiber samples within these weight percentages are still at the transition state to percolation ( $3.2 \times 10^{-3}$  to  $10^{-1}$  S/cm). With the weight percentage of 10% of MWCNTs incorporated in the nanofibers, the nanofibers presented particular high conductivity (1.8 S/cm), which means the MWCNTs/PU nanofibers with remarkable conductivity could be successfully fabricated. From the above, if more MWCNTs were dosed, the conductivity of the MWCNTs/PU nanofibers might be much higher. The newly fabricated MWCNTs/PU nanofibers can be involved in the field of the high-performance mechanical actuation system like elastic electrical artificial skin and in the integrated actuators, due to the excellent conductivity of the nanofibers.

#### 4. CONCLUSIONS

Conductive MWCNTs/PU nanofibers in which different content of the MWCNTs was incorporated were fabricated successfully via electrospinning technique with bead

defects avoided. The ionic liquid was used to pretreat MWCNTs and conduce the MWCNTs to disperse into the PU solutions more stable. Through pretreating by ionic liquid, hydrophobic groups adsorbed on the surface of the MWCNTs, hence, the bonding between MWCNTs and PU was strengthened and more MWCNTs were incorporated into the PU matrix. The morphologies and ultimate properties of the electrospun MWCNTs/PU nanofibers with different content of the MWCNTs were investigated in this study and the data demonstrated that the dispersion condition of MWCNTs affected significantly on the morphologies and properties of the MWCNTs/PU nanofibers fabricated. Further, the more MWCNTs were incorporated into the nanofibers, the higher conductivity of the MWCNTs/PU nanofibers were possessed. Thus, the newly fabricated MWCNTs/PU nanofibers can be involved in the field of the high-performance mechanical actuation system like elastic electrical artificial skin and in the integrated actuators, due to the excellent conductivity of the nanofibers.

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