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Conductivity of carbon nanofiber/polypyrrole conducting nanocomposites †

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Abstract

Carbon nanofiber (CNF) / Polypyrrole (Ppy) composite materials were fabricated by two newly invented processes - filtering, washing and drying the mixture of CNF dispersion and Ppy-NMP solution (FWP process) and heating an aqueous solution of CNF (SH process). CNF/Ppy composite materials have never been reported before in any other research papers. Conductivities of the composite films were obtained by using a four-probe method. To compare the conductivity of CNF/Ppy with that of a pure single-walled carbon nanotube (SWNT), SWNT films were also fabricated and voltage was measured. SEM images were taken for both a surface and a cross-section of composite samples fabricated by the two processes. The CNF/Ppy by FWP was a little brittle because of the low solubility of Ppy in the NMP, and on the other hand, the same material by SH became flexible enough. The conductivity of the pure SWNT film was as high as double the similar case. The conductivity of the pure SWNT film was 20.11 S/cm and 0.013 cm thick. The CNF/Ppy composite films with the thicknesses of 0.062 cm and 0.085 cm gave a conductivity of 63.32 S/cm and 40.57 S/cm, respectively, which are higher than that of the pure SWNT film or SWNT/Polyaniline (PANi) film. The good conductivity of CNF/Ppy composites shows the improved potential for developing the materials for a small actuator.

Keywords: Carbon nanofiber; Conductivity; Nanocomposite; Polypyrrole

1. Introduction

Conducting polymers (CPs) have many attractive properties such as electro-chromism, electro-luminescence, chemical vapor/gas sensitivity, piezo-sensitivity, electromechanical response, and optical switching which make them potentially applicable to artificial muscles or small actuators. CPs may be operated at less than 10 V and generate strains of 12% [1]. Stresses induced from CP actuators are around 5 MPa [2], which is much higher than 0.3 MPa [3] from a natural muscle. However, there are some disadvantages, i.e., low Young's modulus, low conductivity, and low actuating force, which restrict the broad application of CPs.

In an effort to make the characteristics of CPs more suitable for electromechanical devices, people have started to focus on some other new materials that have good electromechanical properties and can be easily compounded of CPs. Since its first discovery in 1991 [4], the carbon nanotube (CNT) has shown remarkable properties which make it an attractive material in a broad range of applications. Due to the excellent strength and stiffness of CNT, it can make up for the weakness of CPs once when it is compounded. In addition, its high conductivity also attracts many researchers for the improvement of conductivity in some polymers which are non-conducting or low conducting. The CNT itself is also a good candidate for an actuator. The CP volume change was first re-

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ported by Burgmayer and Murray [5]. Ionic movement and subsequent volume changes in CPs are the fundamental of the motion in CP actuators.

Tahhan et al. [6] compounded single-walled carbon nanotubes (SWNTs)/Polyaniline (PANi) composite materials and tested their properties for actuators. Kim and Liu [7] developed the strain-voltage relationship of a CNT/CP composite film-type actuator and improved the fabrication process of a SWNTs/PANi composite actuator.

Carbon nanofiber (CNF) has similar properties to CNT, and is much cheaper than CNT, owing to the manufacturing process. Therefore, the CNF can be a good substitute for CNT. The remarkable properties of CNF such as high stiffness and strength, large thermal and electrical conductions were reported recently [8, 9]. In the present work, a pure SWNT film was fabricated and its conductivity was obtained by a four-probe method. A CNF/ Polypyrrole (Ppy) composite film was then made by a chemical blending method and its electrical conductivity was investigated and compared with that of a pure SWNT film. Up to now, the combined CNF and Ppy composite material has not been compounded because Ppy is hard to dissolve into a solution. Naturally the conductivity of CNF/Ppy has been rarely investigated, even though CNF/Ppy is potentially a good material for a small actuator.

2. Fabrication of films

2.1 Fabrication of pure SWNT films

SWNTs with the purity of 90% were utilized. SWNTs (80mg) and 1g of TritonX100 1% (w/w) surfactant solution was added to 50ml of distilled water. This dispersion was sonicated by a sonic dismembrator for more than 6 hours. The purpose of sonication is to release SWNTs from twisting each other. The dispersion was filtered through a previously wetted PVDF (Polyvinylidene Fluoride) membrane in an ethanol/distilled water mixture (50:50). Then, methanol was applied for removing the TritonX100. The filtering and washing processes were done by using a filtration assembly and a vacuum pump. Finally, the SWNT film was dried naturally before peeling off.

Figs. 1 and 2 show SEM pictures of the surface and cross-section of the pure SWNT film. The slender and fiber-like one is an SWNT and large particles are agglomerates of SWNTs. From these figures, it is shown that the length of each SWNT is about 200nm and the diameter is less than 10nm. The agglomerates can be formed by bonds between SWNTs during the process.

2.2 Fabrication of CNF/Ppy composites

Straight type CNF with a purity of 95% was dissolved into a TritonX100 1% (w/w) surfactant solution, then sonicated with the sonic dismembrator for more than 6 hours and the powder of Ppy was dissolved in NMP (N-methyl Pyrrolidine) to make a solution. Two solutions were mixed together with the weight ratio 3:1 of Ppy (150 mg) and CNF (50 mg) and then the mixture was filtered through a previously wetted PVDF membrane in an ethanol/distilled water mixture (50:50). The methanol was also applied for removing the TritonX100 and a filtration assembly and a vacuum pump were applied for filtering and washing processes. The extracted sample film was then soaked in HCl (1mol/L) to make a form of composites. Thereafter, the film was dried in the air before peeling off. This whole fabrication process,

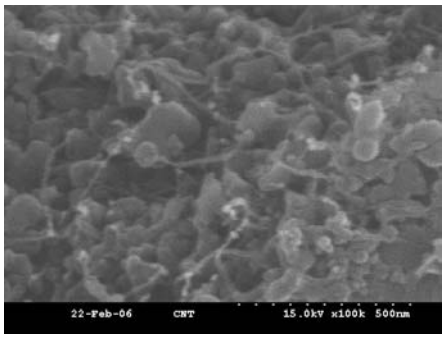

Fig. 1. SEM image of the surface of a pure CNT film.

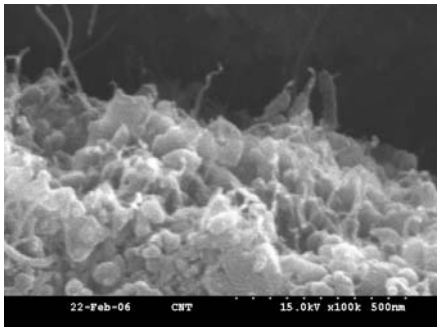

Fig. 2. SEM image of the cross-section of a pure CNT film.

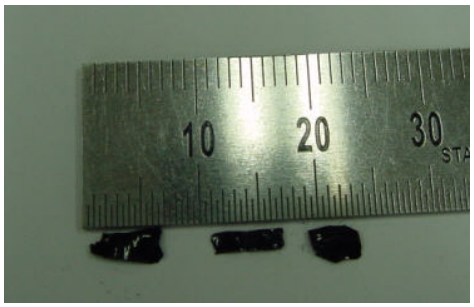

Fig. 3. CNF/Ppy composite samples fabricated by an SH process.

which is basically based on filtering and washing with powder (FWP) called a FWP process takes at least 70 hours in a laboratory. The composite films fabricated by the process seemed to be a little brittle. The composite sample was split into several pieces of itself after being dried in an ambient air at room temperature. This phenomenon is due to the fact that Ppy is usually difficult to dissolve in any solvent. The solution of Ppy in NMP is more like a dispersion.

In order to improve the FWP process which takes more than 70 hours and results in a little brittle material, an improved process based on a solution and heating (SH) process was invented. Because of the low solubility of Ppy, a Ppy solution (100ml, 5%, 1g/ml) was used instead of powder. The PPy solution 100ml purchased from Aldrich and the sonicated CNF dispersion (with 1.67g CNF) were blended in a beaker together and then heated on a hotplate at the temperature of 50^{O}C. After water evaporation in the aqueous solution, flexible (not fragile) composite films as shown in Fig. 3 were left at the bottom. However, composite materials were broken into pieces if heating temperature was over 60^{O}C.

Figs. 4 and 5 show the surface and the cross-section of a composite film fabricated by FWP, respectively. As shown in the figures, the CNFs what look like long threads have a diameter of more than 100 nm. Compared with Figs. 1 and 2, the diameter of CNF is much larger than that of SWNT, nearly 20 times. The white agglomerates like particles are Ppy matrix. It is clearly shown that in the CNF/Ppy composite, CNFs play the roll of fibers and Ppy acts like a matrix. Figs. 6 and 7 show the surface and the cross-section of a composite film fabricated by the improved SH process, respectively. The SEM micro-structures of the materials were similar to those by FWP shown in Figs. 4 and 5.

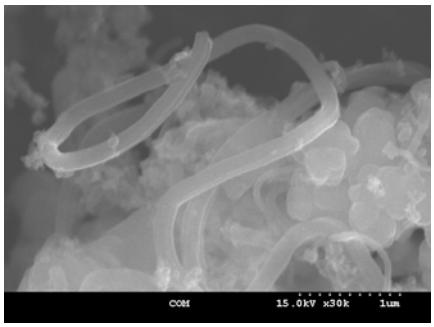

Fig. 4. SEM image of the surface of a composite film fabricated by an FWP process.

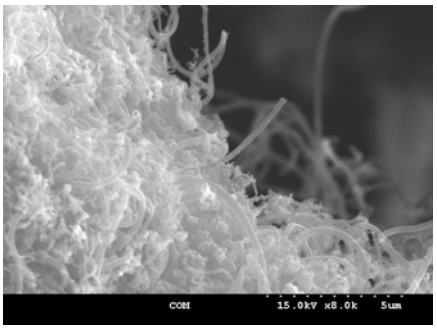

Fig. 5. SEM image of the cross section of a composite film fabricated by an FWP process.

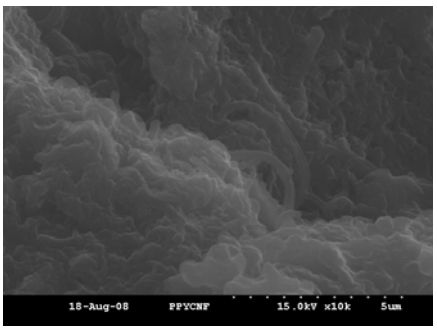

Fig. 6. SEM image of the surface of a composite film fabricated by an SH process.

3. Conductivity

The voltage was measured with a four-probe or Kelvin probe method when a current was applied [10]. Each sample may have a different voltage reading due to different electric resistance in materials. This is the most common way to obtain conductivity.

As shown in Fig. 8, there are four probes arranged in line and the distances between the adjacent probes are equal to each other. A current source is used for

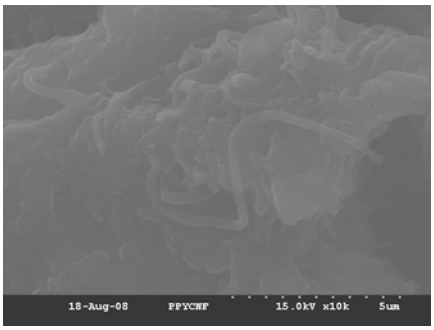

Fig. 7. SEM image of the cross section of a composite film fabricated by an SH process.

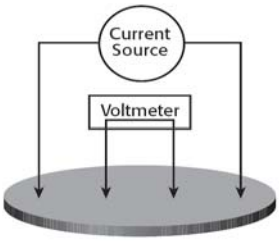

Fig. 8. Four-probe resistivity method.

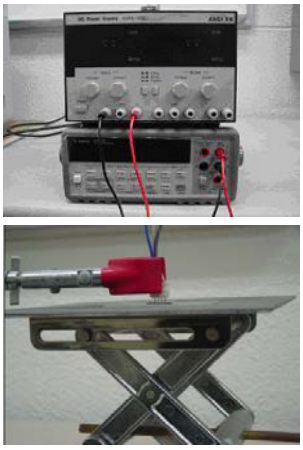

Fig. 9. Experimental setup for conductivity measurement.

supplying an electric current through the outer two probes and a voltmeter measures the voltage between the inner two probes. When differently specified currents are supplied to the same sample material several times, the voltages are measured. Then, the conductivities may be obtained from Eqs. (1) and (2). This type of measurement usually results in errors due to the probe resistance, the spreading resistance under each probe, and the contact resistance between each metal probe and the composite film surface.

Table 1. Conductivity of a pure CNT film

h Thickness (cm)	I Current (A)	ΔV Voltage (V)	C Conductivity (S/cm)
0.013	0.4	0.34	19.98
	0.6	0.50	20.38
	0.8	0.68	19.98
	Average		20.11

Fig. 8 shows the experimental schematic of the measuring method. Fig. 9 shows the setup for voltage measurement in which the DC power supply ADPS-503D supplies the current and is connected to outer two probes and Agilent 34401A is used to measure the voltage between the inner two probes. The conductivity is calculated by following two relationships:

$$R = 4.53\ h\ (\frac{\Delta V}{I}) \tag{1}$$

$$C = \frac{1}{R} \tag{2}$$

where R is the volume resistivity (Ω-cm), ΔV is the measured voltage potential (volts), I is the source current (amperes), and h is the sample thickness (cm). It is noticed from the relationship that conductivity is inversely proportional to the thickness of materials. As the thickness increases, the conductivity decreases.

The conductivities of CNF/Ppy (1:3) composite films and a pure SWNT film were calculated, based on Eqs. (1) and (2), and are listed in Tables 1, 2, and 3. The thicknesses of samples in the tables are different because of difficulties in obtaining the desired thickness in a controlled way. The film materials were retrieved from materials left at the bottom of a beaker after filtering or heating an aqueous mixed solution of CNF and Ppy therefore, the thickness is uncontrollable.

The conductivity of the present pure SWNT film with a thickness of 0.013 cm was 20.11 S/cm (see Table 1) and that of the similar SWNT samples with 0.0049 cm thick [6] was 11.70 S/cm. When compared simply, our number itself is about as high as double the other even if the thickness is different. The conductivity is inversely proportional to the thickness of materials, as shown in Eq. (1). Therefore, the thicknesses can be adjusted equivalently to each other. If the thickness, 0.0049 cm, was increased to 0.013

Table 2. Conductivity of a CNF/Ppy composite film fabricated by an FWP process

h Thickness (cm)	I Current (A)	ΔV Voltage (V)	C Conductivity (S/cm)
0.062	0.4	0.023	61.92
	0.6	0.033	64.74
	0.8	0.045	63.30
	Average		63.32

Table 3. Conductivity of a CNF/Ppy composite film fabricated by an SH process

h Thickness (cm)	I Current (A)	ΔV Voltage (V)	C Conductivity (S/cm)
0.085	0.4	0.026	39.95
	0.6	0.038	41.01
	0.8	0.051	40.74
	Average		40.57

cm, the conductivity would be converted to (0.0049/ 0.013) 11.70 = 4.41 S/cm. In this way, ours becomes higher 4.5 times.

The conductivity of SWNT/PANi was 53 S/cm (0.0169 cm thick) [6] and that of our CNF/Ppy by the FWP process (see Table 2) is 63.3 S/cm (0.0620 cm thick), which is even higher than that of SWNT films. If Ref. [6] was converted to the thickness of 0.0620 cm, the equivalent conductivity would be down to 14.44 S/cm. The conductivity of CNF/Ppy by the SH process (see Table 3) is 40.57 S/cm (0.085 cm thick). If it is converted equivalently to 0.0620 cm thick, the conductivity becomes 55.6 S/cm which is a little lower than 63.3 S/cm (by FWP). A little drop in conductivity is because TritonX 100 which hinders conduction cannot be removed completely by heating. The CNF/Ppy composite films were never fabricated before and show a better conductivity than SWNT/PANi. The improved conductivity seems due to the enhanced connectivity of long carbon nanofibers. This simple improvement of CNF/Ppy may lead to better conducting polymer actuators and expanded applications.

4. Conclusions

Pure SWNT and CNF/Ppy composite (1:3) films were fabricated by powder- and solution-based processes on a laboratory level for possible applications in small sensors and actuators. Especially, the fabrication of CNF/Ppy composite films has not been reported in any other papers before. The conductivities of the film samples were investigated experimentally. The pure SWNT film which is 0.013 cm thick showed a conductivity of 20.11 S/cm, which is as high as double the value in Ref. [6]. The CNF/Ppy composite film fabricated by the FWP process was 0.062 cm thick and the conductivity was 63.32 S/cm. The flexible CNF/Ppy (0.085 cm thick) fabricated by the SH process showed similar converted conductivity of 55.6 S/cm after the thickness conversion (40.57 S/cm measured). The newly invented aqueous solution-based fabrication process (SH) newly invented produced more flexible CNF/Ppy composite films than FWP. The newly developed CNF/Ppy materials showed better conductivity than SWNT/PANi [6]. The electrical conductivity is one of the key factors required for sensors or actuators. The higher conductivity of CNF/Ppy has a good potential for a small actuator material.

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