카본나노튜브/도전성폴리머(CNT/EAP) 복합재 필름의 제조 및 특성분석

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Fabrication and Straining Model of a CNT/EAP Composite Film

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Abstract

The relationship between strain and applied potential was derived for composite actuators consisting of single-wall carbon nanotubes (SWNTs) and conductive polymers (CPs). During deriving the relationship, an electrochemical ionic approach is utilized to formulate the electromechanical actuation of the composite film actuator. The results show that the well-aligned SWNTs composite actuator can give good actuation responses and high actuating forces available. The actuation is found to be affected by both SWNTs and CPs components and the actuation of SWNTs component has two kinds of influences on that of the CPs component: reinforcement at the positive voltage and abatement at the negative voltage. CNT/EAP was fabricated successfully using the chemical polymerization method .

Key Words: Carbon nanotube, Conducting polymer, CNT/CP composite, Actuator

1. Introduction

Many efforts to develop an innovative actuator which consists 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 CPs (conducting polymers) films. SWNTs also exhibit strains due to electrochemical redox at low bias voltage (non-Faradic electrochemical charging) [1], 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 CPs 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 availablestress. SWNTs can also improve the life cycle of the actuators. In order to develop a SWNTs/CPs actuator, it is important to derive the relationships between strain and applied potential for predicting its behavior.

2. Voltage-Strain Relationships

A typical SWNTs/CPs composite actuator consists of a unit cell structure. When the potential difference is applied, a double layer capacitor is formed at electrolyte/composite film interface, and at the same time it is discharged by the ions diffusion. The ions diffused into the composite film are then neutralized by

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the charges within the film. Based on the method that was suggested by Madden *et al.*[2] to the polypyrrole actuator, the actuator's admittance transfer function, *Y(s)*, can be obtained, which combines the effects of diffusion, capacitance and electrolyte resistance as;

$$Y(s) = \frac{\delta + \sqrt{\frac{D_c}{s}} \cdot \tanh(\frac{d}{2} \cdot \sqrt{\frac{s}{D_c}})}{[\delta + \sqrt{\frac{D_c}{s}} \cdot \tanh(\frac{d}{2} \cdot \sqrt{\frac{s}{D_c}})] \cdot R_e + \frac{\delta}{C_{dl} s}} \tag{1}$$

where R_e is the resistance of electrolyte, D_c the coefficient of ionic diffusion in the film, C_{dl} the double layer capacitance, δ the double layer separation, and d is the thickness of the composite film. Note that the diffusion coefficient is different from that of pure polymer electrode due to SWNTs. In fact, each carbon nanotube acts as an electrode so that ions need not travel a long distance [3]. In this model, the polymer resistance is assumed to be negligible compared to the electrolyte resistance.

The combined strain of the composite actuator can be expressed as

$$\begin{aligned} \varepsilon_T(s) = \{[a_1 \cdot \frac{\alpha}{s \cdot V_f} \cdot s \cdot C_{dl} \cdot (\frac{d}{2\delta}+1) \cdot \\ + a_2 \cdot \frac{0.2 \times (0.1 \times 2\sqrt{3} \mp K) \cdot M_C \cdot C_G}{F} \cdot \\ [1 - s \cdot C_{dl} \cdot (\frac{d}{2\delta}+1) \cdot R_e]\} \cdot U(s) \end{aligned} \tag{2}$$

where $a_1 = \frac{E_c}{E_T} \cdot V_P$ and $a_2 = \frac{E_P}{E_T}(1 - V_P)$. This equation can be converted to a time domain by Lapalce transform,

$$\varepsilon_T(t) = \mathrm{L}^{-1}[\varepsilon_T(s)] \tag{3}$$

Here, the electrolyte resistance, R_e, and the thickness of the film, d, can be readily measured. The double layer capacitance, C_{dl}, and the specific capacitance of SWNTs, C_G, also can be measured, fit, or the accepted value can be used. The double layer separation, δ, can be approximately related to C_{dl}. For the given SWNTs that is used to reinforce the composite film, K is a constant.

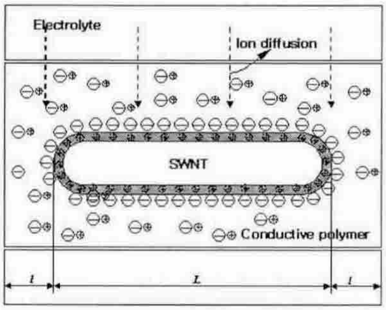


Fig. 1 The ionic distribution on a SWNT coated with Polypyrrole nanocomposite [3]

3. Fabrication

Conducting polymers and carbon nanotubes (CNTs) are among the main components providing a new class of carbon-based advanced materials. As a general rule, two methods are used to prepare these composites: one consists of direct mixing of compounds, and the other is by chemical synthesis. The former procedure can lead to a doping process as observed generally by mixing a polymer and a doping agent. The latter consists of a chemical or electrochemical polymerization of the monomer with addition of carbon nanoparticles as a supplementary reactive agent. In both cases, the final product is a composite of increased conductivity, as reported previously for composites such as SWNTs/polypyrrole [4]. In our experiment, the chemical polymerization method was used. Reagents and materials are SWNT, aniline monomer, HCl, ammonium/potassium persulfate, N-methyl pyrrolidine (NMP), Triton X100, ethanol, deionized water, NaNO3, NaOH, and NaCl.

Single-walled CNT (80-90% purity) is used as received to fabricate the mixture film of carbon nanotubes and conducting polymer. SWNTs are added to 5 ml of aniline with different contents of 1.0, 2.5, and

5.0% wt. (weight percent with respect to aniline monomer). The mixture was heated at reflux condenser for 3 hoursin the dark, the original colorless aniline solution first became brownish and then turned dark red, indicating that SWNTs have been dissolved into aniline. After being cooled to room temperature, a SWNT solution was obtained by filtration through a 0.1μm PVDF membrane.

Polymerization was carried out as follows: a solution of 1 *M* HCl containing 0.325 *M* aniline dissolved SWNTs in various mixture ratios was stirred at 0 5°C and then an equal volume of precooled (5°C) oxidant solution containing 0.125 *M* ammonium persulfate in 1 *M* HCl was slowly added dropwise to the well-stirred solution. The mixture was left for polymerization for 2 hours at 0 - 5°C under constant stirring. The polymerization of aniline-dissolved SWNTs can be observed by the color change of the solution. After a few minutes, the solution became green. The SWNTs/Polyaniline composites were obtained by filtering and rinsing the reaction mixtures with deionized water followed by drying under vacuum at 80 °C for 24 hours. Using the similar method to pure polyaniline film, the mixture was added to NMP to make up a 2% (w/w) solution. The solution was cast on glass slides placed on a hot plate and left to dry before peeling off. The composite film sample fabricated is showed in Fig. 2.

4. Discussions

Fig. 3 displays strains calculated under the applied voltage. The data were obtained form the experimental result [3] of the CNTs-PAn composite actuator. The composite film thickness, $d = 0.169*10^{-4}$ m, area $A = 1.8*10^{-5}$ m^2, $Re = 175$ Ohm. The double layer capacitance $C_{dl} = 0.2$ A is likely in the range of 0.1 *A* to 0.4 *A* [5], and the double layer thickness can be determined from C_{dl}, $\delta = 2.37*10^{-9}$ m (determined from C_{dl}). The value of $K = -0.1562$ is obtained by relating Eq. (2) to the experiment data of pure SWNT actuator. $C_G = 40$ F/g, $Mc = 12$, $F = 9.64846*10^4$, $E_c = 10$ GPa and $E_p = 0.9$ GPa are typical Young's moduli of SWNTs and polyaniline. Two results show that the calculated data are correlated very well with the experiment.

Fig. 4 displays the actuation strains and induced stresses for various CPs volume fractions and equivalent Young's moduli of SWNTs based on the same parameters used for Fig. 3. It is shown that the alignment of the SWNTs affects on actuation of composite actuator remarkably. For the same CPs volume fraction, the well-aligned actuators have smaller strain as in Fig. 4(a), but larger induced stresses as in Fig. 4(b). However, well-aligned SWNTs composites need less SWNTweight fraction under the same strain requirement. So the optimal SWNTs/CPs composite actuator may be achieved through well-aligned SWNTs in CPs matrix. Besides that, there are some other factors that affect the strain-voltage relationship of the actuator, such as the type of ions in the electrolyte, the conductivity of the filmand the input voltage.

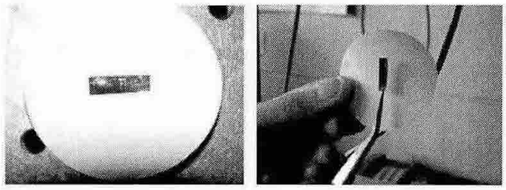
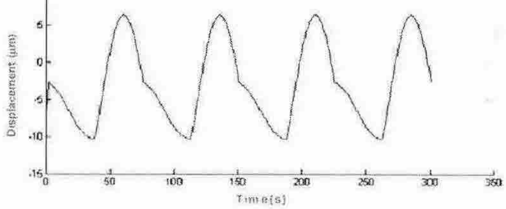
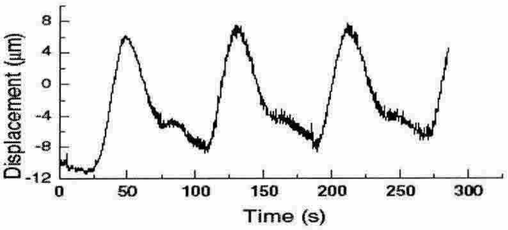


Fig. 2 A fabricated CNT/CP film sample

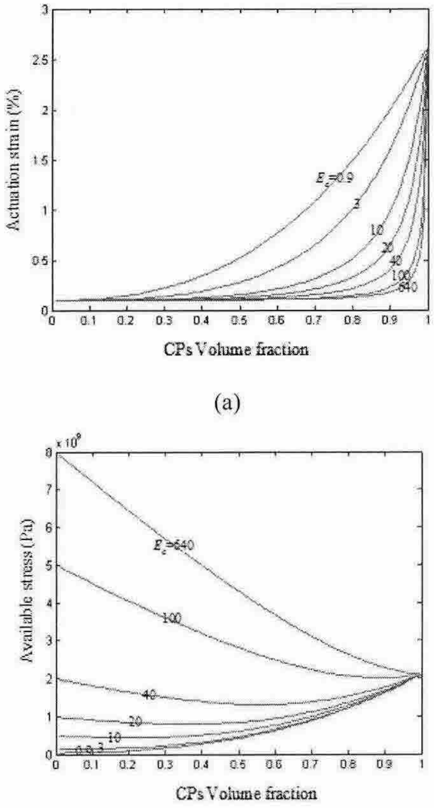


(a)



(b)

Fig. 3 (a) Displacement resulted and (b) experimental results [11] of a CNTs-PAn actuator



(a)

(b)

Fig. 4 (a) Actuation strains and (b) induced stresses

4. Conclusions

The strain-voltage relationships of a SWNTs/CPs composite actuator at a low frequency has been derived using an electrochemical unit cell model. Based on the relationship, the actuating strains and stresses of the actuator were obtained under various applied voltages. The actuation is found to be affected by SWNTs and CPs components. The actuation of the SWNTs has two different influences on that of the CPs reinforcement at a positive voltage and abatement at a negative voltage. Additionally, the SWNTs reinforcement plays an important role in a actuation response due to its high Young's modulus. The performance of the SWNTs/CPs actuator can be optimized based on well-aligned SWNT and choice of suitable electrolyte and applied voltage. The tests of conductivity and strains is underway to check the performance of the film sample.

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