BENDING BEHAVIOR OF A THIN SINGLE-LAYER CARBON-NANOFIBER/POLYPYRROLE COMPOSITE FILM

S.Zhang, C. Kim*
Department of Mechanical Engineering, Kyungpook National University, Daegu, Korea
* Corresponding author (kimchul@knu.ac.kr)

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1 Introduction

In decades, conducting polymers attract researchers with their good electromechanical performances. They are suitable to be used as smart materials for actuators and sensors. The volume change (i.e., strain) in CPs is caused by doping and dedoping of counter ions during a redox reaction [1]. Some researchers focused on the reinforcement of CP with metal fibers of carbon fibers. CNFs have a high stiffness and strength, good thermal and electrical conductivities were reported recently [2], what make it possible to be used as a reinforce fiber. CNF/PPy film has been fabricated in a physical method by Kim and Zhang [3]; however the flexibility was not good. Wang et al. [4] and Sabsiena et al. [5] fabricated monolithic polyaniline actuators with a long lifetime (>3000 cycles). Han and Shi [6] developed a single-layer PPy film which can operate a bending actuation and investigated its behaviors. Toi and Jung used an ionic transportation equation to analysis the motion of ions in order to investigate the actuation of a polypyrrole-based actuator [7]. Most of CP bending actuators consists of bi- or tri-layers. The bending actuation usually caused by the actuation difference between different layers.

In this paper, single-layer PPy film and CNF/PPy composite films were fabricated by the electrochemical polymerization process, and then their electrical conductivities and bending deformations were measured. The CNF/PPy composite film was especially developed for the first time in this study. We demonstrated convincingly that a single-layer CNF/PPy composite film can be bent without bi- or tri-layers structure, which makes this finding be differentiated from other previous works. Electrical conductivity was measured by the four-probe method. Mechanical properties are obtained by a UTM. Ionic transportation equation is studied and it will be used for our future works. The results found in this research show that CNF/PPy film can be well used as a smart material for actuators or sensors.

2 Preparations of CNF/PPy

CNF/PPy composite which has been developed newly can be fabricated, based on the process applied to fabricate PPy. Polypyrrole was polymerized by the oxidation of pyrrole monomers. The polymerization was done under an external constant current applied to the electrode, as in Fig. 1. The electrolyte was consisting of propylene carbonate, pyrrole, and LiTFSI. During the polymerization, the pyrrole will deposit on the working electrode. The TFSI- is a counterion that can balance the charge. PC is used as a solvent. To fabrication the CNF/PPy composite, the CNF should be stained on the on the surface of working electrode. Then CNF/PPy film can be obtained on the side with CNF, and the other naked side will produce PPy film.

Liquid pyrrole monomer was added to a propylene carbonate solution of LiTFSI. Ni sheets (3cm x 4cm) were used as working electrode and counter electrode. The distance between working electrode and counter electrode is fixed to 3mm. DC power supply ADPS-503D was used to give a constant current, anode was connected with a working electrode and a cathode was connected with a counter electrode [8].The working electrode was soaked in CNF dispersion, the CNF dispersion was stained on the surface of the electrode. Water is evaporated by heating the electrode and then only CNF was left. CNF was cleaned on one side of the electrode and the other side with CNF will face to the counter electrode during succeeding polymerization. Weight ratio of CNF is controlled by polymerization time as the polymerization rate of PPy is 0.012g/hour has tested. CNF/PPy films with the CNF weight ratios of 3%, 5%, 7% and 10% were fabricated. All the samples were cut into 5mm x 25mm for next extension and bending tests (Fig. 2).

3 Electromechanical Properties

The electrical conductivity of samples (PPy film and CNF/PPy films) was measured by a classical four-probe method. All the samples have the thickness of 0.015 ± 0.002 cm. The results are summarized in Table 1.The conductivity increases following the CNF weight ratio increasing, the increasing is approximately linear.

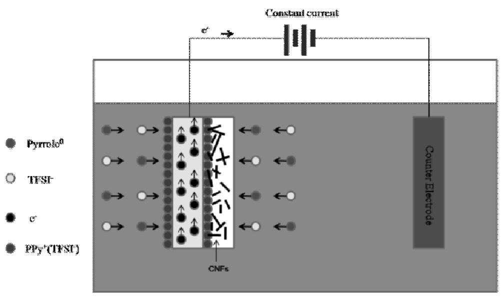


Fig.1. Polymerization process

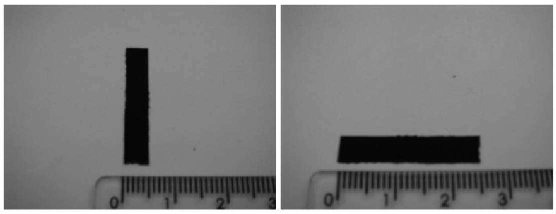


Fig.2. Images of test samples

Table 1. Conductivity of samples

Samples		Thickness (cm)	Conductivity (S/cm)
PPy		0.013	77.9
CNF/PPy	3%	0.013	85.0
	5%	0.014	91.6
	7%	0.016	109.3
	10%	0.017	124.3

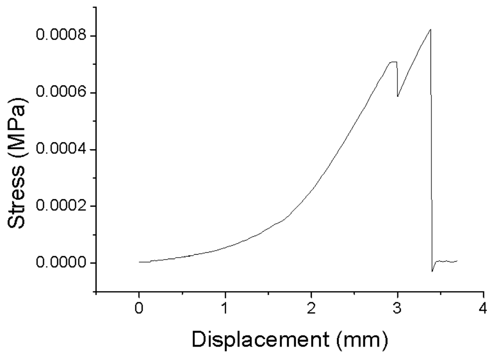


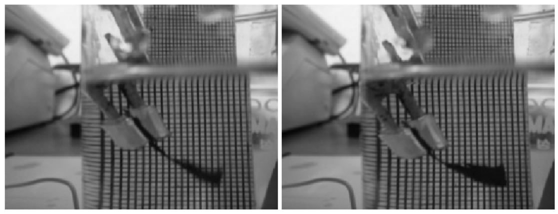
Fig.3. Figure of stress-displacement curve for CNF/PPy film (5%)

To investigate the mechanical property of the material, a tension test is undergoing. Fig. 3 shows a stress-displacement curve of CNF/PPy (5%) composite film. The test was done by a UTM (universal test machine), the sample was cut into 20mm x 5mm (20mm is the original length of the sample for test, the real length of the sample should be larger), the test was under loading of 100N with the speed of 5mm/min. the tests are undergoing, other samples will be tested later. It is supposed that the CNF can improve the mechanical properties of PPy.

4 Bending Actuation Test

Bending actuations were tested for both PPy film and CNF/PPy films. $\pm 1.5V$ AC driving potential was supplied. Solution consists of PC (200mL) and LiTFSI (2g) was used as an electrolyte. A counter electrode (Ni) is needed to form a circuit loop. Bending actuation usually happens in a bi-layer or tri-layer actuator because of the different strain generates from each layer but rarely found in a very thin single-layer film. It is a very particular phenomenon that a thin film can be bent with a single-layer structure. This is because the different surface situations of two sides of the films. During a redox reaction, TFSI ions move into the small holes on the electrode side of a film and make holes swell. On the solution side, the ion injection effect is not so obvious because of the surface is rough. Therefore, the swelling on the electrode side is more active than the solution side, this cause the bending actuation of the single layer film. Figure 4 shows the initial state and final state of a bending cycle.

The driving voltage (AC) is 0.5Hz that means the film can finish 2 bending cycles during 1 second. The bending actuation decays during the test process. The first bending cycle generate the largest tip deflection. The max tip bending deflection is 1.9 mm for a 2.5cm long PPy film, 3% CNF/PPy film showed 1.5 mm max tip bending deflection, 5% CNF/PPy film showed 1.3 mm tip bending deflection and 7% CNF/PPy film showed 1.2 mm tip bending deflection. The work lifetime of PPy film is 630 cycles, the 3% CNF/PPy can actuate for 1020 cycles, the 5% CNF/PPy can actuate for 1040 cycles and the 7% CNF/PPy can actuate for 1070 cycles. The CNF can increase the working lifetime more than 60%. The bending test is still undergoing. The testing results are shown in Table. 2.



(a) initial state (b) final state

Fig.4. Bending actuation test

Table. 2. Testing results for bending actuation.

Samples	Max tip deflection (mm)	Number of cycle
0% (PPy)	1.9	630
3% (CNF/PPy)	1.5	1020
5% (CNF/PPy)	1.3	1040
7% (CNF/PPy)	1.2	1070

5 Ionic Transportation Equation

As mentioned in the introduction, conducting polymer actuator works with the motion of ions. There exists a balance between the electric force and a viscous resistance as well as a diffusion force. It can be described by the following equation [7]:

$$\eta_1 \frac{\partial Q(x,t)}{\partial t} = kT \frac{\partial^2 Q(x,t)}{\partial x^2} - \frac{\partial Q(x,t)}{\partial x} \left\{ \frac{e}{\varepsilon_e S_x} \left[\int_0^t i(\tau) d\tau + Q(x,t) - Q(x,0) \right] \right\} \quad (1)$$

The initial and boundary conditions are [9]:

$$\{Q(x,0)\} = N_a e S_x c_0 x \quad (2a)$$

$$\{Q(0,t)\} = 0, \{Q(d,t)\} = N_a e S_x c_0 d \quad (2b)$$

The electric charge density $c(x,t)$ can be calculated by:

$$Q(x,t) = N_a e S_x \int_0^x c(\xi,t) d\xi \qquad (3)$$

The description of the equation in details can be found in references [7] and [9]. The equations above can be used to analyze the process of the ions motion during the actuation. It is expected that this equations can be modified for analysis of bending actuation of the CNF/PPy film.

6 Conclusions

CNF/PPy composite single-layer films were fabricated by an electrochemical polymerization process. CNF/PPy films with four different CNF weight ratios were obtained by the controlling of polymerization time. The electrical conductivity of samples improved significantly as the CNF weight ratio increased. The mechanical properties were tested by UTM. It was noticed that adding CNF could improve the mechanical properties of pure PPy. It is remarkable that even a single-layer CNF/PPy composite film can result in bending. CNF increases the work lifetime from 630 cycles of PPy film to about 1070 cycles of CNF/PPy (7%) films. The development of ionic transportation equation can investigate the depth of ion penetration and will modify the analysis of bending actuation of the CNF/PPy film.

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References

[1] P. Burgmayer and R. W. Murray "An ion gate membrane: electrochemical control of ion permeability through a membrane with an embedded electrode". *J. Am. Chem. Soc.*, Vol. 104, pp 6139–6140, 1982.

[2] J. Xua, J. P. Donohoeb and Jr. C. U. Pittman "Preparation, electrical and mechanical properties of vapor grown carbon fiber (VGCF)/vinyl ester composites". *Composites: Part A,* Vol. 35, pp 693–701, 2004.

[3] C. Kim and S. Zhang "Conductivity of carbon nanofiber/polypyrrole conducting nanocomposites". *J. Mech. Sci. Tech.,* Vol. 22, pp 1537–1543, 2008.

[4] H. L. Wang, J. B. Gao, J. M. Sansinena and P. McCarthy "Fabrication and characterization of polyaniline monolithic actuators based on a novel configuration: integrally skinned asymmetric membrane". *Chem. Mater.*, Vol. 14, pp 2546–2552, 2002.

[5] J. M. Sabsinena, J. B. Gao and H. L. Wang "High performance, monolithic polyaniline electrochemical actuators". *Adv. Funct. Mater*, Vol. 13, pp 703, 2003.

[6] G. Y. Han and G. Q. Shi "Electrochemical actuator based on single-layer polypyrrole film". Sensors and Actuators B, Vol. 113, pp 259–264, 2006.

[7] Y. Toi and W. Jung "Computational modeling of electrochemical-poroelastic bending behaviors of conducting polymer (PPy) membranes". Journal of Computational Science and Technology, Vol. 2, 4, pp 523-534, 2008.

[8] S. Hara, T. Zama, W. Takashima and K. Kaneto "TFSI-doped polypyrrole actuator with 26% strain". J. Mater. Chem.., Vol. 14, pp 1516-1517, 2004.

[9] S. Tadokoro, S. Yamagami and T. Takamori "An actuator model of ICPF for robotic applications on the basis of physicochemical hypotheses". Proceedings of the 2000IEEE International Conference on Robotics & Automation, San Francisco, CA, pp 1340-1346, 2000.