Carbon nanotube를 포함한 PVDF/DMF 용액의 전기방사

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Electrospinning of poly(vinylidene fluoride) with carbon nanotubes

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1. Introduction

Polymer composites with carbon nanotubes have recently been investigated for improving certain properties i.e., electrical, optical and mechanical properties[1-3]. Kymakis et. al. have reported the electrical and optical properties of single wall carbon nanotube-poly(3-octylthiophene) composites[4]. Polyurethane dissolved in dimethylformanide (DMF) were electrospun by Demir et. al.[5]. Norris et. al. have reported the electrostatic fabrication of ultrafine conducting fibers with polyaniline/polyethylene oxide[6]. They have obtained the electrical conductivity of casting film and its electrospun fiber mat. Reneker group have suggested the optimum conditions for the electrospinning, such as viscosity, applied electric field, with PEO solution[7].

In this research, we studied the effect of single wall carbon nanotubes (SWNTs) contents on the electrical conductivity of the polymer solution, spin-coated thin film and electrospun fiber mat. The viscosity and surface tension of carbon nanotube(CN) PVDF/DMF solutions were also measured for the solutions.

2. Experimental

2.1 Materials

The polyvinylidene fluoride (PVDF), Kynar 760, was supplied by the ATOCHEM NORTH AMERICA INC. The single wall carbon nanotubes (CN) used in this study were purchased from the CNI (Carbon Nanotechnologies Incorporated) and were synthesized by the chemical catalysts method.

2.2 Surface tension and viscosity

We measured the surface tension using the wilhelmy plate method with SIGMA 70. The viscosity of solutions were measured by falling ball method. The room temperature viscosity of glycerine was 816 centipoise[8].

2.3 Conductivity

The room temperature conductivity of solutions were measured using the two-probe technique with parallel ITO-coated glass. Al was evaporated on the spin-coated film for the electrical conductivity measurement. The conductivity of the electrospun fiber mat was measured by inserting the mat between ITO and a metal electrode.

2.4 Preparation of solution

CN was dispersed in DMF using the ultrasonification. The 20 wt% PVDF/DMF solution was made for a stock solution. CN concentration was varied from 0 to 0.015 wt% for the 20 wt% PVDF/DMF solution.

2.5 Spin-coated film preparation

CN in PVDF/DMF solution was spin-coated at 5000rpm on the ITO glass.

2.6 Electrospinning setup

The electrospinning apparatus, as shown in Fig.1, used a high voltage generator with MODEL 200E and MODEL PMT 50A/N. The solutions were spun from a 50ml syringe with a 18 gauge needle. Various electrically grounded materials, such as aluminum plate were used as collection targets.

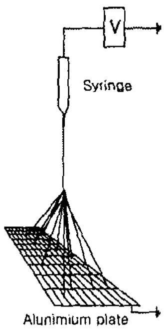


Fig. 1 Schematic of electrospinning process.

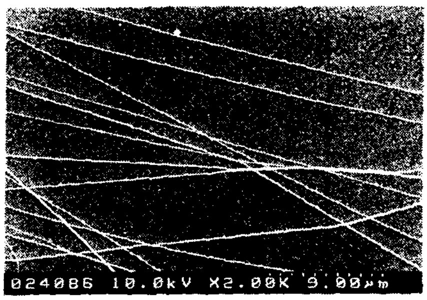


Fig. 2 SEM micrograph of the electrospun fiber mat at 2kV.

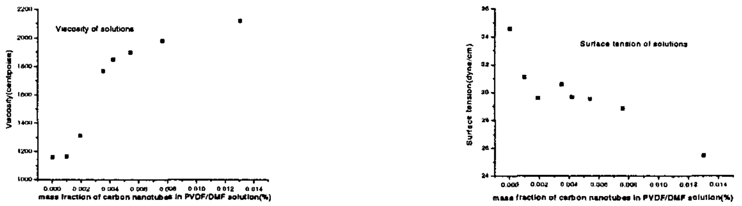
2.8 Scanning electron microscope (SEM)

The electorspun fiber mats have been analyzed using the scanning electron microscopy(SEM), S-4200. Fig. 2 shows the SEM images of the electrospun fiber mat.

3. Results and discussion

Different concentrations of polyvinylidene fluoride(PVDF) in DMF, varying in the range 10-20 wt% were prepared. Stable jet formation was observed for the solutions above 15 wt% at room temperature. At concentrations below 10 wt%, electrospraying took place. Continuous fibers formed between 15 and 20 wt% solutions (In terms of solution viscosity, it is over 1000 cP). We decided to use

20 wt% PVDF/DMF solution throughout our experiment. Fig. 2 shows a SEM image of electrospun fiber mat. It show In the 20 wt% of PVDF/DMF solution, we added the CN in various concentrations. The viscosity and surface tension of CN/PVDF in DMF solution is shown in Fig. 3. The viscosity increases as CN content increases with abrupt increase at 0.003 wt% CN content. But the surface tension decreases as CN content increases. Surface tension of PVDF is 33.2 mN/m(=dyne/cm)[9]

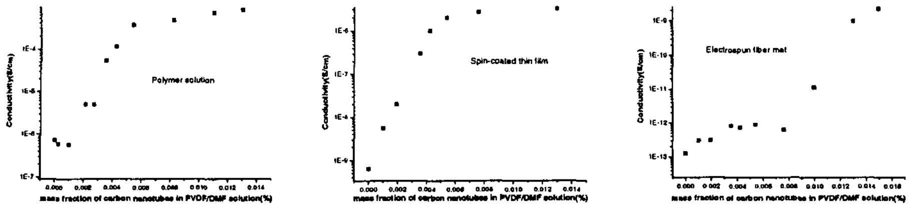


(a) (b)

Fig. 3 Viscosity (a) and surface tension (b) of solutions variation vs. mass fraction of CN in PVDF/DMF solutions.

We measured the conductivity of the solutions, spin-coated thin film and electrospun fiber mats. We observed all samples-solutions, spin-coated films and fiber mats-increasing the conductivity in proportion to increase the contents of CN. Fig.4-(a) shows the conductivity of CN/PVDF in DMF solutions, as the CN contents increases, the electrical conductivity of the solutions can increase by up to four orders of magnitude. The weight fractions of CN below a certain wt%, the nanotubes are almost isolated with the electrical conductivity governed mainly by the electrical characteristics of the polymer solution. As the fraction of CN increases further, the average distance between the nanotubes becomes sufficiently small. It is described by percolation theory.

Spin-coated films and electrospun fiber mats also were similar increasement of conductivity about four orders of magnitude. The percolation theory was also applied to spin-coated film and fiber mat. Comparing the film and electrospun fiber mat, the conductivity of the electrospun fiber mats is significantly lower than that for a spin-coated films. As we can see from the SEM micrograph of the electrospun fiber mat is highly porous. Owing to this porous, the conductivity of fiber mat is lower than film's one. However, it is reasonable to expect that the conductivity of an individual electrospun fiber will be higher than that of the electrospun fiber mat.



(a) (b) (c)

Fig. 4 Electrical conductivity of the solutions (a), spin-coated films (b) and electrospun fiber mats (c) variations vs. mass fraction of CN in PVDF/DMF solution

4. Conclusions

Nano-structured PVDF nanofiber with CN was prepared by electrospinning at 5kV at 20 wt% polymer concentration. The electrical conductivity of solution, spin-coated film and electrospun fiber mat increase as the following order; electrospun fiber mat <spin-coated film <CN/PVDF DMF solution. The percolation threshold of CN concentration is as follows; in solution 0.005 wt%, spin-coated film 0.005 wt%, electrospun fiber mat 0.01 wt%.

Acknowledgement

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