High-temperature property of flexible polyvinylidene fluoride/ (Na0.5K0.5)NbO3 vibration energy harvester

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Flexible polyvinylidene fluoride/(Na0.5K0.5)NbO3 (PVDF/NKN) composite harvester was first characterized at high temperature. The origin of high flexibility is the unique structure assembled by alternately stacking four-sheets and three-fabrics (4-3 harvester). The 4-3 harvester was fabricated by uniformly dispersing piezoelectric NKN particles within a PVDF-sheet and a PVDF-fabric layer. Electric power-output of the 4-3 harvester was measured by using a custom-designed apparatus in the temperature range from 25 to 150°C and was compared with that of PVDF/BaTiO3 (BT) harvester. The PVDF/NKN 4-3 harvesters and PVDF/BT 4-3 harvesters showed significantly different temperature dependences in the temperature range from 25 to 150°C. Electric power-output obtained at 25°C by applying an oscillation at 75 Hz in the thickness direction for the PVDF/NKN 4-3 harvesters and PVDF/BT 4-3 harvesters were 5.7 and 3.5 nW/cm² per an amplitude, respectively. In particular, at temperature above 130°C, the PVDF/NKN 4-3 harvester showed a stable output performance from 3.3 to 3.8 nW/cm², whereas the PVDF/BT 4-3 harvester demonstrated no electric power-output. Thus, the harvester composed of high Tc piezoelectric particles such as NKN is suitable as a vibration energy harvester operated under high-temperature environment.

Key-words : Piezoelectric vibration energy harvester, Polymer/ceramic composite, Lead-free piezoelectric material, Sodium potassium niobate, Electrospinning, High-temperature measurement

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1. Introduction

Energy harvesting technologies such as solar photovoltaic generation, wind power generation, and vibration-powered generator have been paid much attention as an eco-friendly energy technology because they can convert an energy discarded from the surrounding environment into electrical energy.1–5 Among these technologies, piezoelectric vibration energy harvesters (PVEHs) has been expected to realize the stand-alone power system for the sensor device. Using PVEHs as an electric power supply system in the sensor devices, it is possible to obtain relatively high electric power-output which is enough to operate the sensor devices, thus, it will be possible to reduce a number of cables for driving the devices and to miniaturize the industrial sensor devices.6–10

Numerous studies have been performed so far to improve the generating efficiency of PVEHs.11–15 For instance, designing more efficient piezoelectric device structure such as cantilever shape, thin-film, and fiber structures has been studied.16–20 The combination of flexibility and power generation is important to convert vibration into electric energy for PVEHs. Therefore, a combination of piezoelectric ceramics and polymers in the best way to obtain both advantages of two materials such as good power generation and a mechanical flexibility. Our groups have proposed that the novel multilayer structure composed of piezoelectric (Na,K)NbO3 (NKN) particles and fibrous polymer.21 It showed good mechanical flexibility and a maximum power-output of 145 nW/cm² per an amplitude in the longitudinal direction, and the power-output depended on a direction of the applied vibration due to a change of strain propagation from polymer matrix to piezoelectric ceramics. The multilayer structure was composed of four-polyvinyl alcohol (PVA)-sheets and three-polyvinylidene fluoride (PVDF)-fabrics. NKN particles were uniformly dispersed within the PVA sheets and the PVDF fabrics. The polymer sheets and fabrics with uniformly-dispersed NKN particles were laminated alternately (4-3 harvester). In our previous reports, electric power-outputs of the proposed 4-3 harvester was investigated only at room temperature.21 Sensor devices are also in great demand at high-temperature environment less than 150°C such as a muffler-part and an engine-room of automobile. Seon-Bae Kim et al.22 have investigated the effect of temperature on the electric power-output for lead zirconate titanate (PZT)-bulk and PZT-MEMS harvester. PZT-MEMS harvester showed lower thermal degradation rate than PZT-bulk harvester in the temperature range from 25 to 100°C. Furthermore, Jingen Wu et al.23 have reported that electric power-output property of BiScO3–PbTiO3 (BSPT) bimorph-PVEHs which have a high curie temperature (Tc ~450°C). A voltage of the BSPT bimorph-PVEHs initially increased in the temperature range from 25 to 150°C, however, the voltage decreased dramatically above 150°C. This phenomenon was related to the change of piezoelectric constant ε33 with increasing temperature and thermal depolarization effect of the BSPT. Generally, bulk ceramic bimorph-PVEHs showed a

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high generation performance, however, bulk ceramics are susceptible to fatigue crack when subjected to high frequency cyclic loading or large displacement. Development of flexible PVEHs composed of polymer/piezoelectric composite is important for a practical application of the PVEHs because the PVEHs should be placed at curved surface such as the muller-part. High flexibility of polymer matrix is useful to attach the PVEHs to anyplace. In spite of the fact that many kinds of the PVEHs of polymer/piezoelectric composite have been studied, there is no information about temperature dependency of electric power-output properties as far as we searched.

In this study, a 4-3 harvester composed of PVDF sheets and fabrics with uniformly-dispersed NKN particles were fabricated. PVDF is suitable for the high-temperature environment because it is one of the super engineering plastics, and it has good heat resistance properties (the melting point: 150–170°C). We measured the electric power-output of the PVEHs by the custom-designed apparatus. Furthermore, the $d_{33}$ values of the heat-treated harvester were measured to determine the depolarization temperature ($T_d$) of NKN particles, and the relationship between electric power-output and the $T_d$ was also investigated.

2. Experimental methods

NKN powder was synthesized through a solid-state reaction method. $\text{Na}_2\text{CO}_3$ (99.9%), $\text{K}_2\text{CO}_3$ (99.9%), and $\text{Nb}_2\text{O}_5$ (99.9%) were weighted according to the formula ($\text{Na}_{0.5}\text{K}_{0.5}$)$\text{NbO}_3$ and mixed by a wet-ball-milling for 16 h. The mixed powder was sintered by two-step thermal treatments at 910°C for 10 h and at 1098°C for 2 h. The sintered powder was ground for 30 min to obtain a homogeneous powder. Polyvinylidene fluoride (PVDF, Takiron Co., Ltd., Japan) was dissolved into N,N-dimethylformamide (DMF, Kishida chemical Co., Ltd., Japan) at 110°C to prepare a PVDF solution. The initial concentration of this solution was 1.0 g PVDF per 30 mL DMF. The NKN powder was added with the ratio of 50 vol% into the PVDF solution and that slurry was stirred for 1 h, and the PVDF/NKN sheets in the thickness of 40 μm were obtained by an extrusion technique on an alumina plate at 110°C from slurry. PVDF/NKN composite fabrics were prepared as follows. The NKN powder was added with the ratio of 50 vol% put into a PVDF solution (ca. 0.12 g/mL) and then carbon particles (JEOL Ltd., Japan) were mixed with the ratio of 1% into the PVDF/NKN slurry to rise electrical conductivity. It is known that a uniform fiber is formed via electrospinning by rising electrical conductivity of the slurry. The mixed PVDF/NKN slurry solution was placed in a 5 mL plastic syringe (Terumo Co., Ltd., Japan) with a needle inner diameter range of 0.80 mm. The flow speed was 1.5 mL/h and the distance from the tip of a syringe to a grounded collector was 10 cm. PVDF/NKN composite fabrics were obtained by the electrospinning 18 ± 1 kV voltage. Both the fabricated PVDF/NKN fabrics and the PVDF/NKN sheets were cut into $28 \times 13$ mm. Four-PVDF/NKN sheets and three-PVDF/NKN fabrics were laminated alternately and pressed by a hot pressing at 40 MPa and 95°C. The 4-3 lamination was polarized by corona poling method in the thickness direction under ~20 kV for 30 min. An Ag electrode was formed on the facing surfaces of the pole samples and a Cu-tape was attached on that Ag electrode. The prepared vibration energy harvesters (4-3 harvester) were sealed with PTFE-tape film (Chukoh Co., Ltd., Japan) to adhere the surface electrode. Furthermore, by use of BaTiO$_3$ powder (BT; Kojundo chemical laboratory Co., Ltd., Japan), PVDF/BT vibration energy harvesters were also fabricated by a same fabrication method of 4-3 harvester of PVDF/NKN.

![Fig. 1.](image)

Fig. 1. (a) Schematic illustration of the measurement apparatus for in-situ temperature dependence of electric power-output, (b) side elevation of the measurement apparatus, (c) temperature schedule.

Microstructure and morphology of PVDF/particle fabric were investigated by scanning electron microscopy (SEM; Technex Mighty-8, Japan). The fibrous diameter distribution of the fabric was determined from over 150 fibers in the SEM images at 5000× magnification using an Image J software. As heat-resistance test of piezoelectric properties, 4-3 harvesters were placed on a hot-plate and heated for 20 min at the certain temperature in the temperature range from 25 to 250°C. After cooling of the 4-3 harvesters to room temperature, the piezoelectric $d_{33}$ values were measured by a quasi-static $d_{33}$ meter (Academia Sinica ZJ-6B, China) at 110 Hz. To measure a temperature dependency of the electric power-output, a custom-designed apparatus was constructed as schematically shown in Fig. 1. The harvester was fixed at one side, and an external repeated vibration was induced to the thickness direction in the stroke of 2.6 μm at temperature from 25 to 150°C and frequency at 75 Hz. In order to stabilize the temperature, the direction of applied vibration was limited to the thickness direction. The harvester was connected with the external resistor, and impedance matching was optimized to obtain maximum electric power-output (Fig. 2). The output voltages were monitored by an oscilloscope (Keysight Technologies, USA) and the electric power-output was calculated. Strain gauges were bonded on the samples, and the tensile mechanical properties of PVDF/NKN laminated composites were measured in the temperature range from 25 to 100°C by a compression stress tester (Imoto Co., Ltd., IMC-90FB, Japan). Young’s modulus was calculated from the value of their strain in the strain range from 0.05 to 0.15% at each temperature.

3. Results and discussion

3.1 Structural characterization

There was no difference in appearance of the PVDF/NKN and PVDF/BT vibration energy harvesters, and the thickness of two harvesters was both approximately 300 μm. Figure 3 showed SEM images and histograms in diameter of the PVDF/NKN and PVDF/BT fibers. The average particle sizes of NKN particles and BT particles were 1.9 ± 0.6 and 0.8 ± 0.3 μm in diameter, respectively. The average particle sizes were almost same as sizes of starting powders. The average fiber diameter of PVDF/NKN and PVDF/BT fiber were 139 ± 54 and 144 ± 53 nm, respectively. There was no significant change of the diameter in PVDF/
NKN and PVDF/BT fiber. In addition, both NKN and BT particles were well dispersed in the three-dimensional PVDF fiber and entangled in the PVDF polymer chain. Thus, there was no significant difference between their morphologies. It is interesting that the type of raw material and particle sizes doesn’t affect neither fiber diameter distribution and fiber morphology.

3.2 Electric power-output characterization

Figure 4 showed piezoelectric $d_{33}$ values after the heat-treatment in temperature range from 25 to 250°C. Although a melting point of PVDF is around 160°C, interestingly, PVDF composed ceramics did not melt above $T_m$ and kept the shape until 250°C. The $d_{33}$ values for the 4-3 harvesters of PVDF/NKN and PVDF/BT were $12 \pm 1.7$ and $7.9 \pm 1.4$ pC/N after heat-treatment at 25°C, respectively. The $d_{33}$ value of a 4-3 harvester fabricated from only pure PVDF was also measured, and it was ~1.0 pC/N. Therefore, we think the piezoelectric performance is closely related to the property of dispersed piezoelectric ceramics and a flexibility of the polymer matrix. The $d_{33}$ values for the 4-3 harvester of PVDF/BT linearly decreased with increasing heat-treatment temperature, and the $d_{33}$ values were 0 pC/N at temperature above 145°C. The 4-3 harvester of PVDF/NKN showed a stable piezoelectric performance from 25 to 115°C. Although the $d_{33}$ values for the 4-3 harvester of PVDF/NKN were gradually decreased from 145°C, the 4-3 harvester still showed 6.8 pC/N even after heat-treatment at 250°C. Matsudo et al. have reported the temperature dependence of the electromechanical coupling factor $k_p$ for NKN ceramics. The $k_p$ value at room temperature was 0.37 and the values were stable until $T_{DK,T}$ (~210°C). The $k_p$ was gradually decreased above $T_{DK,T}$. Thus, the degradation of the $d_{33}$ values for the 4-3 harvester of PVDF/NKN above 210°C was caused by the depolarization of NKN particles. V. Sencadas et al. reported that the melting point ($T_m$) of poled and non-poled β-PVDF were 156.3 and 160.1°C, respectively. The $T_m$ of PVDF is decided according to the crystalline phase and poled condition, and flexible fabric layer having a large specific surface area is sensitive to heat. Thus, the melting of PVDF caused the structure change of flexible fabric layer, and the $d_{33}$ values for the 4-3 harvester of PVDF/NKN could be decreased from 145 to 250°C.

The temperature dependencies of electric power-output characteristics were measured in the thickness direction by the custom-designed equipment at 75 Hz in the temperature range from 25 to 150°C (Fig. 5). From the SEM images, there were no difference in the fiber morphology of PVDF/NKN and PVDF/BT. On the other hand, their temperature dependencies of the electric power-output were significantly different. The 4-3 harvester of PVDF/BT generated 195 mV and 3.5 nW/cm² per an amplitude at 25°C. The electric power-output of the 4-3 harvester of PVDF/BT was gradually decreased in the temperature range from 25 to 120°C, and no power output signal was observed above 130°C. This results showed a similar decreasing tendency of piezoelectric $d_{33}$ values for the 4-3 harvester of PVDF/BT with increasing temperature. It is seen that the electric power-output and depolarization for temperature were related closely. In contrast, the 4-3 harvester
of PVDF/NKN generated 250 mV and 5.7 nW/cm² per an amplitude at 25°C, and both output voltage and electric power-output were almost constant from 25 to 70°C. Although the electric power-output was gradually decreased from 80°C, the 4-3 harvester of PVDF/BT still showed generated performance at 150°C, and its power-output was 3.8 nW/cm² per an amplitude. These differences should be related to the depolarization temperature (T_d) of the dispersed piezoelectric particles into PVDF. It is well known that the Curie temperature (T_C) for BT is ~130°C, and the depolarization occurs above T_C.27) It is assumed that the electric power-output of the 4-3 harvester of PVDF/BT gradually decreased by the depolarization of BT particles with increasing temperature, and above T_C, polarization of the BT particles was not enough to generate electric power-output. On the other hand, NKN has a higher T_C (~400°C) than that of BT. Our previous studies have revealed that the d_{33} value of NKN ceramics showed an increase tendency up to 150°C by inverse method and strain measurement method.28,29) Therefore, the electric power-output of the 4-3 harvester of PVDF/NKN was generated even at 150°C due to the high depolarization temperature of NKN.

**Figure 6** showed a comparison between the ratio of output voltage and piezoelectric constant d_{33} for 4-3 harvester of PVDF/NKN. The solid line is an output voltage and the dashed line is a piezoelectric constant d_{33}. With increasing temperature, the change ratio of d_{33} values was approximately 10% from 25 to 145°C, however, the change ratio of output voltage was 18% from 25 to 150°C. The difference appeared especially in the temperature range from 80 to 150°C.

Figure 7(a) showed the strain-stress curves for 4-3 lamination of PVDF/NKN in the temperature range from 25 to 100°C. The max strain was 0.42% at 25°C, and it decreased with increasing temperature. Finally, the max strain decreased to 0.22%. On the other hand, max stress was constant up to 40°C, and it gradually decreased from around 10.1 to 2.89 MPa. Figure 7(c) showed the Young’s modulus estimated from the strain-stress curves for 4-3 lamination of PVDF/NKN in the temperature range from 25 to 100°C. Young’s modulus was linearly decreased from 3.35 to 2.76 GPa with increasing temperature from 25 to 100°C. This result indicated that flexibility of the 4-3 lamination of PVDF/NKN was maintained in the temperature range from 25 to 100°C, and the 4-3 lamination of PVDF/NKN became more flexible with increasing temperature. It has been reported that an amorphous relaxation of PVDF existed around 70°C.30,31) This relaxation induces some mobility within the chains that may initiate the loosening of molecular orientation.25) Thus, the decrease tendency...
of Young’s modulus of the 4-3 lamination were related to the property of polymer material.

In terms of the temperature dependency of the electric power-output, the 4-3 harvester of PVDF/NKN showed the decrease tendency from 80°C. We expected that the electric power-output for the 4-3 harvester of PVDF/NKN showed stable values up to 150°C, because the crystal structure of NKN forms an orthorhombic perovskite at wide temperature from room temperature to approximately 200°C. Accordingly, the decrease of electric power-output for the 4-3 harvester of PVDF/NKN could be related the hardness variation of the polymer/ceramic multilayer structure, especially the hardness variation of the polymer material with temperature due to the molecular motion of PVDF. Therefore, a polymer layer with high temperature resistance is necessary to utilize the characteristic of NKN and to use the harvester for high temperature environment.

4. Conclusions

In this study, the flexible energy harvester with 4-3 multilayer structure was fabricated by laminating the super engineering polymer sheets and fabrics with uniformly dispersed BT or NKN particles, and the temperature dependency of electric power-output was investigated in the temperature range from 25 to 150°C. The electric power-output of the PVDF/BT 4-3 harvester was linearly decreased with temperature, and above 130°C, the PVDF/BT 4-3 harvester didn’t generate the power-output. On the contrary, even at 150°C, the PVDF/NKN 4-3 harvester generated 80% of output voltage at 25°C. The decrease could be related to the thermal property of polymer matrix rather than the property of NKN particles which have high Tc. Therefore, using a polymer matrix which has both flexibility and high temperature resistance above 150°C, the harvester including NKN particles is applicable to high-temperature application.

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