Thick film polymer-ceramic composites for pyroelectric applications

M. Dietze, J. Krause, C.-H. Solterbeck, and M. Es-Souni

Institute of Materials and Surface Technology, University of Applied Science Kiel, Grenzstr. 3, 24149 Kiel, Germany

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Thick films of 0-3 composites of lead-zirconate-titanate ceramic and polyvinylidene-trifluorethylene copolymer have been produced by spin coating on gold-coated silicon wafers. The dielectric properties were investigated as a function of ceramic volume fraction and temperature. Pyroelectric measurements were undertaken by temperature modulation with a Peltier element. Additionally, the pyroelectric response has been investigated up to 3000 Hz using a modulated laser. The piezoelectric response of the composites obtained by using a laser vibrometer are also reported. It is shown that the dielectric constant increases with increasing volume fraction of ceramic and that it reaches a maximum at a temperature in the range of 65–70 °C due to the ferroelectric-paraelectric phase transition of the polymer matrix. The pyroelectric coefficient increases to 92 μC m⁻² K⁻¹ at a ceramic volume fraction of 20%. Furthermore the effective piezoelectric charge coefficient $d_{33}$ of the composite almost vanishes at this composition. This composites show relatively high pyroelectric figures of merit and may be a potential candidate for pyroelectric sensor applications.


I. INTRODUCTION

Composites of ferroelectric ceramic inclusions in a polymer matrix have been widely investigated as promising candidates for many applications such as pressure and pyroelectric sensors as well as hydrophones.⁴ These composites combine the advantages of the polymer matrix, such as good mechanical properties, low density and acoustic impedance, and flexibility, with those of the ceramic phase which provides high piezoelectric and pyroelectric properties.⁴ Following the concept of connectivity introduced by Newnham et al.,³ this kind of composites is known as 0-3 composite which means that the ceramic inclusions are homogeneously dispersed in the polymer matrix without touching each other.

Composites with 0-3 connectivity have several advantages over other kinds of composites. They are easy to produce, the volume fraction of the ceramic phase can be varied in a wide range, and it is possible to process film composites with well established techniques such as spin coating.

It has been shown that the pyroelectric constant of a ferroelectric polymer can be increased by addition of a ceramic component.⁶,⁷ Furthermore the piezoelectric response of the resulting composite can be decreased by proper composition control and poling method.⁷,⁸ This is an advantage for pyroelectric sensors, because no complex compensation of the piezoelectric activity is needed. Although the pyroelectric constant of the polymer and the composites is lower than that of pure ceramics,¹⁰ the figures of merit show good values because of the low dielectric permittivity of the composites compared to ceramic.

In this paper ferroelectric 0-3 composites of polyvinylidene-trifluorethylene (PVDF-TrFE) containing lead zirconate titanate (PZT) powder were prepared as films of 5 μm thickness on gold-coated silicon wafers via spin-on technique. A previous work on 0-3 composites with a PVDF-copolymer matrix has been conducted on thick, free standing films of about 20–100 μm processed by compression moulding.⁶,⁷ Only few papers report of composites prepared by spin coating on substrates.⁸ However, even in these works the composites were heated above their melting temperature to increase adhesion to the substrate and density. In this work no pressure or heating above the melting temperature of the copolymer is used. It is shown that for low ceramic volume contents of up to 20 vol % the composites are dense. The composites are characterized in terms of microstructure and functional properties. It is shown that these composites have promising potentials for use as pyroelectric sensors.

II. EXPERIMENT

The ceramic powder used was a commercial PZT powder (PZ21) from Ferroperm-piezo® (Denmark). The powder was modified for better dispersion by adsorbing oleic acid (Riedel-de Haën) on the surface. Adsorption was done by adsorbing 2 wt % Triton X-100 (Alfa Aesar) with respect to the ceramic powder. A 7 vol % polymer solution was prepared by dissolving PVDF-TrFE copolymer powder (56:44, Solvay Solexis S.A.S, France) in acetylacetone (Fluka). An appropriate amount of ceramic powder was subsequently dispersed in this solution by stirring and ultrasonication. Films of 5 μm thickness were produced by spin coating this mixture on gold-coated silicon wafers. Samples were kept on a hot plate at 130 °C for 15 min to let the solvents evaporate. After that, the samples were cured at 140 °C for 12 h to ensure that all of the solvent is removed and to increase the crystallinity of the copolymer.

Poling of the composites can be very difficult due to the high mismatch of the dielectric constants and the resulting...
applied electrical field to the components, especially for low volume fractions of the ceramic. On one hand, according to Zeng et al., a long poling time at high temperature is necessary to pole the ceramic inclusions in 0-3 composites. On the other hand, the PVDF-TrFE cannot be poled at temperatures higher than its ferroelectric to paraelectric transition temperature of 70 °C. Therefore, poling must be conducted in two steps. Poling of such composites is often realized by contact poling. However, this method can lead to electrical breakdown of the sample due to the high electrical fields necessary for poling. A more suitable method for poling composites is the corona poling method. Taking the above mentioned facts into account the composites prepared were poled by corona poling at 120 °C under a dc voltage of 12.5 kV for 2 h followed by poling at room temperature for 1 h. After poling Au front electrodes were sputtered. For dielectric, piezoelectric, and ferroelectric measurements 3 mm gold electrodes were used, while for pyroelectric measurements electrodes with a diameter of 0.6 mm were used.

Impedance measurements were carried out in the frequency range from 100 Hz to 1 MHz using a computer controlled impedance analyzer (Agilent 4192) equipped with a heating stage.

Dynamical pyroelectric properties were measured using a self-made experimental setup including a computer controlled laser vibrometer (Polytec OFV 353 sensor head and OFV 3001 vibrometer controller), digital signal processing (DSP) lock-in amplifier, frequency generator and voltage source. The vibrometer was operated in the most sensitive velocity range (1 mm s⁻¹ V⁻¹). The effective thickness mode piezoelectric coefficients d₃₃,eff of the composites were determined at 5 kHz, outside resonance. Microstructures of the samples were investigated by means of a scanning electron microscope (Phillips XL30).

III. RESULTS AND DISCUSSION

A. Microstructure

The microstructure of a sample with 30 vol % PZ21 is shown in Figs. 1 and 2. The volume content of the ceramic powder was determined by removing the film from the substrate and measuring the weight before and after burnout of the polymer. Figure 1 shows the surface of a composite film. It can be seen that the film is quite homogeneous and the ceramic particles are well distributed, with only a small tendency to agglomeration. A cross section of the composite film is shown in Fig. 2.

B. Dielectric measurements

The temperature dependence of the dielectric constant at 1 kHz of composites with 0–30 vol % ceramic is shown in Fig. 3. It can be seen that the dielectric constant increases as a function of temperature at 1 kHz.
The dependence of the dielectric constant on the volume fraction of the ceramic powder can be described by two analytical models, following Bruggeman,

\[
1 - \Phi_C = \left( \frac{\varepsilon - \varepsilon_C}{\varepsilon_p - \varepsilon_C} \right)^3 \frac{\varepsilon_p}{\varepsilon},
\]

and the well-known Maxwell-Wagner model,

\[
\varepsilon = \frac{2(1-\Phi_C)\varepsilon_p + (1+2\Phi_C)\varepsilon_C}{(2+\Phi_C)\varepsilon_p + (1-\Phi_C)\varepsilon_C \varepsilon_p},
\]

where \( \varepsilon \) is the dielectric constant, \( \varepsilon_p \) and \( \varepsilon_C \) are the dielectric constants of the polymer matrix and the ceramic inclusions, respectively, and \( \Phi_C \) is the ceramic volume fraction.

Figure 4 shows the measured dielectric constant as function of the ceramic volume content compared to the calculated curves using either Bruggmann or Maxell-Wagner models. It can be seen that the latter describes well the results for ceramic volume fractions up to 20%, but the discrepancy increases for higher volume fractions. However, it is known that the Maxwell-Wagner model is only applicable at relatively low inclusion volume fractions. The discrepancy shown by the calculations based on the Bruggeman model is probably due to the boundary conditions of the model not being satisfied. In fact, the Bruggeman model postulates small inclusion sizes with respect to the film dimension. Particle size measurements of the ceramic particles by laser scattering show a mean particle size of 0.7 \( \mu m \) which is about 14% of the film thickness (5 \( \mu m \)). Thereby, the conditions of the model are no more fulfilled.

C. FE-simulations of the dielectric properties of 0-3 composites

As discussed above, neither of the analytical models describes well the dielectric properties of the 0-3 composites in the whole composition range. Thus finite-elements (FE) modeling was applied to these composites. The distribution of the ferroelectric ceramic particles in the polymer matrix is supposed to be of statistical nature, and the problem is addressed by creating many random geometries, solving the electromechanical equations and evaluating the effective dielectric constant. Since many piezoelectric ceramic particles must be considered for each geometry, only two-dimensional (2D) simulations are feasible. The simulation domain measures 50 \times 10 \( \mu m^2 \), where the length corresponds to the thickness of the experimental membranes. The width limits the computational domain and is extended to infinity by periodic boundary conditions. The piezoceramic inclusions are assumed to be circles with an average radius of 0.5 \( \mu m \). For each circle a radius is randomly picked such that the distribution is a Gaussian with a standard deviation of 0.15 \( \mu m \). The circles are—one by one—randomly placed in the simulation domain such that they do not overlap or touch. By selecting the number of circles the volume ratio of the piezoceramic particles in the polymer can be adjusted. As the domain gets more and more filled only smaller circles can be added and the effective average radius decreases. The problem is solved by using a larger nominal radius for the random selection; the effective average radius then turns out to be correct. For this procedure a MATLAB (The Mathworks Inc. Boston, USA) script is developed. It creates geometries for Comsol Multiphysics (Comsol AB, Stockholm, Sweden) up to volume ratios of 35%.

The simulation solves electrical and mechanical responses of the membrane to an applied voltage (i.e., the electric field is in thickness direction). The full piezoelectric coupling takes effect in the PZT particles, which are assumed to be all polarized perpendicular to the plane of the membrane, whereas the polymer membrane is considered not active.

The phenomenon is described by the deformation vector \( \mathbf{u} \) and the electrostatic potential (\( \Phi \)). The constitutive law relates the cinematic quantities (strain \( S \) and electric field \( E \)) to the dynamic quantities, which are the stress \( T \) and the electric displacement field \( D \). In the simple, and in many cases sufficient approximation, the constitutive law is linear and can be written as

\[
T = cS - eE,
\]
\[ D = \varepsilon S + \varepsilon E, \]  

(4)

where \( \varepsilon \) is the elastic compliance, \( \varepsilon \) is the electromechanical coupling, and \( \varepsilon \) is the permittivity (that all have tensorial character in general).

For piezoelectric materials such as PZT the coupling \( \varepsilon \) is nonzero. In these simulations the polymer is considered inactive and \( \varepsilon \)=0, that means that electrical and mechanical behaviors are independent of each other. Because the polymer has embedded PZT particles there is, however, an indirect coupling.

The equations for the static case follow from the law of virtual work and can be directly used for finite-element analysis,

\[ dS_T - dE_D = 0. \]  

(5)

The analysis of these simulations focuses on the electric response and computes an efficient dielectric constant for vanishing external stress.

The values for the polymer matrix was obtained by measuring the pure polymer film \( \varepsilon_r(1 \text{kHz})=17.7 \), while the ceramic value was taken from the Technical data sheet, \( \varepsilon_r(1 \text{kHz})=3800 \).

The results of the FE simulation are shown in Fig. 4. For a low volume content of 10 vol \% ceramic the numerical model shows a good agreement with the measured data. For higher volume contents the calculated dielectric constants are smaller than measured. As mentioned above samples with 30 vol \% ceramic seem to have some porosity and therefore are not compared to the model.

More precise simulations are limited by the computing power, in the sense that the width of the domain is limited, the number of particles is limited, and most of all that only 2D simulations are possible.

## D. Pyroelectric properties

The measurement method for the pyroelectric coefficient is outlined below. A sinusoidal temperature variation is applied to the sensor element via a Peltier element. The temperature variation is measured with a thermocouple element directly on the sample surface and the pyroelectric current signal is recorded on a front electrode next to the thermocouple element. Because of the slow response of the thermocouple the signal is recorded on a front electrode next to the thermocouple element suitable frequencies for the sinusoidal temperature variation are around 10–50 mHz. The method is coupled element suitable frequencies for the sinusoidal temperature variation is measured with a thermocouple element.

The pyroelectric coefficient of the composites from 0–30 vol \% ceramic is shown in Fig. 5. The pure polymer film shows a pyroelectric coefficient of approximately 50 \(\mu\text{C m}^{-2}\text{K}^{-1}\), which is in good agreement with values reported in literature. The pyroelectric coefficient is almost doubled for a ceramic content of 20 vol \%, with a value of 92 \(\mu\text{C m}^{-2}\text{K}^{-1}\). The pyroelectric coefficient increases for higher ceramic volume fractions. This may be due to increasing porosity. The measured pyroelectric coefficient is significantly higher than that reported for other composites based on PVDF. Malhomme et al. produced a PZT/poly(vinylidene fluoride-hexafluoropropylene) composite with 50 vol \% ce-

![Image](image.png)

**FIG. 5.** Pyroelectric coefficient \( p \) as a function of ceramic volume content.
They reported a pyroelectric coefficient which is strongly dependent on temperature reaching values of around 450 μC m$^{-2}$ K$^{-1}$ at 70 °C. However, at 40 °C their pyroelectric coefficient was 40 μC m$^{-2}$ K$^{-1}$ and decreased further at lower temperatures. Similar results were obtained by Ploss et al. who prepared a composite of PVDF-TrFE and PbTiO$_3$ and measured a pyroelectric coefficient of about 20 μC m$^{-2}$ K$^{-1}$ for both phases poled in the same direction. Ploss et al. used a copolymer with a pyroelectric coefficient of 20 μC m$^{-2}$ K$^{-1}$ and a mean ceramic particle size of 100 nm. The higher values of the pyroelectric coefficient obtained in this work may be explained in terms of the better properties of the copolymer used, the poling procedure described above, and the larger size of the ceramic particles used which should exhibit better ferroelectric properties (a pyroelectric coefficient of 630 μC m$^{-2}$ K$^{-1}$ was obtained from 640 μm thick disks of pressed and sintered PZ21 powder after corona poling at 120 °C for 0.5 h with 10 kV).

Several figures of merit (FOMs) are used to describe the performance of a material for pyroelectric sensor applications. Often just the FOM resulting from Eq. (12) is used,

$$ F = \frac{p}{\varepsilon_r}. $$  \hspace{1cm} (12)

However, Eq. (12) does not take other material properties into account which are important for pyroelectric sensor applications. More suitable FOMs are the current FOM ($F_i$) which is proportional to the current responsivity,

$$ F_i = \frac{p}{c'}, $$ \hspace{1cm} (13)

and the voltage FOM ($F_V$), which is proportional to the voltage responsivity,

$$ F_V = \frac{p}{c' \varepsilon_0 \varepsilon_r}. $$ \hspace{1cm} (14)

If the noise of the pyroelectric detector is dominated by the ac dielectric loss of the pyroelectric element, the most important FOM is the so called detectivity FOM ($F_D$),

$$ F_D = \frac{p}{c' \varepsilon_0 \varepsilon_r \tan \delta}. $$ \hspace{1cm} (15)

For Eqs. (12)–(15), $p$ is the pyroelectric coefficient, $c'$ is the volumetric specific heat, $\varepsilon_0$ and $\varepsilon_r$ are the permittivity of free space and relative permittivity of the material, respectively, and $\tan \delta$ is the dielectric loss. From Eqs. (12)–(15) one can see that to increase the FOM it is necessary to increase $p$ while decreasing $c'$, $\varepsilon_r$, and $\tan \delta$. Composites of ceramics and polymers are one possibility to fulfill these requirements. Table I summarizes the measured values of $\varepsilon_r$, $\tan \delta$, and $c'$ as well as the calculated FOMs, and compares them to those of a PZT thick film from literature.

The measured values of the volumetric specific heat for the polymer are in good agreement with values reported in literature. We assume that the volumetric specific heat of the ceramic used is equal to that reported in Ref. 19. This value is slightly higher than that of the copolymer. The increase of the volumetric specific heat with increasing ceramic content for all samples except for the sample with 30 vol % ceramic can be explained in terms of the lower density of the composites. The decrease for the samples with 30 vol % is probably due to the higher porosity mentioned above.

It can be seen that $F_i$ and $F_D$ of the samples with 10 and 20 vol % ceramic are substantially higher than those of pure PVDF-TrFE films, while $F_V$ is higher only for samples with 10 vol % ceramic. For samples with 30 vol % ceramic the FOMs decrease again, because of the decreasing pyroelectric coefficient and the increasing dielectric constant. Compared to a PZT thick film from literature $F_D$ is a little bit smaller but $F_V$ and $F_i$ are quite high. This means that detectors made of the composite materials will show a slightly higher Johnson noise than those made of PZT thick films, but higher voltage and current responses.

Table I. Volumetric specific heat and dielectric and pyroelectric properties of the composite films investigated. The results of a PZT thick film from literature are also shown.

<table>
<thead>
<tr>
<th></th>
<th>PVDF-TrFE</th>
<th>PVDF-TrFE</th>
<th>PVDF-TrFE</th>
<th>PVDF-TrFE</th>
<th>PZT thick film (Ref. 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 vol % PZ21</td>
<td>20 vol % PZ21</td>
<td>30 vol % PZ21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c'$ (MJ m$^{-3}$ K$^{-1}$)</td>
<td>2.2</td>
<td>2.6</td>
<td>2.9</td>
<td>2.7</td>
<td>2.5</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>18</td>
<td>22</td>
<td>29</td>
<td>34</td>
<td>558</td>
</tr>
<tr>
<td>$\tan \delta$</td>
<td>0.053</td>
<td>0.041</td>
<td>0.034</td>
<td>0.036</td>
<td>0.022</td>
</tr>
<tr>
<td>$p$ (μC m$^{-2}$ K$^{-1}$)</td>
<td>52</td>
<td>80</td>
<td>92</td>
<td>73</td>
<td>352</td>
</tr>
<tr>
<td>FOM (μC m$^{-2}$ K$^{-1}$)</td>
<td>2.9</td>
<td>3.6</td>
<td>3.2</td>
<td>2.2</td>
<td>0.6</td>
</tr>
<tr>
<td>$F_i$ (pm/V)</td>
<td>23</td>
<td>31</td>
<td>32</td>
<td>27</td>
<td>14</td>
</tr>
<tr>
<td>$F_V$ (m$^2$/C)</td>
<td>0.146</td>
<td>0.159</td>
<td>0.125</td>
<td>0.091</td>
<td>0.028</td>
</tr>
<tr>
<td>$F_D$ (10$^{-6}$ Pa$^{-1/2}$)</td>
<td>8</td>
<td>11</td>
<td>11</td>
<td>8</td>
<td>15</td>
</tr>
</tbody>
</table>
The present work. This can be explained by the much higher $d_{33}$ of the powder used which is specified with 630 pC/N for bulk ceramics.\textsuperscript{17}

Pyroelectric activity cannot be achieved without piezoelectric activity in monolithic ferroelectric materials. It can be only achieved in composites. Such materials may be interesting for the production of pyroelectric sensors, because there is no need for a compensation of the piezoelectric activities due to vibration or pressure changes.

IV. CONCLUSIONS

Thick films of 0-3 PZT-PVDF-TrFE composites have been produced by spin coating on gold coated silicon substrates. As expected the dielectric constant increases with increasing ceramic volume fraction. The results cannot, however, be described by analytical connectivity models, but a 2D FE simulation model is shown to fit well the experimental results. A pyroelectric coefficient of 92 $\mu$C m$^{-2}$ K$^{-1}$ has been measured for composites with 20 vol % ceramic. The composites exhibit a good pyroelectric voltage response when they are heated with a modulated laser source. For the composites with 10 and 20 vol % ceramic, voltage and current figures of merits are higher than for PZT thick films, while $F_D$ is a little smaller, because of the higher dielectric loss of the composites. The piezoelectric properties have been also characterized, and it is shown that the charge coefficient $d_{33}$ of the composite vanishes at volume fraction of 20%, due to the $d_{33}$ of the copolymer and the PZT being of opposite signs. This composite can be seen as a suitable sensor material for pyroelectric applications, since compensation circuits for piezoelectricity would not be needed.

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