Analysis of temperature effect in dielectric response of electrostrictive polymers for pseudo-pyroelectric operations

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A B S T R A C T

Thanks to their flexibility and easy processability, electroactive polymers have gained a lot of attention over the last decades. More specifically, dielectric electrostrictive polymers have been demonstrated to provide interesting ways for mechanical actuation and energy harvesting or for electrocaloric applications. This Letter aims at presenting an additional application potential of such materials, showing their ability in terms of converting thermal energy into electrical energy. More particularly, it is shown that such materials, once polarized through the application of a bias electric field, allows a polarization variation with the temperature, yielding the so-called pseudo-pyroelectric effect. Theoretical analysis, supported by experiments, therefore demonstrates that such a material can exhibit pseudo-pyroelectric activity that can be tuned with the applied electric field.

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1. Introduction

Thermal to electrical energy conversion has been of particular interest over the last decades in order to dispose of efficient temperature sensors and electrothermal coupling devices (for instance energy harvesting and solid-state cooling). Hence, the development of materials featuring high pyroelectric activities has recently attracted many researchers. In particular, ferroelectric monocrystals exhibiting ultra-high electrothermal activity have been extensively studied over the last decades. For instance, Sebald et al. demonstrated that $< 111 >$ oriented $0.75\text{Pb}\left(\text{Mg}_{1/3}\text{Nb}_{2/3}\right)\text{O}_3 - 0.25\text{PbTiO}_3$ single crystal can exhibit pyroelectric coefficients up to 1300 µC m^{-2} K^{-1} at 40 °C ([1]) (the pyroelectric coefficient being strongly dependent to the temperature). However, recent trends in electrothermal conversion (electrocaloric and pyroelectric effects) have focused on the use of polymers and composites, such as poly[(vinylidenefluoride-co-trifluoroethylene] (P(VDF-TrFE)) copolymer which is ferroelectric and naturally pyroelectric with a pyroelectric coefficient up to 50 µC m^{-2} K^{-1} for pure copolymer ([2,3]) and 140 µC m^{-2} K^{-1} for calcium and lanthanum-doped lead titanate/poly(vinylidene fluoride-trifluoroethylene) (PCLT/PVDF-TrFE) composites ([4]). In the same way, Malmonge et al. reported that Lead Zirconate Titanate/ poly(vinylidene fluoride-hexafluoropropylene) (PCLT/ PVDF-

HFP) composites also exhibit very high pyroelectric coefficients of more than 400 µC m^{-2} K^{-1} around 70 °C ([5]).

In addition to ferroelectric materials, dielectric electrostrictive polymers such as poly(vinylidenefluoride-trifluorethylene-chlorofluoroethylene) [P(VDF-TrFE-CFE)] terpolymer have also been widely investigated ([6–9]) in terms of electrical to thermal energy conversion (electrocaloric effect). Such an interest in polymeric materials for electrothermal conversion lies in their easy processing, conformability and low price. More particularly, their low heat conductivity and possible small thickness yielding a low thermal capacitance (and thus lower time response) make them a premium choice for application as electrothermal transducers. While many researches on dielectric polymers focused on the electric to thermal conversion (*i.e.*, electrocaloric effect) for instance for solid-state cooling, very few investigated the possibility of using the converse effect (*i.e.*, pyroelectric activity) for their use as sensors or energy harvesters, while in the mechanical domain, number of studies reported their possible use as pseudo-piezoelectric materials ([10–12]).

Indeed, the increasing demand in terms of left-behind wireless self-powered sensors has placed a significant attention on energy harvesting products able to supply electrical energy to electronic devices. Among available energy sources in close environment, temperature has been of great interest for the design of small-scale energy harvesters ([13–16]), allowing the disposal of self-powered electronics systems able to work from heat energy, for instance for battery-less temperature measurement ([17]), application in wearable self-powered devices ([18]) or condition monitoring in harsh environment ([19]). In terms of sensing, pyroelectric elements are

widely used in infrared detection ([20,21]), thermal imaging ([22]) or optical measurements ([23]). However, their fixed pyroelectric constant (for a given working temperature) does not allow scaling the measurement temperature range and associated sensitivity at the material level. Furthermore, such materials being active, they may also generate charges/voltage when subjected to temperature variation, which can be particularly harmful for the associated electronic board. Hence, even when shut down and not in operation, ones have to pay careful attention in handling or storing pyroelectric-based sensing devices. On the other hand, materials that do not feature spontaneous polarization and yield an electrothermal coupling activated and controlled by the application of an electric field would allow not only avoiding overvoltage but also tuning their sensitivity by tailoring the electric field polarizing the material.

Hence, as a first step, this Letter proposes to investigate the dielectric response of electrostrictive poly(vinylidenefluoride-trifluorethylene-chlorofluoroethylene) [P(VDF-TrFE-CFE)] terpolymer that can eventually be of significant interest for electrothermal energy harvesting or sensing. The paper is organized as follows. Section 2 exposes the physical origin of the electrothermal coupling in such dielectric electrostrictive materials, along with theoretical developments based on a Debye–Langevin formalism described in ([24,25]). From this modeling, Section 3 provides some theoretical considerations on the use of the pseudo-pyroelectric effect. Then, experimental investigations and comparisons with theoretical predictions are exposed in Section 4. Finally, Section 5 briefly concludes the paper, recalling the main findings of this study and the perspectives that can be drawn.

2. Electrothermal coupling origin and theory

This Section aims at conceptually and theoretically investigating the coupling between thermal and electrical domains for the considered materials (*i.e.*, dielectric electrostrictive polymers). The model is based on the mean dipole orientation that is influenced by both the electrical field and temperature through thermal agitation for the latter. Hence, as depicted in Fig. 1, when an electric field is applied to the material, electric dipoles gets aligned therefore inducing polarization and charges appearing on the surface (Fig. 1(b)). However, as temperature increases, thermal agitation introduces some disorder in the dipole alignment (Fig. 1(c)), leading to decreased polarization and surface charges for the same applied electric field. This therefore allows obtaining a temperature-dependence of the polarization and surface charges allowing using the material as pseudo-pyroelectric element.

More specifically, assuming that the material has only one dominant phase, and according to Boltzmann's statistics and using Debye/Langevin formalism, the polarization $\mathcal{P}$ may be expressed as ([24]):

$$\mathcal{P} = N(\theta)\mu\left[\coth\left(\frac{\mu E}{k_B\theta}\right) - \frac{k_B\theta}{\mu E}\right] \tag{1}$$

where $N(\theta)$ is the temperature-dependent dipole density, μ the dipolar moment and k_B the Boltzmann constant. E and θ refer to the applied electric field and temperature, respectively. Hence, the expression of the polarization variation $d\mathcal{P}$ with respect to the variation in the electric field dE and temperature $d\theta$ is therefore given by:
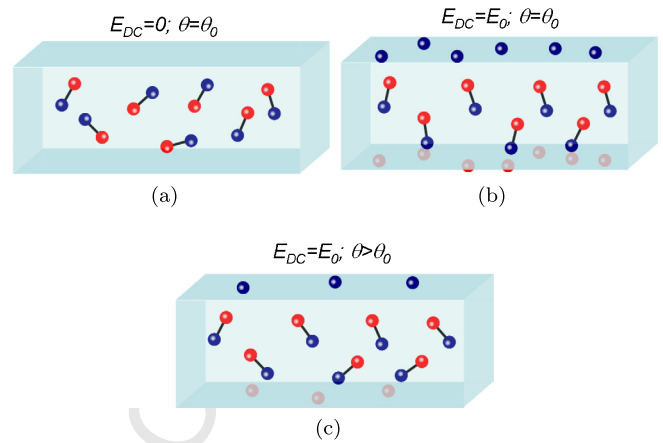

Fig. 1. Principles of the pseudo-pyroelectric operation: (a) when no electric field is applied, dipoles are randomly oriented with a zero mean polarization; (b) a polarization appears as an electric field is applied; (c) when the temperature increases, the thermal agitation of dipoles leads to a decrease of the mean polarization, as the required energy to overcome the thermal agitation increases.

$$\begin{aligned}
d\mathcal{P} &= \frac{d\mathcal{P}}{dE}dE + \frac{d\mathcal{P}}{d\theta}d\theta \\
&= \frac{N(\theta)\mu^2}{k_B\theta}\left[\left(\frac{k_B\theta}{\mu E}\right)^2 - \operatorname{csch}^2\left(\frac{\mu E}{k_B\theta}\right)\right]dE \\
&\quad + N(\theta)\mu\left\{\frac{\mu E}{k_B\theta^2}\left[\coth^2\left(\frac{\mu E}{k_B\theta}\right) - 1\right] - \frac{k_B}{\mu E}\right\}d\theta \\
&\quad + \frac{\partial N(\theta)}{\partial\theta}\mu\left[\coth\left(\frac{\mu E}{k_B\theta}\right) - \frac{k_B\theta}{\mu E}\right]d\theta
\end{aligned} \tag{2}$$

Assuming that the electric field remains almost constant and equal to E_0, the polarization derivative with respect to the temperature, namely the pseudo-pyroelectric coefficient p, is therefore given as:

$$\begin{aligned}
p = \left.\frac{\partial\mathcal{P}}{\partial\theta}\right|_{E_0} &= N(\theta)\mu\left\{\frac{\mu E_0}{k_B\theta^2}\left[\coth^2\left(\frac{\mu E_0}{k_B\theta}\right) - 1\right] - \frac{k_B}{\mu E_0}\right\} \\
&\quad + \frac{\partial N(\theta)}{\partial\theta}\mu\left[\coth\left(\frac{\mu E}{k_B\theta}\right) - \frac{k_B\theta}{\mu E}\right]
\end{aligned} \tag{3}$$

which can therefore be tuned through the electric field E_0. Furthermore, considering that the material does not experience any phase transition in the temperature working range, the dipole density N may be considered constant with the temperature so that Eq. (3) simplifies to:

$$p = \left.\frac{\partial\mathcal{P}}{\partial\theta}\right|_{E_0} \approx \frac{N\mu^2 E_0}{k_B\theta^2}\left[\coth^2\left(\frac{\mu E_0}{k_B\theta}\right) - 1\right] - \frac{Nk_B}{E_0} \tag{4}$$

which can be rewritten using the dielectric susceptibility χ_0 and saturation electric field E_{sat_0}, both at a given temperature θ_0:

$$p = \left.\frac{\partial\mathcal{P}}{\partial\theta}\right|_{E_0} \approx \frac{3\chi_0}{\theta_0}\left\{\left(\frac{\theta_0}{\theta}\right)^2\left[\coth^2\left(\frac{E_0}{E_{sat_0}}\frac{\theta_0}{\theta}\right) - 1\right] - \left(\frac{E_{sat_0}}{E_0}\right)^2\right\}\times E_0 \tag{5}$$

with ([24]):

$$\begin{aligned}
\chi_0 &= \frac{N\mu^2}{3k_b\theta_0} \\
E_{sat_0} &= \frac{k_b\theta_0}{\mu}
\end{aligned} \tag{6}$$

Such an expression can actually be further simplified considering low electric field operations ($\frac{E_0}{E_{sat_0}}\frac{\theta_0}{\theta} \ll 1$), yielding:

$$p = \left.\frac{\partial\mathcal{P}}{\partial\theta}\right|_{E_0} \approx -\frac{N\mu^2}{3k_B\theta^2}E_0 = -\frac{\chi_0\theta_0}{\theta^2}E_0 \tag{7}$$