DIELECTRIC PERMITTIVITY OF THERMOPLASTIC POLYURETHANE/PZT COMPOSITE FOAMS

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Abstract

The touch sensitivity of piezoelectric-based sensors is inversely proportional to their dielectric permittivity. Introducing a cellular structure into these sensors can decrease the permittivity while enhancing their mechanical flexibility. In this work, various cellular thermoplastic polyurethane (TPU)/lead zirconate titanate (PZT) composites having several PZT contents were fabricated using physical foaming, and their dielectric properties and microstructure were studied. Composite foams with PZT contents of 2.5-10vol.%, relative densities of 0.2-1, and void fractions of 50-75vol.% were obtained, providing a platform to assess the evolution of relative permittivity with the foaming degree. The relative permittivity continuously decreased in both the neat TPU and TPU/PZT composites, up to a maximum of 4 times, as the volume expansion increased. At higher expansion ratios, the relative permittivity of the composites appeared to be independent of the PZT loading, due to the volumetric dominance of the low-dielectric air phase. The experimental relative permittivity measurements also showed good agreement with the predictions made by the Yamada model, extended to ternary system of piezoceramic polymer composite foams. Voltage sensitive foams can have applications in aerospace, robotics, and flexible electronics.

Introduction

Over decades, great attention has been paid to ceramic piezoelectric materials. Although these materials can have large piezoelectric charge constants \(d_{33}\), they are very brittle and difficult to shape into mechanically compliant structures [1]. On the other hand, polymers are a group of materials that can be ductile and malleable. Ceramic filled flexible polymer composites are thus becoming an emerging class of mechanically flexible piezoelectric materials. They combine the high piezoelectric coefficient of ceramics with the desirable mechanical properties and processing capability of polymers. Even with the mechanical flexibility, piezocomposites have a few shortcomings, e.g. not being lightweight enough for some applications and having low piezoelectric voltage constant \(g_{33}\). The low \(g_{33}\) of these composites is due to the low \(d_{33}\) of the polymer matrix.

Thermoplastic polyurethane (TPU) is a block copolymer, composed of soft and hard segments, providing the possibility to tune its elasticity [2]. TPU can thus be a highly flexible polymer, and desirable as matrix for applications where conformability is a priority. However, in piezoceramic polymer composites, due to the high ceramic filler loadings needed, the resultant composite is usually not flexible.

Foaming of polymers has been studied and used to enhance the flexibility of composites [3-5]. Foams are made up of a polymer matrix and gas inclusions together to form a cellular structure with lower density and more conformability. Introducing cellular structure into piezoceramic polymer composites could then enhance their flexibility.

On the other hand, cellular structure can enhance the touch sensitivity of piezo-composites. In the past, many efforts have been done to enhance the sensing efficiency of piezoceramic composites [6-9]. The primary performance indicator of a piezoelectric material is the piezoelectric voltage constant \(g_{33}\), which quantifies the touch sensitivity and is described as:

\[
g_{33} = \frac{d_{33}}{\varepsilon_{33}}
\]

The introduction of cellular structure to piezoceramic polymer composites can result in a decreased dielectric constant \(\varepsilon_{33}\) [10]. Assuming that introducing cellular structure will not affect the overall value of \(d_{33}\) [11], the decreased permittivity will in turn enhance the sensing capability \(g_{33}\) in Eq. 1. Therefore, the combination will be a more flexible and conformable material with a higher \(g_{33}\) compared to the unfoamed piezo-composite [12, 13].

Very limited work, however, has been done so far on the foaming of piezoceramic polymer composites. There are only two pieces of literature demonstrating the foaming of piezoelectric composites. De Boom [12] foamed polyurethane (a thermoset)/PZT composites with magnetic stirring and whipped cream maker method. McCall et al. [13] worked on PDMS (a rigid thermoplastic)/BTO/MWCNT composites and foamed them via the sugar-templating method. In both cases, the foaming methods used are not practical and scalable. Hence, coming up with a better method to foam the composites could broaden the production of these composites.

In addition, there is no work on the piezocomposite foams based on flexible thermoplastic polymers. Using a
flexible polymer as the matrix could enhance the flexibility even more and make it possible to employ composites with high filler loading while maintaining flexibility. In this work, TPU was selected as the matrix, because of its wide range of flexibility and foamability, due to its high CO₂ solubility [14-17].

In this study, we report, for the first time, the fabrication of piezoceramic thermoplastic composite foams, prepared using physical foaming method, with a range of expansion ratios and cellular structures and characterized their relative permittivity and cellular morphology. Here, we successfully decrease the ε₃₃ of the TPU/PZT composite, over a range of PZT contents. Furthermore, the experimental data are compared with that of the theoretical Yamada model and some predictions are established for the composites with higher PZT contents.

Experimental Procedure

1. Materials

The commercially available TPU (Elastollan 1185A, BASF Ltd., USA), having a density of 1.12 gr.cm⁻³ and a glass transition temperature of -38 °C was used as the base resin. The PZT powder, with an average particle size of 1 μm was supplied by Hammond Lead Products (USA). Supercritical CO₂ was purchased from Oxar Company and used as the physical blowing agent.

2. Sample Preparation

2.1. Preparation of TPU/PZT composites

The composites were produced by solution casting, using tetrahydrofuran (THF) as the solvent. Prior to the casting, TPU pellets were oven-dried at 90 °C for 2 h to remove any excess moisture. Then, TPU pellets and PZT powder were separately dispersed in THF with a magnetic stirrer. After the complete dissolution of TPU, the PZT mixture was added to the TPU slurry to keep the filler concentration at 2.5, 5, 7.5 and 10 vol.% Then, the mixture was put in an ultrasonic bath and sonicated for 0.5 h to prevent the filler precipitation. Finally, the mixture was casted in Petri-dishes and left under a fume hood overnight for complete drying. Any remaining moisture was then removed by drying the composites in a vacuum oven at 100 °C for 4 h.

The solvent-cast film was then formed into 0.7 mm sheets using a hot press (Carver Inc., Wabash, IN) at 170 °C, 5 MPa for 10 min.

2.2. Fabrication of TPU/PZT Foams

The foaming of neat TPU and the composites was conducted using supercritical CO₂ as the blowing agent via the batch foaming process. Figure 1 illustrates the schematic of the batch foaming setup. The hot-pressed samples were cut in strips of 10 × 10 × 0.7 mm³ and put in a pressure vessel. The vessel then was pressurized and heated up to the desired foaming pressure and temperature which ranged from 10 to 34 MPa and 90 to 125 °C, respectively. Different combinations of pressure and temperature were employed, in order to achieve the same void fractions for the composites with different PZT loadings. The gas saturation time was fixed at 1.5 h, which was assumed to be long enough to reach sorption equilibrium [15]. Foaming was then initiated by a pressure quench down to atmospheric pressure.

![Figure 1. Schematic illustration of batch-foaming setup.](image)

Characterization

The microstructure and cellular morphology of the TPU/PZT foams were examined using a JEOL JSM-6060 scanning electron microscope (SEM). The samples were cryo-fractured using liquid nitrogen before sputter coating. The densities of the solid (ρₘ) and foamed (ρₙ) composites were measured using the water-displacement method (ASTM D792-08). The volume expansion ratio (ϕ) and the void fraction (Vₕ) were then calculated using the following equations, respectively:

$$\phi = \frac{\rho_m}{\rho_f} = \frac{1}{1-V_f}$$  \hspace{1cm} (2)

$$V_f = \frac{\rho_m - \rho_f}{\rho_m} \times 100$$  \hspace{1cm} (3)

The dielectric constant of the samples was measured using a Hewlett Packard 4192A LF impedance analyzer with 16451B dielectric test fixture over the frequency range of 5 Hz to 13 MHz. The following equation can be written for the sample under test:

$$\varepsilon = \varepsilon_0 \varepsilon_r = \frac{C_p}{A}$$  \hspace{1cm} (4)

where ε is the dielectric constant (permittivity) of the sample, ε₀ is the space permittivity, εₑ is the relative permittivity (or relative dielectric constant) of the sample, Cₚ is the capacitance, A is the area of the electrode and ᴛ is the thickness of test sample. Thus the relative permittivity can be obtained by measuring the capacitance value and using the following equation:

$$\varepsilon_r = \frac{C_p}{\varepsilon_0 A}$$  \hspace{1cm} (5).
Results and Discussion

1. **Microstructure**

The cellular morphology of the neat TPU and TPU/PZT composite foams at expansion ratio of 2 is given in Figure 2. As shown, higher PZT contents depicted a higher cell density and smaller cells, except the 5vol.% PZT samples, which had bigger cells than 2.5vol.% PZT samples. The major intention was to obtain the same expansion ratio in various TPU/PZT composites with different PZT contents. To achieve this, different foaming conditions (temperature and pressure) were applied for different PZT contents. Therefore, the differences in the cellular structure are a consequence of different foaming conditions as well as different concentration of PZT particles, as heterogeneous cell nucleating agents. However, all the TPU/PZT foams exhibited relatively similar cellular morphologies with small cell sizes in the range of 1 - 30μm (Figure 2) and can be classified as microcellular foams.

![Figure 2. SEM micrographs of cellular (a) neat TPU and TPU/PZT composites containing (b) 2.5vol.%, (c) 5vol.%, (d) 7.5vol.%, and (e) 10vol.% PZTs at the expansion ratio of φ=2 (Vf=50%).](image)

Figure 3, shows a magnified micrograph of TPU-2.5 vol.% PZT sample with 50% void fraction (φ=2) showing the dispersion of PZT particles.

![Figure 3. SEM micrograph of cellular TPU-2.5 vol.% PZT composite with 50% void fraction (ϕ=2) showing the dispersion of PZT particles.](image)

2. **Relative Permittivity of solid TPU/PZT**

Figure 4, shows the broadband relative permittivity of TPU/PZT composites as a function of frequency at several PZT contents. As expected, the permittivity of the composites increased with increasing the PZT loading and the permittivity values showed relatively frequency independent behavior. The measured data are consistent with the values reported in the literature [18, 19].

![Figure 4. Broadband relative permittivity of TPU/PZT composites at various PZT loadings.](image)

Figure 5 also depicts the changes in the relative
permittivity of the solid TPU/PZT composites with different PZT contents, up to 10vol.%. The experimentally measured values of the relative permittivity at 1 MHz have been used to evaluate $\varepsilon_r$. The solid and dashed lines represent the experimental results and predictions using the Yamada model, respectively. The experimental data were compared with the following expression, developed by Yamada [20]:

$$
\varepsilon_r = \varepsilon_1 \left\{ 1 + \frac{nV(\varepsilon_2 - \varepsilon_1)}{2\varepsilon_1 + (\varepsilon_2 - \varepsilon_1)(1 - q)} \right\}
$$

(6)

where $\varepsilon$ is the dielectric constant of the composite, $V$ is the volume fraction of the PZT and $n$ is a parameter related to the geometry of the ceramic particles. The dielectric constant of TPU ($\varepsilon_1$) and PZT ($\varepsilon_2$) used here are 6.4 and 1850, respectively.

As it was expected, the relative permittivity of the solid samples increased with increasing the PZT content, as the $\varepsilon$ of PZT is $\sim$ 300 times more than that of TPU. It can be seen from Figure 5 that there exists a remarkably good agreement between the measured values and the predictions by the Yamada model for the solid samples.

![Figure 5. Relative permittivity vs PZT content for solid PZT/TPU samples, compared with the prediction of Yamada model (dashed line).](image)

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3. **Effect of foaming on the relative permittivity of TPU/PZT**

Figure 6 shows the relative permittivity of the neat TPU and TPU-5vol.% PZT samples as a function of void fraction. The relative permittivity of both neat TPU and TPU/PZT composite reduced to less than 2.5 with the addition of 75% void fraction. In both cases, a decrease of $\sim$70% was achieved with 75% void fraction, which is the maximum decrease in permittivity in all the samples. The Yamada model was also extended for the ternary system of TPU/PZT/air, in an attempt to predict the relative permittivity of the composite foams. As seen in Figure 6, a relatively good agreement was obtained between the experimental values and Yamada model for both neat TPU and TPU/PZT composites indicating the capability of Yamada model to predict the relative permittivity of ternary systems.

![Figure 6. The variation of the relative permittivity (at 1 MHz) of neat TPU and TPU-5vol.% PZT composite foams as a function of void fraction.](image)

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Figure 7 shows the variation of the relative permittivity of TPU/PZT composite foams with PZT content at several fixed expansion ratios (void fractions). In general, the curves shifted downwards as the expansion ratio increased, demonstrating an inversely proportional relation between the relative permittivity and the void fraction. The overall relative permittivity decreased by $\sim$50-80% by increasing the void fraction up to 75%. The relative permittivity clearly decreased when the samples were foamed, but showed a nearly constant behavior versus PZT content for a given expansion ratio, especially at higher expansion ratios, and also showed little difference between consecutive void fractions. This can be attributed to the dominance of low-permittivity air phase at high void fractions. It is expected that the sensitivity to PZT content would increase as the content increases. The erratic behavior of the foams having different PZT content and the same expansion ratio can be attributed to the inconsistencies in the foaming conditions.

![Figure 7. Relative permittivity of TPU/PZT composites as a function of PZT content at the expansion ratios (void fractions) of $\varphi=2$ ($V_f =0.5$), $\varphi=3$ ($V_f =0.67$), $\varphi=4$ ($V_f =0.75$).](image)

Figure 7. Relative permittivity of TPU/PZT composites as a function of PZT content at the expansion ratios (void fractions) of $\varphi=2$ ($V_f =0.5$), $\varphi=3$ ($V_f =0.67$), $\varphi=4$ ($V_f =0.75$).
To observe the effect of increasing the PZT content and void fraction together on the relative permittivity of the composites, and also to extend the experimental observations to higher PZT contents, a 3-D plot of a tri-phase composite was simulated using Yamada model and presented in Figure 8. As the PZT content is increased, the effect of foaming on dielectric constant is also signified. According to this model, TPU-40vol.%PZT samples will experience a maximum of ~4 times decrease in dielectric constant with addition of 75% void fraction, compared to ~2 times decrease in TPU-10vol.%PZT samples.

![Figure 8. 3-D Yamada simulation of the relative permittivity of TPU/PZT composite foams as a function of PZT content and void fraction.](image)

According to equation 1, in order to obtain a greater $g_{33}$, the PZT content as well as the void fraction should be simultaneously increased. The high amount of PZT is needed in order to achieve high $d_{33}$, and a high void fraction is needed to decrease $g_{33}$. Considering only the effect of the permittivity on the piezoelectric voltage constant, (i.e. constant piezoelectric charge constant) the $g_{33}$ would increase twofold for TPU/10vol.%PZT and fourfold for TPU/40vol.%PZT composites.

**Conclusions**

Composite foams of TPU/PZT with different PZT contents (ranging from 0 to 10vol.%) and various void fractions (0 to 75vol.%) were prepared using solution casting followed by physical batch foaming with supercritical CO$_2$. The foams demonstrated microcellular structures at all the PZT contents. The relative permittivity increased with an increase in the PZT content. Overall, the introduction of cellular structure decreased the relative permittivity. The relative permittivity exhibited an inversely proportional relation with the void fraction, and a maximum of 4 times decrease was obtained at 75% void fraction. At the higher void fractions, the relative permittivity appeared to be independent of PZT loading, due to the dominance of low-permittivity air phase. The experimental relative permittivity measurements also showed good agreement with the predictions made by Yamada model, extended to ternary system of piezoceramic polymer composite foams. Voltage sensitive foams can have applications in aerospace, robotics, and flexible electronics.

**References**