

## Research Article

# Ferroelectric Composites Based on PVDF/P (VDF-Trfe) Ferroelectric Films and Graphene/Graphene Oxide: Experimental Observation and Molecular Modeling

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## Keywords

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- Graphene/graphene Oxide
- Composites
- Molecular modeling
- Piezoelectricity

## Abstract

Recent advantages in experimental and computational studies of new composite nanomaterials based on polymer ferroelectrics and graphene/graphene oxide are presented. Main results of the computational molecular modeling of various nanostructures and the piezoelectric properties of the composites from polyvinylidene fluoride (PVDF)/poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) films and graphene/graphene oxide (G/GO) were reviewed and analysed in comparison with the experimental data at the nanoscale, particularly with atomic force and piezo-response force microscopy (AFM/PFM) data. The performed computational molecular modeling of the graphene/graphene oxide (G/GO) and PVDF ferroelectric polymer composite nanostructures, were studied by the different methods using HyperChem tool: molecular mechanics (MM) methods (BIO CHARM), quantum mechanical (QM) calculations based on density functional theory and semi-empirical PM3 method. Experimentally the switching behavior, piezoelectric response, dielectric permittivity and mechanical properties of the films were investigated and found to depend on the presence of G/GO concentration. Experimental results qualitatively correlate with those obtained in the calculations. Particularly, computed data of the piezoelectric coefficients  $d_{33}$  for developed PVDF-G/GO models are in line with observed experimental behavior with concentration changes of GO components. The results obtained in the reviewed and analysed present study provide important insights into our understanding of the mechanisms of piezoelectricity in such new nanocomposites, give us new prospective for further creation, development and applications of novel ferroelectric polymer-graphene/graphene oxide nanocomposites as multifunctional nanomaterials.

## ABBREVIATIONS

GrPVDFnc: Graphene-PVDF nanocomposites

## INTRODUCTION

The attention of researchers to the development, creation and investigation of the properties of new nanocomposite materials is constantly growing all over the world. Of special interest here are polar and ferroelectric materials, since they have numerous applications in a wide variety of fields, owing to their properties, such as polarization, piezoelectricity and pyroelectricity, etc. [1-5], particularly at the nanoscale level too [3], and for nanobiomaterials purposes [4,5]. Among these materials, new nanocomposites based on the combination of the polymer ferroelectrics and graphene /oxide graphenes 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 is important for many multifunctional applications, both traditional and completely new (for example, for the molecular storage systems and environmental protection, in the nanobiotechnology, and nanobiomedicine, both for sensors and as new smart bioimplants) [11]. The study of these new objects have a special interest, which is focused on finding a composite material based on polymers and low-dimensional 2D nanostructures of carbon (graphene (G), carbon nanotubes (CNT)), as their exhibits an unusual and prospective electrical and mechanical characteristics. The study of such systems is dictated also by the urgent necessity to overcome some limitations in mechanical and electrical parameters of usual ferroelectric polymers as alone.

Polymer ferroelectrics, especially such as poly(vinylidene fluoride) (PVDF) and poly(vinylidene fluoride-trifluoroethylene)

P(VDF-TrFE) copolymers [2,3,12], and especially in their formation as a thin high-ordering Langmuir-Blodgett (LB) films [nn] are already sufficiently well studied [13-29], (both experimentally and theoretically, including using detailed molecular modeling [22-29]) and have numerous applications.

Graphene and graphene oxides (G/GO) [6-11], as well as other carbon materials (for example, carbon nanotubes (CNT) [30-32], which after it unroll turn into a plane is forming a regular layer of graphene) also have a lot of research, especially after the works [33,34], which led to the obtaining of the Nobel prize.

But the joint combination and study of the conjugate properties of such nanomaterials as PVDF-Graphene, PVDF-GO and P(VDF-TrFE)-G/GO composites based on these two main components have begun relatively recently. Although new interesting and important results have already been obtained, studies of the properties and prospects of such nanocomposites of PVDF-G type are only unwrapped and expanding, and many new data are still to be obtained here. Recent studies show, that their properties can be varied by using different polymers and crystalline ferroelectrics, which gives an additional advantage for their use in functional devices, for example, such as pyro- and piezo- sensors, ultrasound transducers etc. In recent past, composites with ferroelectric polymer matrix based on PVDF/P(VDF-TrFE) have been explored by many researchers [35]. This is due to fact that, these polar polymers base is characterized by most high piezoelectric coefficients as compared to other polymer materials, and at the same time graphene particles embedded in a ferroelectric polymeric matrix is expected to provide highly unipolar states and a large electromechanical and pyroelectric activity. Additionally it is expected that, the polymer matrix doped with graphene can exhibit anomalous low coercive field without influencing its piezoelectric properties, which provides an additional degree of freedom for tailoring the properties of composites. Thus, it also allows the use of these composite ferroelectric polymer-based materials in various piezoelectric and pyroelectric sensor systems with wide multifunctional applications. Polymer/graphene composites and polymer/carbon nanotube (CNT) composites have also been studied using computational molecular mechanics (MM) and molecular dynamics (MD) methods [36]. However, there are only a few reports of the computational molecular modeling of the interfacial properties of polymer/GO composites [37], so further computational and molecular modeling studies in this field are urgently needed.

Experimentally such new nanocomposite P (VDF-TrFE)/GO thin films were recently designed and investigated using piezoresponse force microscopy (PFM) in our group [6,11]. The distribution of the local piezoresponse poling area and the effect of the graphene sheet on P(VDF-TrFE)/GO thin films were measured: increasing the GO component from 0% to 2% was found to reduce the piezoresponse, with the value of the experimentally measured effective piezoelectric coefficient  $d_{33eff}$  dropping to only half that observed for pure PVDF [28]. In order to identify possible reasons and mechanisms for this behaviour, computational molecular modeling of G/PVDF and GO/PVDF systems was performed in the work reported in the present paper [38,39]. The resulting computational data were

analysed and compared with experimental data obtained from PFM observations of similar composite systems [39].

The present brief review is devoted to discussing and analyzing of such recently obtained results on PVDF-graphene nanocomposites, both in the experiment and in modeling as well the further prospective of the studying their properties. But the most focus in this review will be devoted to computational molecular modelling of their structures and calculations of these nanocomposites properties using HyperChem molecular modelling tool [38].

## EXPERIMENTAL DETAILS

Various experimental approaches were used for these composites fabrication in different works. Composite thin film of the copolymer P (VDF-TrFE) with graphene oxide (GO) were prepared by spin coating method in considered works [6,11]. The obtained films were investigated using piezoresponse force microscopy (PFM).

The preparation of nanocomposites for experimental studies were described in details in [6]. Here we present only short description for main basic features. Initial graphene oxide (GO) was prepared by the chemical exfoliation of graphite (Graphite powder, < 45 mm, 99.99%, Sigma-Aldrich) [6,11,40]. For the composite sample preparation, poly (vinylidene fluoride-trifluoroethylene) copolymer with a TrFE content of 30% was used. The P (VDFTrFE) copolymer was chosen, because it favors crystallization from a solution or melt directly to the ferroelectric b-phase. Composite films with different concentration of GO (0–2 wt%) were prepared by spin coating technique using P(VDF-TrFE)-GO solutions with film thickness of 500–550 nm as described in Refs. [6,11,40].

Atomic Force Microscopy (AFM) measurements were carried out using a Veeco AFM Multimode Nanoscope (IV) MMAFM-2, Veeco microscopy. PFM measurements were performed using AFM instrument with an external lock-in amplifier (EG&G 5205 Lock-in Amplifier) used to apply ac and dc voltages. Local piezoelectric properties of the films were visualized simultaneously by using AFM in contact mode and PFM methods [6,11,41,42]. The PFM technique is based on the detection of the mechanical response of the sample to an applied electric voltage due to converse piezoelectric effect. A conductive Si cantilever (Nanosensors, nominal force constant 15 N/m) was used to both apply the voltage to the surface and to measure mechanical response of the sample. The details of the methods and measurements technique of the voltage applied to the sample were described in Refs. [6,11,41- 43].

## COMPUTATIONAL AND INITIAL MODELING DETAILS

In the works [6,11,39], several types of molecular models for PVDF (b-phase)-graphene and GO (PVDF-G/GO) ferroelectrics systems were developed and investigated using HyperChem tool [38]. In all cases were used the same approaches for PVDF modeling as in Refs. [25-29]. Different computational methods were used, including molecular mechanics (MM) methods (such as BIO CHARMM), quantum mechanical (QM) self-consistent field (SCF) Hartree-Fock (HF) calculations based on density functional

theory (DFT) and semi-empirical method (PM3), in restricted Hartree-Fock (RHF) and unrestricted Hartree-Fock (UHF) approximations. The main approach used here for molecular modeling is to obtain the minimum of the total, or potential energy surface (PES), of the all studied molecular systems in both the MM and QM methods. The optimization of molecular geometry is executed using the Polak-Ribiere (conjugate gradient) algorithm, which determines an optimized geometry at the minimum energy point (through PES run to the minimum point) [38]. The initial molecular model of the PVDF chain was used and necessary parameters were taken from paper [28] (Figure 1a, b) with 12.5 elementary molecular units similar as in [25-27]. The approach for the modeling and calculations methods of PVDF chain behavior in electrical field (Figure 1c) and the algorithm for computed data of piezoelectric coefficients were also used from work [28].

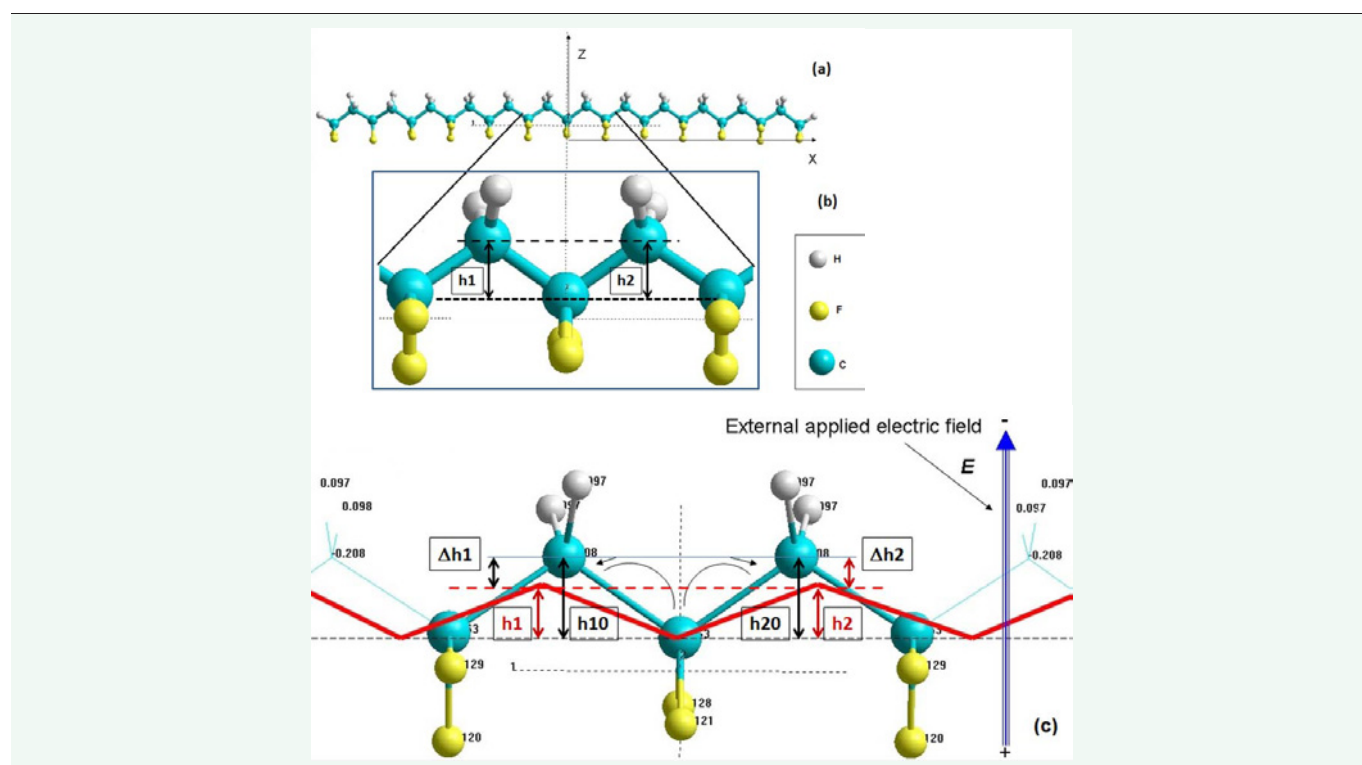
## RESULTS AND DISCUSSION

### Main experimental data

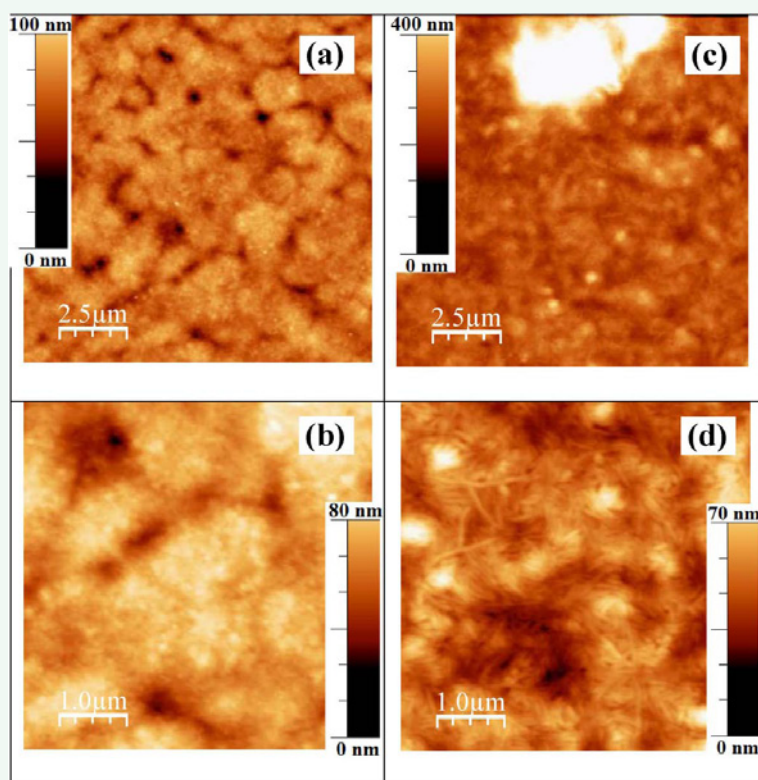
The X-ray diffraction (XRD) for several studied samples was performed in the work [6]. In initial P (VDF-TrFE) sample, two main phase (a and b) was observed. However, in the XRD patterns of the GO/P (VDF-TrFE) composites, peaks related to only b phase of P (VDF-TrFE) was present. The formation of the b phase in this case can be explained by the adsorption of PVDF chains onto GO sheets [44]. An increase in the inter-planer spacing observed in composite from 8.42 to 8.84 Å was evident when compared to pure GO sample. This result suggests that the incorporation of GO particles in polymer matrix governs the

polymer chain movement and consequently affects the molecule polarization. PVDF-GO composites with varying composition were investigated at the local level to understand the underlying mechanisms of the ferroelectric behavior in these films. Figure 2 demonstrates the morphology of P (VDF-TrFE)/GO as observed by AFM measurements. The average thickness of film as obtained from the AFM analysis was found to be in the range of 200–400 nm. In addition, it is observed that GO particles present on the surface and in the body of the film have a size of less than 1 μm. Roughness and average grain size were also found to increase for GO composite. The RMS roughness and average grain size of GO and its composite were found to be 11.8 nm, 83.3 nm and 1.2 μm, 3.7 μm, respectively [6]. Figure 3 shows image of P (VDF-TrFE)-graphene thin films after poling. Here, we present only some examples of the experimental results obtained. More detailed experimental data are given in Refs. [6,11,39]. To investigate macroscopically a piezoelectricity of the films, the domain structure was written in an area of 10×5 mm<sup>2</sup> (as illustrated in Figure 3) by applying dc voltage (−50 V/+50 V) more than its coercive voltage with a slow scanning velocity ( $V_{tip} = 2.5 \text{ mms}^{-1}$ ).

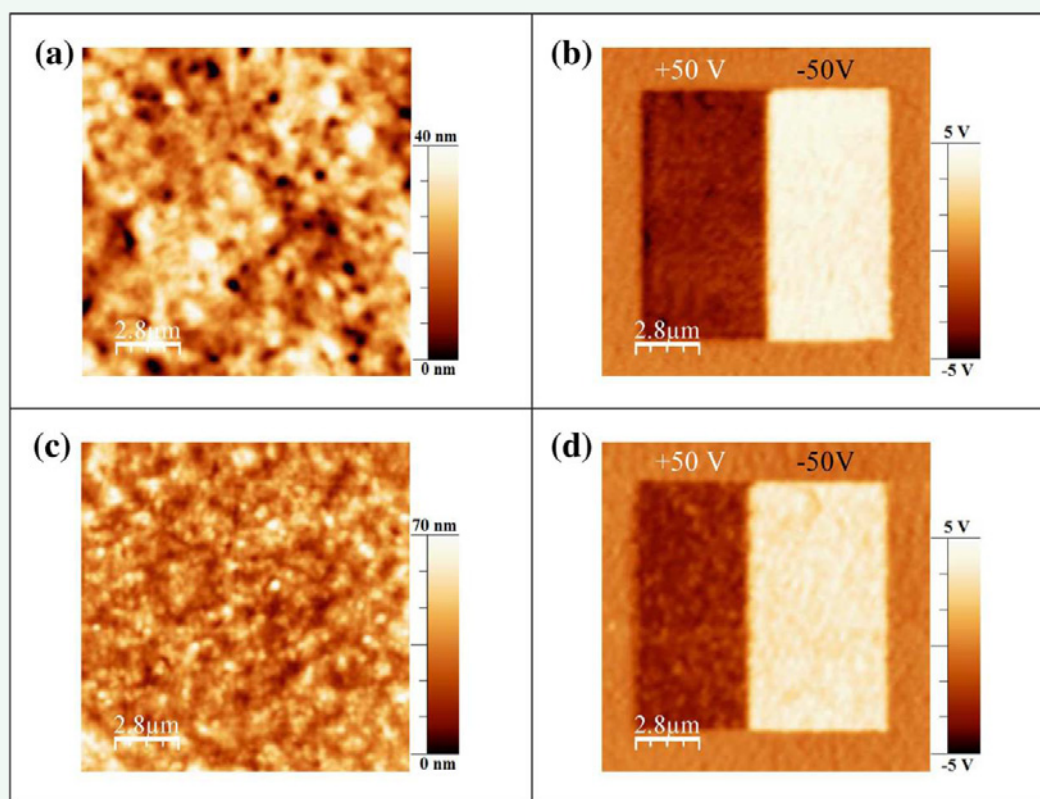
After calibration were obtained the next values of  $d_{33\text{eff}}$  for our films: 38.0 pm/V for pure P (VDF-TrFE) and 30.1 pm/V for P (VDF-TrFE)/GO composite films [6]. It is seen that the pattern of polarization is similar to the local piezoresponse hysteresis loops (Figure 4) [6,11]. Interesting that this data is very close to calculated from model [28]. The experimental results obtained (Figure 4) clearly show that as GO concentration rises, the piezoelectric coefficient  $d_{33}$  (which is effective and registered directly in mV units in this case) changes its value tending to decrease.



**Figure 1** Model of PVDF chain ([28,39]): (a) – PVDF with 12.5 units (marked as PVDF12) and (b) – its central part, (c) – PVDF chain deformation under applied electrical field: red color line show the deformed PVDF chain skeleton after relaxation in the applied external electric field  $E$ .



**Figure 2** AFM images of the P (VDF-TrFE) and P (VDF-TrFE)-graphene oxide thin films. (a and b)-P (VDF-TrFE) and (c and d)-P (VDF-TrFE)-graphene oxide thin films.



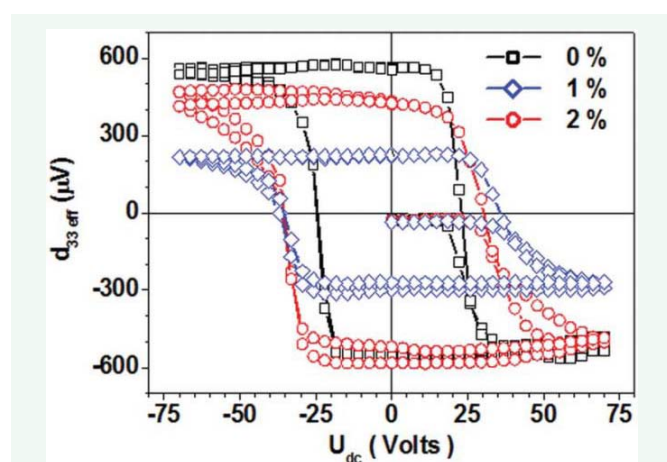
**Figure 3** AFM Topography (a and c) and PFM image (b and d) for P(VDF-TrFE) (a and b) and (c and d) P(VDF-TrFE)-graphene oxide films.

## Computational modeling results and discussions

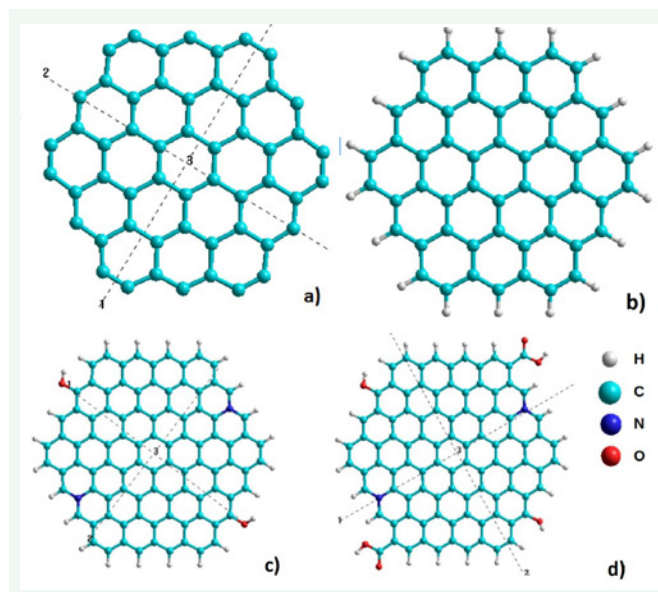
To understand the mechanism of piezoresponse evolution of the composite, we used our previous computational molecular models of PVDF chain (Figure 1a, b), its behavior in electrical field (Figure 1c) and computed the data for piezoelectric coefficients [28]. The symmetrized models of graphene oxide based on graphene layer consisting of 54 carbon atoms (Figure 5a, b) and 96 carbon atoms: with oxygen and OH groups (Figure 5c), marked by Gr96N2O2H2, and with COOH groups (Figure 5d), marked shortly for simplicity by Gr96O, as arranged by hydrogen were used [6,11,28,39].

In these works were proposed and developed several simplest models for PVDF/Graphene oxide complex (Figure 6) and computed their piezoelectric coefficients by the same calculations algorithms as declared in Refs. [25,28,39]. Here firstly it were constructed the molecular models of PVDF/Graphene oxide composites in 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) as show in Figure 6. For deeper understanding, here were considered two versions of the mutual rotation of the graphene layers in relation with PVDF chain. The main calculated results are presented in Table 1.

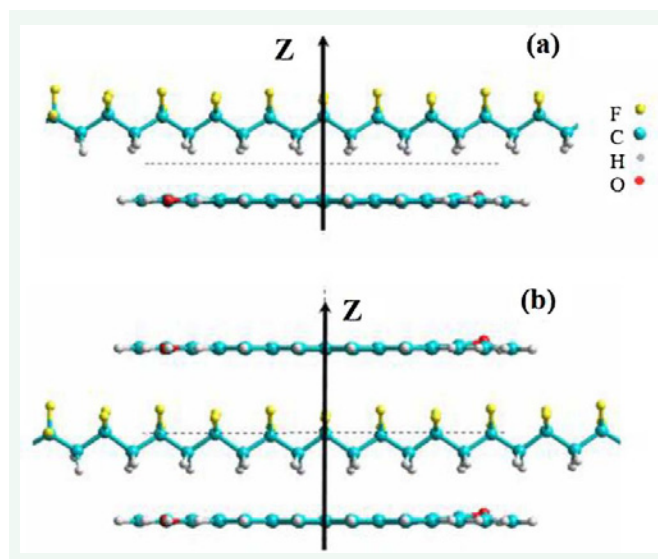
Experimental results qualitatively correlate with those obtained in the calculations (Figure 7). We can assume that experimental data obtained for the P (VDF-TrFE)-GO composite film can be associated with the model constructed for the case of PVDF with graphene oxide from one side only. This leads to a reduction in the piezoresponse coefficient. Increasing of GO content most probably corresponds to the model assuming sandwich clusters in the composite. Experimentally, piezo signal is reduced for 1% of GO content due to the statistical disorientation of graphene oxide and PVDF layers, and uncontrolled thickness of the individual layers of graphene oxide and PVDF. Statistical disorder does not yield an exact match with the simulation. Even



**Figure 4** Piezoresponse hysteresis loops of P(VDF-TrFE)-graphene oxide thin films with different concentrations of GO.  $|U_{ac}| = 3$  V, 50 kHz.



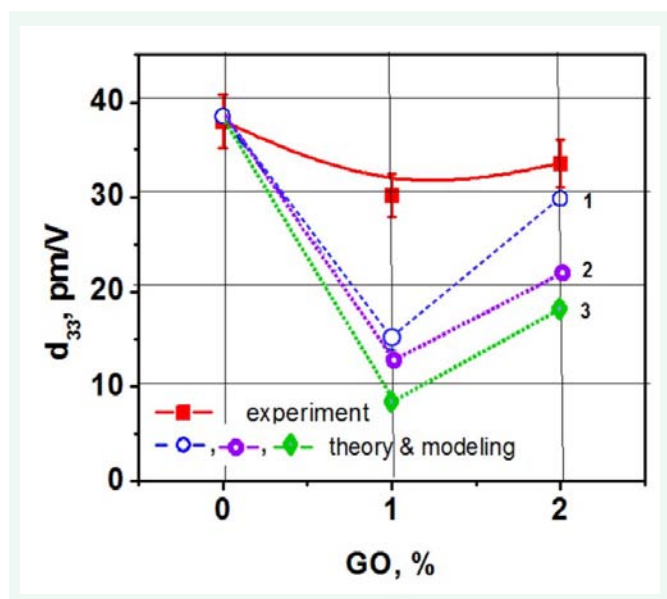
**Figure 5** Upper line – Graphene models from one layer: a) with 54 carbon atoms (marked as Gr54) and b) with 54 carbons atoms arranged by hydrogen atoms (marked as Gr54H). Down line - Graphene oxide layers models from 96 carbon atoms arranged with hydrogen atoms: (a) with 2 OH group and 2 nitrogen atoms (marked as Gr96N2O2H2), (b) the same, but with additionally 2 COOH groups (marked shortly as Gr96NO).



**Figure 6** Models of PVDF/GO structures, interacted with one H-side. (a)-PVDF/GO, Type 1, (b)-interacted with both H- and F-sides: sandwich structure GO/PVDF/GO, Type 2.

at low concentrations, there is the effect of molecular order, but for these composites the probability that the sandwich structures are formed is quite significant. In the case of the controlled hetero-structures one can assume much greater effect.

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 (Figure 8). Thus graphene oxide grain has a layered structure with separated



**Figure 7** Concentration dependencies of the piezoelectric coefficient after poling. For theoretical data: upper blue dashed lines correspond to the GO model with COOH groups, and two lower dashed lines data – for the GO models with OH groups in GO layers.

layers. Separated sheets are more ease at the edges of the sheets. So, the grain boundary will split on the graphene oxide grains and PVDF fills all cavities in the composite. 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 PFM measurements (Figure 8a). Figure shows the contour boundaries of graphene grain. In the grain boundary an increased intensity of piezoresponse was observed (Figure 8b). This is possibly due to the alternating structure (Figure 8c). This suggests that in the heterostructures under controlled alternating layers, this effect will be clearer and they can be controlled.

To explain this observation more complicated multi-layered model of PVDF-GO composite structures were recently proposed and developed (Figure 9,10) [45,46]. For example, the influence of G/GO composition layers (described above), which is observed experimentally by atomic and piezo-force microscopy methods [6] can be considered in the frame of these new proposed models. One of the peculiarities of these new developed models are the curvature of the optimized structural layers (Figure 10 c,d), which could be close to observed in experiments [6]. The computed value of piezoelectric coefficient is  $\sim 22$  pm/V for the last models (Figure 10c, d), that is in line with [6,11,28,39]. This new model now is in progress for further detailed studies.

## CONCLUSIONS

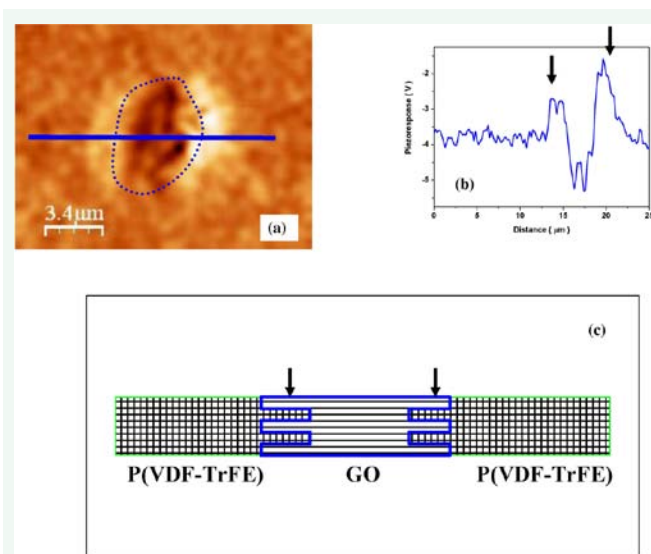
The summarized models of PVDF/Graphene oxide composite with oxygen and OH groups and with COOH groups arranged by hydrogens were used for PVDF/Graphene oxide complex viz. 1) with H-side (hydrogen atom) connected from PVDF to graphene oxide, 2) with F-side (fluorine atom) connected from PVDF graphene oxide and 3) Graphene Oxide/PVDF with both

sides (sandwich type). The results of theoretical modelling show qualitative agreement of the piezoelectric properties with the experimental data obtained considering the PFM images with area poling and justify a decrease of piezo-coefficient  $d_{33eff}$  values under the influence of G/GO layers. Modelling of sandwich structures of PVDF/GO and PFM measurements on the graphene oxide grains show the prospects of the multilayer structures of these composites with a significant increase in piezoelectric parameters. The P (VDF-TrFE)/GO ferroelectric films prepared by the spin coating technique were investigated by the PFM technique. The writing of polarization areas was done by biasing the AFM tip in the course of scanning during a fixed time. Molecular modeling results were found to compliment the experimental PFM measurements.

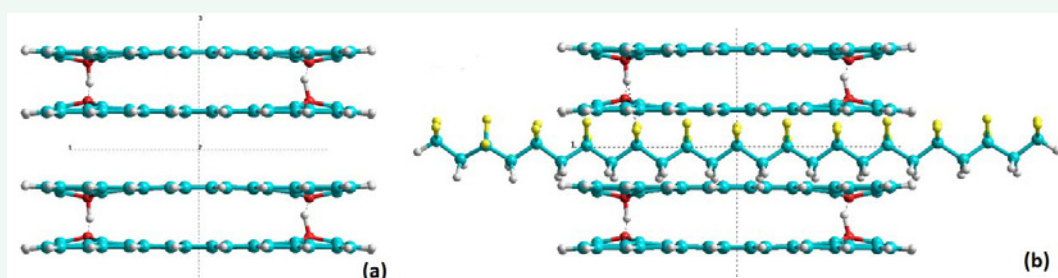
**Table 1:** The piezoelectric coefficients  $d_{33}$  calculated for different types of structures of Graphene Oxide with OH and COOH groups and PVDF (electric field  $E_z \sim 514$  GV/m, for comparison the data from our paper [23] were taken).

#	Type of structure	$\langle d_{33} \rangle$ , pm/V
1	PVDF12/Gr54-H-side	-12.29
2	PVDF12/Gr54-F-side	-12.16
3	PVDF12 / Gr96N202H2	- 14.6
4	PVDF12 /Gr96NO	- 13.5
5	Gr96N202-H2 / PVDF12 / Gr96N202-H2	- 29.8
6	Gr96NO /PVDF12/ Gr96NO (rot1)*	-22.8
7	Gr96NO /PVDF12/ Gr96NO (rot2)*	-14.5
8	Gr96NO /PVDF12/ Gr96NO(average from above rot1 and rot2)	-18.7
9	PVDF12[28]	-38.5*
10	P(VDF-TrFE) [6]	38.0**
11	P(VDF-TrFE)/GO [6]	30.1**

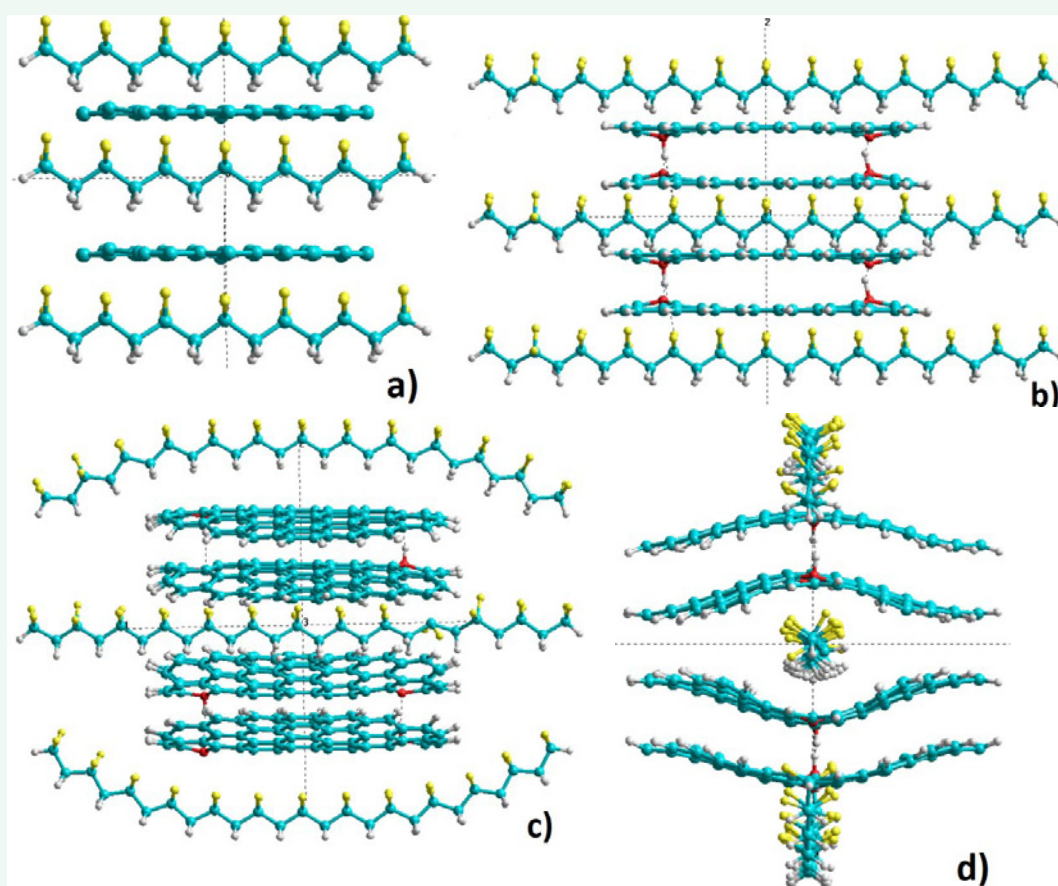
\*) Data computed in [28] for pure PVDF chain from 12.5 units.  
\*\*) Data obtained experimentally in [6] from PFM measurements.



**Figure 8** PFM image (a), one of dots-GO grain, (b-cross-section along blue line L and (c)-model of P (VDF-TrFE)-GO-P(VDF-TrFE). Arrows indicates the boundary areas.



**Figure 9** Models with two hydrogen-bonded G layers and PVDF chain: a) only 2 double layers GO model with 2 H-bonds, b) interacted PVDF chain between 2.



**Figure 10** Several models of multi-layered GO-PVDF structures: a) 3 PVDF6 chains and 2 GR54, b) 3 PVDF12 chains and 2 double H-bonded GO layers, c) and d) last optimised model by MM method (BIOCHARM) with incurved structures in Y and X plane of HyperChem.

The computational studies of the PVDF-G/GO molecular models were constructed and their optimized structures were investigated using various methods from HyperChem package and on the developed algorithm for piezoelectric coefficient calculations from our previous work [23]. Analysis of switching behavior of the films obtained from the distribution of local piezoresponse signal after poling and computational molecular modeling for several molecular order of P(VDF-TrFE) and GO suggests that two main order types can be realized in the composites: two layers P(VDF-TrFE)/GO and three-layer sandwiched GO/P(VDF-TrFE)/GO. Two layers P(VDF-TrFE)/GO structures are associated with decreased d33 value, whereas

sandwich structure GO/P(VDF-TrFE)/GO favors to increased magnitude of the piezoresponse. Mixed and statistic distribution of these possible order types in the P(VDF-TrFE)/GO ferroelectric films with small ( $\gg 1-2\%$ ) GO concentration may be the cause of the ferroelectric anomalies observed for these composites. Computed data of the piezoelectric coefficients d33 for developed PVDF-G/GO models are in line with observed experimental behavior with concentration changes of GO components.

The results obtained have an important insight into our understanding of the mechanisms of piezoelectricity in such composite new nanomaterials and give us new prospective for further creation and applications of ferroelectric polymers-

graphene/graphene oxide composite nanomaterials. Thus, it appears that the total polarization of the nanocomposite decreases with increasing GO concentration. However, these data require further investigation to correlate them with the computed and measured piezoelectric coefficient data discussed above. Another research direction involves the fabrication of ultrathin Langmuir-Blodgett PVDF or P (VDF-TrFE) films [3,15-17,21-24] deposited directly onto a G/GO layer in order to obtain highly ordered multilayered ferroelectric composites with excellent polarization and piezoresponse properties.

## ACKNOWLEDGEMENT

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