Ferroelectric PVDF films and graphene-based composites

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Abstract. Advantages in the studies of new composite nanomaterials based on polymer ferroelectrics and graphene are presented. We analyzed the main results of the computational molecular modeling of nanostructures and the pyroelectric properties of the composites from polyvinylidene fluoride (PVDF) films and graphene layers. The pyroelectric effect was modelled and pyroelectric coefficients were calculated for several models using molecular dynamics simulation with quantum-chemical semi-empirical PM3 method from HyperChem tool. The results obtained provide important insights into our understanding of the mechanisms of pyroelectricity in the new nanocomposites, give us new prospective for further studies of the ferroelectric polymer–graphene multifunctional nanomaterials.

1. Introduction

All polymer ferroelectrics, including polyvinylidene fluoride (PVDF) and copolymers, as any ordinary ferroelectrics, have a set of common ferroelectric properties: critical behaviour in the phase transition point vicinity, spontaneous polarization and nonlinear switching of the polarization, Curie-Weiss law for dielectric permittivity, piezoelectricity and pyroelectricity phenomena, etc. [1-3]. These properties have many practical applications, and most of them concern with piezoelectricity and pyroelectricity [4-7]. Among various types of polymer ferroelectrics, of special interest are the so-called thin and ultra-thin ferroelectric films fabricated by spin coating technique and by Langmuir-Blodgett (LB) methods [3]. These films have unique mechanical flexible properties which are very important for biomedical applications. These properties exist in the more complex composite ferroelectrics materials and films based on polymer ferroelectrics combined with graphene and graphene oxides [6, 8, 9].
We witness ever growing attention of researchers to the development, creation and investigation of the properties of new nanocomposite materials all over the world. Of special interest are ferroelectric materials, since they have numerous applications in a wide variety of fields, owing to their properties, such as polarization, piezoelectricity and pyroelectricity [1-5]. The most important of these composite materials are new nanocomposites based on the combination of the known polymer ferroelectrics and graphene/oxide graphenes, which are most pronounced [6-11]. These materials have a unique combination of the properties of ferroelectrics (polarization, piezo-/pyro-properties, etc.) and possess high elastic and mechanical properties, which are very important for many multifunctional applications [11].

Polymer ferroelectrics poly (vinylidene fluoride) (PVDF) and poly (vinylidene fluoride-trifluoroethylene) P(VDF-TrFE) copolymers [2, 3, 10, 12], especially in the formation of thin high-ordering Langmuir-Blodgett (LB) films [3, 10, 13, 14] are already sufficiently well studied [13-21] (both experimentally and theoretically). Computational molecular modeling and calculations of pyroelectric and piezoelectric properties, were usually performed using HyperChem package [22] with semi-empirical quantum-chemical method PM3 [20-23]. But for calculation of the piezoelectric and pyroelectric coefficients it is necessary to know the temperature dependence of the polarization [1-3]. These data can be obtained by using the molecular dynamics approach [20-22], which is included in HyperChem tool. This method was widely used in other investigations aimed at determining the dynamical dependence of the specific parameters of the studied system, such as the behavior of the polarization switching time in the similar thin ferroelectric films, for example [21]. In this work we use the dynamics of the polarization changes as the temperature of the modeled system rises so that to calculate the pyroelectric coefficients.

2. Computational and initial modelling details
In papers [6, 11, 23], several types of molecular models for PVDF (β-phase)-graphene and GO (PVDF-G/GO) ferroelectrics systems were developed and investigated using HyperChem tool [22]. In all the cases we used the same approaches for PVDF modeling as in Refs. [19-21]. Different computational methods were used, including molecular mechanics (MM) methods and quantum-chemical semi-empirical method (PM3), in restricted Hartree-Fock (RHF) and unrestricted Hartree-Fock (UHF) approximations. The initial molecular model of the PVDF chain was proposed and first-ever elaborated in paper [20] with 12.5 elementary molecular units as it was done in [19-21, 23].

From the main phenomenological theory of ferroelectrics it is known that the values of piezoelectric and pyroelectric coefficients are defined by relations described in [1-3]. Experimentally these coefficients in such samples are thin and LB polymer ferroelectric films are measured by interferometric and thermal modulation methods described in details in [3, 12-20].

3. Results and discussions: pyroelectric coefficients calculations by molecular dynamics method
Molecular dynamics (MD) method calculations allow us to obtain the temperature dependence of many physical characteristics of the studied systems. Particularly, one of the important characteristics for ferroelectrics is the polarization dependence on temperature changes. In this work the simulation of this temperature dependence was made using special MD option in HyperChem tool [21, 22]. We used a special set of parameters necessary for MD run: run time (~ 2.5 ps), step size for MD run (~ 0.001 ps), bath relaxation time (~ 0.001 ps) and simulation temperature T, which was changed from T = 0 K up to the phase transition of first order (PT1) temperature T0 = ~313 K for the selected physical points. Each MD run took place at constant temperature in vacuum for the molecular chain (PVDF12) being modeled and for two composite models: with one Graphene layer, oriented to F-side of PVDF (model PVDF12+Gr96H), and for model with two Graphene layers, with sandwiched PVDF (model PVDF12+2Gr96H). The proposed and developed models are shown in figure 1, 3, 4. Firstly, PVDF12 chain was investigated at different temperatures to reveal how its polarization depends on temperature (figure 1 and figure 2).
To check these data we performed calculations using the well-known relation from Landau-Ginzburg-Devonshire (LGD) phenomenological theory of the ferroelectrics with the first order phase transition (PT1 at $T_0$ as phase transition temperature and with Curie point at $T_c$ temperature) using formula for PT1 in the dimensionless form in Fridkin book [3]:

$$P = P_{00} \sqrt{1 + \sqrt{1 - t}},$$

where

$$t = \frac{3}{4} \frac{T - T_0}{\Delta T_c}, \quad \Delta T = T_c - T_0 \approx 70 \text{ K}, \quad T_0 = 313 \text{ K}, \quad P_{00} = 0.109 \text{ C/m}^2.$$

![Figure 1. Molecular dynamics simulation of initial PVDF12 chain with temperature changes: a) initial PVDF at $T=0$ K, b) PVDF chain after MD run at $T=273$ K (as one of the examples of MD run).](image)

The plots in the inserted “simulation window” show the changes of the averages energies (in kcal/mol) during simulation time (in ps): kinetic $E_{\text{KIN}}$ (red), potential $E_{\text{POT}}$ (green) and total $E_{\text{TOT}}$ (blue).
Figure 2. Dependence of the PVDF polarization on the temperature: a) data calculated using formula (1) for PT1, b) data from MD run for different temperatures with PM3 calculation at the each step.

These parameters and polarization $P_0$ are recalculated using known values of the LGD expansion coefficients from [1 -3] into this simple dimensionless form. These calculated data of polarization $P(T)$ are presented in figure 2. It can be seen that despite some deviations, due to statistical errors of MD run, both the dependencies demonstrate the same behavior and the polarization values calculated are close to known experimental data [1-3, 13-18].

From these data obtained we can easily calculate the pyroelectric coefficient of the pure PVDF by the molecular model: $p = \Delta P/\Delta T = \sim 34 - 41 \, \mu C/(m^2*K)$, which is in line with many known data for PVDF and its copolymers systems [1-3, 13-23].

Next MD run was performed for model with one Graphene layer (see in figure 3) and for two Graphenene layers with PVDF in the sandwich model (figure 4). Corresponding computed data of pyroelectric coefficients are collected in table 1. These are very interesting results, which show that Graphene components embedded into common composite material lead to observed changes and differences in the pyroelectric coefficients values. This influence depends greatly on the Graphene content: for one layer model we have a rise in PVDF component and a higher total value of the pyroelectric coefficient, while for two layers model, the PVDF component is slightly less (but nevertheless is higher than for pure PVDF) and the total value of the pyroelectric coefficient is nearly tenfold lower than in one layer model.
Figure 3. Molecular dynamics simulation of the total changes of the PVDF12+Gr96H model with temperature: a) initial state at T=0 K, b) after MD run at T = 293 K. Inserted plots are the same as in figure 1.

Table 1. Pyroelectric coefficients MD calculated data.

| Model         | MD run     | p(PVDF), μC/(m²K) and PVDF only component in composite system | p(composite), μC/(m²K) in Total system |
|---------------|------------|----------------------------------------------------------------|---------------------------------------|
| PVDF12        | Various, average | 34.1 – 40.8                                                   | -                                     |
| PVDF12+Gr96H  | 1          | 117.7                                                           | 111.13                                |
|               | 2          | 158.5                                                           | 160.5                                 |
| PVDF12+2Gr96H | 1          | 86.4                                                            | 17.5                                  |
|               | 2          | 89.8                                                            | 18.8                                  |
4. Conclusions

The developed models and MD run methods allowed us to calculate the temperature dependence of the polarization and calculate the values of the pyroelectric coefficients for pure PVDF and for the composites of PVDF with Graphene layers. The values of the pyroelectric coefficient obtained for pure PVDF are in line with known data, the data computed for composite materials are new and predict complex unlinear behavior as Graphene content may change. But in any case it was shown that in proposed and developed composite systems the value of the pyroelectric coefficient could be higher than in the initial matrix of pure PVDF materials. The data obtained and conclusion are new and very important. These data were obtained for the first time. Notes that the data obtained predict the behavior of the new composites system based on graphene and ferroelectric copolymers.

From this point of view further experimental research direction must involves the fabrication of ultrathin Langmuir–Blodgett PVDF or P(VDF-TrFE) films [3, 15–17, 21, 23] deposited directly onto a G/GO layer in order to obtain highly ordered multilayered ferroelectric composites with excellent polarization and piezoresponse properties. This new approach will be the next step on the way of creating new high-quality composites for multifunctional applications. The models proposed and developed here only exactly show us this way, because these models are more ideal and ordered systems than experimentally investigated films, fabricated by spin coating method, and they are especially close to the thin Langmuir–Blodgett films.

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Figure 4. Molecular dynamics simulation of the total changes of the PVDF12+2Gr96H model with temperature: a) initial state at T=0 K, b) after MD run at T = 293 K. Inserted plots are the same as in figure 1.
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