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V I Egorov[1,*], O G Maksimova[1], H Koibuchi[2], G Jug[3], C Bernard[4,5], J-M Chenal[6], O Lame[6], G Diguet[4], G Sebald[4], J-Y Cavaillé[4], T Takagi[4,7]

[1] Cherepovets State University, Cherepovets, Russian Federation
[2] National Institute of Technology (KOSEN), Sendai College, Natori, Japan
[3] DiSAT, Insubria University, Como, Italy
[4] ELyTMaX UMI 3757, CNRS-Université de Lyon-Tohoku University International Joint Unit, Tohoku University, Sendai, Japan
[5] Frontier Research Institute for Interdisciplinary Sciences (FRIS), Tohoku University, Sendai, Japan
[6] Materials Engineering and Science (MATEIS), CNRS, INSA Lyon UMR 5510, Université de Lyon, Villeurbanne Cedex, France
[7] Institute of Fluid Science (IFS), Tohoku University, Sendai, Japan

E-mail: *rvladegorov@rambler.ru

Abstract. We apply the Finsler geometry (FG) modeling technique to study the electric field-induced strain in ferroelectric polymers. Polyvinylidene difluoride (PVDF) has a negative longitudinal piezoelectric coefficient, which is unusual in ferroelectrics, and therefore the shape changes in this material are hard to predict. We find that the results of Monte Carlo simulations for the FG model are in good agreement with experimental strain-electric field curves of PVDF-based polymers in both longitudinal and transverse directions. This implies that FG modeling is suitable for reproducing the reverse piezoelectric effect in PVDF.

1. Introduction

The reverse piezoelectric effect in ferroelectrics is widely used for creating actuators to convert the electrical energy into the mechanical energy, or vise versa. One of the most important goals in material science is to develop flexible elastic materials with piezoelectric properties. For this purpose, polyvinylidene difluoride (PVDF)-based polymers need to have increased mechanical strength, shock resistance, and flexibility compared with low-weight molecular ferroelectrics. However, PVDF has an unusual shrinking behavior along the direction of the external field, of which the mechanism is not yet completely understood [1]. Furthermore, the shape-change of the material caused by the electric field is typically very complex and difficult to simulate.

Finsler geometry (FG) technique has been successfully applied for modeling the deformation of materials with an anisotropy of mechanical properties like rubbers and soft biological materials [2, 3]. Also, the shape transformation of liquid crystal elastomers under external electric fields has been studied by this technique [4]. In the present work, we further extend the FG model for describing the reverse piezoelectric effect in ferroelectric polymers. In the FG model, Finsler metric is used instead of Euclidean metric, which is always used in simulations of surface

models for membranes. The Finsler metric is defined by using an internal degree of freedom σ, which represents the dipole moment in the case of PVDF. This approach precisely or effectively implements the role of the positional and directional degrees of freedom in polymers.

2. The model

More detailed description of 3D FG model is reported in [5]. For the simulation of a field-induced deformation, we modify the Hamiltonian in [5] by taking into account an additional dipole interaction with the external electric field. In this section, the 3D FG approach is briefly outlined. The continuous Hamiltonian S_1 corresponding to the Gaussian bond potential is given by:

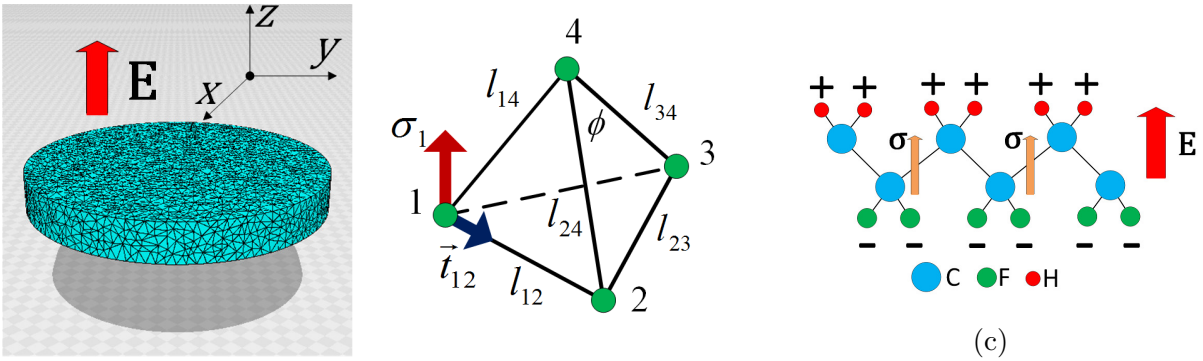
$$S_1 = \int \sqrt{g} g^{ab} \frac{\partial \vec{r}}{\partial x_a} \frac{\partial \vec{r}}{\partial x_b} d^3x, \tag{1}$$

where $\vec{r}$ is a position vector of a three-dimensional body with coordinates $x_a (a = 1, 2, 3)$. The symbol g^{ab} is the inverse of metric tensor g_{ab} and g is its determinant.

To define the discrete Hamiltonian, we use a thin cylindrical body (Fig.1(a)). This body is discretized by tetrahedrons using the Voronoi tessellation. We introduce a variable σ_i, which corresponds to the direction of the dipole moment at the vertex i. The discrete metric tensor has the form: $g_{ab} = \begin{pmatrix} v_{12}^{-2} & 0 & 0 \\ 0 & v_{13}^{-2} & 0 \\ 0 & 0 & v_{14}^{-2} \end{pmatrix}$. This form is obtained from Euclidean metric by replacing its diagonal elements with v_{ij}^{-2}, where v_{ij} is the Finsler length given by the projection $\sigma_i \cdot \vec{t}_{ij}$ of σ_i on link $\vec{t}_{ij}$ of the tetrahedron such that

$$v_{ij} = \sqrt{1 - |\sigma_i \cdot \vec{t}_{ij}|^2} + v_0, \tag{2}$$

where $\vec{t}_{ij}$ is an unit tangential vector of the bond ij (Fig.1(b))), and $v_0 = 0.001$ is a cutoff. Almost all ferroelectric polymers have a dipole moment, which is oriented perpendicular to the carbon skeleton (the structure of β-PVDF is illustrated in Fig.1(c)).



(a) (b) (c)

Figure 1. (a) The three-dimensional thin cylinder discretized by tetrahedrons, (b) a tetrahedron on which the discrete Hamiltonian is defined, and (c) the molecular structure of β-PVDF.

Replacing the integration in Eq.(1) with a sum over tetrahedrons and including the symmetric terms obtained by index replacement with the factor 1/4, we have a discrete version of S_1 [5]. With some extra terms, the discrete Hamiltonian for the FG model of the ferroelectric polymer is given by:

$$
\begin{aligned}
&S = \gamma S_1 + \kappa S_2 - bS_3 - cS_4 + U_{3D} + U_{vol}, \quad S_1 = \textstyle\sum_{ij} \Gamma_{ij} l_{ij}^2,\ \Gamma_{ij} = \left(1/\bar{N}\right) \sum_{\rm tet} \gamma_{ij}({\rm tet}),\\
&S_2 = \textstyle\sum_i (1 - \cos(\phi_i - \pi/3)), \quad S_3 = \sum_i \sigma_i \cdot \vec{E}, \quad S_4 = \sum_i (\sigma_i \cdot \vec{E})^2,\\
&U_{3D} = \begin{cases} \infty & (V_{tet} \le 0) \\ 0 & (V_{tet} > 0) \end{cases}, \quad U_{vol} = \begin{cases} 0 & |V - V_0| \le \Delta V) \\ \infty & (\text{otherwise}) \end{cases},
\end{aligned}
\tag{3}
$$

where l_{ij} denotes a length of the bond ij. The coefficients $\Gamma_{ij} (\Gamma_{ij} = \Gamma_{ji})$ are given by the sum of tetrahedrons sharing the bond ij, and γ_{ij}(tet) for the tetrahedron of vertices 1234 are determined via components of the metric tensor such that [5]:

$$
\begin{aligned}
&\gamma_{12} = \tfrac{1}{4}\left(\tfrac{v_{12}}{v_{13}v_{14}} + \tfrac{v_{21}}{v_{23}v_{24}}\right), \gamma_{13} = \tfrac{1}{4}\left(\tfrac{v_{13}}{v_{12}v_{14}} + \tfrac{v_{31}}{v_{32}v_{34}}\right), \gamma_{14} = \tfrac{1}{4}\left(\tfrac{v_{14}}{v_{12}v_{13}} + \tfrac{v_{41}}{v_{42}v_{43}}\right),\\
&\gamma_{23} = \tfrac{1}{4}\left(\tfrac{v_{23}}{v_{21}v_{24}} + \tfrac{v_{32}}{v_{31}v_{34}}\right), \gamma_{24} = \tfrac{1}{4}\left(\tfrac{v_{24}}{v_{21}v_{23}} + \tfrac{v_{42}}{v_{41}v_{43}}\right), \gamma_{34} = \tfrac{1}{4}\left(\tfrac{v_{34}}{v_{31}v_{32}} + \tfrac{v_{43}}{v_{41}v_{42}}\right).
\end{aligned}
\tag{4}
$$

The second term κS_2 in Eq.(3) plays a role of deformation strength against bending and shear deformation, both of which have an influence on the material shape. ϕ_i in S_2 is an internal angle of the triangle. The third term bS_3 is an energy of the dipole interaction with the external electric field, which causes the piezoelectric effect. cS_4 is the potential describing the quadratic electrostrictive effect. U_{3D} is a constraint for the volume of the tetrahedron for not being negative. To prevent the volume from changing, the last term U_{vol} is introduced, where ΔV is a mean value of the volume of one tetrahedron and V_0 is an initial volume of the whole cylinder which is determined by the simulation without U_{vol} in the absence of external electric field.

3. The simulation results

In this work, we use a cylinder of size $(N, N_B, N_T, N_{tet}) = (10346, 69964, 116041, 56422)$, where N, N_B, N_T, N_{tet} denote the total number of vertices, bonds, triangles, and tetrahedrons, respectively. The ratio of the cylinder height and its diameter is equal to 0.125. For this cylinder, the simulation of electric field-induced deformation is carried out by Monte Carlo method. The Monte Carlo (MC) updates of locations of vertices and σ are performed using the standard Metropolis algorithm. The uniform external electric field is applied along the axis of the cylinder i.e. along the z axis. The snapshots in Figs. 2(a)-(d) show how the shape of the cylinder is changed. We can see that the height shrinks and the diameter expands with increasing electric field.

The absolute value of thickness strain $|\varepsilon_z|$ and diameter strain ε_d vs. the external electric field E for different values of the bending stiffness are presented in Figs.2(e),(f). The values of c and $b = \sqrt{c}$ were chosen by data analysis for the best correspondence of the experimental and the simulation data. We compare our simulation results for longitudinal shrinking with experimental data of highly electrostrictive networks of β-PVDF [6]. For the transverse stretching comparison, the strain-field diagram of P(VDF-TrFE-CFE) films is used [7]. To summarize, the simulation results are in good agreement with experimental data in both longitudinal and transverse directions.

From the comparison of the energy cS_4 and the physical dielectric energy, we obtain $cE^2 k_B T/a^3 = \epsilon_0 \Delta\epsilon E_{exp}^2$ [4], where $\epsilon_0 = 8.85\times10^{-12}$[F/m], $\Delta\epsilon$ is the dielectric anisotropy, a is the lattice spacing, $k_B T$ is given by $k_B T = 4\times10^{-21}$[J] at room temperature. If the experimental data ε_z or ε_d at E_{exp} in units of [10^6V/m] are comparable with those simulation data at E, then we conclude that $E = 10^{-6} E_{exp}$ [4]. In this case, we have $a = \left(ck_B TE/\epsilon_0 \Delta\epsilon E_{exp}\right)^{1/3} \simeq (7.7\times10^{-8})\,(c/\Delta\epsilon)^{1/3}$ [m]. Using the value of $\Delta\epsilon = 0.25$ [8] and the input $c = 0.024$[MV^{-2}], we find that $a \simeq 3.5\times10^{-8}$[m] in β-PVDF model, which is clearly larger than the van der Waals

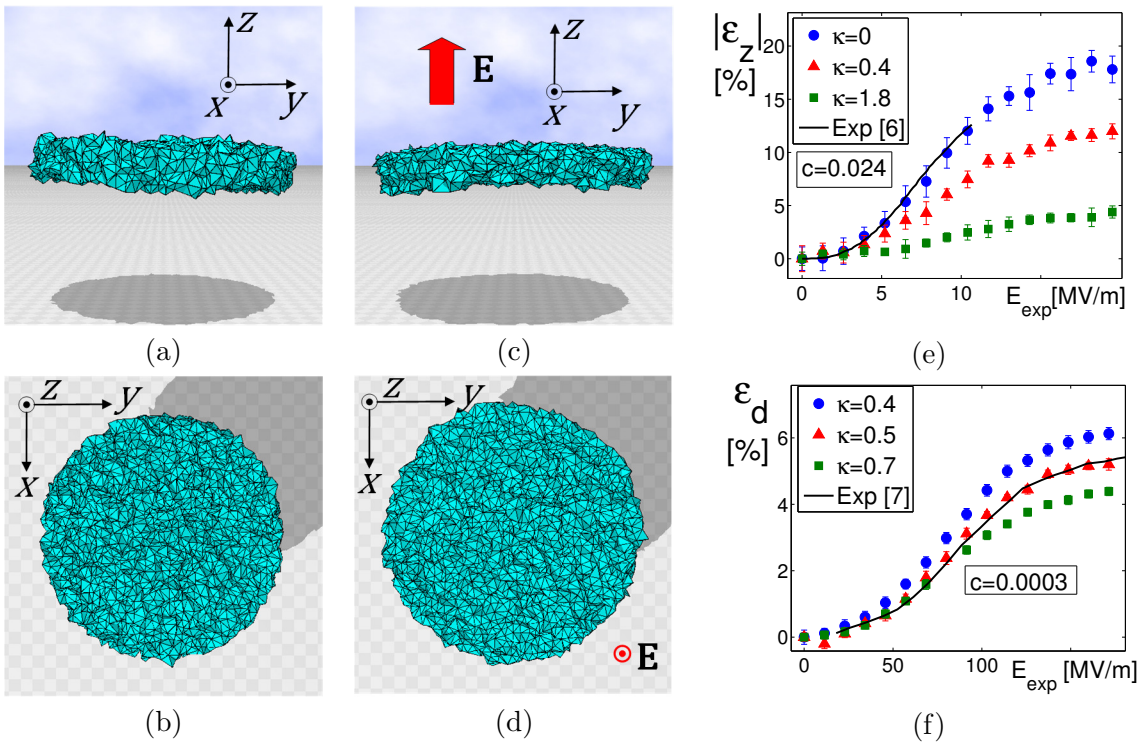


Figure 2. Snapshots of the cylinder with the external field: (a),(b) $E_{exp} = 0$, and (c),(d) $E_{exp} = 20$ with the bending stiffness value $\kappa = 0.4$. (e) The thickness-strain $|\varepsilon_z|$ v.s. E_{exp} and (f) the diameter-strain ε_d vs. E_{exp} with several different κ values.

distance $D_{\mathrm{VWD}} \simeq 10^{-10}$[m]. In P(VDF-TrFE-CFE) model with $c = 0.0003$[MV^{-2}], we have less value of the lattice spacing $a \simeq 8.1 \times 10^{-9}$[m], which is reasonable because the experimental samples of P(VDF-TrFE-CFE) were thinner than ones of β-PVDF.

4. Conclusion

We propose a simulation model on the basis of Finsler geometry for describing the reverse piezoelectric effect in PVDF. The simulation results of deformation, induced by the electric field, are in good agreement with reported experimental data for both longitudinal shrinking and transverse stretching. Hence, we conclude that this model is suitable to predict the shape transformation of PVDF-based actuators.

Acknowledgments

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