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Polarization switching in PVDF ferroelectric polymer composites containing graphene layers: molecular dynamic simulations

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ABSTRACT

The study of composite nanostructure containing ferroelectric polymer PVDF and graphene layers was carried out in this work by molecular modeling methods and the PM3 semi-empirical method of quantum molecular dynamic (MD) calculations using HyperChem software.

It is firstly shown here that the inclusion (addition) of graphene layers to the ferroelectric PVDF polymer increases the coercive field of the composite structure and decreases the polarization switching times of this composite heterostructure. New compositions of such nano- and heterostructures with altered or adjustable times of polarization switching and coercive fields can be constructed based on the obtained calculation results. It provides new opportunities for device constructions such as sensors for nanotechnological and biomedical applications.

1. INTRODUCTION

Ferroelectric polymers and polymer films, including based on polyvinylidene fluoride (PVDF) and poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)), are of considerable interest for various applications due to their convenient and specific properties (piezoelectric and pyroelectric, specially polarization switching) [1-6]. Recently, researchers have been particularly interested in studying their properties at the nanoscale, because these thin and ultrathin PVDF/P(VDF-TrFE) films obtained by the Langmuir-Blodgett (LB) method [6-16] being two-dimensional ferroelectrics [6, 9, 10, 17, 18] demonstrate the phenomenon of polarization switching at the nanoscale with local switching of ferroelectric polarization [6–18], local piezoelectric effect [8-10, 16] and pyroelectric properties in wide-range diapason [13, 18-20]. These properties are extremely important both for understanding the main fundamental processes and phenomena of ferroelectricity at the atomic-molecular level, and for new promising applications in a wide variety of fields of nanosciences and various nanotechnology. Nanomaterials based on ferroelectric polymers can be easily adapted to the production of nanodevices of various geometries, for example, nanolayers, nanofibers, combined heterostructures, etc.

Recently the PVDF/P(VDF-TrFE) and graphene/graphene oxide (G/GO) nanocomposites was made in the form of layers and fibers [21-29]. Such materials demonstrate changes of piezo- and pyro-electric properties depending on concentration of the G/GO components in their structures [20, 27, 28]. These features turn out to be highly important for the creation of new composite materials with adjustable properties.

An important parameter of thin polymer ferroelectrics is also the polarization switching times [18, 19, 30, 31]. Particular interest here is the possibility of using such ultra-thin ferroelectric films in various increasingly miniature nano-devices, switches and sensors. A significant dependence of the polarization switching times on the thickness of the films (the number of layers or unit cells) was established and recently investigated both experimentally and theoretically, using various modeling methods, including molecular dynamics (MD) simulation [30].

It was shown that, within the size *l*, comparable or smaller than the critical domain nuclei *l** ($l \le l^*$) [18, 19], the ferroelectric phenomena in such nanoscale ferroelectrics is fully described by the Landau-Ginzburg-Devonshire (LGD) theory and the polarization switching kinetics is corresponding to Landau-Khalatnikov equations [18, 19, 31]. Near the critical values of the electric field E close to the intrinsic coercive one *Ec*, the dependence of the important switching parameter (switching time τ_S) on electrical field magnitude is determined by the linear relation between square of the inverse switching time τ and the applied electric field E (for $E > Ec$) according to [31]:

$$1/(\tau)^2 \sim (E - Ec) \qquad (1)$$

The relation (1) allows us to calculate this dependence in the vicinity of the coercive field [17-19].

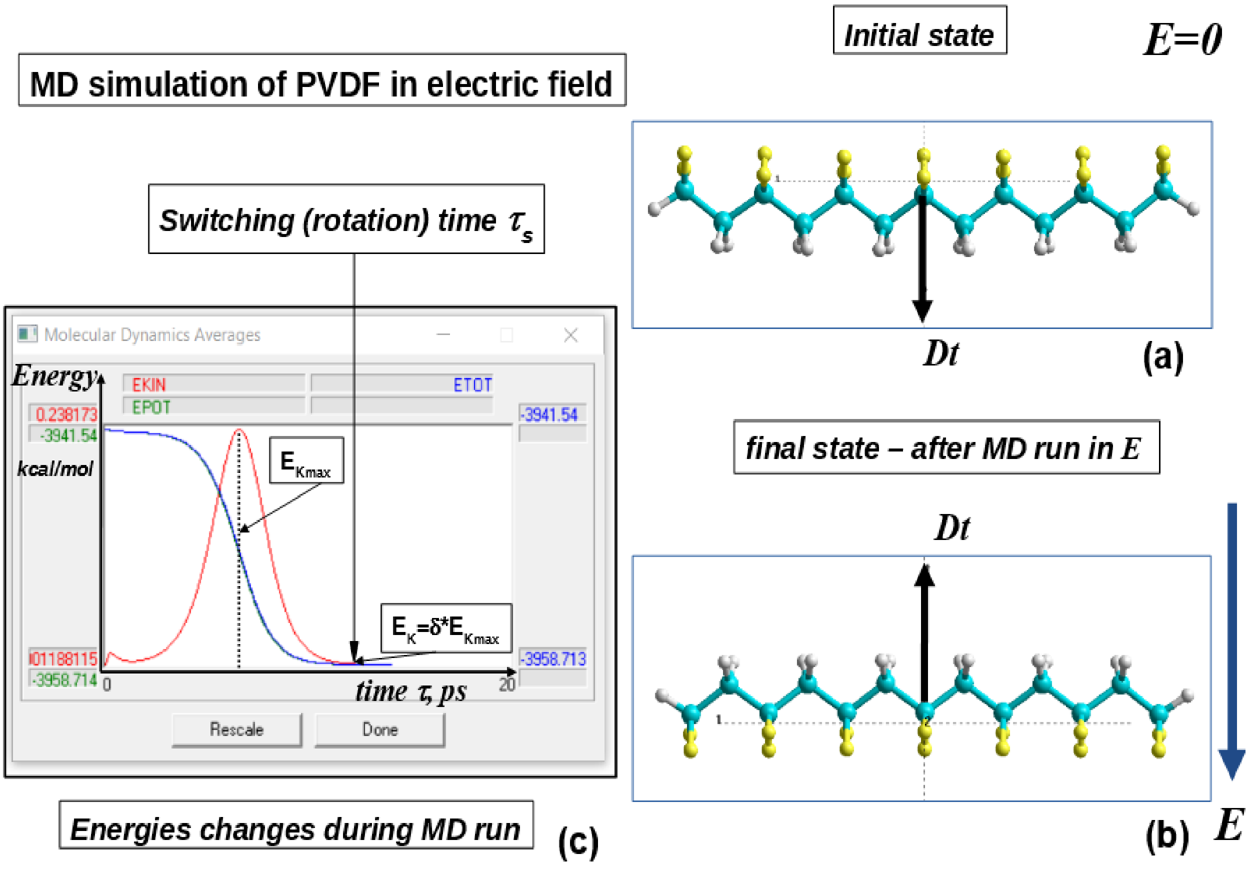

Figure 1. Principles of the molecular dynamics (MD) simulations run (example of PVDF6 chain) using PM3 RHF method calculations by HyperChem software at each MD run step:

(**a**) initial state; (**b**) final state after the MD run with dipole moment ***Dt*** orientation turned (switched) in the opposite direction in the applied electric field E; (**c**) changes of the MD average energies trajectory over time during the MD run (in ps units) and the time of the switching τ_s for this PVDF system (RED – kinetic energy, BLUE – total energy, GREEN – potential energy). Colour for model: Carbon atom C is CYAN, Fluorine atom F is YELLOW and Hydrogen atom H is GREY.

The influence of graphene layers inclusions on the switching times in composites based on polymer ferroelectrics, has not yet been studied at all. The similar influence of graphene oxide should be investigated too.

Although, this phenomenon is of considerable interest and can determine the properties of newly made composite and hybrid nanomaterials with controlled switching times, which would undoubtedly be very promising for many practical applications. In this research, the dependence of the change in the polarization switching time in thin PVDF film layers on the embedded graphene layer was studied by quantum molecular dynamics methods with quantum chemical semi-empirical calculations at each step of the molecular dynamics run using the HyperChem software [33]. The quantum-mechanical calculations at each step of the MD were carried out using semi-empirical methods PM3 in RHF approximation developed by authors earlier in [17-19, 27-30, 32].

2. COMPUTATIONAL METHODS AND MODEL DETAILS

In this work, we used the basic approaches and models developed by us in previous works [17-20, 26-30, 32]. To reveal the main effect of the influence of graphene on the polarization switching times in the polymer ferroelectric PVDF, we considered the model of PVDF as chains of n = 6 basic elementary units $(C_2H_2F_2)_n$. This model is named here as “PVDF6”. Firstly we carried out a study of the polarization switching of such a PVDF6 chain using molecular dynamics (MD) simulation methods, similar to methods used in our previous researches [30] (Fig. 1).

The simulation results are given in comparison with data published in [17-20, 26-30, 32]. These obtained results and main principles of MD simulation are additionally discussed and shown below in section 3.

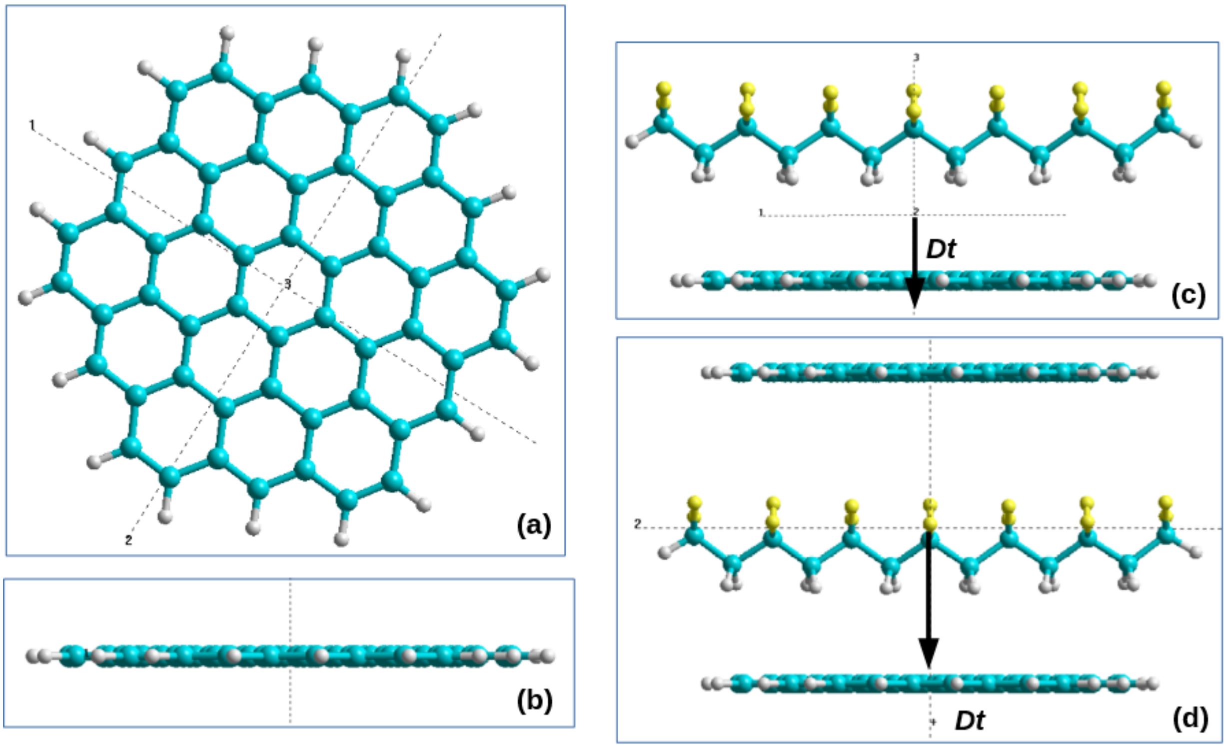

Figure 2. Models of initial states for one Graphene layer and one PVDF6 chain: a) Graphene layer model Gr54H with 54 carbon atoms C (CYAN), arranged round by the hydrogen atoms H (GRAY),

in Z-plane; b) the same in Y-projection plane; c) “PVDF6+G54H_H-C” model in the initial state of PVDF6 chain and Gr54H with “H-C” positions; c) the sandwich structure “Gr54H+PVDF6+Gr54H” model in the initial state. Initial dipole moment ***Dt*** orientation is shown by vector – black arrow.

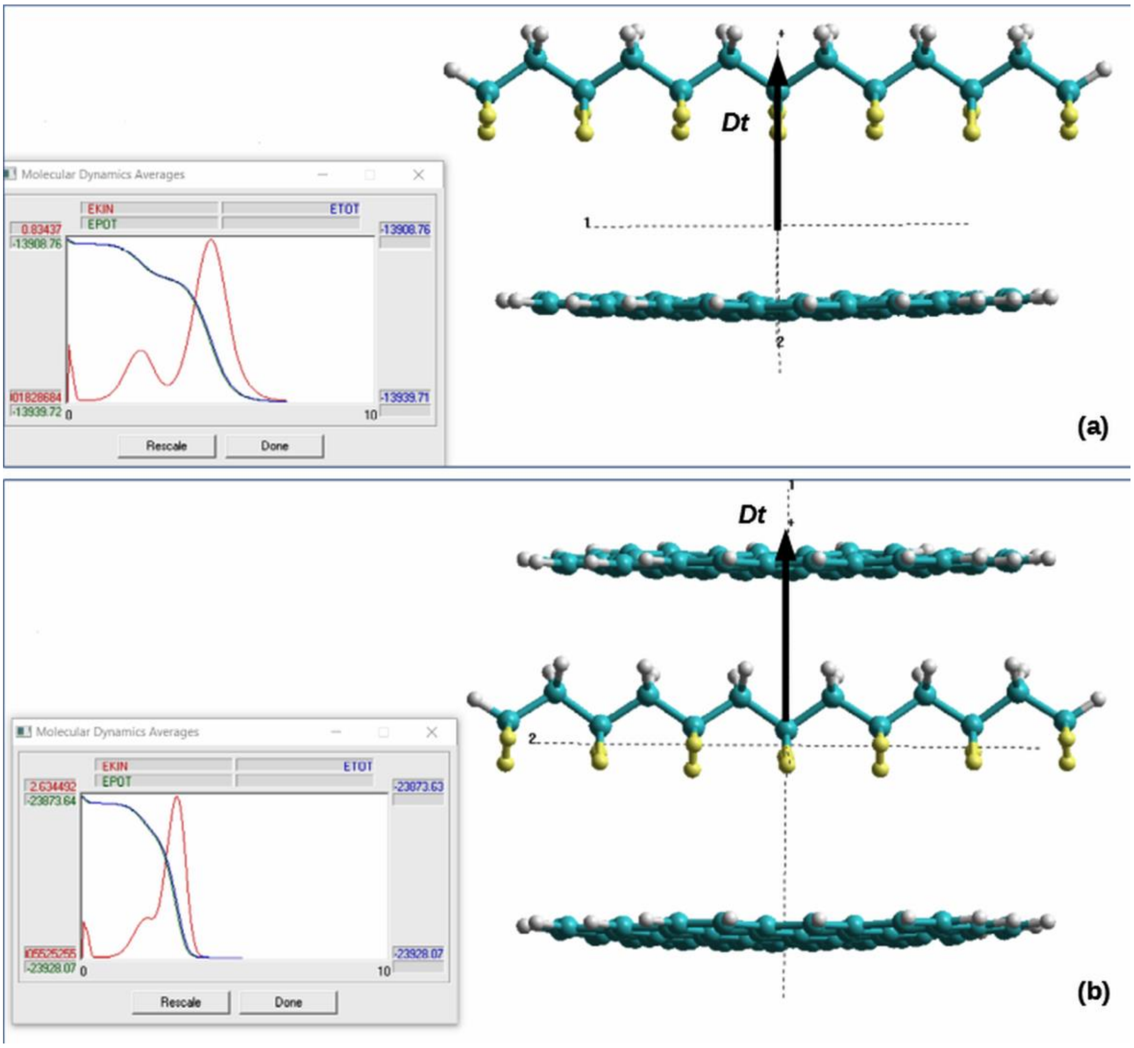

Figure 3. Final states of the “PVDF+Gg54H” models after PVDF chain and total dipole Dt rotation (switching) in the applied electric field E:

a) one-side “PVDF6+G54H_H-C” model with switched opposite orientation of the total dipole moment ***Dt*** in comparison with initial state on Fig. 2 c;

b) sandwich “G54H+PVDF6+G54H” model with the same opposite switched ***Dt*** in comparison with initial state shown on Fig. 2 d. On right side of each pictures shown examples of the MD average energies trajectory over time during the MD run similar as on Fig. 1.

Further, the model of the graphene layer developed earlier will be used [24, 25, 27, 29]. This simplest model consists of 54 carbon C atoms surrounded on the edge by hydrogen atoms H [29] (Fig. 2 a, b). This model is named here as “Gr54H”.

We consider two types of the models as the main composite (hybrid) structures “PVDF6+Gr54H”:

1) one-sided model “PVDF6+G54H_H-C”, where the PVDF chain (or layer) is directed to the graphene layer by hydrogen atoms H (Fig. 2 c);

2) two-sided model (or sandwich model) “G54H+PVDF6+G54H”, where the PVDF chain (or layer) is surrounded on both sides by two graphene layers (Fig. 2 d).

This model construction approach is similar to the model, which we used for calculating the piezoelectric coefficients of similar PVDF and graphene composites [28, 29].

The semi-empirical PM3 method in the restricted Hartree-Fock (RHF) approximation [32, 33] was used for the quantum calculations of the initial structures of all models and for calculations

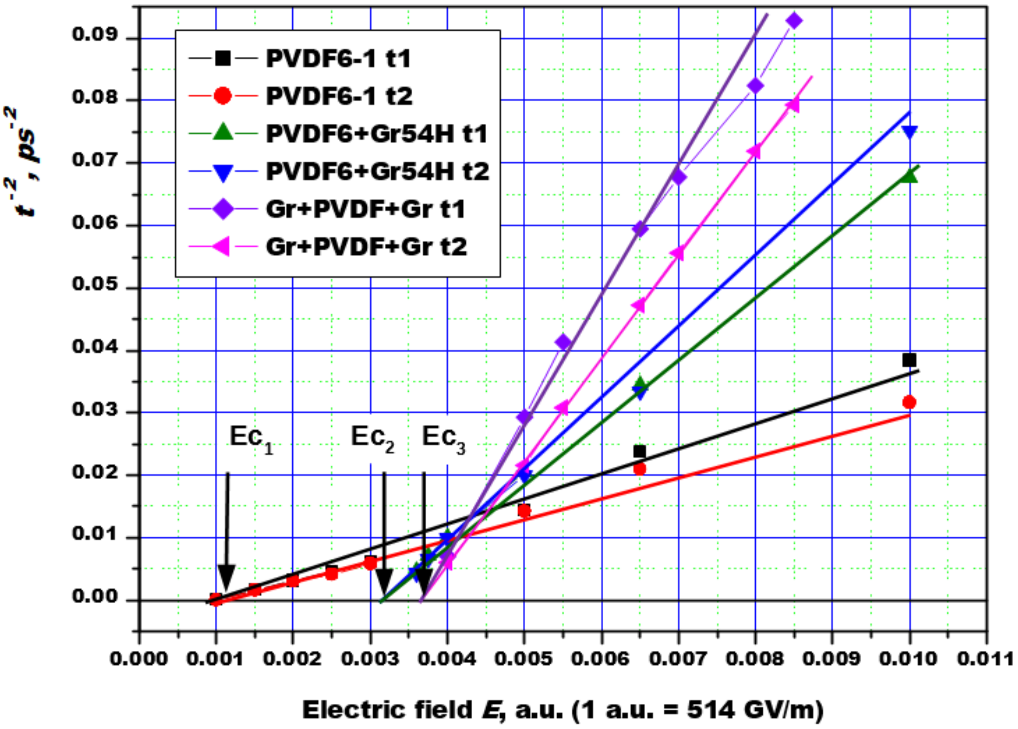

Figure 4. Square of the inverse switching time τ (1) as a linear function of the electric field E for different models, taking into account the spread of data accuracy between the values of t1 and t2.

during the MD run at each of its steps. This PM3 method is included in the HyperChem package [33].

The main part of all quantum-chemical calculations in HyperChem was made using Single Point (SP) calculation method. For cases of the hysteresis loop calculations, when is necessary to take into account the changes of geometry of the molecular systems, the optimization of molecular systems and finding of their optimal geometry is performed using the Polak–Ribere (conjugate gradient method) algorithm, included in HyperChem package [33]. This approach is especially important for the case of the dipole moment rotation switching (and polarization switching) in the applied electric field at the critical point of the systems. Simulation of the system under an imitated applied constant electric field is available in HyperChem packages too [33].

The main approach used in this work is MD simulation run and changes of the modelled structures under applied electric field ***E*** with its various values using HyperChem software [33]. Performing of such MDS calculations and runs requires specifying a certain set of parameters, which are set in the MD option of the HyperChem program. The main initial parameters are following: MD calculations perform at constant temperature (for each used electric field value) in vacuum, with bath relaxation time = 0.05 ps; for MD run parameter “run time” = 5 – 20 ps (depending of necessary time interval, in which switching process observed) and with “step size” = 0.0005 – 0.001 ps, which is varied depending of applied electric field and the rate of the molecular chain rotation.

2. MAIN RESULTS AND DISCUSSIONS

Results of MD run calculations obtained for various electric field applied values E, directed opposite the electric field arisen by the PVDF dipole moment vector, show that during this MD run the PVDF

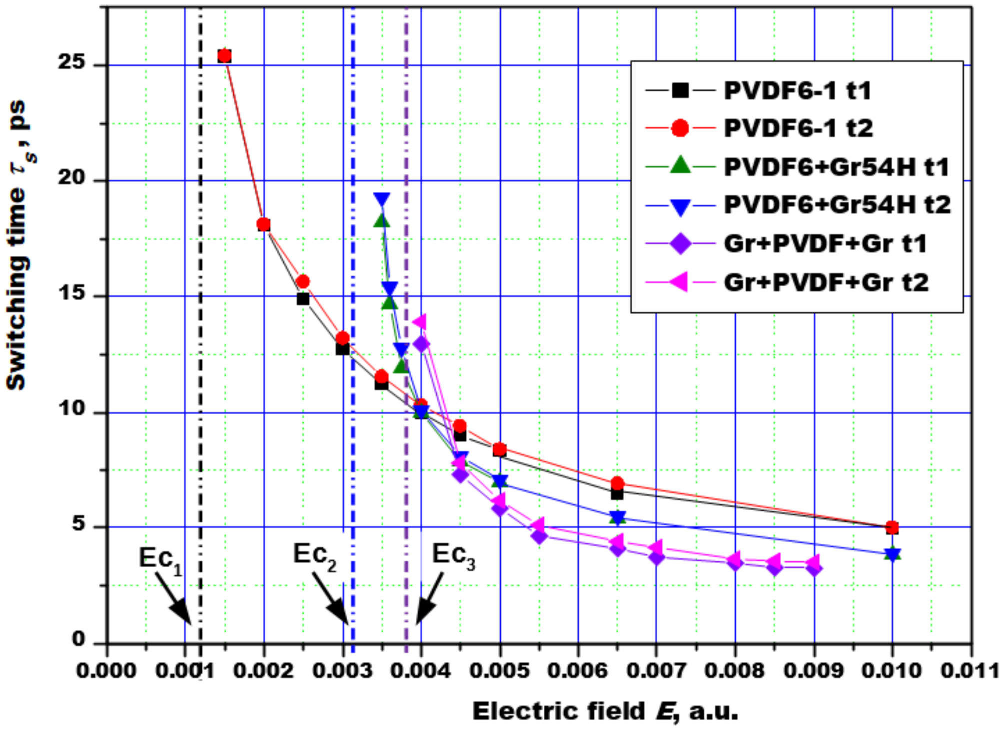

Figure 5. Behaviour of the switching time τ (1) as a function of the electric field E for different models, taking into account the spread of data accuracy between the values of t1 and t2.

chain and its total dipole ***Dt*** turn gradually so, that it eventually rotates in the opposite direction in the final state. As results, all initial models (shown on the Fig. 1 a, Fig. 2 c, d) undergo different structural changes under the influence of electric fields of different magnitudes - rotation of the PVDF dipole structure is performed with different speeds depending of the electric field value. Some examples of the final states of different considered models after a such flipping (switching) are shown in Fig. 1 b, Fig. 3.

The corresponding changes of all MD average energies with time are shown as example in Fig.1c. The final time of two-chain rotation (switching time τ) was estimated from these MD energies trajectories at the criteria $\delta \sim E_K/E_{Kmax} \leq 0.01 – 0.001$, where E_K is the kinetic energy at the final point and E_{Kmax} is the kinetic energy at the maximum of the chain rotation (as shown in Fig. 1 c). The calculated data and performed MD run in various electric field show clearly the different behaviour of the PVDF chain at the strong and at the low electric field and allow us to obtain the critical behaviour at the electric field $E \sim Ec$ at the low limit of this electric field, $E \rightarrow Ec$ for $E > Ec$.

Results of the switching time τ variations obtained from MD run calculations for various electric field values ***E*** are presented below on Fig. 4 and Fig. 5. The data obtained is very interesting.

First, the behaviour of the PVDF chain alone was considered (Fig. 1 c, d). It is in good comparison with previous calculations [17-19, 30] shown a linear behaviour (1) with coercive field *Ec* ~ 0.5 GV/m (Fig. 4).

Second, the behaviour of one-side heterostructure “PVDF6+G54H_H-C” model was investigated (Fig. 3 a, Fig. 4, Fig 5). The result showed that the rotation (switching) time τ_s became shorter, that is, the rotation is faster under the influence of the graphene layer. The coercive field is increased up to *Ec* ~ 1.5 GV/m.

On the other hand, it is interesting and important that in this case the graphene layer itself does not

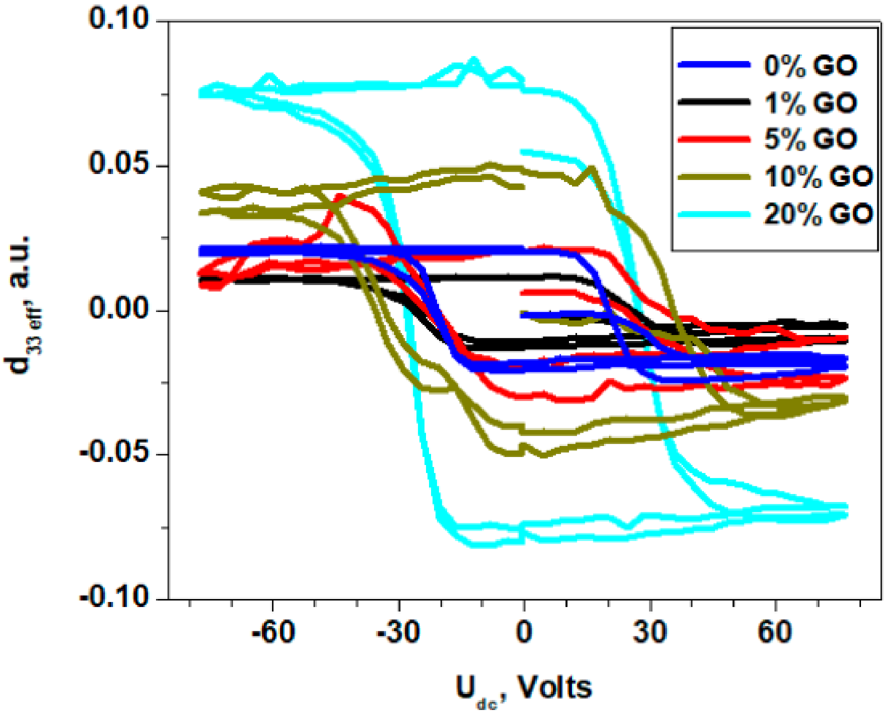

Figure 6. Piezoresponse hysteresis loops of P(VDF-TrFE)-graphene oxide fibers with different concentration of GO. *U*ac = 7.5 V, 40 kHz (data from [25]).

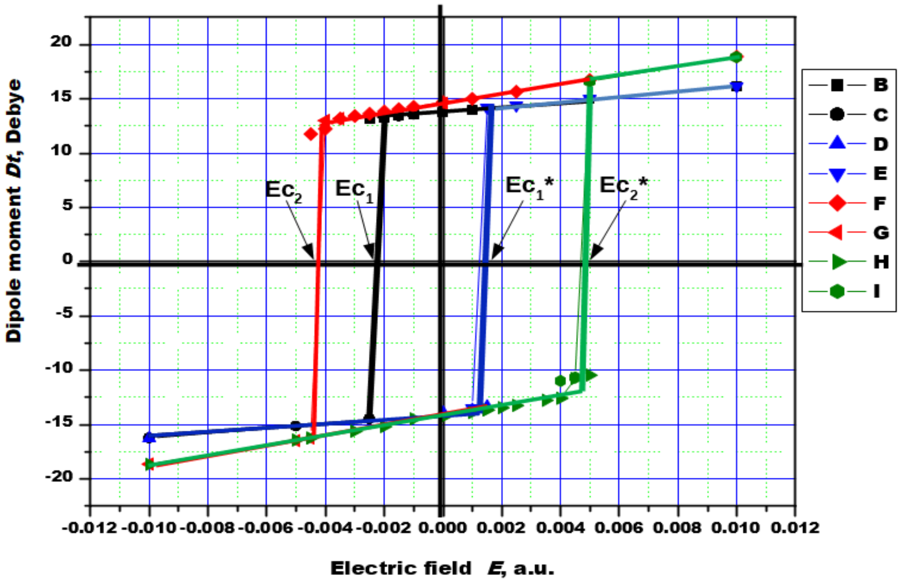

Figure 7. Calculated hysteresis loop of PVDF6 model (B-C down, D-E up branches) and for "PVDF6+G54H_H-C" model (F-G down, H-I up branches) with increased coercive field *Ec*: from Ec_1 up to Ec_2 for left side and from Ec_1* up to Ec_2* for right side (due to some asymmetry of hysteresis loop for various electric field direction in relation to the $C_2H_2F_2$ dipoles in PVDF6 chain).

overturn, but mainly retains its previous position. Rotated only PVDF chain.

Third, the behaviour of the sandwich "Gr54H+PVDF6+Gr54H" hetero-structure shows even shorter switching times (Fig. 3 b, Fig. 4, Fig. 5) and increasing of coercive field up to *Ec* ~ 2 GV/m.

Thus, the calculations performed by the quantum MD simulation method show that, under the influence of graphene layers, the switching times τ in the ferroelectric PVDF polymer decrease and coercive field *Ec* increase. And this can have important technological and practical implications and applications.

It should also be noted the fact that in the works [24, 25], in which the properties of the similar composite “PVDF + Graphene”, but some more complex composition (with Graphene oxide and P(VDF-TrFE)), were studied - and it was found that the addition of graphene/graphene oxide increases the value of the coercive field in comparison with the pure polymer composition (Fig. 6).

Moreover, with an increase in the graphene concentration, this shift towards an increase in the coercive field value increased more and more (up to a certain level of graphene concentration) (Fig. 6).

This fact is confirmed in our presented calculations (Fig. 4, 5).

In addition to calculating the switching times, here we calculated the hysteresis loop of pure PVDF and the hysteresis loop for the PVDF + Gr54H (H-C) model (Fig. 7) and obtained a clear increase in the width of the hysteresis loop, that is, an increase in the value of the coercive field, under the influence of the addition of graphene layer.

5. CONCLUSIONS

The calculations and MD simulations presented in this article unambiguously show that the coercive field increases and the polarization switching time decreases under the influence of graphene layers in thin layers of polymer ferroelectrics. These results of modeling and calculations, of course, require experimental verification. This can be done directly by production of samples of the type of PVDF layers deposited by the LB method on graphene layers or similar hetero-structures (of different thicknesses and / or different numbers of layers - similar, for example, to the work [13]). Following measurements of the hysteresis loops and switching times (similar to the works of the [12-16]) of these samples could be done for the proceeded experimental verification of obtained in this work results.

The results of performed investigation are undoubtedly important and relevant, since they demonstrate the direction of the necessary structural modifications of newly produced nanomaterials with predetermined and desired properties. In this case, we get the opportunity to regulate and control the switching times and the magnitude of the coercive field, which are extremely important parameters for new designed nanodevices (for example, memory devices or switching sensors) based on polymer ferroelectrics and graphene/graphene oxide layers and similar two-dimensional heterostructures.

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