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Modelling of the Piezoelectric and Pyroelectric properties of the Ferroelectric composites thin films based on the polyvinylidene fluoride (PVDF) with Graphene and Graphene Oxide layers and fibers

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ABSTRACT

Recent results in modelling and computational studies of new composite nanomaterials based on polymer ferroelectrics and graphene/graphene oxide structures are reviewed. Main findings of the computational molecular modelling and calculations of the plane layered and fibers nanostructures, as well as multi-layered structures, and the piezoelectric and pyroelectric properties of the composites, consisting of polyvinylidene fluoride (PVDF) thin films and graphene/graphene oxide are analysed. The piezoelectric and pyroelectric effects were modelled, both piezo- and pyro-electric coefficients were calculated for several models, using various methods from HyperChem software tool, including molecular dynamics (MD) simulation with quantum-chemical semi-empirical PM3 method. The results obtained provide important insights into our understanding of the mechanisms of piezoelectricity and pyroelectricity in these new nanocomposites, give us new perspectives for further studies of the ferroelectric polymer-graphene nanomaterials.

1. INTRODUCTION

Polymer ferroelectrics, such as polyvinylidene fluoride (PVDF) and its copolymers, have a set of common ferroelectric properties [1-3]. These properties have many practical applications, and most of them connected with piezoelectricity and pyroelectricity [1-7]. Among various types of polymer ferroelectrics, thin ferroelectric films fabricated by spin coating technique or by Langmuir-Blodgett (LB) methods are especially interesting [3]. These films have unique mechanical flexible properties which are very important for many applications, including biomedical ones. These properties are also characteristic to more complex composite ferroelectric materials and films based on polymer ferroelectrics combined with graphene (G) and graphene oxides (GO) [6, 8, 9], which are presented in [6-11]. These materials have a unique combination of ferroelectric properties (high polarization and its switchable properties, piezo- and pyroelectricity, etc.) and have high elastic and mechanical characteristics [11]. Polymer ferroelectrics PVDF and their copolymers, such as poly(vinylidene fluoride-trifluoroethylene) P(VDF-TrFE) [2, 3, 12], especially in the form of thin highly-ordered Langmuir-Blodgett (LB) films [3, 13, 14], are thoroughly studied (both experimentally and theoretically) [12-21]. Computational molecular modeling and calculations of physical properties of such ferroelectric polymers, were performed using HyperChem package [22] which contains semi-empirical quantum-chemical method PM3 as well as some other methods and approaches [19-22]. So, on the basis of the molecular models proposed and developed in [19], the approaches and algorithms were developed to describe piezoelectric properties in materials, such as PVDF and P(VDF-TrFE), and calculations of the piezoelectric coefficients were performed [20]. Then, using the method of molecular dynamics (MD) the mechanisms of polarization switching in such polymer ferroelectrics were investigated [12, 21], by quantum calculations by PM3 approximation at each step of MD run.

Further attempts to incorporate graphene-like structures (G and GO) into new composites with ferroelectric polymers PVDF and P(VDF-TrFE), were performed, both experimentally and using computational molecular modelling [6, 11, 23, 24]. Also, using the same MD run method, pyroelectric coefficients in PVDF and PVDF-G were calculated [24-26]. In this work we consider some complex compositions of this type, consisting of PVDF and G or GO [26-29]. We also give a short review of the models aimed at investigation of their piezo- and pyroelectric properties.

2. COMPUTATIONAL AND MODELLING DETAILS

Molecular models for pure PVDF (in ferroelectric β-phase), and for composites of PVDF with graphene PVDF-G and with graphene oxide PVDF-GO, as common ferroelectric systems were developed and investigated [6, 11, 23], using HyperChem tool [22]. Different computational methods, including molecular mechanics (MM, Amber, MM+, BIO CHARM) methods and quantum-chemical semi-empirical method (QM,PM3, ZINDO-1), in restricted Hartree-Fock (RHF) and unrestricted Hartree-Fock (UHF) approximations, were used.The molecular model of the PVDF chain (denoted by PVDF12) was proposed by us earlier in [19] and then was used and developed in [20, 21, 23] to determine the effect of the electric field on the polarization and for calculation of the piezoelectric coefficients, when applying an external electric field E (using the HyperChem software [22]). Figure 1 shows our original model [19] and its central part used in these piezoelectric effects calculations [21, 23].The aim of the usage of both the MM and QM methods used for

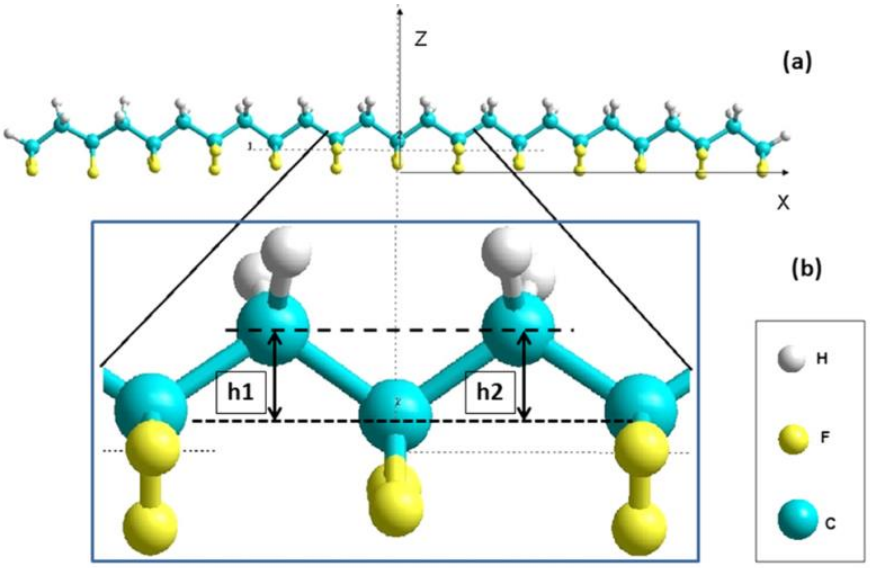

Figure 1. Model of PVDF chain: (a) PVDF with 12.5 units (marked PVDF12) and (b) Its central part.

molecular modeling is to search and to obtain the minimum of total or potential energy surface (PES), of the investigated molecular systems which correspond to optimal atomic configuration of the system. Finding of such optimal geometry of all system investigated is executed using the Polak–Ribere (conjugate gradient method) algorithm, which which is included into the HyperChem package [22]. These various computational methods were used for the detailed debugging, validation and testing of the models. For final current calculations of the optimized models the methods BIO CHARM and PM3 in RHF approximations were used mainly in this work.

Further, the G and GO models were developed and several models of their composites with PVDF were proposed [6, 11, 23]. Such initial models with 96 carbon atoms (Gr96H) in one layer are presented in Figure 2 (a, d), as well as G-layers models with PVDF chain in various configurations in Figure 2 (b, c, d, e, f). For calculation of the piezoelectric coefficients the special algorithm elaborated for thin films in our previous works [20-23] was used and now it is applied for fiber models too. These data obtained are presented and analyzed in Sec. 3.1 and 3.3.

For calculation of the pyroelectric coefficients it is necessary to know the temperature dependence of the polarization [1-3]. These data can be obtained by using the MD run approach [20 - 22], which is included in HyperChem tool too. This method was similarly used and developed early, for example, for investigation of the polarization switching time in similar thin ferroelectric films [21], using quantum method PM3. Now we use this MD approach to study the dynamics of polarization change, which take place as the temperature of the studied system rises, which enables us to calculate

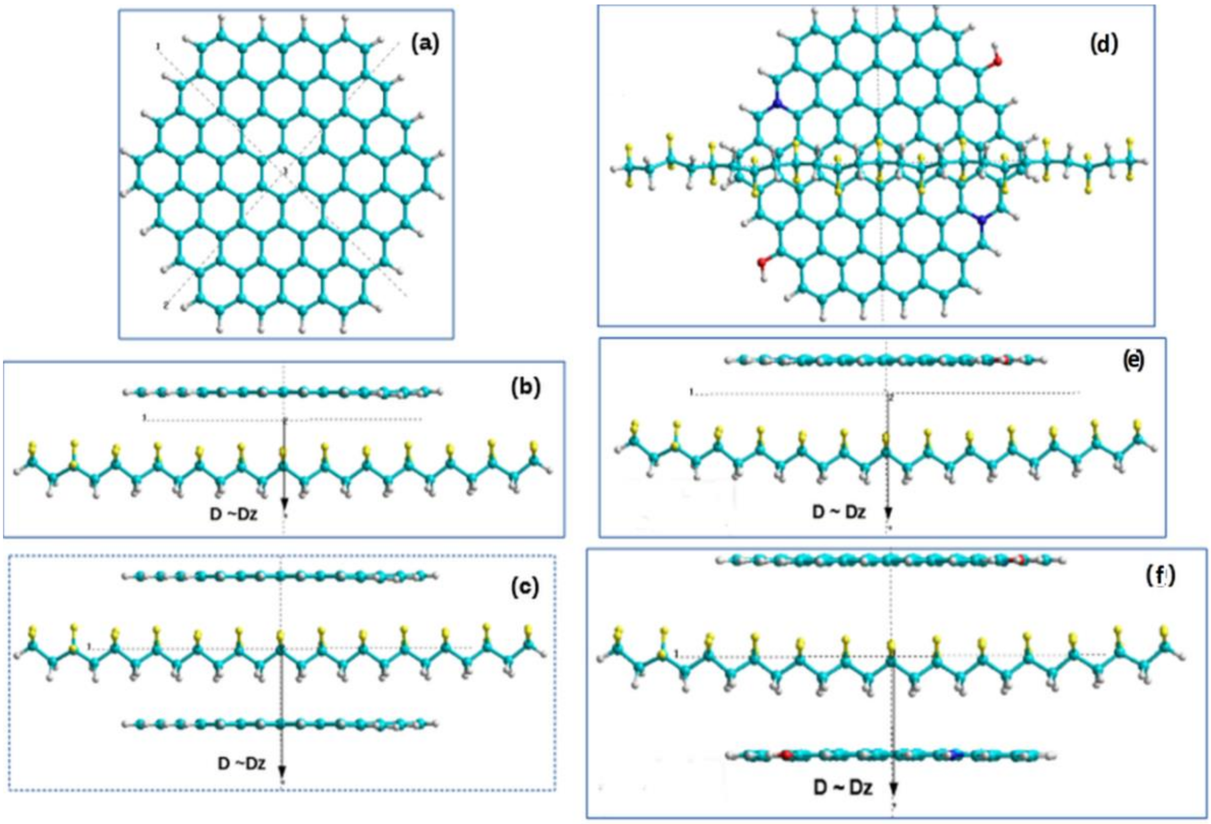

Figure 2. Initial states for several models for the composites of PVDF with G/GO:
(a) initial G layer model from 96 carbon atoms arranged by hydrogen atoms H (Gr96H), in Z view projection, (b) PVDF chain and G layer (PVDF12+Gr96H) in Y view, (c) PVDF and 2 G layers (PVDF12+2Gr96H) in Y view, (d) GO layer (with 2 nitrogen atoms N and 2OH groups) and PVDF chain (PVDF12+Gr96H2N2O2H) in Z view, (e) the same model in Y view, (f) PVDF and 2 GO (PVDF12+2Gr96H2N2O2H).

the pyroelectric coefficients. Such an approach was used to determine pyroelectric coefficients, for example, in our recent work for the PVDF-G composite [24]. In present work, additionally some more complex various model compositions, consisting of PVDF and either G or GO are considered and analysed in Sec. 3.2.

To check these molecular modeling and MD run data in our work [24] was proposed to perform the polarization calculations using the well-known relation from Landau-Ginzburg-Devonshire (LGD) phenomenological theory of the ferroelectrics with the first order phase transition (PT1) [1-3]. From the basic phenomenological theory of ferroelectrics it is known that the values of piezoelectric and pyroelectric coefficients are defined by relations described in [1-3], through the behavior of polarization P depending on temperature T by square root law. This behavior is determined by LGD theory parameters: Curie-Weiss constant *C*, Curie temperature T_0, dielectric constant e_0, phenomenological coefficients a, b, g and the value of the spontaneous polarization P_{S0} at the phase transition temperature $T=T_c$ for the case $E = 0$. Using such square root formula for PT1 from LGD theory in the dimensionless form with reduced temperature *t* (similarly as [3, 24]), it could be written:

$$P = P(E=0) = \pm P_{S0}\left[\frac{2}{3}\left(1+\sqrt{1-t}\right)\right]^{\frac{1}{2}},$$

$$P_{S0}^2 = -\frac{3}{4}\frac{\beta}{\gamma},\ t = 4\alpha\frac{\gamma}{\beta^2},\ \alpha = \frac{(T-T_0)}{C\varepsilon_0},\ T < T_0 \qquad (1)$$

For PVDF known data of the LGD theory coefficients and PT1 parameters [3, 24] lead to the value of $P_{S0} \sim 0.11$ C/m^2, that allow us to calculate *P*(*T*) dependence on temperature *T* and therefore pyroelectric coefficients. These data are used and analyzed in Sec. 3.2.

2. MAIN RESULTS OBTAINED FROM MOLECULAR MODELLING STUDIES AND DISCUSSION

3.1. Piezoelectric coefficients calculations

The mechanism of piezoresponse evolution of the composite was studied using our previous computational molecular models of PVDF chain (Figure 1(a) and (b)). The behavior of piezoelectric response in an electric field and the data on the average piezoelectric coefficients (calculated using algorithm [20, 23]): here **$<d_{33}> = (\Delta h_i/U)*\varepsilon$**, where **U** is voltage for the applied electric field value and **Δh_i** is a change of PVDF chain's skeleton height **h_i** (i=1, 2 as is shown in Figure 1) which takes place after geometry optimization at each step of calculations for every applied electric field value, **ε** is dielectric permittivity (ε = 10).

Additionally, the piezoelectric coefficient calculated with the use of the electromechanical coupling relation: **$d_{33} = 2Q\varepsilon\varepsilon_0 P$** (where **Q** is electrostriction coefficient, **P** is polarization) [20]. The symmetrized models were used both for graphene oxide based on graphene layer consisting of 54 carbon atoms (Gr54) and 96 carbon atoms (Gr96). These graphen oxides contained oxygen, OH groups (marked by Gr96N2O2H2), and COOH groups (marked shortly for simplicity by Gr96NO), surrounded by hydrogen (Gr54H, Gr96H) [6, 11, 23]. In these works several simplest models were developed for PVDF/Graphene oxide complex (Figure 2) and their piezoelectric coefficients were computed by the same calculation algorithms as described in detail [20, 23]. There we started with considering the simplest models of PVDF/Graphene oxide composites in the main three variants: 1) with H-side (hydrogen atom side) connected from PVDF to the graphene oxide, 2) with F-side (fluorine atom side) connected from PVDF to graphene oxide (these both first variants show approximately the same values of piezoelectric coefficients) and 3) Graphene Oxide/PVDF with both sides (sandwich type). The more complex models were considered too. It is interesting that the data obtained depend on the orientation of the GO layer: we compare two different orientations marked as "rot1" and "rot2." Similarly a more complex new multi-layered structure was considered in [27]. This work is developed further. The main calculated results are presented in Table 1.

Experimental results qualitatively correlate with those obtained in the calculations [6, 11, 20, 23, 30]. We can assume that experimental data obtained for the P (VDF-TrFE)-GO composite film at the low GO content can be associated with the model constructed for the case of PVDF with

Table 1. Calculated values of the piezoelectric coefficients <d_{33}> for PVDF-G/GO composites.

#	Type of the model structures	<d_{33}>, pm/V	Experimental <d_{33}>, pm/V
1	PVDF12/Gr54-H-side	-12.29	
2	PVDF12/Gr54-F-side	-12.16	
3	PVDF12 / Gr96N2O2H2	- 14.6	
4	PVDF12 /Gr96NO	- 13.5	
5	Gr96N2O2-H2 / PVDF12 / Gr96N2O2-H2	- 29.8	
6	Gr96NO /PVDF12/ Gr96NO (rot1)*	-22.8	
7	Gr96NO /PVDF12/ Gr96NO (rot2)*	-14.5	
8	Gr96NO /PVDF12/ Gr96NO (average rot1&rot2)	-18.7	
9	Multi-layered models [27]	-22	
10	PVDF12 [20]	-38.5	-20.0 … -39.0 (cited in [20])
11	P(VDF-TrFE) [6]		-38.0
12	P(VDF-TrFE)/GO [6]		-30.1
13	P(VDF-TrFE) [30]		-25.0 … -55.0
14	P(VDF-TrFE)/BPZT [30]		-18.0 … -40.0

graphene oxide from one side only. This leads to a reduction in the piezoresponse coefficient. This effect may be due to the possible effect of shielding from the graphene layer on the charges and the PVDF dipoles. An increase in the GO content most probably corresponds to the model where the availability of sandwich clusters in the composite is implied.

Quality manifestation of the effect of the graphene oxide grains on the piezoelectric properties of the composite films can be observed at the boundaries of graphene grains [6, 11]. That may lead to the formation of alternating layers of graphene oxide and PVDF on the boundary grains. Based on the results of our simulations the piezoresponse for sandwich structures PVDF/GO must be increased (Table 1). This is qualitatively observed from our piezo-response force microscopy (PFM) measurements [6, 11], and demonstrates a possible existence of such effects which take place due to their layered structure. This suggests that in the heterostructures under controlled alternating layers, this effect will be clearer and they can be controlled.

3.2. Pyroelectric coefficients determination by molecular dynamics method

Simulation of any system by molecular dynamics (MD) method allows us to obtain the temperature dependence of many physical characteristics for studied systems. The important characteristics for ferroelectrics is the polarization dependence on temperature changes (which is described by a well-known square root low [1-3]). Such simulation of the temperature dependence using special MD option in HyperChem tool [12, 21, 22] was made in

Table 2. Pyroelectric coefficients from MD calculated data [26] and obtained from experiments [25].

Type of model system or samples	*p*, μC/(m^{2}K) (average by several MD run)		V_G/V, V_{GO}/V	*p*, μC/(m^{2}K), experim. data [25]	
Pure PVDF12	34.1 - 40.8			39.5 for P(VDF-TrFE) (70:30)	
Composites	with G	with GO		Non-polarized samples with GO	Polarized samples with GO
PVDF12+Gr96H	135.8		0.65	-	-
2PVDF12+Gr96H	64.9		0.48		
PVDF12+2Gr96H	18.2		0.79		
2PVDF12+2Gr96H	22.9		0.65		
PVDF12+Gr96H2N2O2H		29.2	0.65	33.3	15.0
2PVDF12+Gr96H2N2O2H		57.2	0.48		
2PVDF12+Gr96H2N2O2H (MM+)		48.9			
PVDF12+2Gr96H2N2O2H (MM+)		27.4	0.79		
2PVDF12+2Gr96H2N2O2H		58.3	0.65		

this work. A special set of parameters necessary for MD run are described earlier [24], as well as the MD run calculation algorithm. The semi-empirical quantum method PM3 in RHF approximation was used for all these calculations and for each MD run step. These data allow us to obtain the polarization values for all the systems modelled under all changes of the temperatures and then to calculate the pyroelectric coefficients as **$p = \Delta P/\Delta T$** [1-3, 24]. For each temperature polarization was determined, through optimized dipole moment and volume of the full system, and corresponding value of the pyroelectric coefficient was calculated at each step.

From these data obtained the pyroelectric coefficient for the pure PVDF chain molecular model was calculated: **$p = \Delta P/\Delta T = \sim 34 - 41$** μC/(m^2*K), which is in line with many known data for PVDF and copolymers systems [1-3, 13-23] (see Table 2).

To check these data we additionally performed calculations using square-root relation (1) for polarization depending on temperature by Landau-Ginzburg-Devonshire (LGD) theory of the ferroelectrics [3, 24]: these data calculated are comparable with the data obtained by MD run. The MD runs were performed for several complex models [26] (some of which are shown in Figure 2 for the initial states). Corresponding data of the pyroelectric coefficients for all computed models [26] are collected in Table 2. These are important results, which show that G and GO components embedded into composite material lead to observed changes and differences in the pyroelectric coefficients values. This influence depends greatly on the G and GO content: for one G layer model we have a rise of the pyroelectric coefficient (as compared with pure PVDF), while for 2 G layers model (sandwich) value of the pyroelectric coefficient is nearly tenfold lower than in the case of one G layer model. The data obtained show that the values of the pyroelectric coefficients computed by the MD run method proposed are very close to experimental data from [25] as well as for PVDF and P(VDF-TrFE) from many other published data [1-3, 13-18].

3.3. Nanofibers composites

Piezoelectricity in macromolecule polymers has been gaining immense attention, particularly for applications in biocompatible, implantable, and flexible electronic devices. This paper [28] describes composite fibers of copolymer poly trifluoroethylene wiz. (P(VDF-TrFE)) with graphene (G) and graphene oxide (GO). Experimental and theoretical investigations were done to understand the effect of the G and GO concentration on polarization behavior of bulk composites and composite fiber microstructures. The electromechanical properties of the PVDF/G and PVDF/GO nanofibers are investigated in terms of piezoresponse mapping, local hysteresis loops, polarization reversal by advanced piezoresponse force microscopy (PFM) and Kelvin Probe Force Microscopy (KFM).

In order to understand the mechanism of piezoresponse evolution of the composite we used the models of PVDF chains, interacting with Graphene/GO layers, the data on its behavior in an electric field and the data computed for piezoelectric coefficients using HyperChem, as described above. But, the new curved models of the PVDF chains as well as the G/GO layers were developed [28] in these cases (see Figure 3 as a simple model case: pure PVDF (a) and with one curved Graphene layer (b)). Experimentally measured results qualitatively correlate with the data obtained in these calculations (Table 3) [28, 29].

An optimization strategy which determines the changes in the atomic configuration of studied clusters [20,23] assumes several steps of models, the first one considers an absence of electric field which allows to find the initial optimal atomic positions of modelled composite structure and to determine the initial optimal parameters of PVDF chain heights in its central part (h1, and h2). The second step of model considers an external electric field Ez with Z orientation (along the main polarization vector of PVDF), this model allows to find out the optimal geometry for new atomic configuration under action of electric field. The third step of model assumes the changes of the main parameters (h1 and h2, Figure 3) from initial optimal parameters, which allows to determine the deformation Dh1 and Dh2, and to calculate the corresponding values of voltage U = Ez*h and, finally, the piezoelectric coefficient $d_{33} = \varepsilon(\Delta h/U)$ was computed, using a dielectric permittivity value of ε = 10 [20, 23]. Comparison with the data known for d_{33} attributed to initial PVDF samples testifies that under the influence of graphene oxide layer the piezoelectric coefficient d_{33} of new composite structure is decreased. It has nearly three times

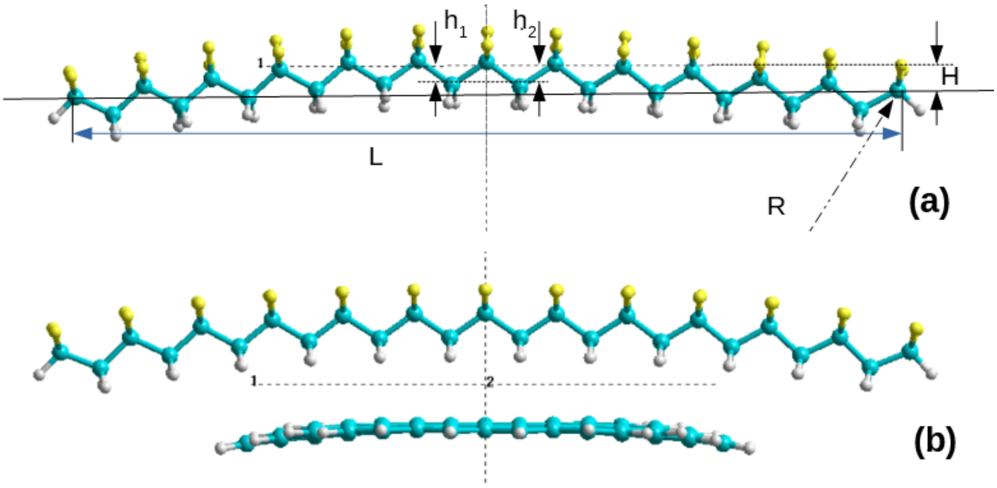

Figure 3. Model of curved PVDF chain (a) and curved composite PVDF-Graphene (b), R - radius of curvature, L - chord of curvature, H - hight of curved chain on length of chord L; h_1 and h_2 are similar as above in [20, 23].

Table 3. The piezoelectric coefficients d_{33} calculated for different types of structures of Graphene Oxide with OH and COOH groups and PVDF: for flat layer models and for curved fiber models (for comparison data from paper [20, 23] were taken, data present only in absolute values, without its negative sign).

#	Models Content	Flat models* d_{33}, pm/V	Films (experimental) d_{33}, a.u., V	Curved models d_{33}, pm/V	Fibers (experimental) d_{33}, a.u.
0	PVDF pure (chain)	38.5	7.5	22.3	20.8
1	PVDF/G54 1 side	12.2	-	-	-
2	PVDF/G54H 1 side	9.8	-	16.7	11.1
3	G54H/PVDF/G54H 2 sides (sandwich)	19.0	-	34.8	22.7
4	G96H/PVDF/G96H 2 sides (sandwich)	-	-	51.9	46.9
5	PVDF/GO1 1 side	14.6	5.9		
6	PVDF/GO2 1 side	13.5	-		
7	GO1/PVDF/GO1 2 sides (sandwich)	18.7	6.7		
8	GO2/PVDF/GO2 2 sides (sandwich)	29.8			

***** [20,23]

Abbreviations used in Table 3 are the following: GO1 is graphene oxide which contain COOH groups ($Gr96N_2O_2H_2COOH_2$, which was abbreviated as Gr96NO in [23, 28, 31]), GO2 is graphene oxide with OH group written as formula $Gr96HN_2O_2H_2$ above.

lower value: d_{33} = 14.6 pm/V (or pC/N) for the simple flat models (with one side H or F of PVDF chain—Figure 2a), which interacting with one GO layer (with OH groups), as compared with the average value of the pure PVDF d_{33} = 38.5 pm/V (pC/N). It is important to note, that the sign of d_{33} coefficient is negative in all cases as it was established in [22, 23] for the initial pure PVDF, it is caused by specific mechanism of PVDF chain deformation under an applied electric field. In the case of flat with double graphene oxide layers (sandwich model structure) the piezoelectric coefficient d_{33} is increased to the value of d_{33} = ~ 29.8 pm/V (pC/N) (Figure 2b, and see in Table 2, data for flat models).

The experimental results qualitatively correlate with those obtained in the calculations (see Tables 2 and 3). We assume that the experimental data obtained for the composite with small amount of graphene oxide correlate to the model constructed for the PVDF chain interacted with graphene oxide from one side only. The results obtained for this case show a reduction in the piezo-response as well as in the piezoelectric coefficient. From the other side, piezoelectric properties of the composites with larger GO content correspond to the model assuming the sandwich-like clusters in the composite. The experimental data testify a decrease in the piezoelectric signal in these composites which is caused by statistical dispersion and disorientation of graphene oxide layers and PVDF chains (or layers). Uncontrolled thickness of the individual layers of graphene oxide and PVDF component can also affect piezoelectric properties of the composites. Statistical disorder obtained in these cases could not yield an exact match with the simulation performed. However, even at low concentrations, the effect of molecular ordering is observed, and for 20% GO composite the probability of the formation of sandwich structures (as proposed in our modeling) is quite significant. Furthermore, in the case of controlled hetero-structures we can consider a much greater effect and results will be closer to experimental.

The case of model with curved PVDF chain and Graphene layers were considered and discussed here also [6, 26, 27, 29-30]. This situation could be corresponding to the fiber′s surface—it is a curved surface with some radius R. In the experimental case it is approximately ~R ~50...100 nm. But in our modeling, we use approximately R ~10 nm (and more) for most bright and expressive influence of such curvatures, which imitates the curved surface. This radius could be simply determined from usual geometry using formula (see about of some geometrical chord (with high H and length L) determinations on Figure 3a:

$$R = (H^2 + L^2/4)/(2H) \qquad (2)$$

It is known from the literature that for the case of curved (or flexible) polymers such as PVDF and related materials, the piezoelectric coefficients are changed in this case [31, 32]. But all computed data used here for our calculation of d_{33} shown the series of such curved models in this case are similar as in our previous flat models and following results of calculated piezoelectric coefficients are presented in Table 3 (last two columns for curved models).

It should be noted that different types of oxidation (O, OH, COOH etc.) may notably change the functional properties of the composites and appropriate calculations becomes to be quite difficult for conventional computer modelling while these models will be considered in our further works. However, despite on used different units for values of the piezoelectric coefficient, current results clearly show the same trend of changes both for the computed and measured data (see Tables 1, 2).

4. CONCLUSIONS

The developed models [19-23] and MD run methods [24] allowed us to calculate the temperature dependence of the polarization and calculate the values of the piezoelectric and pyroelectric coefficients for pure PVDF model and for the composites models of PVDF with Graphene and Graphene oxide layers [26, 27, 28, 30]. The values of the piezo- and pyroelectric coefficients obtained for pure PVDF are in line with many known data, the data computed for composite materials are new and predict complex nonlinear behaviour which may take place if Graphene content changes. In some cases (with one G layer models) it was shown that in proposed and developed composite systems the value of the pyroelectric coefficients could be higher than in the initial matrix of pure PVDF materials, while in other cases (for sandwich G models), it can be lowered as compared with initial pure PVDF. These questions need further deepest studies. These data obtained are new and very important. The data obtained predict the novel features of the behaviour of such new composites system based on graphene and ferroelectric copolymers. It is worth noting that the calculated values of the pyroelectric coefficients for various composites from PVDF with G/GO components are close to the values, which are obtained from pyroelectric currents measurements for similar P(VDF-TrFE)/GO composites samples [25]. But, it must be emphasized that these samples were prepared by crystallization from a solution and this fabrication method is different from highly ordered Langmuir-Blodgett technique. For further studies we must focus on the fabrication of the ultrathin Langmuir-Blodgett PVDF or P(VDF-TrFE) films [3, 15-17, 21, 23] deposited directly onto a G/GO layer, which allow us to obtain a very highly ordered multilayered ferroelectric composites with excellent polarization and piezoresponse, as well as pyroelectric properties. This approach must be the next step on the way of creating such new high-quality composites for multifunctional applications. The models developed here predict the important new features and behaviour of these new graphene-PVDF-based composites systems and exactly show us this new way.

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