Fabrication of Carbon Nanotube Polymer Actuator
Using Nanofiber Sheet

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Abstract. Carbon nanotube polymer actuators were developed using composite nanofiber sheets fabricated by multi-walled carbon nanotubes (MWCNTs) and poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP). Nanofiber sheets were fabricated by electrospinning method. The effect of flow rate and polymer concentration on nanofiber formation were verified for optimum condition for fabricating nanofiber sheets. We examined the properties of MWCNT/PVDF-HFP nanofiber sheets, as follows. Electrical conductivity and mechanical strength increased as the MWCNT weight ratio increased. We fabricated carbon nanotube polymer actuators using MWCNT/PVDF-HFP nanofiber sheets and succeeded in operating of our actuators.

1. Introduction

Recently, soft materials that have the ability to convert electrical energy directly into mechanical work [1-3] have attracted a lot of attention [4] because it is expected to be applicable to robots, tactile and optical display, prosthetic devices, medical devices [5] and microelectromechanical system [6]. Among these soft materials, low-voltage driven electroactive polymer (EAP) actuators that can operate quickly and softly are focused on [7] due to lightness [8], easy of fabrication, and flexibility. Therefore, the EAP actuators can be used as artificial muscle [9] for various bio-medical and human affinity applications. Although ordinary EAP actuators operate only in electrolyte solutions [10], Ding et al. reported ‘dry’ EAP actuators that work in air, using ionic liquids (ILs) and conductive polymer [11]. ILs have low volatility [12], exhibit high ionic conductivities [13] and wide potential windows, which are advantageous for quick response actuators and high electrochemical stability components. However,
Conductive polymer-based actuators have essential drawbacks in their lifetime and responsiveness, because the motion is driven via oxidation/reduction of the conjugated polymers [6]. There were also some reports about actuators using single-walled carbon nanotube (SWCNT) [5, 14] and these actuators are driven via electrical charge/discharge of SWCNTs [6]. However, the actuation occurs only in electrolyte solutions. Therefore, carbon nanotube polymer actuators using ILs were proposed [2, 4, 15, 16]. Carbon nanotube (CNT) has an advantage of superb electrical conductivity [17], surface width [18], and mechanical strength [19]. Therefore, many potential applications have been proposed for CNT such as conductive and high strength composites, energy storage, and conversion devices, and semiconductor devices [20]. Mukai et al. reported the mechanism of this actuator using ILs as follows: when voltage is applied to the electrodes, the internal ions move and then EAP actuator is caused a volume change between the positive and negative electrodes. As a result, the actuator bends [2]. Carbon nanotube polymer actuators are currently being studied aiming at further improvement of the performance such as displacement and response speed in order to apply actuator to various fields [21]. Achieving this improvement, nanofiber sheet fabricated with conjugated polymer was proposed. Increasing the interfacial area between the electrolyte and the conjugated polymer should lead to a larger volume change of electrode films. In order to increase the interfacial area, nanofiber sheet of conductive polymer which has large specific surface area was applied to actuator’s electrodes [22]. Therefore, we propose to fabricate carbon nanotube polymer actuator using electrolyte film containing ILs and multi-walled carbon nanotube (MWCNT) composite nanofiber electrode films which has larger specific surface area than bulk film to improve furthermore actuator performance. We used MWCNT and poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) as materials of electrode film. MWCNT/PVDF-HFP nanofiber sheet was fabricated by electrospinning. Electrospinning is one of the popular methods for fabricating nanofiber sheets [23], because it can be used in the processing of polymers into nanofiber sheet by applying a high voltage between the grounding collector and spinning nozzle [24]. Nanofibers have outstanding properties such as large surface area, high length/diameter ratio, and flexible surface functionality [25]. Therefore, actuators which are fabricated by electrospinning have several advantages of good dispersion, enhanced flexibility, and ability to produce different form by varying essential factors [26].

In this study, we fabricated MWCNT/PVDF-HFP nanofiber sheet using electrospinning method and adjusted flow rate and polymer concentration in electrospinning solutions for optimum performance in order to obtain nanofiber sheet having less spherical substances called beads, because beads is generated by the incorrect concentration of polymer solution, flow rate, and viscosity of electrospinning solution. We examined morphologies and characterizations of MWCNT/PVDF-HFP nanofiber sheet such as electrical conductivity and mechanical strength. Furthermore, we fabricated carbon nanotube polymer actuator using nanofiber electrode films and operated actuators at DC 6 V.
2. Experimental

2.1. Materials

MWCNTs (purity of 95%, length of 1-10 μm, number of walls are 3-15) were purchased from Plasma Chem. and used as electrical conductive and mechanical strength material. The ionic liquids (IL), 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMI[BF$_4$]) and PVDF-HFP (M$_w$ = ~400 kDa) were purchased from Aldrich and their chemical structures are shown in Figure 1(a) and (b). 4-Methyl-2-pentanone (MP) $\geq 99.5\%$, propylene carbonate anhydrous (PC), and N, N-dimethylformamide (DMF) were purchased from Nacalai tesque. The chemicals mentioned above were used without any further purification.

2.2. Fabrication of the electrode film

MWCNTs were dispersed in DMF using ultra sonication for more than 24 h. Then, PVDF-HFP was dissolved in the obtained MWCNTs dispersion at 120°C for 2 h. The weight ratio of MWCNTs to PVDF-HFP was in a range from 0.0 to 10.0wt%. Using this MWCNT/PVDF-HFP solution, MWCNT/PVDF-HFP nanofiber electrode films were fabricated by electrospinning method. Figure 2 shows a schematic illustration of the experimental set-up for electrospinning [26, 27]. The MWCNT/PVDF-HFP solution for electrospinning was injected to a syringe pump and electrospinning was performed at 10 kV to the syringe nozzle. Flow rate of the solution was 0.2-3.0 mL/h. An 18-gauge spinning nozzle with a 0.94 mm inner diameter was employed. The distance between the end of the nozzle and the surface of the rotary collector was 3 cm. The rotary collector for collecting nanofibers was 10 cm diameter, 15 cm width. In order to fabricate aligned MWCNT/PVDF-HFP nanofibers [28-30], the rotary collector was rotated at 1.5-7.3 m/s (300-1400 rpm).

![Chemical structure of EMIBF$_4$](image1)

![Chemical structure of PVDF-HFP](image2)

![Diagram of Electrode film and Electrolyte film](image3)

**Figure 1.** Chemical structures of (a) EMIBF$_4$, (b) PVDF-HFP and (c) configuration of the MWCNT/PVDF-HFP actuator.
2.3. Fabrication of the electrolyte film

The electrolyte film was fabricated by casting 300 μL of electrolyte solution consisting of 80 μL of EMIBF₄ (in Figure 1(a)), 130 mg of PVDF-HFP (in Figure 1(b)), 3 mL of MP, and 207 μL of PC on aluminum substrate (the size is 2.5 cm × 2.5 cm). The solvent was then completely removed at 80°C for 2 h. The thickness of the electrolyte film was measured using a digital micrometer (Mitutoyo).

2.4. Fabrication of actuator using MWCNT/PVDF-HFP nanofiber electrode film

The configuration of MWCNT/PVDF-HFP actuator [31] is illustrated in Figure 1(c). An actuator had a three-layer structure having the electrolyte film between the MWCNT/PVDF-HFP nanofiber sheets and is fabricated by hot-press at 130°C for 10 min with 7.5 MPa. The nanofiber electrode film and the electrolyte film, with thickness of 20-40 μm and 50-60 μm, were used to fabricate actuator.

2.5. Characterization

A scanning electron microscope (SEM, KEYENCE VE-8800) was operated at 5-8 kV, and the average nanofiber diameters were measured from SEM images using the software package (Image J) from 100 places/specimen. The alignment intensity of MWCNT/PVDF-HFP nanofibers was measured with SEM images using the software package (Fiber Orientation Analysis Ver. 8.13) [32]. Electrical conductivities of aligned MWCNT/PVDF-HFP nanofibers in the alignment direction were measured by the two-terminal method with a digital multimeter (Model617, TOYO corporation) at room temperature and relative humidity of 40-50%. Mechanical strength of aligned MWCNT/PVDF-HFP nanofibers in the
alignment direction were measured with a tensile tester (FGPX-02, NUDEC-SHIMPO) at an elastic stress speed of 10 mm/min at room temperature. The electrical conductivity and the mechanical strength measurement were performed 3 times/specimen. Viscosity of MWCNT/PVDF-HFP solution was measured with VISCOMATE (CBC Co., Ltd. VM-10A-L).

3. Results and discussion

3.1. Morphology of MWCNT/PVDF-HFP nanofiber sheet

3.1.1. Effect of flow rate and polymer concentration

Electrospinning is popular method for fabricating nanofiber. However, this method needs to adjust various condition such as applied voltage, polymer concentration in spinning solution, and flow rate [33, 34]. Therefore, we tried various condition of electrospinning such as flow rate and polymer concentration in order to search for the best condition for fabricating MWCNT/PVDF-HFP nanofiber sheet. Figure 3(a), (b), and (c) show the SEM images of MWCNT/PVDF-HFP nanofiber sheet fabricated under different flow rate. The flow rate for each sample was 3, 1 and 0.2 mL/h, respectively. In this experiment, we fabricated MWCNT/PVDF-HFP nanofiber sheet using solution containing 10wt% CNT and fixed peripheral velocity of collector at 7.3 m/s. In Figure 3, spherical substances called beads decreased as the flow rate decreased. The beads are made in places of nanofiber under incorrect conditions of electrospinning because the nanofiber formation unstabilized due to the instability of the jet of polymer solution [35].

Figure 4(a), (b) and (c) show the SEM images of MWCNT/PVDF-HFP nanofiber sheet fabricated using different polymer concentration of 10, 12 and 15wt% in electrospinning solution, respectively. In this experiment, we fabricated MWCNT/PVDF-HFP nanofiber sheet using solution containing 10wt% CNT. In addition, we fixed peripheral velocity of collector at 7.3 m/s and flow rate at 1mL/h. As shown in Figure 4, the beads decreased as polymer concentration increased. In general, when the concentration of solution increases, the viscosity of solution also increases. Therefore, I investigated the

![Figure 3](image-url)  
Figure 3. SEM images of MWCNT/PVDF-HFP nanofiber sheet fabricated under different flow rate of (a) 3 mL/h, (b) 1 mL/h and (c) 0.2 mL/h.
relationship between the viscosity of the electrospinning solution and nanofiber formation. Figure 5 shows the viscosity of electrospinning solution as a function of CNT weight ratio for two types of polymer fraction in solution. Figure 6 shows the SEM images of MWCNT/PVDF-HFP nanofiber sheet containing different CNT weight ratio of (a)2wt%, (b)5wt% and (c)10wt% (polymer 15wt% in solution), respectively. In Figure 6, as the CNT weight ratio to polymer increased, the viscosity of electrospinning solution increased. In Figure 6, as the CNT weight ratio increased, it can be confirmed form SEM images that nanofibers with less beads are fabricated. Therefore, we considered that the viscosity of electrospinning solution affected the nanofiber formation. We speculated from Figure 3-6 that it is important for fabricating nanofiber sheet with less beads to adjust flow rate and the viscosity of spinning solution.

Figure 4. SEM images of MWCNT/PVDF-HFP nanofiber sheet fabricated using different polymer concentration of (a) 10wt%, (b) 12wt% and (c) 15wt% in electrospinning solution.

Figure 5. The viscosity of electrospinning solution as a function of CNT weight ratio for two types of polymer weight in solution.
3.1.2. Effect of peripheral velocity of collector

We also examined the effect of peripheral velocity of collector on nanofiber alignment. Figure 7 shows SEM images of MWCNT/PVDF-HFP nanofiber sheet collected with different peripheral velocity (1.5-7.3 m/s) and Figure 8 shows the alignment intensity [32] of MWCNT/PVDF-HFP nanofiber sheet as a function of peripheral velocity of collector which was measured from SEM images of Figure 7 and other data (not shown). As shown in Figure 7 and 8, the nanofibers were aligned as the peripheral velocity of collector increased. There was report that the trajectory of the continuous electrospinning jet is affected by the rotation of the collector [34]. In electrospinning, when the nanofibers are attached electrostatically onto collector surface, it stretches the following tow of nanofiber from its spiraling path to align with the rotation direction of the collector. Therefore, the effective draw is increased when the peripheral velocity of collector increased, resulting in better alignment of the collected nanofibers. Therefore, we

Figure 7. SEM images of MWCNT/PVDF-HFP nanofiber sheet collected different speed (1.5-7.3 m/s).
confirmed that nanofibers fabricated by electrospinning are able to align along rotating direction at high peripheral velocity of collector.

3.1.3 Effect of CNT weight ratio on nanofiber diameter

Figure 9 shows the average diameter of aligned MWCNT/PVDF-HFP nanofibers as a function of CNT weight ratio. In Figure 9, the average diameters of aligned MWCNT/PVDF-HFP nanofibers were 170 (CNT 0wt%), 120 (CNT 2wt%), 110 (CNT 5wt%), 100 (CNT 7wt%) and 90 nm (CNT 10wt%), respectively. The average diameters of aligned MWCNT/PVDF-HFP decreased as the CNT weight ratio increased. As Mazinani et al. have explained [36], we considered that high electrical conductivity of CNT affected the decrease of nanofiber diameter because of increased stretching force in nanofibers by increased charge in sprayed liquid drops from spray nozzle during electrospinning.

Figure 9. The average diameters of aligned MWCNT/PVDF-HFP nanofibers as a function of CNT weight ratio.
3.2. Characteristics of MWCNT/PVDF-HFP nanofiber sheet

The electrical conductivity and the mechanical strength of aligned MWCNT/PVDF-HFP nanofiber sheet were measured in the alignment direction. Figure 10(a) shows the electrical conductivities of aligned MWCNT/PVDF-HFP nanofiber sheets as a function of CNT weight ratio to the weight of PVDF-HFP in nanofiber sheet. Their electrical conductivities were measured by two-terminal method at room temperature and relative humidity of 40-50%. As shown in Figure 10(a), electrical conductivities of MWCNT/PVDF-HFP nanofiber sheets were $2.9 \times 10^{-10}$ (CNT 0wt%), $6.6 \times 10^{-2}$ (CNT 2wt%), 1.3 (CNT 5wt%), 3 (CNT 7wt%), and 12 S·m$^{-1}$ (CNT 10wt%), respectively. The electrical conductivity in the alignment direction increased as the CNT weight ratio increased. These results are considered due to good electrical conductivity of CNTs. In addition, we also considered that increase of electrical conductivity is not linear but curvilinear as the CNT concentration increased, which is because of rapid increase of connection between MWCNTs in PVDF-HFP nanofibers around the 7wt% (CNT weight ratio). Figure 10(b) shows the mechanical strengths of aligned MWCNT/PVDF-HFP nanofiber sheet in the alignment direction as a function of the CNT weight ratio in nanofiber sheets. Their mechanical strengths were measured by measuring tensile strengths using a tensile tester at an elastic stress speed of 10 mm/min at room temperature. In Figure 10(b), tensile strengths of aligned MWCNT/PVDF-HFP nanofiber sheet were improved by introducing CNT in nanofiber due to good mechanical strength of CNTs.

3.3. Operating of actuator

In order to confirm whether operating MWCNT/PVDF-HFP nanofiber electrode actuator is possible, we tried to fabricate polymer actuator using MWCNT/PVDF-HFP nanofiber sheets for electrodes, which sandwiched IL/PVDF-HFP electrolyte film by hot-press. We used MWCNT/PVDF-HFP nanofiber sheet in the alignment direction as a function of CNT weight ratio.

![Figure 10](image-url)
nanofiber sheet same as experimental condition in Figure 3 (b). Figure 11 shows the optical images of bending actuator at (a) - 6 V, (b) 0 V and (c) 6 V. In Figure 11, we confirmed that actuator was bending. This actuator bent to the left at (a) - 6 V and to the right at (c) 6 V.

4. Conclusions
In this paper, we fabricated carbon nanotube polymer actuator consisted of a EMIBF$_4$/PVDF-HFP electrolyte film between MWCNT/PVDF-HFP nanofiber electrode films fabricated by electrospinning method. Nanofibers with less beads are fabricated by adjusting flow rate and polymer concentration. In addition, it was found that the nanofibers were aligned as the peripheral velocity of collector increased, electrical conductivity and mechanical strength of nanofibers increased as the MWCNT weight ratio to the polymer increased, and the actuator moved to the right or left at DC 6 V between the electrodes. It was considered above results that EAP actuator has wide range of applications such as artificial muscle and so on because of their various advantage such as flexibility and lightness. Therefore, it is important to improve the EAP actuator performance, and this study has possibility of opening a novel route for improving EAP actuator performance using polymer nanofibers containing CNT.

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