Corona Poling Conditions for Barium Titanate/Epoxy Composites and their Unsteady Wind Energy Harvesting Potential

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Corona Poling Conditions for Barium Titanate/Epoxy Composites and their Unsteady Wind Energy Harvesting Potential

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The objective of this paper is to design and fabricate barium titanate (BTO)/epoxy composites, investigate the effect of poling conditions on their piezoelectric properties, and obtain their unsteady energy harvesting potential. The poling condition test deals with the effect of the poling conditions on the piezoelectricity of BTO/epoxy composites. The specimens are polarized by corona poling under different conditions, and their piezoelectric coefficient d_{33} is measured. The distribution of the piezoelectric particles in the matrix is studied using scanning electron microscopy (SEM), and the microstructure of the particle is investigated using X-ray diffraction (XRD). A wind harvesting test was then performed, and the output voltage is measured for the composite sheets under unsteady air flow. This study opens the way for the development of flexible energy harvesting devices.

1. Introduction

Piezoelectric ceramics and composites have found extensive application in sensors, electronic devices, and energy harvesting devices.[1] To support the sustainable development of society and human health, the development of lead-free piezoelectric materials has become a new and intensive research area in recent years. Barium titanate ($BaTiO_3$ or BTO) is a well-known lead-free material. However, due to the brittleness of this ceramic material, the applications of BTO are limited. Recently, high-quality lead-free BTO nanofibers were obtained using a sol–gel based electrospinning technique, and a flexible piezoelectric device was fabricated from aligned BTO nanofibers and a polydimethylsiloxane (PDMS) polymer matrix.[2] Inker-modified BTO nanoparticles have been incorporated into poly (ethylene glycol diacrylate) (PEGDA) composite film devices.[3] A BTO/PDMS composite film with a 20 wt% mass ratio of BTO nanoparticles has shown high performance.[4] The roles and effects of multi-walled carbon nanotubes (MWCNT) (0.0–5.0 wt%) and BTO nanofibers (10–50 wt%) in the electrical, dielectric, and piezoelectric properties of PDMS-based nanogenerators have been systematically investigated.[5] Bowland et al.[6] studied ways of synthesising textured BTO films on carbon fiber fabrics and their integration into a carbon fiber composite with power generation and sensing capabilities. More recently, Narita et al.[7] developed piezoelectric hybrid carbon fiber-reinforced polymer (CFRP) composite laminates by embedding BTO with potassium sodium niobate ($K_{1-x}Na_xNbO_3$, KNN) nano-particle filled epoxy interlayers, and successfully polarizing the composite specimens. They showed that the output voltage of the piezoelectric CFRP composite due to the impact load is stable the day after the material is polarized.

It is well-known that the poling process is a crucial step to induce the piezoelectric response of a piezoelectric material. Optimized poling conditions are a very important tool for improving the piezoelectric properties of lead-based or lead-free ceramics, including poling temperature, poling voltage, poling time, etc. The poling conditions affect the piezoelectric properties of a material by changing its microstructure.[8] As shown in **Figure 1**, the material is initially cubic and becomes tetragonal by elongating along a cube axis when BTO cools to 5 °C from its Curie temperature. The tetragonal BTO shows piezoelectric properties due to the lattice asymmetry. Upon further cooling to −90 °C, the lattice transforms to orthorhombic.

Poling of piezoelectric ceramics and composites is typically performed in a temperature-controlled oil bath by applying a large DC electric field directly to the electrode faces of the specimen. However, this conventional DC technique has many disadvantages; for example, electroding of the material is necessary, and poling is limited to specimens with a small area. In addition, localized dielectric breakdown at weak spots such as pinholes short-circuits the electrodes, preventing further poling. To improve the poling of piezoelectric materials, the corona discharge technique has been used. In this method, an electric charge from a corona needle is sprayed onto the surface of the specimen, which rests on a grounded plate, creating an electric field between the faces of the specimen. This method can be used to pole specimens with large surface area, and due to the absence of electrodes, there is no shorting of the specimen at weak spots.[9]

Although there are several studies of the poling conditions for BTO ceramics, the effects of poling conditions on BTO/epoxy

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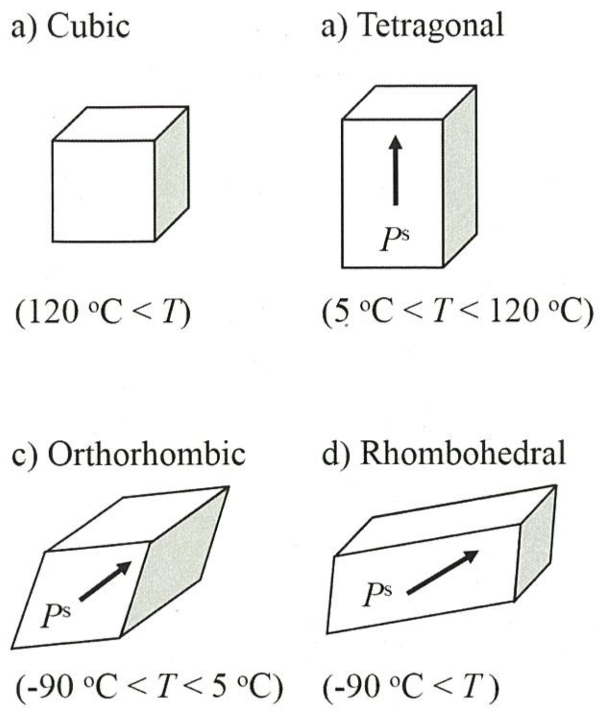

Figure 1. Crystallographic changes in the BTO unit cell with spontaneous polarization P_s at different temperatures.

composites have rarely been studied, and it is important to investigate the piezoelectric behavior of BTO/epoxy composites polarized under different conditions.

The objective of this study is to design, fabricate, and characterize a BTO/epoxy composite sheet. Combining the BTO with epoxy can not only increase the toughness of the material but also reduce its weight and cost. BTO/epoxy composite sheets were developed, and the relationships between the poling conditions, piezoelectricity, and phase structure were studied. The applications of BTO/epoxy composite material can also be expanded, particularly to energy-harvesting devices. The unsteady wind harvesting properties of BTO/epoxy composite were measured.

2. Experimental Section

2.1. Material Preparation

BTO/epoxy composites were prepared using BTO particles (Nippon Chemical Industrial Co. Ltd., Japan) and a commercially available epoxy resin (EP-106NL, Cemedine Co. Ltd., Japan). The particle size of the BTO was approximately 1.04 μm, and the volume fraction of BTO particles was held constant at 32 vol%.

The fabrication method is shown in **Figure 2**a. The epoxy was first mixed with BTO particles at the designed volume fraction, and the mixture was then stirred for 30 min and defoamed for 10 min using a Thinky AR-100 conditioning mixer (Thinky Co., Japan). The well-stirred mixture was then poured into the mould and heated to 60 °C to reduce its mucosity, and 20 min of vacuum-pumping were conducted to eliminate air bubbles from the mixture. Following this, the composite was solidified in the oven at 135 °C for 45 min. Finally, the composite sheets were cut to the desired size, as shown in Figure 2b and **3**a. The length, width, and thickness of the test specimen for the poling conditions were 12, 3, and 0.2 mm, while those for the unsteady wind energy harvesting test were 25, 10, and 0.2 mm, respectively.

2.2. Poling Treatment

Prior to the poling treatment, an electrode made of conductive copper tape with a thickness of 0.1 mm was applied to the lower surface of the specimen. Figure 2(c) and 3(b) and (c) show the appearance of the specimens and their thicknesses. In this study, all of the specimens were polarized in the thickness direction.

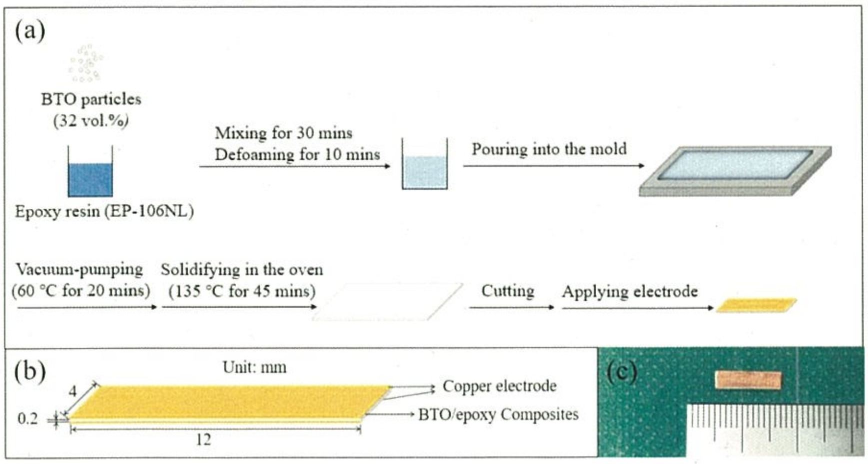

Figure 2. Fabrication of the BTO/epoxy composite: a) fabrication method; b) diagrammatic sketch of the poling condition test specimen; and c) appearance of the poling condition specimen.

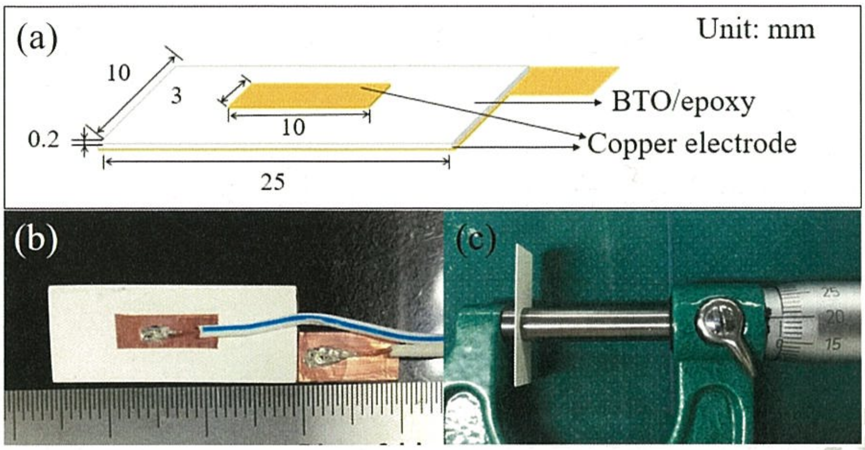

Figure 3. Specimen for the unsteady wind energy harvesting test: a) diagrammatic sketch; b) appearance; and c) thickness of the specimen.

Figure 4a displays the electrical circuit used for corona poling. It consists of a tungsten needle (referred to as a corona needle) that is connected to a high-power supply voltage V_N and suspended above the specimen, which is placed on a heat plate. The bottom surface of the specimen with the electrode is connected to the ground. When the corona discharge is triggered by the application of a high voltage, electric charge from a corona needle is sprayed onto the surface of the specimen which rests in a grounded plate, creating an electric field between the specimen faces. The charges remain on the surface, generating a poling electric field between the top surface and the ground. We assume that the voltage in the upper side of the specimens is equal to the voltage of the corona needle. Furthermore, the heat plate can heat the specimen to a specific temperature during poling.

In the poling conditions test, the following conditions were used to investigate the effect of the poling conditions on the longitudinal direct piezoelectric coefficient d_{33} for BTO/epoxy composites. In order to eliminate errors caused by abnormal data, three specimens were used for each condition.

The specimens were polarized under the following conditions:

(1) 25–100 °C, 40 kV mm^{-1}, 10 min, corona needle at 15 mm distance;
(2) 100 °C, 40 kV mm^{-1}, 0–40 min, corona needle at 15 mm distance;
(3) 75 °C, 0–45 kV mm^{-1}, 10 min, corona needle at 15 mm distance; and
(4) 65 °C, 15 kV mm^{-1}, 10 min, corona needle at 6–15 mm distance.

After the poling treatment, the upper electrode was applied to the upper surface of the specimen. The electrical properties of all BTO/epoxy composites were measured more than a day after poling.

Furthermore, to study the changes over time in the piezoelectricity of the BTO/epoxy composite after poling, three specimens were polarized at 65 °C, 40 kV mm^{-1}, for 30 min, and with a corona needle distance of 15 mm, and the values of d_{33} for the specimens were measured within 0–7 days after poling.

In the unsteady wind energy harvesting test, which is discussed later, three specimens were polarized at 65 °C, 40 kV mm^{-1}, for 30 min, and with a corona needle distance of 15 mm.

2.3. Characterization

The cross-sectional morphology of the BTO/epoxy composite sheets was observed using scanning electron microscopy (SEM)

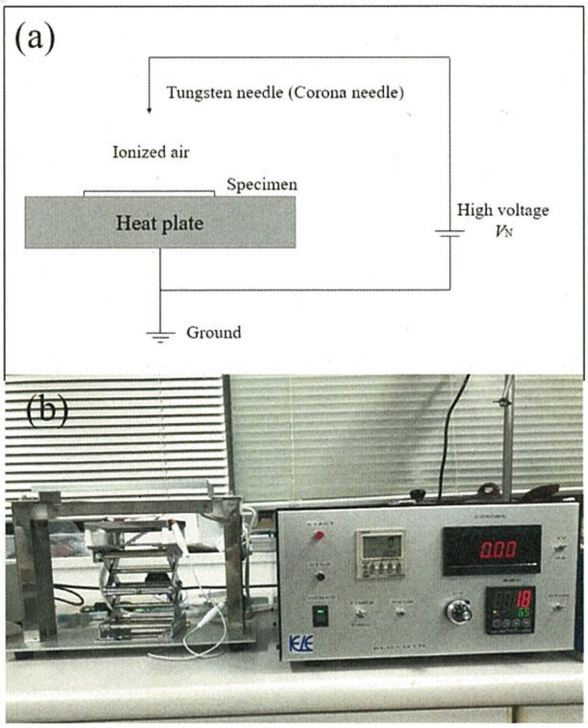

Figure 4. Corona poling: a) electrical circuit for corona poling; and b) corona poling equipment.

with a JSM-7800F model microscope (JEOL Ltd., Japan). The specimens were gold plated prior to SEM characterization. The piezoelectric coefficient d_{33} was measured using a piezo-d_{33} meter (YE2730A, Sinocera Piezotronics, Inc., China). The crystalline structure and phase of the BTO/epoxy composite specimens were subsequently determined using a Rigaku SmartLab (Rigaku Co., Japan) operating at 45 kV and 200 mA, using a Cu K_α wavelength of 0.15406 nm. Peaks were recorded in the 2θ range 20–60°.

2.4. Unsteady Wind Energy Harvesting Test

A diagrammatic sketch of the unsteady wind energy harvesting test is shown in **Figure 5**. It is well-known that natural wind conditions are unsteady and discontinuous. In order to imitate this discontinuous natural wind, three- and five-leaf fans were designed, fabricated, and used to transform the continuous air flow from the air duct into a discontinuous flow. The fans consisted of a 3D-printed core and polyethylene terephthalate (PET) leaves with a thickness of 0.5 mm. Figure 5(a) and (b) show the size and appearance of the three- and five-leaf fans, respectively.

Figure 5(c) shows the equipment used in the unsteady wind energy harvesting test. The specimen was first connected to a data logger (Keyence NR-500, Keyence Co., Japan) and computer, and then fixed 10 mm away from the fan. The original continuous air flow with the speed of $v_o = 2\,\mathrm{m\,s^{-1}}$ was passed through the duct and was changed by the fan fixed in front of the duct. The resulting discontinuous air flow v_f acted on the specimens, and the real-time output voltage of the specimen was recorded by the data logger and computer.

In order to ensure the authenticity and universality of the data, three specimens were used in the test in each group, and each specimen was tested three times.

3. Results and Discussion

3.1. SEM

SEM was used to evaluate the composite microstructures and the dispersion of the BTO particles within the epoxy matrix. **Figure 6** shows the SEM micrographs of the cross-section of the BTO/epoxy composite. From the figure, it can be seen that

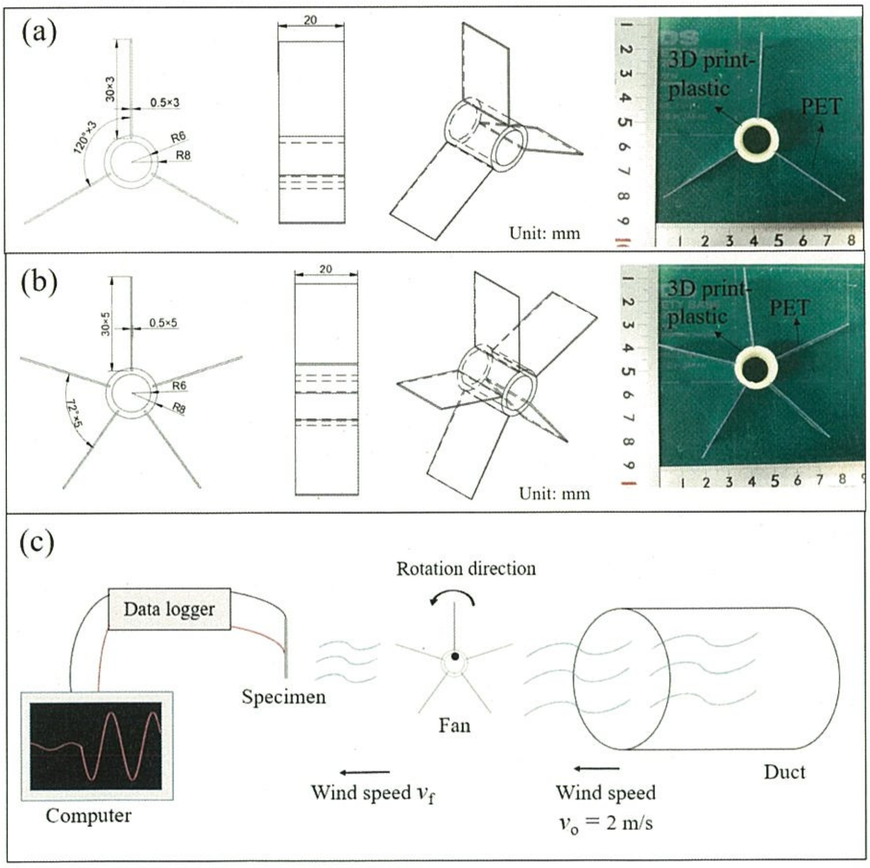

Figure 5. Diagrammatic sketch of the wind energy harvesting test: a) three-leaf fan; b) five-leaf fan; and c) equipment for unsteady wind energy harvesting test.

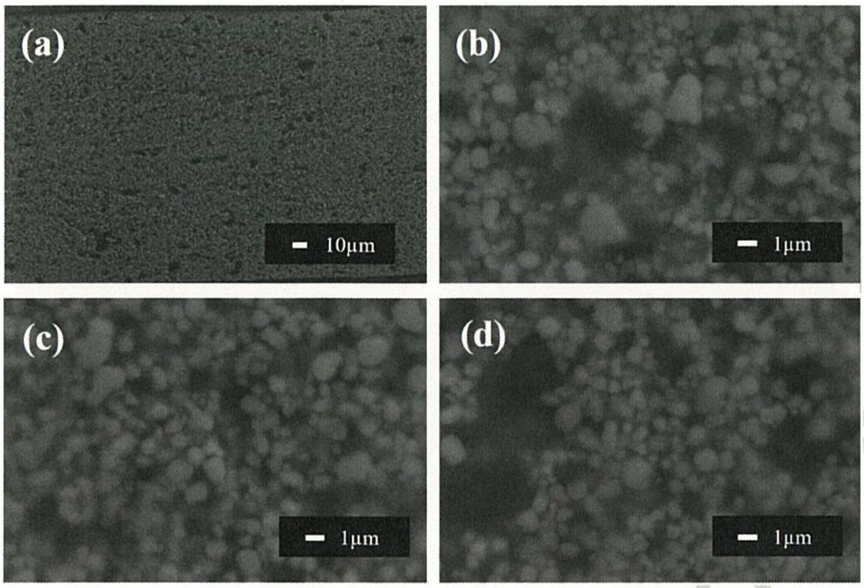

Figure 6. SEM micrograph of the cross section of the BTO/epoxy composite: a) overall view; b) upper view; c) central view; and d) lower view of BTO/epoxy composite.

the dispersion of the BTO particles over the upper, central, and lower parts is similar and that there is no precipitation of particles at the bottom. In general, the BTO particles are relatively evenly distributed within the epoxy matrix, proving that they are well mixed. However, there are some voids in the composite, with sizes of approximately 1–50 μm^2.

3.2. Effects of the Poling Conditions

Figure 7 shows the effects of the poling conditions on the piezoelectric coefficient d_{33} for the BTO/epoxy composite. The d_{33} for polarized BTO/epoxy varies in the range 0.4–3.0 pC/N. Theoretically, a suitable poling temperature can make the electric domain easier to rotate, which is helpful in increasing the piezoelectricity of piezoelectric materials. From Figure 7a, it can be seen that the value of d_{33} for BTO/epoxy composites at first increases with an increase in the poling temperature, and then decreases after a critical temperature of 65 °C is reached. At 65 °C, the value of d_{33} is 2.5 pC/N, which is 6.25 times in the value at 25 °C (average value 0.4 pC/N). It is clear that the value of d_{33} for the BTO/epoxy composites is greatly improved by the change in poling temperature. The BTO/epoxy composite shows relatively high piezoelectric properties at a poling temperature of 65 °C.

Figure 7b shows the voltage dependence of d_{33} for the BTO/epoxy composite. When the poling voltage reaches 20 kV mm^{-1}, d_{33} increases with poling voltage, and then becomes saturated and remains near to the saturation value (about 2.3 pC/N). The saturation poling voltage for the BTO/epoxy composite is approximately 40 kV mm^{-1}.

On the other hand, the value of d_{33} for specimens polarized at 15 kV mm^{-1} remains at zero, meaning that 15 kV mm^{-1} is not sufficient to pole the BTO/epoxy composite. To better understand the reason for this, we reduced the distance between the corona needle and the specimen from 15 mm to 6 mm and then measured d_{33} for the specimens. The results are shown in **Table 1**, which show that d_{33} does not increase when the distance between the specimen and corona needle is reduced. We therefore assume that 15 kV mm^{-1} is not sufficient to make the electric domain rotate or move.

The effect of poling time on the piezoelectric coefficient d_{33} of BTO/epoxy composites is depicted in Figure 7c. It can be seen that the value of d_{33} reaches 1.5 pC/N (average value) within 30 min, which is 3.4 times that of the specimen poled for 5 min at same poling voltage and temperature (average value 0.5 pC/N). This agrees with a previous study showing that the poling degree increases with poling time before the specimen is broken.[10] Furthermore, Figure 7(d) shows that d_{33} for the BTO/epoxy decays after poling. The d_{33} of the BTO/epoxy composite decreases by about 10% within seven days after poling.

The relative permittivity ε_r of the specimens was also measured, and approximately $\varepsilon_r = 16$ was obtained. The values were small and not affected by the poling conditions. A low permittivity is desired to increase energy harvesting characteristics.

Besides, it is clear that increasing the volume fraction of BTO particles increases the piezoelectric coefficient d_{33} of the composite. The specimens made with 44 vol% of BTO particle were also fabricated and polarized under 65 °C, 40 kV mm^{-1}, and 30 min by corona poling machine. The d_{33} of the specimens is approximately 4.3 pC/N. However, the higher volume content of the BTO particles makes the composite brittle and loses our purpose. Hence, in this investigation, the content was kept at 32 vol%.

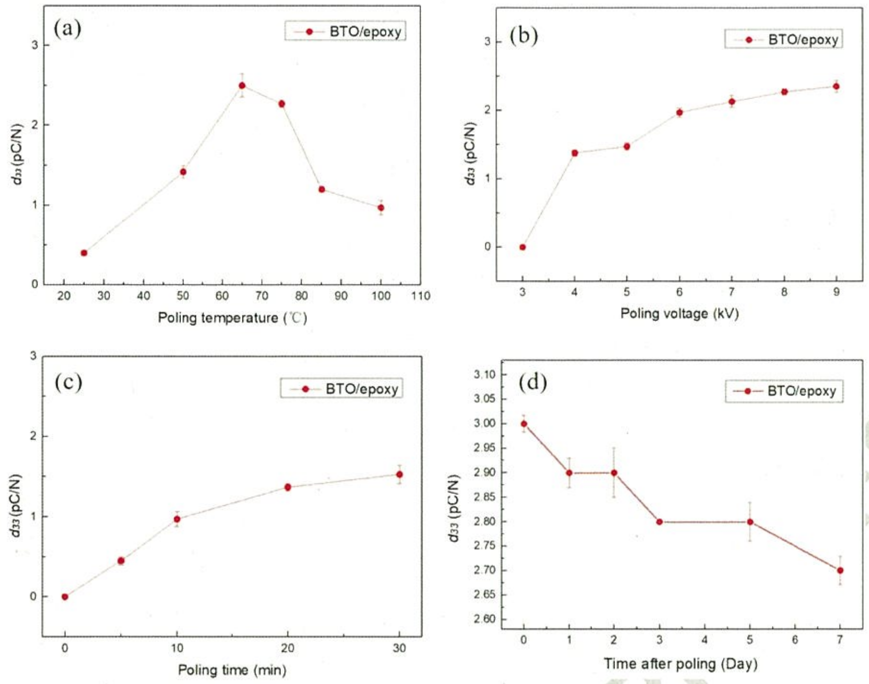

Figure 7. d_{33} for BTO/epoxy composite polarized under different poling conditions: d_{33} changes with a) poling temperature (40 kV mm^{-1}, 10 min); b) poling voltage (75 °C, 10 min); c) poling time (100 °C, 40 kV mm^{-1}); and d) time after poling (65 °C, 40 kV mm^{-1}, 30 min).

3.3. X-Ray Diffraction (XRD)

The BTO/epoxy composite sheets were polarized at different poling temperatures, and the details of the poling conditions are shown as follow:

(1) B-0: unpoled;
(2) B-65: 65 °C, 40 kV mm^{-1}, 30 min, corona needle at 15 mm distance; and
(3) B-100: 100 °C, 40 kV mm^{-1}, 30 min, corona needle at 15 mm distance.

To explain this phenomenon based on the microscopic structure, the XRD patterns of the specimens are obtained. **Figure 8** shows the XRD patterns for BTO/epoxy composite at different poling temperatures. Clear splitting of the (200) and (002) reflections near $2\theta = 45°$ is observed in B-0 and B-65, meaning that the BTO is in the tetragonal phase.[11] However, their ratio of intensity in (002) and (200) ($I_{(002)}/I_{(200)}$) is different which indicates that the fraction of tetragonal phase changes after 65 °C's poling. Murugaraj and Kutty[12] have given the relationship between the integrated intensity of (200) plus (020) and (002) reflections and fraction of tetragonal phase in the BTO ceramics: with the fraction of tetragonal phase increase with the increase of the intensity ratio. The intensity ratio of B-0 equal to 0.66 while the ratio of B-65 is 0.73, which indicates that the B-65 contents more tetragonal phase than B-0. So it is the increase of the tetragonal phase causes the increase of the piezoelectricity of the material after 65 °C's poling. Besides, BTO/epoxy polarized at 100 °C is characterized by (220)/(020) peak splitting at about 45°, which indicates that it is the orthorhombic phase. From the result of Section 3.2, the BTO/epoxy polarized under 100 °C has lower piezoelectricity than the material polarized under 65 °C. We assume that the phase transition from tetragonal to orthorhombic makes the decrease of the piezoelectricity of the material.

Table 1. Effect of distance to corona needle.

Number	Material	Poling temperature [°C]	Poling voltage [kV mm^{-1}]	Poling time [min]	d_{33} [pC/N]
B-25	BTO/epoxy	25	40	10	1.3
B-65	BTO/epoxy	65	40	10	2.9

3.4. Unsteady Wind Energy Harvesting of BTO/Epoxy Composite

Prior to the unsteady wind energy harvesting test, three specimens were polarized by corona poling, and the average d_{33} of the specimens was 5.5 pC/N. The details of the poling conditions and the values of d_{33} for the specimens are shown in **Table 2**.

Figure 9 displays the results of unsteady wind energy harvesting using BTO/epoxy composite. As shown in Figure 9a, the output voltage change ΔV for the five-leaf fan was 3.66 mV (average value), which was larger than that for the three-leaf fan (1.38 mV).

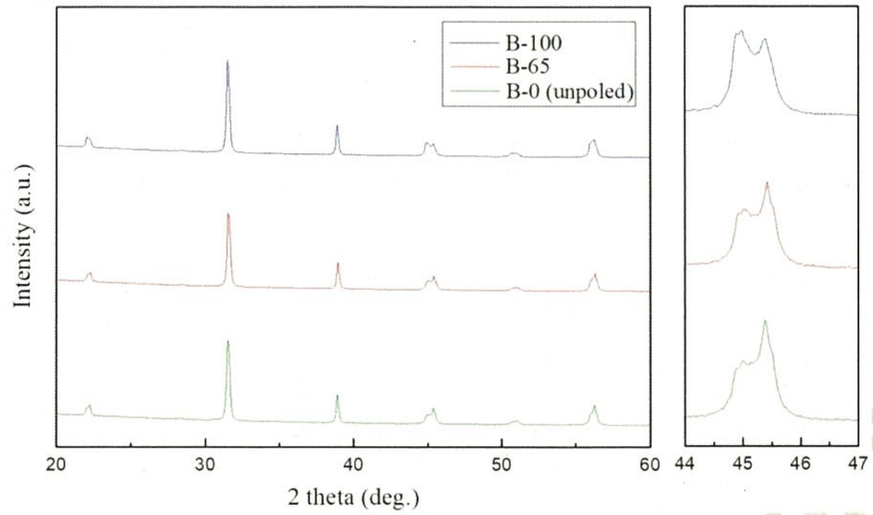

Figure 8. XRD pattern for BTO/epoxy composite at different poling temperatures.

Table 2. Details of wind harvesting specimens.

Number	Material	Poling temperature [°C]	Poling voltage [kV mm^{-1}]	Poling time [min]	d_{33} [pC/N]
B-W-1	BTO/epoxy	65	40	30	5.2
B-W-2	BTO/epoxy	65	40	30	6.1
B-W-3	BTO/epoxy	65	40	30	5.3

From the real-time output voltage shown in Figure 9b and c, we can see that the variation in the frequency for the three-leaf fan group is larger than for the five-leaf fan. This is due to the different number of leaves, and the weight of the fan causes the frequency of the discontinuous air flow v_f to change. The speed of the discontinuous air flow from the three-leaf fan is much higher, approximately 1.5 m s^{-1}, while that from the five-leaf fan is approximately 0.8 m s^{-1}.

It is interesting that the lower wind speed produced more electrical energy. We assume that this is due to the frequency,

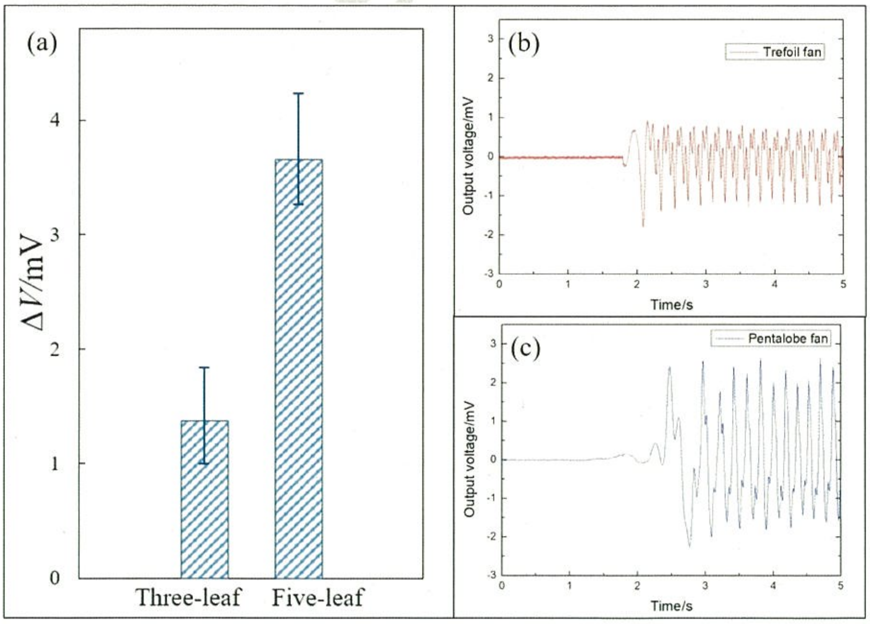

Figure 9. Results of the wind energy harvesting test: a) output voltage of different fans; b) real-time output voltage with the three-leaf fan; and c) real-time output voltage with the five-leaf fan.

which is much lower for the five-leaf fan than for the three-leaf fan under the same air flow. For a piezoelectric material, the changes of electric filed are decided by the stress amplitude applied on the material. The constitutive equations of the piezoelectric effect can be written as[13]:

$$\varepsilon = s\sigma + dE \tag{1}$$

$$D = d\sigma + \epsilon E \tag{2}$$

where σ and ε are stress and strain; D and E are the electric displacement and electric field intensity, and s, d, ϵ are the elastic compliance, piezoelectric coefficient, and permittivity, respectively.

If the wind frequency becomes high, the changes in the stress applied to the specimens will also take place faster. When a new air pulse arrives at the specimens, the stress inside the material has not yet been completely released, meaning that the changes of the stress will become lower and the output voltage will become smaller.

Overall, the BTO/epoxy composite can generate more energy under a lower-frequency air flow.

Here the specimens were cooled to room temperature without the corona voltage. If the voltage is not switched off at high temperature, the material would not depolarise. This might be the best to optimize the poling conditions. Work is currently being pursued.

4. Conclusions

In summary, a lead-free piezoelectric particle-polymer BTO/epoxy composite was fabricated successfully, and a corona poling method was used to improve the piezoelectric properties of the composite. The effects of both the phase transition and poling conditions on piezoelectricity were studied.

For the BTO/epoxy composites polarized by corona poling, the piezoelectric coefficient d_{33} reaches a saturation value at a poling time of 30 min and a poling voltage of 40 kV mm^{-1}. BTO/epoxy at a poling temperature of 65 °C shows the highest piezoelectric coefficient d_{33} due to the increase of the fraction of tetragonal phase. The value of d_{33} for the BTO/epoxy will then decay after poling. The experimental results show that a large value of d_{33} (approximately 3.0 pC/N) for the BTO/epoxy composite can be achieved by corona poling at an optimal poling temperature of 65 °C, a poling voltage of 40 kV mm^{-1}, and a poling time of 30 min.

Moreover, the polarized BTO/epoxy composite can generate energy from a very light, unsteady wind, and the size of the voltage collected is related to the frequency and speed of the wind. The BTO/epoxy composite can generate 3.66 mV under low frequency and low speed (0.8 m s^{-1}) wind conditions.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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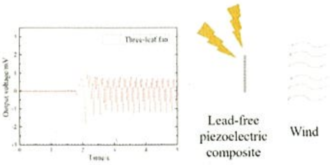

The lead-free piezoelectric 0–3 composite made by barium titanate nano-particle and epoxy is fabricated and used to harvest energy for unsteady wind. To get better energy harvesting properties, the composite is polarized by corona poling method, and the optimal corona poling condition of the composite is also found.