Orientation Dependence of Power Generation on Piezoelectric Energy Harvesting Using Stretched Ferroelectric Polymer Films

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Abstract. The piezoelectric vibration energy harvesters were fabricated by using uniaxially stretched poly (vinylidene difluoride/trifluoroethylene) copolymer (P(VDF/TrFE)) film, and the relationship between piezoelectric power generation and molecular orientation was investigated. The molecular orientation in the stretched P(VDF/TrFE) films was evaluated with polarized Fourier transfer infrared (FT-IR) spectra measurement. In stretched films, the main-chains of P(VDF/TrFE) were aligned along the stretching direction. The piezoelectric properties and the electric power generation of stretched P(VDF/TrFE) films were strongly depended on their molecular orientation, measuring by cantilever-type energy harvesters. The piezoelectric coefficient ($e_3$) and output power observed in the energy harvester with the film stretched in the longitudinal direction of cantilever were 16.9 mC/m² and 222 nW, respectively. These values were approximately 2.1 and 3.5 times these of the unstretched elements.

1. Introduction

Vibration energy harvesting using piezoelectric material have attracted much attention in the recent years [1-4]. Inorganic piezoelectric materials with high piezoelectric coefficient have been widely used for vibration power generation, however, the resonant frequencies of these harvesters are higher than that of environmental vibration. To effective use the environmental vibration, the resonant frequency should be adjusted to around that of environmental vibration widely distributed under 100 Hz. The soft organic ferroelectrics are promising candidates for the element of the vibration harvester because of their low resonance frequency, whereas, the low output power of them has been reported.

In our previous work, we used poly (vinylidene difluoride/trifluoroethylene) (P(VDF/TrFE)) (Fig.1 (a)) which is the typical organic ferroelectric polymer [5-6], and tried to improve the performance of harvesters with the multi-stacked P(VDF/TrFE) films. The energy harvester with the cantilever

![Figure 1. Chemical structure of P(VDF/TrFE) (a) and schematic structure of cantilever-type energy harvester (b).](image-url)
structure generated electric power with a resonant frequency of approximately 25 Hz that is comparable to the environmental vibration. The power density of four-layered harvesters was larger than that of the single layer harvester [7]. Moreover we fabricated energy harvester with stretched P(VDF/TrFE) films and investigated the relationship between piezoelectric power generation and molecular orientation in P(VDF/TrFE) films [7]. Therefore, in this study, the fabrication of the energy harvesters using the uniaxially oriented P(VDF/TrFE) films and the piezoelectric power generation of these harvesters were reported in more detail.

2. Experimental methods

P(VDF/TrFE) was dissolved in methyl ethyl keton, and spin-coated onto a silicon substrate. The thickness of the P(VDF/TrFE) films was 2.0μm, approximately. The P(VDF/TrFE) layer was peeled off from the substrate. The free-standing P(VDF/TrFE) films was uniaxially stretched to ratio of 300 % in air, and aneled at 140 ºC for 2h. The stretched film, onto which the 80 nm Al electrodes were deposited, was laminated to the 25-μm-thick poly(ethylene naphthalate) (PEN) substrate. The cantilever structure consisted of Al/P(VDF/TrFE)/Al was used as a design for power generation and piezoelectric measurements. This structure is illustrated in Fig.1 (b). For poling, a triangular external electric field was applied to these energy harvester at room temperature. The piezoelectric properties were evaluated using a laser Doppler vibrometer and optical microscope (Ono Sokki LV-1720). The displacement of the cantilever corresponding the piezoelectric vibration was measured with applying a sinusoidal voltage between the top and bottom electrodes. The electric power generation was measured by applying mechanical vibrations with an acceleration of 10 m/s².

3. Results and discussion

Figure 2 shows the polarized Fourier transfer infrared (FT-IR) spectra of stretched P(VDF/TrFE) films. In the spectrum which was measured with the incident light polarized perpendicular to the stretching direction, the high-intensity absorption at 1400 cm⁻¹, corresponding to the CH₂ wagging mode, was
observed; on the other hand, the intensities of absorption peaks at 1290, 1190, 880 and 840 cm\(^{-1}\) are much weaker than those in the spectrum with parallel polarization. These absorption peaks were assigned to CF\(_2\) antisymmetric stretching, which is perpendicular to the polymer chains [8]. These results suggested that the main-chains of P(VDF/TrFE) were aligned along the stretching direction.

The current density electric field (J–E) curve of the stretched P(VDF/TrFE) film was shown in Fig.3. This measurement was carried out by applying a triangular electric field. There are two peaks in the negative and the positive electric field, respectively. These peaks indicated polarization switching. The remnant polarization was 70 mC/m\(^2\) which was comparable to the value of the unstretched P(VDF/TrFE) film.

The properties of vibration power generators were measured around the resonant frequency approximately 25 Hz. The three type cantilever structure are illustrated in Fig.4, and the resonant frequency, effective voltage, output power generation, and piezoelectric constant \(e\) of these energy harvesters were shown in table 1. In unstretched P(VDF/TrFE) film (Type A), the piezoelectric constant \(e\) was 8.24 mC/m\(^2\); and this value of P(VDF/TrFE) film stretched in the longitudinal direction (Type B) and widthwise direction (Type C) of cantilever was 16.9 and 2.19 mC/m\(^2\), respectively. The highest \(e\) value was observed in Type B energy harvester, in which main-chains of P(VDF/TrFE) were aligned to the longitudinal direction of the cantilever. The output power of Type A, B and C energy harvesters were 61.2, 222 and 22.4 nW, respectively. The highest value also observed in Type B energy harvester. Here, this value of P(VDF/TrFE) film stretched in the longitudinal direction and widthwise direction of cantilever was approximately 3.5 and 0.4 times these of the unstretched elements, respectively [7].

Table 1. Maximum output power and piezoelectric constants of unstretched and stretched P(VDF/TrFE) films.

|                        | Type A Unstretched P(VDF/TrFE) film | Type B Stretched longitudinal direction | Type C Stretched widthwise direction |
|------------------------|-------------------------------------|----------------------------------------|--------------------------------------|
| Resonant frequency (Hz)| 24.1                                | 24.6                                   | 23.3                                 |
| Effective voltage (mV) | 423                                 | 735                                    | 330                                  |
| Piezoelectric coefficient \(e\) (mC/m\(^2\)) | 8.24                                | 16.9                                   | 2.19                                 |
| Output power (nW)      | 61.2                                | 222                                    | 22.4                                 |

Figure 4. Schematic structures of cantilever-type energy harvesters.
These results suggested that the molecular orientation in P(VDF/TrFE) films affected the piezoelectric constant and output power, and the optimal molecular orientation for vibration power generations was to be parallel their long chain axis to the longitudinal direction of the cantilever.

In conclusion, we fabricated the cantilever-type energy harvesters using stretched and unstretched ferroelectric polymer films. In the energy harvester in which P(VDF/TrFE) main-chains were aligned to the longitudinal direction of the cantilever, the highest $e$ and output power values were observed. Thus, the uniaxially oriented P(VDF/TrFE) films showed potential for the element of the vibration harvester using in the environmental vibration.

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