A Prediction of Permittivity of Dielectric Elastomer using an Equivalent Capacitance Model and its Effect in Material Designing and Manufacturing

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Abstract: Using elastomers filled with high dielectric constant particles is a very common method to prepare dielectric elastomers (DE). In this paper, silicone elastomer filled with high permittivity particle calcium copper titanate (CCTO) was employed to fabricate high dielectric constant DE. For the purpose of evaluating dielectric properties of DE, an equivalent capacitance method was used to calculate the permittivity of DE samples, and compare the calculated value with experimental data to analyze the material structure influence on dielectric properties. An effective model was finally obtained for material design.

Keywords: Dielectric Elastomer, Permittivity, Composites nanostructure.

1. Introduction
Dielectric elastomers (DE) are attracting attentions for its large strain, fast response, light weight, low modulus, reliability and high energy density [1]~[3]. As an electroactive polymer with the highest potential, DEs have been widely employed in artificial muscles, biomimetics, and micro-robotics as actuator, sensor, and generator [4]~[7].

Dielectric elastomer actuator (DEA) is formed of a membrane of DE sandwiched between two flexible electrodes. Applied with voltage on the electrodes, the DEA will strain due to the electric field pressure from surface electrostatics, “Maxwell pressure”, the thickness strain of a DEA can be approximated by:

\[ S = -\frac{P}{Y} = -\frac{\varepsilon_0 \varepsilon_r E^2}{Y} \]  

Where \( P \) is Maxwell pressure on the material; \( Y \) is Young’s modulus; \( \varepsilon_0 \) is the vacuum permittivity; \( \varepsilon_r \) is the relative permittivity.

Researchers have been working on improving the dielectric property of DEs. Z.G. Suo proposed a theory coupled large deformation and electric potential, and described nonlinear and nonequilibrium behavior of DEs [8]. Filling silicone with TiO2 particles can improve the permittivity of material without increasing the Young’s modulus have been reported by several groups [9]~[14]. D. Yang etc. fabricated a DE with high dielectric strain by filling various types of TiO2 and they also found that the size of TiO2 particles influenced the dielectric strain greatly [15], and we performed further research on this subject. We chose various types of the high permittivity particle calcium copper titanate(CCTO) with different sizes as filler, and poly(dimethyl siloxane) PDMS as matrix to prepare DEs, and analyze the influences by particle size[16]~[18].

Because the actuation strain are in a small range and causing a large measurement error, we decided to measure the capacitance of samples to evaluate the dielectric property of DE, and the relationship between capacitance \( C \) and dielectric constant is given by

\[ C = \frac{\varepsilon_0 \varepsilon_r S}{d} \]  

where \( S \) is area of the electrical conductor; \( d \) is thickness of the insulator layer. The size of particle fillers only affects the Young’s modulus, while the permittivity of composite material is determined by the permittivity and volume fraction of the filler. We have several models to describe composite’s permittivity such as Lichtenecker Model (eq.3), Bruggeman Model (eq.4), Maxwell-Garnett Model (eq.5), etc. Y. Rao proposed a EMT model (eq.6) to describe the permittivity of ceramic/plastic composite, which works well even at high ceramic volume loading [19].

\[ \log \varepsilon_{eff} = V_1 \log \varepsilon_1 + V_2 \log \varepsilon_2 \]  

\[ \varepsilon_{eff} = \varepsilon_2 + 3f \varepsilon_2 - \frac{\varepsilon_1 - \varepsilon_2}{3} \]  

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In this paper, we used an equivalent capacitance model to predict the permittivity of material, and compared the differences between calculated value and experimental data.

2. Methods

2.1 Material and methods

Three types of calcium copper titanate with different particle sizes (300nm-, 1μm-, and 60μm-) were obtained from Jiangsu WuXi Kai-Star Electro-optic Materials Co., Ltd., China. H₂C₂O₄·H₂O, Ca(NO₃)₂·4H₂O, Cu(NO₃)₂·3H₂O, Ti(OC₄H₉)₄, Mg(NO₃)₂·6H₂O, tetrahydrofuran, and absolute ethanol were provided by Sinopharm Chemical Reagent, China. Poly (dimethyl siloxane) (PDMS) (RTV-3483), matching curing agent (RTV-3083) and compliant electrode materials (Molykote HP-800 Grease) were purchased from Dow Corning Corporation. Polypropylene glycol (Specification: PPG-400) was supplied by Jiangsu Haian petrol Chemical Plant of China.

The CCTO particles were initially mixed with PDMS, and tetrahydrofuran as solvent at room temperature by stirring for 20 min. Subsequently, curing agent was blended with the composites further to get suspension. Then, the suspension of CCTO/PDMS composite was poured into a self-manufacture PTFE mold and heated in an oven at 30°C for 24h. Finally, the thickness of the composites was controlled to be 0.5 mm.

For the other group of samples, self-prepared CTO and M-CCTO were used as filler. CTO and M-CCTO particles were synthesized by the coprecipitation method with oxalic acid as precipitators. Typically, 0.6 mol of H₂C₂O₄·H₂O was dissolved in 500 ml of ethanol and some ammonia was dripped onto it. 0.3 mol Ti(OC₄H₉)₄ was added into solution with stirring for 3h to adjust the pH to 3.0 and a suspension was obtained. A mixed solution of 0.075 mol of Ca(NO₃)₂·4H₂O, 0.225 mol Cu(NO₃)₂·3H₂O, 40g PPG-400 and 150 ml distilled water was dropped into the suspension with magnetic stirring for overnight. Subsequently, the precursor was obtained by filtration and washed with ethyl alcohol and water, dried at 80°C overnight. The precursor was then transferred into a corundum crucible and heated at 700°C for 3 h. After cooling to room temperature, the product was collected and denoted as CCTO in the end.

2.2 Calculation

We divided the material into cube cells with a side length of a, each contains one particle, the particle’s volume are determined by the filler volume fraction ϕ. Thus \( b^2h = \phi a^3 \). The cell was further divided into several partial capacitors (Fig. 1), and their capacitances were calculated individually. We calculated the total equivalent capacitance of cell as a circle formed by the partial capacitors (Fig. 2).

The total equivalent capacitance of cell is

\[
C_{cell} = C_1 + C_2 + C_6 + C_7 + \frac{1}{\varepsilon_1 \varepsilon_2 \varepsilon_3} \quad (7)
\]

And we have:

\[
C_1 = C_2 = \varepsilon_0 \varepsilon_m \left( \frac{a-b}{2} \right) \quad (8)
\]

\[
C_3 = C_4 = \frac{2 \varepsilon_0 \varepsilon_m b^2}{a-h} \quad (9)
\]

\[
C_6 = C_7 = \frac{\varepsilon_0 \varepsilon_\text{m} (a-b) b}{2a} \quad (10)
\]

\[
C_5 = \frac{\varepsilon_0 \varepsilon_m b^2}{h} \quad (11)
\]

Where \( \varepsilon_\text{m} \) is the permittivity of matrix, and \( \varepsilon_p \) stands for the the permittivity of particle. Assume \( h = mb, \phi a^3 = hb^2 \) and integrate equation (7-11), then we have:

\[
C_{cell} = \left[ 1 - \left( \frac{\phi}{m} \right)^3 \right] \varepsilon_0 \varepsilon_\text{m} \alpha + \frac{\phi^2}{m} \varepsilon_0 \varepsilon_\text{m} \alpha \frac{1}{\varepsilon_p} \left[ \frac{1}{1 - m} \left( \frac{\phi}{m} \right)^2 \right] + \varepsilon_m \left( \frac{\phi}{m} \right)^3 \quad (12)
\]

Due to the anisotropy of the particle, we introduced a distribution parameter to modify the equation for the purpose of
a precise result, and then we have

\[ C_{\text{cell}} = \left[ 1 - \left( \frac{\phi}{m} \right)^2 \right] \varepsilon_0 \varepsilon_m \varepsilon_{\text{PDMS}} + \frac{\phi}{m} \varepsilon_0 \varepsilon_m \varepsilon_{\text{PDMS}} \]

According to equation (2), we have

\[ \varepsilon_{\text{eff}} = \frac{C_{\text{cell}}}{C_0} = \frac{C_{\text{cell}}}{\varepsilon_0 a^2} = \frac{C_{\text{cell}}}{\varepsilon_0 a^2} \left[ 1 - m \left( \frac{\phi}{m} \right)^2 \right] + \frac{n \left( \frac{\phi}{m} \right)^2 \varepsilon_m \varepsilon_{\text{PDMS}}}{n - m \left( \frac{\phi}{m} \right)^2 \varepsilon_m \varepsilon_{\text{PDMS}}} \]

This model is only effective in low load of particle volume fraction and requires similar particle morphology.

3. Result and Discussion

We take aspect ratio \( m = 0.15 \) from SEM picture of the particles, and the dielectric constant of CCTO used in experiment is \( \varepsilon_{\text{PDMS}} = 20000 \), the dielectric constant of PDMS is \( \varepsilon_m = 4.31 \), and we used one group of samples to calculate the distribution parameters \( n = 0.52 \). We obtained calculated values of this model and compared it with Lichtenecker Model and data of other groups of experiments (Fig. 3, Fig. 4).

Lichtenecker Model: \( \log \varepsilon_{\text{eff}} = V_1 \log \varepsilon_1 + V_2 \log \varepsilon_2 \)

Where \( V_1, V_2 \) are volume fraction of two compositions of composite and \( \varepsilon_1, \varepsilon_2 \) are permittivity of two compositions.

Fig. 3 and Fig. 4 showed that the model fits the experimental data well with the samples made with lower size (300nm and 1 m). The samples with higher particle size has a much lower value than the calculated value and this might be due to the deposition of large particles while fabrication. The uneven dispersion structure of the material caused our model’s failing in this situation. Even though we have obtained a model which is more precisely than the Lich model, in fact the result of our model is quite similar to other models such as Maxwell-Garnett Model and Y. Rao’s model. But their model only considered the effect of volume fraction for their models are designed to describe properties of solids like ceramics and metal. In our model, the capacitance change of the material can be easily calculated when the structure changes when strain occurs. Thus, we assume that this model is more convenient to use in an elastomer based composite.

4. Conclusions

Equivalent capacitance model is used to predict the effective dielectric constant of the elastomer-ceramic composite. The model includes fitting factor \( n \) accounts for the distribution of particles was used to describe the coupling between material structure and dielectric property. This model can also be applied to DE in a stretched situation.

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References

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