IMPROVED FABRICATION AND TESTS OF A CNT/PANI COMPOSITE FILM ACTUATOR

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Keywords: *polyaniline, composite actuator, conducting polymer, conductivity*

Abstract

Many efforts to develop an innovative actuator which consist of SWNTs and conducting polymer have been made for last several years for its possible application to operate MEMS devices or small insect-like robots. In this nanocomposite film actuator, the SWNTs electrodes exhibit a unique pore structure and high efficiency of specific surface areas, which can be considered as the surface-area-enhancing component in composite films. Therefore, the composite pseudocapacitance is increased remarkably. This large capacitance suggests that the composite film can be used for local energy storage as well as actuation. Carbon nanotubes have high electrical conductivity that can increase the charging-discharging rate and improve the electrodic performance of conducting polymers films. SWNTs also exhibit strains due to electrochemical redox at low bias voltage (non-Faradic electrochemical charging), which is enough for actuating MEMS devices. In addition, SWNTs show very high Young's modulus so that they can function as reinforcing fibers to the conducting polymers matrix in the composite actuator. As a result, it is possible to make a SWNTs/CPs composite actuator that can show both high actuation strain and high available stress. SWNTs/CPs film actuator was fabricated and the strain was measured. The original length was l_0*=12.69mm. The extension was measured by the laser displacement meter,* Δl*=0.043mm.*

1 Introduction

Conducting polymer (CP) has some unique properties such as electro-chromism, electro-luminescence, chemical vapour/gas sensitivity, piezo-sensitivity, electromechanical response, and optical switching which make them potentially useful for artificial muscles and small actuators. However, in order to utilize these materials more effectively, these have to be modified with functional groups for enhancing the sensitivity, selectivity, response characteristics etc. The incorporation of functional groups such as phthalocyanine, ferrocene, rhodamine etc. into conducing polypyrrole, polyaniline and polythiophene has led to tremendous enhancement of sensitivity and selectivity.

The volume changes of CPs were reported the first time by Burgmayer and Murray [1] and are due to ionic movement produced during an electro-chemical redox. The ionic movement and the subsequent volume change in CPs are the fundamental of the motion in CP actuators. A conductive polymer actuator consists of an anode, a cathode and an electrolyte. Both anode and cathode can be made of CP and electrolyte can be either liquid or solid. The actuators with a liquid electrolyte only work in a liquid medium and those with a solid electrolyte operate in the air. These actuators work by electrochemical transfer of ions between the electrodes through the electrolyte. The mass and volume of electrolyte must be strictly controlled and appropriate for ionic conductivity.

Since several remarkable properties of carbon nanotubes were found in 1991 [2], their applications have been investigated in broad areas. They have one hundred times the tensile strength of steel, thermal conductivity better than all but the purest diamond, and electrical conductivity similar to copper, but with the ability to carry much higher currents.

From what mentioned above, it is known that SWNT (single-walled carbon nanotube)/CP composites may result in artificial muscle-type actuators where the CP component contributes to a high actuating strain and the CNT component to a high Young's modulus. Tahhan et al. [3] fabricated SWNT/PANi actuators and measured actuating strains subjected to voltage. Kim and Liu [4] developed a strain-voltage relationship of a CNT/CP composite actuator. In this paper, the improved SWNTs/PANi composite films applicable to an artificial muscle were fabricated using a new process of manufacture that consists of 90% pure single-walled CNT and chemical polymerization. The strains and the electrical conductivity have been measured and compared with analytical results calculated by the electromechanical constitutive equations.

2 Fabrication of Films

2 1 Fabrication of Polyaniline Film

Deionized aniline (0.1 *M*, Aldrich) was added to an aqueous solution of HCl (1 *M*, Aldrich). The solution was placed in an ice bath. Polymerization was initiated by adding 41 *ml* of an aqueous solution of ammonium persulfate (8.35 g, 0.1*M*) in a dropwise manner at a rate of 5 ml/min. The reaction mixture was continuously stirred during polymerization, and in the course of the reaction, the color of the mixture turned from pink to copper to dark blue. After polymerization, the dark blue precipitate was filtered and washed with deionized water and methanol. The powder was de-doped by stirring it in a solution of 0.1 *M* ammonium hydroxide for 18 hours. The resulting mixture was filtered by vacuum filtration and washed repeatedly with deionized water to obtain the PANI (emeraldine base (EB)) powder. The PANI powder was washed with deionized water until the wash solution was colorless. The purified PANI powder was dried in an oven at 60°C overnight.

PANI solution (2wt%) was prepared at room temperature by dissolving the PANI powder in N-methyl pyrrolidine (NMP). The PANI powder was added very slowly into the solvent to avoid gelation. It is very important to add EB powder gradually into the NMP. The PANI solution was then filtered through a PVDF filter to remove any undissolved and shear-induced agglomerates. This solution was used to prepare the PANI films actuators.

The films were made by pouring small quantities of the PANI solution onto specimen slides. And the film size can be controlled by the amount of coasted solution. The slides were then placed in an oven under 60°C to remove the solvent by evaporation. After drying for more than 24 hours, these spiders were immersed in a water bath for 30 mins to float the films off the specimen slides. The films were then dried on a filter paper and stored in a sealed container. The resulting film was soaked in HCl (1 M) to convert it into the PANI (acid) form, which was electrically conductive.

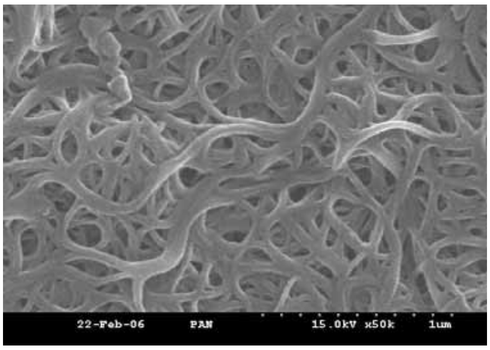
2 2 Fabrication of SWNT/PANi Composite Film

SWNTs (90% purity) and 1 g of TritonX100 1% (w/w) surfactant solution were mixed with distilled water to make dispersion. This dispersion was sonicated for 6 hours to avoid the binding of SWNTs together. The powder of PANi was put into the N-methyl pyrrolidine (NMP). These two solutions were mixed together and the weight ratio of the SWNTs and PANi was 3:1. The mixture was, then, filtered through a PVDF membrane which was previously wetted in an ethanol/distilled water mixture (50:50). Ethanol is used for removing the TritonX100. After that, the film was soaked in HCl (1mol/L) for composite. At last, the film was dried naturally and peeled off.

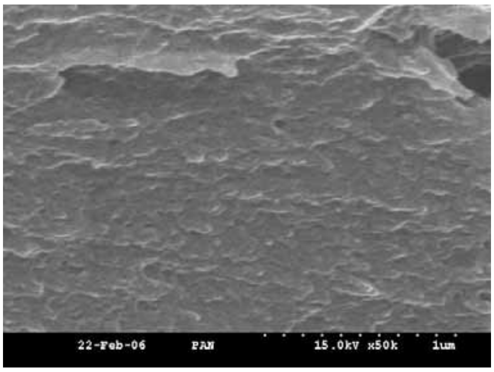
Tahhan et al. [3] fabricated the SWNTs/PANi composite film by coating the PANi (4% NMP solution) onto the CNT (carbon nanotube) mat. As an artificial muscle actuator, this film is not flexible enough, and it is apt to be fragile. It is, therefore, difficult to make a film in a large size. The new fabrication method in this paper, uses SWNTs powder and TritonX100 1% (w/w) surfactant mixed with distilled water, and then mixed with PANi (NMP solution), and improves the flexibility. Fig. 1 shows a SWNTs/PANi composite film sample. This thin film showed the motions of expansion and contraction.

Figs. 3 (a)(b) and (c)(d) show SEM pictures of the surface and cross section of the PANI film sample and the SWNTs/PANI composite film sample, respectively. Fig.3 (e)(f) of SEM pictures give clear indication of diameter of PANI and SWNTs/PANI composites, respectively.

Fig. 1. A SWNT/PANi composite film sample



(a)



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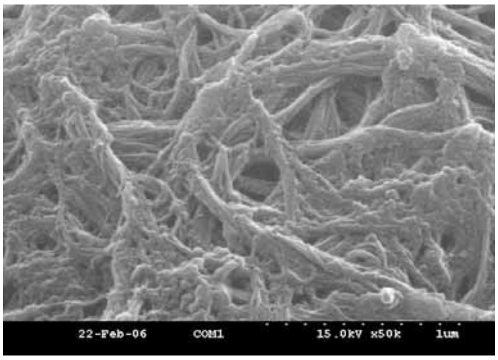

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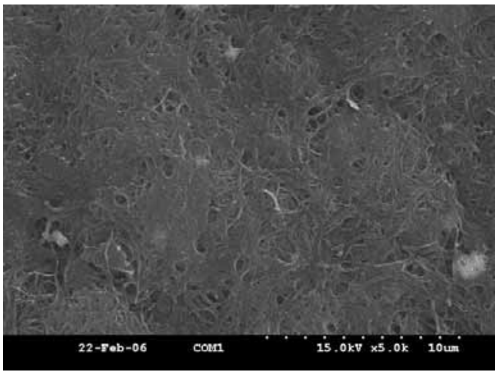

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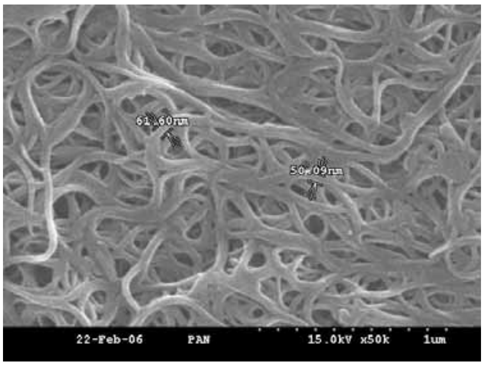

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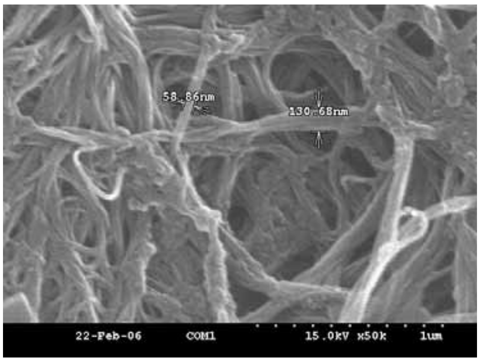


(f)

Fig. 2. SEM pictures of samples

3 Measurements of Conductivity and Strain

3.1 Conductivity

The four-point, or Kelvin probe method is the most common way to measure conductivity. The outer two probes are used as a current supplier and the inner two probes are used as a voltmeter. Using four probes eliminates measurement errors due to the probe resistance, the spreading resistance under each probe, and the contact resistance between each metal probe and the composite film. This technique involves bringing four equally spaced probes into contact with the material of unknown resistance [5].

The volume resistivity is calculated by Eq. (1), and then the conductivity can be obtained from Eq. (2).

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

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

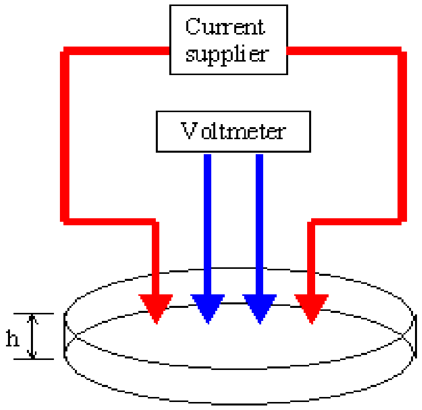


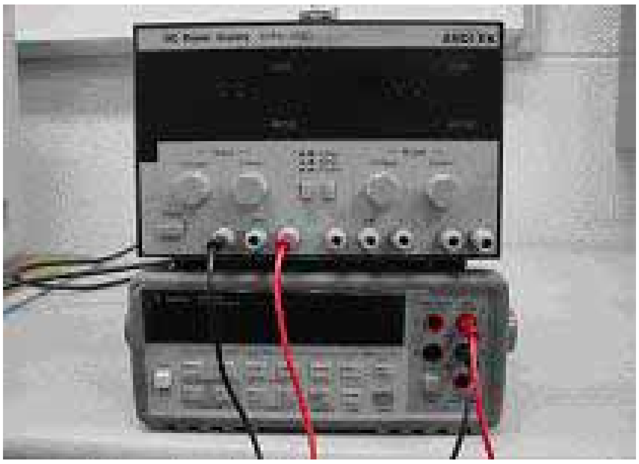
Fig.3. Four-point collinear probe resistivity method

where ρ is the volume resistivity (Ω-cm), ΔV is the measured voltage (volts), I is the source current (amperes), and h is the sample thickness (cm). The conductivity of SWNTs/PANI (3:1) composite film and PANI film were measured using the Four-Point collinear probe method, and the results is shown in Table 1 and Table 2 respectively.

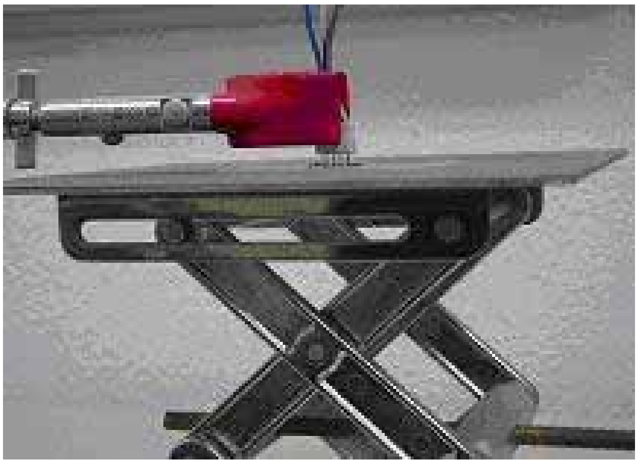
Fig. 4 shows the conductivity measurement system in which DC power supply ADPS-503D supplied the current and connected to the outer two probes, and the Agilent 34401A is used to measure the voltage between the inner two probes.

3.2 Strain Test

The actuation strain, ε, due to expansion/contraction of the sample is calculated using the Eq. (3)



(a)



(b)

Fig.4. A measurement system for conductivity

Table 1. Conductivity of a SWNT/PANi composite film actuator

h (Thicknss, cm)	I (Current, A)	ΔV (Voltage, V)	C (Conductivity, S/cm)
0.012	0.40	0.12	61.32
	0.45	0.15	55.19
	0.48	0.17	51.94
			56.15 (average)

$$\varepsilon = \left(\frac{\Delta l}{l_0}\right) \times 100\% \tag{3}$$

where l_0 is the original length and Δl is the movement between expansion and contraction. The actuator strain coursed by given voltage was tested by a beam balance apparatus developed by Spinks et al. [6] as shown in Fig. 5.

The strain test system is consisted of a balance, an electrolyzer with electrolyte solution, working electrode, auxiliary electrode, a function generator and a laser displacement meter. A two arms mechanical balance was refitted for our experiment. One arm was connected to the free part of the working electrode, and the other one was under load of the weight of the free part of the working electrode to counterpoise the gravitation force of it, to make sure the sample in our test is in the condition of no load. The electrolyzer can use any glass container with suitable size, in this test a beaker was used. And the electrolyte solution is the aqueous $NaNO_3$ solution. Working electrode has two parts: one is fixed and the other is free.

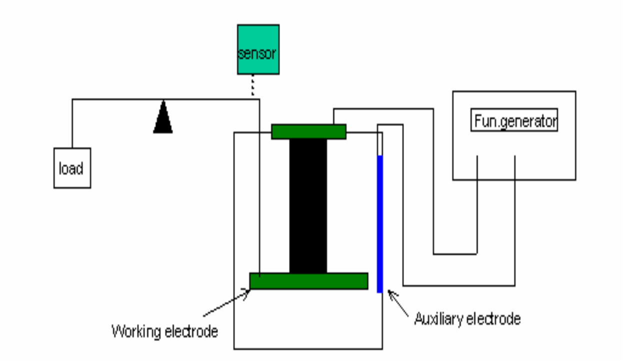


Fig. 5. Schematics of an actuator testing system

Both of them are conductor and in form of clip that can attach the film samples easily. The auxiliary electrode is made of a piece of conductive board. Function generator is the Agilent 33220A, here work as a power supplier. And the laser displacement meter (Omron 3Z4M-J1001-6) is used to test the actuation response.

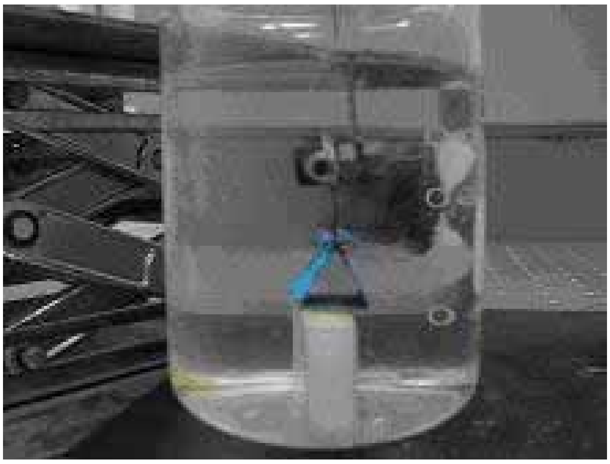
The actuation response of the samples will be tested using beam balance apparatus as described where the sample was immersed in electrolyte solution ($NaNO_3$). The sample is fixed on the working electrodes which are in form of clip. AC voltage is supplied by the function generator, though the working and auxiliary electrodes. The length changes measured using a laser displacement meter. All the parts of the test system are shown in Fig. 6: (a) is the balanced structure, (b) is the operation place and show us the attachment of the samples to the electrodes, and (d) is the connection of the electrodes.

The original length l_0=12.69mm, the extension was tested by the system through the laser displacement meter, Δl=0.043mm, then use Eq. (3), ε=0.34% was gotten. This is a very high strain for this kind of composite material. Tahhan et al. [3] got the strain result: 0.23%. An improvement of 47.8% was gotten.

It was found that the actuation is affected by both the SWNTs and CPs s and the actuations of SWNTs have two kinds of effect to the CPs: reinforcement at positive voltage and abatement at negative voltage.

Simultaneity, a simulation of the strain has done based on the equations which were derived by Kim and Liu [4], and in Fig. 7, the result is shown. This result shows the max strain is 0.3792%, as the experimental strain result is 0.34%.

(a)



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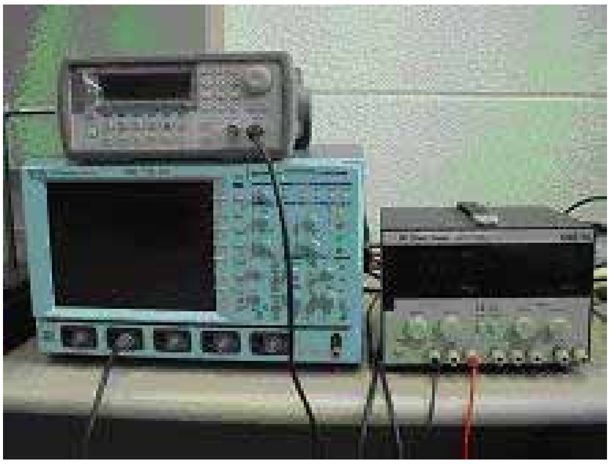

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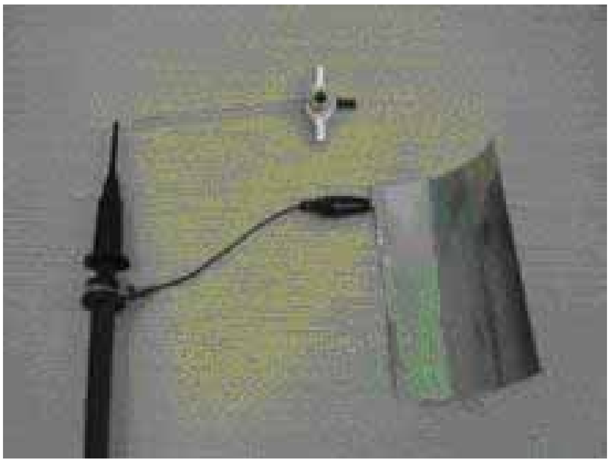

(d)

Fig. 6. Strain test system

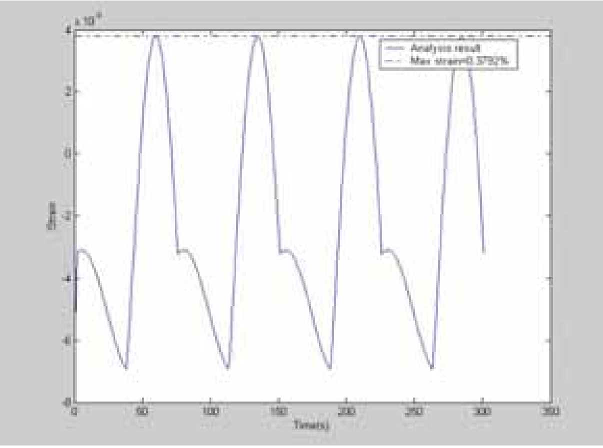

Fig. 7. The simulation result of the strain.

4 Conclusions

SWNT/PANi film samples were fabricated and tested to investigate electro-mechanical characteristics. This actuator sample were made of SWNTs (90% purity) and polymerization with improved fabrication method. Conductivity of a SWNT/PANi film actuator was 56.15 S/cm and that of the pure PANi was 17.38 S/cm. This showed that the composite film was 3.2 times higher than PANi. The measured strain was 0.34% which is higher than other similar experimental values. The improved polymerization technique was proved to be effective to produce a good conducting polymer that is applicable to artificial muscle-type actuators.

References

[1] Burgmayer P. and Murry R.W. "An ion gate membrane: Electrochemical control of ion permeability through a membrane with an embedded electrode". *Journal of American Chemical Society*, Vol. 104, pp 6139, 1982.

[2] Iijima S., "Helical microtubules of graphitic carbon" *Nature* (London), Vol. 354, Nov. 7, pp. 56-58, 1991.

[3] Tahhan M., Truong V., Spinks G.M. and Wallace G.G., "Carbon nanotube and polyaniline composite actuators," *Smart Materials and Structures*, Vol. 12, pp. 626-632, 2003.

[4] Kim C. and Liu X.Y., "Electromechanical behaviors and application of carbon nanotube composite actuator consisting of bundles and mats" *Journal of The Korean Society for Composite Materials*, Vol. 18, pp. 34-39, 2005.

[5] Dygas J.R., Fafil G. and Breiter M.W., "Study of grain boundary polarization by two-probe and four-probe impedance spectroscopy" *Solid State Ionics*, Vol. 119, No. 1, pp. 115-125, 1999.

[6] Spinks G.M., Liu L., Wallace G.G. and Zhou D., "Strain response from polypyrrole actuators under load" *Advanced Functional Materials*, Vol. 12, pp. 437–440, 2002.