PIEZOELECTRIC FOAMS BASED ON CYCLIC OLEFIN COPOLYMER

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Abstract

The preparation and characterization of a new type of highly efficient pseudo-piezoelectric materials (ferroelectret) based on porous cyclic olefin copolymer (COC) is reported in the study. The quasi-static piezoelectric coefficient of the ferroelectrets can reach exceptionally high level ~1100 pC/N, and the materials retains the high piezoelectric activity for temperature up to 170°C. The sample preparation procedures can be divided into three steps. First, patterns on COC film were prepared using laser cutter. Then CO₂ bonding was used to bond different layers together. Finally, contact charging was implemented to obtain desired piezoelectricity. The piezoelectricity was characterized by quasi-static piezoelectric coefficient. Moreover, thermally stimulated discharge was selected to study the thermal stability of the ferroelectret. And hysteresis loop measurements were used to study the charge build up process inside the artificial void. The critical breakdown voltage of the 50µm artificial void sample is about 2500V and agrees with the value calculated from the simplified model. Such material have applications on sensing, actuating and energy harvesting and many other fields.

Introduction

Piezoelectric materials convert mechanical energy to electric energy. Currently the dominant work material is ceramic based piezoelectric materials. Polymer ferroelectret was investigated in Finland since 1989[1]. Polymer based piezoelectric foams have advantages compared to traditional piezoelectric materials such as flexible, environmentally friendly, lightweight and low cost. A large variety of applications are available for polymer ferroelectret, such as flexible sensor[2][3], actuator[4], musical pickup[2], and microphone[5]. Although significant work has been conducted in regard of different materials[6-11], the thermal stability of the charged polymer foams still requires further study. For example, the dominant working piezoelectric foam, polypropylene piezoelectric foams, only have a working temperature of about 70°C[12].

Cyclic Olefin Copolymer (COC) is an amorphous polymer made by chain copolymerization of cyclic monomers such as norbornene or tetracyclododecene with ethene. COC has excellent processability, environmental stability, low dielectric constant, low dielectric losses and excellent mechanical properties and particularly, good thermal stability. Several studies had been done in regard of the piezoelectric foams of this type of material[8][11]. We had initially proved that, by using a none-overlapped frame structure, which can efficiently convert mechanical energy to electrical energy, the piezoelectric coefficient can be significantly increased[8]. We developed manufacturing procedures in which CO₂ bonding
was used because it can avoid large deformation of sample structure compare to other bonding methods, such as fusion bonding[8]. Here we continue to study the thermal stability of the prepared sample and charge build up process. And the piezoelectric coefficients of different COC charged sandwich structure were reported in the study. The thermal stability of the charged structure was studied by thermally stimulated discharge. And the charge build up process inside the artificial void was investigated by hysteresis loop.

**Materials**

The COC used in this study was TOPAS 6017. The material was purchased from Topas Advanced Polymers (Florence, KY).

![Figure 1. Schematic view of the prepared sandwich structure](image1)

Figure 1 shows the schematic view of the prepared sandwich structure. The structure had five layers in total. The top and bottom layers were protective layers which had a thickness of 100µm. And each of the other 3 layers had a thickness of 50µm.

![Figure 2. Cross-section of the structure before and after compression](image2)

Figure 2 shows the cross-section of the sandwich structure before and after compression. The pattern films inside the structure were designed to be non-overlapped to reduce the elastic modulus of the whole structure. Since the piezoelectric coefficient is negative proportional to the elastic modulus[8]. This design can significantly increase the piezoelectric coefficient.

The preparation of the charged laminated sandwich structure can be divided into three general steps, preparation of the patterns, CO₂ bonding for different layers and charging of the sandwich structure.

In the preparation of the pattern on COC film, the film thickness was chosen to be 50µm. Laser cutting was used to make cavities on the COC film. Three different patterns were prepared with different widths of the cavity, 2mm, 2.5mm and 3mm.

In the step of CO₂ bonding, a bonding temperature of 120°C was chosen, which is approximately 60°C lower than the glass transition temperature (180°C) of the COC (TOPAS 6017) since CO₂ bonding can significantly reduce the glass transition temperature of the polymer as well as increase the chain mobility of molecules, making polymer films easy to be bonded together [8]. The bonding pressure was chosen to be 10Mpa.

In the third step, contact charging was used to charge the prepared laminated structure. For the sample prepared for measuring the quasi-static piezoelectric coefficient and thermally stimulated discharge, the charging voltage was chosen to be 5000V. For the hysteresis loop characterization, different charging voltages with a range from 500V to 7500V were applied to the sample with a contact charging. The contact charging equipment used was Heinzinger PNC 1000-6 ump. And the hysteresis loop characterization equipments were TREK model 609B from RADIANT and Precision Premier II.
Result and discussion

Quasi-static piezoelectric coefficient

Quasi-static piezoelectric coefficient is the most common parameter to characterize the performance of piezoelectric material, which was determined by:

\[ d_{33} = \frac{Q}{F} = \frac{\sigma}{p} \]  

where \( d_{33} \) is quasi-static piezoelectric coefficient, \( Q \) is the amount of charge, \( F \) is applied force, \( \sigma \) is charge density, \( p \) is applied pressure.

In the study, three types of prepared samples with different cavity widths of 2mm, 2.5mm and 3mm were measured by applying pressure from 2.45kPa to 24.5kPa.

In the experiments, the induced charge was measured by an electrometer (Keithley 6517A).

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Figure 3. Quasi-static piezoelectric coefficient of prepared sample

Figure 3 shows the quasi-static piezoelectric coefficient of these three types of samples. From the result, a piezoelectric coefficient of about 1100pC/N was observed in the sample of 3mm cavity width with an applied pressure of 2.45kPa, which was about 3 times higher than the commonly reported result[6][10]. This indicates that the non-overlapped design of the structure is very successful. And by varying the width of the cavity, the piezoelectric coefficient differs from about 350pC/N to 1100pC/N. This is because that the bending of the non-overlapped structure can be regarded as a three-point bending. If the length of the 'beam' was changed, the bending modulus would be different. And since the piezoelectric coefficient is closely related to the modulus, there will be a large range of piezoelectric coefficient with different modulus.

Thermally Stimulated Discharge

The thermal stability of the prepared samples was characterized by thermally stimulated discharge (TSD). Since both sides of the sample was coated by metal, the TSD was in short circuit. The temperature was chosen from room temperature to 240°C with a ramping speed of 3°C/min.

The thermal stimulated current was measured by an electrometer (Keithley 6517A).

Figure 4. Thermally stimulated discharge of prepared samples. Samples were the same as the ones for measuring quasi-static piezoelectric coefficient

Figure 4 shows the TSD result of the prepared sample. Two peaks were observed in the result. One occurs at about 120°C while the other one at about 210°C. And integration of the current over time shows that the first peak only counts for 18.5% of
the total charge. This part of charge may represent for the unstable charge inside the artificial void. A further study shown that the quasi-static piezoelectric coefficient could still remain more than 80% of the original performance after a thermal treatment of 170°C, which is consistent with the result got by TSD.

The result shows that the sample have a working temperature of approximately 170°C. If the working temperature of PP foam with 70°C is taken into consideration[12], the thermal stability of the COC based piezoelectric foams is significantly higher than PP.

Hysteresis loop

In this study, hysteresis loop was used to investigate the charge build up process in the artificial void. Different charging voltage were selected to study the hysteresis loop.

Figure 5. Applied voltage over time on the sample

Figure 6. Hysteresis loop of the prepared sample

Figure 7. Quasi-static charge build up in the artificial void

Figure 8. Simplified model for calculating breakdown voltage

From the structure of the sample, a simplified model was show in Figure 8. Electric field was built up during the contact charging. And according to Gauss' theorem

\[ \varepsilon_0 \varepsilon_{COC} E_{COC} = \varepsilon_0 E_{air} \]  

(2)
and Kirchhoff's second law:

$$E_{\text{COC}}h_{\text{COC}} + 2E_{\text{air}}h_{\text{air}} = V_{\text{total}}$$  \hspace{1cm} (3)

where $\varepsilon_0$ is dielectric permittivity of vacuum, $\varepsilon_{\text{COC}}$ is relative permittivity of COC, $h_{\text{air}}$ and $h_{\text{COC}}$ are thickness of air and COC respectively, $E_{\text{air}}$ and $E_{\text{COC}}$ are electric field strength in air and COC respectively, $V_{\text{total}}$ is the applied voltage.

According to the Paschen law, the critical breakdown electric field strength is determined by:

$$E_{bd} = \frac{ap}{\ln(pd) + b}$$  \hspace{1cm} (4)

where $E_{bd}$ is the breakdown electric field strength, $a$ is $4.36 \times 10^7$ V/(atm·m), $p$ is pressure (1 atm in the study), $d$ is the thickness of gas (50µm in the study), $b$ equals to 12.8.

From above, the critical breakdown voltage can be determined by:

$$V_{bd} = \frac{ap}{\ln(ph_{\text{air}}) + b} \left( \frac{h_{\text{COC}}}{\varepsilon_{\text{COC}}} + 2h_{\text{air}} \right)$$  \hspace{1cm} (5)

In the study, with an air gap thickness of 50µm, the breakdown voltage was calculated to be 3141V.

The breakdown voltage of approximately 2500V in the experiment is consistent with the theoretical calculation if the deflection of the sample structure during the process of CO$_2$ bonding was taken into consideration. The deflection of the structure during bonding process will cause the air gap smaller than 50µm, which lower the breakdown voltage described by Formula 5.

In the experiment, the threshold breakdown voltage is about 2500V. Below that voltage, nearly no charge was accumulated during the charging process. When the applied voltage was higher than the threshold breakdown voltage, dielectric barrier discharge occurred and charge started to build up in the artificial void. Particularly, the quasi-permanent charge was approximately linear proportional to the applied voltage after the applied voltage reached the threshold breakdown voltage.

**Conclusion**

In the study, COC based ferroelectret was prepared. The design of non-overlapped structure had been proved to be very successful. High piezoelectric coefficient of approximately 1100pC/N was obtained. Excellent thermal stability of the COC based piezoelectric foam was achieved. And the charge build up process inside the artificial void of the structure was studied by hysteresis loop. A threshold breakdown voltage of about 2500V was observed, which was consistent with the theoretical result. It is shown that the material has excellent thermal stability as well as high piezoelectric coefficient.

**Reference**