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On the interactions between poly(ethylene oxide) and graphite oxide: A comparative study by different computational methods

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The aim of this work is to investigate polymer–substrate interactions for a polymer nanocomposite material: poly(ethylene oxide) (PEO) confined in graphite oxide (GO). Six discrete and simplified models (one for PEO and five for GO) have been chosen in order to reproduce the most likely PEO–GO interactions. Twelve potential interaction energy curves have been built using the models and curve minima have been optimized using the 2nd order Møller-Plesset perturbation theory (MP2)/6-31+G(d) method. The intermolecular interactions have been analyzed in terms of distances, stabilities, and bond critical points properties revealing several dispersion assisted π-interactions and the most stable hydrogen bond interaction between the hydrogen of the GO hydroxyl groups and the oxygen of the PEO. MP2 results have been compared with five density functionals developed by Truhlar and Zhao (M05, M05-2X, M05-2X, M06-HF, and M06-L).

I. INTRODUCTION

Following the discovery of new carbon forms1 (fullerenes, carbon nanotubes, and more recently graphene), a large amount of work has been carried out to date to design and produce composite materials incorporating these complex nanostructured carbons into polymer matrices. The main driving force behind this work has been the modification of the polymer properties, giving rise to improved materials performance: light materials with enhanced mechanical properties, improved fire resistance, controllable viscosity or high electrical conductivity, for instance.

On the other hand, the recent progress in the preparation of graphene-based materials is giving rise to a new revival of the area of graphite intercalation compounds, which started about 150 years ago with the work of Shafhaentl2 obtaining the exfoliation of graphite in 1841, and continued with the work of Brodie3 in 1859, producing graphite oxide for the first time. In this context, graphite oxide (GO) offers unique opportunities associated with its sub-nanometer multilayer structure, hydrophilic character, and possibilities for the large-scale production of high-quality specimens. Being a precursor of graphene by reduction,4,5 GO has attracted the recurring interest of the chemical community over many years. Numerous studies have been done in order to unveil its structure, from the early studies of Hofmann,6 Russ,7 Scholz and Boehm,8,9 and Nakajima10 until the generally accepted structures of Lerf and Klinowski11,12 or Szabó.13 Concerning GO, as the base for intercalation compounds, it has been recently reported that GO can accommodate water14 and other different solvent molecules,15 cationic surfactants,16 alkylamines,17 and alkylchlorosilanes18 as well as macromolecules19–21 without inducing de-lamination of the GO layers. GO is also being considered as a prominent material for the preparation of permeation membranes with unprecedented properties.22

On the other hand, recent inelastic neutron scattering results on poly(ethylene oxide) (PEO) intercalated into sub-nanometer GO layers show that, under these conditions, this polymer adopts a planar zigzag conformation, in no way resembling the characteristic 72 helical structure of the bulk crystal or the random coil conformation of the melt state.21,23 The vibrational density of states and other dynamical processes of PEO also result drastically affected. These works demonstrate that polymer intercalation into GO is a convenient platform for much-needed studies of macromolecules under extreme two-dimensional confinement, a situation for which theoretical predictions have also been reported.24

In spite of the results commented above, the development of new materials based on the combination of polymers and new carbon forms relays on the basic knowledge of the interactions between both components. For instance, in the example discussed above of PEO intercalated into GO layers, it is not obvious to what extent the dramatic changes observed of the structure and dynamics of PEO are controlled by the confining topology or by the particular interactions between PEO and GO. Concerning these questions, it is worthy of remark that some carbon based substrates as GO can present π-type interactions (see, for example, Refs. 25–27) that are not well described in some computational chemistry methods (see Refs. 28–31 as representative references). On the other hand, it is also desirable to remark the increasing interest in the study by means of atomistic classical molecular dynamics...
simulations of complex nanostructures, including polymers and graphene, GO, or related compounds (see, for example, Refs. 32 and 33). It is evident that the precise knowledge of the particular interactions in these systems is of utmost importance to properly define the suitable force-field for this type of simulations.

With these ideas in mind, in this work we have carried out computational simulations of the interactions between discrete models of confined PEO in GO. The computational study of polymer · · · substrate interactions is a complex topic that can be conducted from different points of view.34–37 Our main objectives were: (a) to perform a systematic analysis of the possible polymer · · · substrate interactions for a polymer confined in a carbon based substrate with an accurate computational chemistry standard method such as the 2nd order Møller-Plesset perturbation theory (MP238), and (b) to compare the MP2 results with other ab initio methods for a better evaluation of the behavior of the system. The results obtained by MP2 were compared with five of the new generation density functional theory (DFT) methods developed by Truhlar and Zhao (M05,39 M05-2 ×,40, 41 M06-2 ×, 40, 42 M06-HF,40, 43 and M06-L40, 44) in order to find an ab initio method that can describe the electronic properties of the system with less computational cost. Some other functionals have been tested but they produce poor results (B3LYP45 and B97-146) or convergence problems (M0640, 41 and MPWB1K47) and have not been included in the systematic study of the interactions. The calculations were carried out using the GAUSSIAN0948 package.

The paper is organized in the following way: after the presentation of the used computational methods (Sec. II A), the PEO-GO discrete models will be introduced (Sec. II B), and the results shown and discussed (Sec. III C). The results section is divided in three parts: (Sec. III A) MP2 potential energy curves, (Sec. III B) optimization of the potential curve minima, and (Sec. III C) comparison of the MP2 results with other methods.

II. THEORETICAL METHODS

A. Methodology

Ab initio calculations were performed by means of the GAUSSIAN0948 set of programs. For an introduction to ab initio methods, several textbooks can be recommended.49, 50

The calculation has been performed using several methods. At a first stage, MP238 has been used. The MP2 method was used in its restricted formalism (RMP2) for closed-shell systems and in its unrestricted (UMP2) and restricted open-shell (ROMP2) formalism for open-shell systems. The UMP2 calculations present spin contamination51 problems that are avoided by the ROMP2 formalism, however, the ROMP2 gradient is not available in the GAUSSIAN09 set of programs. Therefore, UMP2 was used for optimization calculations. MP2 method has been widely used to describe the properties of weak interactions (see, for example, Refs. 52–54), but, sometimes, it presents certain limitations, specially for the simulation of π interactions, where it can overestimate the interaction energy, specially in cases where a small basis set has been used (smaller than triple zeta).55–57 The use of a most precise method such as Coupled-Cluster Singles Doubles and Non-iterative Triples Correction (CCSD(T))58 or MP459 should be desirable but our computational resources did not make possible the use for this kind of systems. Hence, in order to have a better idea of the polymer · · · substrate interactions, the MP2 results were compared with five DFT methods developed by Truhlar and Zhao (M05,39 M05-2 ×,40, 41 M06-2 ×, 40, 42 M06-HF,40, 43 and M06-L40, 44).

DFT methods traditionally present several limitations28–31, 46 depending on the quality of the exchange-correlation functional, such as the description of transition metals, thermochemical properties, medium-range correlation energy, barrier heights or non-covalent bond interactions. Among all those, the former is the one in which we would like to focus our interest in this work. Truhlar and Zhao41–47, 55 have developed and tested several DFT functionals in order to improve the traditional limitations. These functionals are mainly based on modifications of the generalized gradient approximation (GGA) with the addition of supplementary variables (meta-GGA) and mixtures of meta-GGA functionals local exchange with the non-local Hartree-Fock exchange (hybrid meta-GGA). In this work, one meta-GGA functional (M06-L) and four hybrid meta-GGA functionals (M05, M05-2X, M06-2X, and M06-HF) were used in their restricted and unrestricted formalisms in order to elucidate the method that better describes the non-covalent interactions.

All the ab initio optimizations were carried out without constraints using the GAUSSIAN09 Berny algorithm,60 in Cartesian coordinates and with the 6-31+G(d)61, 62 basis set. A triple zeta basis set should be desirable for MP2 estimation of π-type interaction energies, but our computational resources do not allow this approximation. The two-bodies interaction energy (Ei) between PEO and GO was calculated by the supermolecule approach with basis set superposition error (BSSE) correction using the Counterpoise method.53 The interaction energy was calculated using the following equation: 

\[ E_i = E_{\text{PEO/GO}} - E_{\text{PEO}} - E_{\text{GO}} \]

where \( E_{\text{PEO/GO}} \) is the total energy of the polymer/substrate model, \( E_{\text{PEO}} \) is the total energy of the polymer model with the entire basis set and \( E_{\text{GO}} \) is the substrate model with the entire basis set.

The intermolecular interactions were studied using Bader’s theory of atoms in molecules.64, 65 The electronic density analysis was performed using the AIMPAC package.66 The analysis was focused on the intermolecular bond critical points, classified as (3,−1) according to their rank and signature. The bond critical point electronic density (ρ(rb)) and its Laplacian (\( \nabla^2 \rho(r_b) \)) were studied in order to estimate the type and the strength of the intermolecular interaction. From Bader’s work, for the closed shell/weak interactions the ρ(rb) value is in the order of 10⁻³ and the \( \nabla^2 \rho(r_b) \) is positive indicating depletion of electron density at the point.

B. Models

In order to study the main interactions between PEO and GO, different discrete models with a limited number of atoms have been selected.
PEO is a well-known synthetic polyether of relatively simple chemical formula (see Figure 1), which in the case of low values of molecular mass (low values of \(n\)) is also known as poly(ethylene glycol). PEO shows a wide range of applications due to properties such as its amphiphilic character, solubility in water and many organic solvents, and low toxicity. In order to study the interactions between PEO and GO, we have taken an extremely simplified approach, representing PEO by the dimethylether (DME) molecule. This simplification can be acceptable taking into account that PEO is a polymer and many of its properties are due to those of its repeating units.

Concerning GO, in this work we have considered as a starting point a simplified version of the generally accepted GO structure of Lerf and Klinowski (see Figure 2). This consists in a non-stoichiometric model, where the carbon plane is furnished with random hydroxyl and epoxy (1,2 ether) functional groups. However, we have not considered the presence of carboxyl groups included in the model of Lerf and Klinowski mainly as carboxylic acids along the sheet edge. Moreover, the presence of holes and vacancies is not taken into account. Within this general scheme, and in order to simulate the possible interactions with PEO, we have chosen five models for the GO substrate. Three of them are polycyclic aromatic hydrocarbons (PAHs): pyrene, triangulene, and coronene and the other two are PAH derivatives with epoxy and hydroxyl substituents in its central part: epoxypyrene, and hydroxytriangulene (see Figure 3).

The Merz-Singh-Kollman (MSK) atomic charges of the molecules are represented in Table I according to the atoms nomenclature shown in Figure 4. In the figure, the maps of electrostatic potential (MEP, red color correspond to negative charges and blue to positives) of the molecules are also represented to illustrate the table data. At a first glance, it can be appreciated that the carbon interacting parts are almost neutral, the oxygen of the hydroxyl group is far more negative than those of the epoxy, and the hydrogen of the hydroxyl group presents a remarkable positive charge density. Thus, from an electrostatic point of view, it seems that the stronger interactions should be with the OH group.

<table>
<thead>
<tr>
<th></th>
<th>DME</th>
<th>D2h</th>
<th>D2h(O)</th>
<th>D3h</th>
<th>D3h(OH)</th>
<th>D6h</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>-0.02</td>
<td>-0.08</td>
<td>0.07</td>
<td>-0.01</td>
<td>0.85</td>
<td>0.00</td>
</tr>
<tr>
<td>C2</td>
<td>0.34</td>
<td>0.27</td>
<td>-0.10</td>
<td>-0.40</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>-0.42</td>
<td>-0.31</td>
<td>0.30</td>
<td>0.50</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>C4</td>
<td>-0.33</td>
<td>-0.36</td>
<td>-0.20</td>
<td>-0.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C5</td>
<td>0.01</td>
<td>0.13</td>
<td>-0.40</td>
<td>-0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C6</td>
<td>-0.10</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>-0.37</td>
<td>-0.27</td>
<td>-0.67</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>0.07</td>
<td>0.37</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIG. 4. MEP of the studied models with the atom nomenclature employed in Table I (a) DME, (b) D$_{2h}$, (c) D$_{2h}(O)$, (d) D$_{3h}$, (e) D$_{3h}(OH)$ and (f) D$_{6h}$. Note that in spite of the symmetry breaking in D$_{3h}(OH)$ due to the hydroxyl group the nomenclature is maintained because the effect is small; the charge densities in the table are the average of equivalent atoms.

III. RESULTS AND DISCUSSION

This section is divided in three parts: (Sec. III A) “MP2 potential energy curves,” the first part, where the MP2 potential energy curves are shown and discussed; (Sec. III B) “optimization of the potential curve minima,” the second part, where curve minima are optimized and their geometric, energetic, and electronic properties are shown and discussed, and, finally (Sec. III C), “comparison of the MP2 results with other methods,” where MP2 potential curves and MP2 optimized structures are compared with those calculated with other methods.

A. MP2 potential energy curves

In a first step, the strength of the possible interactions between DME and substrate models was studied. A complete study of the potential energy landscape for these two molecules is almost impossible and we restrict ourselves to represent only the most relevant interactions. In order to do so, we decided to study only discrete (interactions where each molecule only interacts with one part, avoiding double interactions) and direct interaction (interactions where the molecule parts interact following the less sterically hindered directions). Twelve potential curves have been built at MP2/6-31+G(d) level with the optimized geometries at this level. The curves represent the evolution of the interaction energy ($E_i$) as a function of the intermolecular distance ($d$) for a collection of [DME][PAH] dimers with the different orientations shown in Figure 5. The curve for each orientation will be referred to as $O_1$, $O_2$, $O_3$... $O_{12}$: $O_1$ and $O_2$ curves represent a [DME][D$_{2h}$] dimer (35 atoms) with two possible interactions (O(DME)···bond(D$_{2h}$)) and H(DME)···bond(D$_{2h}$), respectively; $O_3$ and $O_4$ show two possible interactions for a [DME][D$_{2h}(O)$] dimer (36 atoms).
FIG. 6. Potential energy curves for the closed-shell orientations (O1, O2, O3, O4, O11 and O12) at RMP2/6-31+G(d) level.

FIG. 7. Potential energy curves for the open-shell orientations (O5, O6, O7, O8, O9 and O10) at ROMP2/6-31+G(d) (continuous lines) and UMP2/6-31+G(d) (dotted lines) levels.

(O(DME)·O(D2h(O)) and H(DME)··O(D2h(O))); O5 and O6 display the two interactions for [DME][D3h+] (43 atoms) (O(DME)··C(D3h) and H(DME)··C(D3h)); O7, O8, O9, and O10 exemplify four interactions for [DME][D3h(OH)] (45 atoms) (O(DME)··H(D3h(OH)), H(DME)··H(D3h(OH)), O(DME)··O(D3h(OH)), and H(DME)··O(D3h(OH))); and, finally, O11 and O12 illustrate two [DME][D6h] interactions (45 atoms) (O(DME)··cycle(D6h) and H(DME)··cycle(D6h)). The MP2 formalism depends on the multiplicity of the system, consequently, the closed-shell systems (DME)[D2h], [DME][D2h(O)], and [DME][D6h(OH)] are described using the RMP2 and the open-shell systems (DME)[D3h] and [DME][D3h(OH)] with the ROMP2 because of the fact that the UMP2 presents spin contamination problems ((S^2)^UMP2 = 4.0 instead of 3 for [DME][D3h] and (S^2)^UMP2 = 5.5 instead of 3.75 for [DME][D3h(OH)]). However, the curves have also been calculated at UMP2 level for comparison purposes since the ROMP2 gradient is not implemented in GAUSSIAN and hence the UMP2 method has been used instead for optimization. The RMP2 curves for the closed-shell orientations O1, O2, O3, O4, O11, and O12 are displayed in Figure 6 and the ROMP/UMP2 curves for the open-shell orientations O5, O6, O7, O8, O9, and O10 are plotted in Figure 7.

Two of the curves (O3 and O9) are repulsive and the rest present stable minima at distances between 2 and 4 Å which values are represented in Table II. The minima can be classified in four types depending on the type of the interaction: hydrogen bond like interactions (O4, O7, and O10), O···π interactions (O1, O5, and O11), H···π interactions (O2, O6, and O12), and H···H interaction (O8). One of the hydrogen bond like interactions is the most stable (O7, −5.71 kcal/mol) and the other two slightly stable (∼−1 kcal/mol), this can be easily justified based on charge density differences between charge densities of the O (−0.37 e^−) and the H (0.08 e^−) of the DME. The stability of the π type interactions is similar for all the cases (∼−3 kcal/mol) somewhat more stable for O···π interactions than H···π interactions. Eventually, the H···H minimum is a spurious one that cannot be optimized as will be shown in Sec. III B where the interactions will be described in more detail.

The ROMP2 and UMP2 curves for the open-shell orientations depicted in Figure 7 present a similar shape but some stability differences (UMP2 curves are more unstable, as expected due to the spin contamination problems). The average difference between the minima stabilities shown in Table II is 0.44 kcal/mol with similar positions for all the cases and, hence, it can be concluded that UMP2 can be a fair approach of ROMP2 for optimization purposes, nevertheless, the properties should be calculated at ROMP2 level.

B. MP2 optimization of the potential curves minima

The next step in the study of the DME···substrate interaction is to optimize the ten potential energy curves minima at MP2/6-31+G(d) level, using the restricted formalism for closed-shell systems and the unrestricted for open-shell, nevertheless, the open-shell properties are calculated using the ROMP2 formalism. Eight minima, referred as M1, M2,

TABLE II. Stability and intermolecular separation for the potential energy curves minima.

<table>
<thead>
<tr>
<th>Number of atoms</th>
<th>R(OMP2)/6-31+G(d)^a</th>
<th>UMP2/6-31+G(d)</th>
<th>E_i [Kcal/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>35</td>
<td>3.000</td>
<td>−2.56</td>
</tr>
<tr>
<td>O2</td>
<td>35</td>
<td>2.750</td>
<td>−1.54</td>
</tr>
<tr>
<td>O3</td>
<td>36</td>
<td>Repulsive</td>
<td></td>
</tr>
<tr>
<td>O4</td>
<td>36</td>
<td>2.375</td>
<td>−1.37</td>
</tr>
<tr>
<td>O5</td>
<td>43</td>
<td>3.125</td>
<td>−2.99</td>
</tr>
<tr>
<td>O6</td>
<td>43</td>
<td>2.750</td>
<td>−1.82</td>
</tr>
<tr>
<td>O7</td>
<td>45</td>
<td>2.000</td>
<td>−5.71</td>
</tr>
<tr>
<td>O8</td>
<td>45</td>
<td>2.750</td>
<td>−0.43</td>
</tr>
<tr>
<td>O9</td>
<td>45</td>
<td>Repulsive</td>
<td></td>
</tr>
<tr>
<td>O10</td>
<td>45</td>
<td>3.750</td>
<td>−1.06</td>
</tr>
<tr>
<td>O11</td>
<td>45</td>
<td>2.875</td>
<td>−3.56</td>
</tr>
<tr>
<td>O12</td>
<td>45</td>
<td>2.625</td>
<td>−1.99</td>
</tr>
</tbody>
</table>

^aRMP2 for O1, O2, O3, O4, O11 and O12 and ROMP2 for O5, O6, O7, O8, O9, O10.
M3 . . . M8, have been obtained since some of the curve minima lead to the same structure which is the case of the orientations O5 and O6 that converge to the M4 minimum, and the orientations O7 and O8 that take to the M5 minimum. The complete relationship between the Ox and Mx structures is depicted in Figure S171 of the supplementary material, where are shown the starting geometries and the optimized geometries around the xz and xy planes.

Several changes from the starting geometries can be appreciated depending on the type of the interaction. The structures with H···π interactions (O2, O6, and O12) evolve to a structure with a close contact between the C atom and the PAH, those with O···π interactions (O1, O5, and O11) lead to a structure that also presents H···π interactions. However, the structure with H···H interaction (O8) disappears taking the same minimum that O7 structure with a hydrogen bond like interaction. The other two structures with this kind of interaction (O4 and O10) progress to a minimum with closer C–O contacts.

All the optimized minima are stable (between 2.08 and 7.06 kcal/mol) and the analysis of the topology of the electronic density reveals the existence of intermolecular bond critical points in all the structures (see Figure 8 for the position of the bond critical points and the atoms involved in the interaction) with values of the electronic density (0.0052-0.0349 e/\(a_0^3\)) and its Laplacian (0.0168-0.0131 e/\(a_0^5\)) indicative of weak interactions (see Table III for the values of the interaction energy, bond distance, electronic density at the bond critical points, and charge densities of the bond involved atoms).

By far the more stable minimum is M5 (−7.04 kcal/mol) that corresponds to a standard hydrogen bond interaction with the highest value of the electronic density (3.49×10⁻² e/\(a_0^3\)) and its Laplacian (1.31×10⁻¹), the shorter intermolecular bond distance (1.779 Å, a standard distance for a hydrogen bond) and a polar character of the interaction. It is remarkable that the same structure can be obtained starting from both O7 and O8.

![Figure 8](image.png)

**FIG. 8.** Optimized geometries at MP2/6-31+G(d) level (restricted for closed-shell systems and unrestricted for open-shell) with intermolecular bond critical points highlighted (a) O1→M1, (b) O2→M2, (c) O4→M3, (d) O5→O6→M4, (e) O7→O8→M5, (f) O10→M6, (g) O11→M7, (h) O12→M8. The atoms involved in the bond are connected with dotted lines.

| TABLE III. Properties of the optimized structures and their intermolecular bonds: (a) interaction energy at RO/MP2/6-31+G(d) (\(E^{R\text{OPT}MP2}\), restricted MP2 for closed-shell systems restricted open-shell MP2 for open-shell systems), (b) involved atoms (first of them the substrate and second the polymer), (c) intermolecular bond distance (d), (d) electronic density (\(\rho(r_c)\)) at the intermolecular bond critical points, (e) Laplacian of the electronic density \((\nabla^2\rho(r_c))\) at the intermolecular bond critical points and (f) charge density \((\rho(q))\) of the atoms involved in the bond. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \(E^{R\text{OPT}MP2}\) [kcal/mol]\textsuperscript{a} | Involved atoms | \(d\) [Å] | \(\rho(r_c)\) \([10^3 (e/\text{a}_0^3)]\) | \(\nabla^2\rho(r_c)\) \([10^2 (e/\text{a}_0^5)]\) | \(\rho(q)_1\) [e⁻] | \(\rho(q)_2\) [e⁻] |
| M1 | −3.29 | C···C | 3.12 | 6.85 | 2.51 | 0.17 | −0.08 |
| M2 | −2.08 | C···O | 3.22 | 8.36 | 3.01 | 0.06 | −0.28 |
| M3 | −2.11 | C···C | 3.28 | 6.99 | 2.23 | 0.00 | −0.07 |
| M4 | −3.89 | C···H | 2.91 | 5.34 | 1.71 | 0.07 | 0.07 |
| | | C···H | 2.92 | 5.25 | 1.68 | 0.07 | 0.06 |
| M5 | −7.06 | H···O | 1.78 | 34.90 | 13.10 | 0.33 | −0.12 |
| M6 | −2.88 | O···C | 3.11 | 5.90 | 2.83 | −0.74 | −0.12 |
| M7 | −3.47 | O···C | 2.97 | 10.70 | 3.91 | −0.12 | −0.22 |
| | | C···H | 2.79 | 6.78 | 5.20 | −0.13 | 0.10 |
| | | C···H | 3.23 | 5.20 | 2.31 | 0.34 | 0.11 |
| M8 | −2.84 | C···C | 3.19 | 7.05 | 2.72 | 0.18 | −0.03 |

\textsuperscript{a}RMP2 for O1, O2, O3, O4, O11 and O12 and ROMP2 for O5, O6, O7, O8, O9, O10.
FIG. 9. Potential energy curves for the (a) O1, (b) O2, (c) O3, (d) O4, (e) O5, and (f) O6 orientations at MP2, M05, M05-2X, M06-2X, M06-HF and M06-L calculation levels, all of them with 6-31+G(d) basis set. The ab initio formalism (restricted (R), unrestricted (U) or restricted open-shell (RO)) is specified in the legend.

and O8 structures. This interaction is expected to be the more significant in polymer···substrate interactions.

The other minima are less stable (between −2.08 and −3.89 kcal/mol), with a bigger separation and with lower values of the density and Laplacian at the bond critical points, indicating weak van der Waals interaction character. In all cases, the DME interacts with a C atom of the substrate except in M6, where the C atom of the DME interacts with the O in the hydroxyl group. The stability tends to slightly increase with the number of bond critical points. It is possible to define the interactions as dispersion assisted π-interactions attending to the involved atoms and the non-polar character of most of the bond critical points. The relevance of these interactions depends on the number of GO defaults. In systems with a big number of defaults, the most expected interactions are those with the epoxy group (M3) and, specially, those with the hydroxyl group (M5).

C. Comparison of the MP2 results with other methods

In this final part, the 12 potential energy curves (interaction energy vs. distance, referred to as Ox: O1, O2, O3…O12) have been built using five DFT functionals less expensive than MP2 (Figures 9 and 10): M05, M05-2X, M06-2X, M06-HF, and M06-L. The DFT curves are calculated with 6-31+G(d) basis set and are BSSE corrected using Counterpoise method; the closed-shell curves (O1, O2, O3, O4, O11,
FIG. 10. Potential energy curves for the (a) O⁷, (b) O⁸, (c) O⁹, (d) O¹⁰, (e) O¹¹ and (f) O¹² orientations at MP2, M05, M05-2X, M06-2X, M06-HF and M06-L calculation levels, all of them with 6-31+G(d) basis set. The ab-initio formalism (restricted (R), unrestricted (U) or restricted open-shell (RO)) is specified in the legend.

and O¹²) are calculated using the restricted formalism of the functionals and the unrestricted curves (O⁵, O⁶, O⁷, O⁸, O⁹, and O¹⁰) are calculated using the unrestricted functional that does not present problems with spin contamination. In general terms, all the methods present similar results to those of MP2. There are several stability differences but all methods predict minima at similar distances, the stability and distance of the minima for each method are shown in Table IV. The main differences can be appreciated for the case of O⁹, where four of the five methods predict minima (one of them metastable) instead of the repulsive curve at MP2 level. In a following step, the curves minima have been optimized at the same computational level. For most of the cases, the optimized structures (referred as Mx: M¹, M², M³...M¹²) are similar to the MP2 ones. Several properties have been calculated for the Mx structures (see Table S²⁷ of the supplementary material) such as the interaction energy (Eᵢ), the bond distance for the intermolecular interactions (d), the charge density of the atoms involved in an intermolecular interaction (ρ(q)), the electronic density at the intermolecular bond critical points (ρ(rᵢ)), and the Laplacian at these points (∇²ρ(rᵢ)). The average property differences between MP2 and the other methods are shown in Table V. In general, all methods present similar results to the MP2 ones although several differences will be detailed hereafter.

The M05 functional produces similar curves to those of the MP2 method with some differences in the position and stability of the minima: in general, the intermolecular
separations of the minima are bigger than MP2 but the interaction energy smaller. This reveals that MP2 probably overestimates the interaction energies, nevertheless, M05 method is usually the less stable of the DFT methods, so it is possible that this method presents a small underestimation of the interaction energy. This behavior can also be appreciated in the Mx structures, where the intermolecular distance is also bigger and the interaction energy also smaller than MP2, a fact that affects the bond critical points properties, especially for the M1 and M7 structures, where some bond critical points do not appear.

The M05-2X functional curves also present a similar behavior to the MP2 method curves, with like shape and almost the same position of the minima positions but smaller energy (but bigger than M05). Hence, M05-2X is expected to describe better the interaction than the MP2 method without overestimation of the interaction energy. However, the Mx structures are, in general, a bit more stable than those calculated by MP2 in spite of a slightly bigger intermolecular separation. The increase of intermolecular separation yields to small values of the bond critical points properties. The fact that the potential energy curves calculated using this method are less stable than the MP2s and the Mx structures more stable suggest that this method can properly describe the correlation energy for most of the cases and that should be recommended to study the PEO-GO system.

The curves calculated using the M06-2X functional present, in general, minima at shorter distances than MP2, with smaller stabilities in certain cases (O1, O7, O8, O9, O10). This suggests that the method can overestimate the interaction energy even more than MP2. The Mx structures calculated using this method are more stable than those calculated by MP2 with similar or smaller intermolecular distances that yield to bigger values of $\rho(r_c)$ and $\nabla^2 \rho(r_c)$.

The M06-HF functional produces potential curves similar to those of M06-2X with small differences in minimum distances and interaction energies. Their Mx structures are also more stable than MP2 structures but less than M06-2Xs with smaller intermolecular separation than M06-2X for most of the cases. M3 and M7 structures using this method are quite different than MP2 structures.

The M06-L functional curves are also similar to M06-2X and consequently M06-HF. Mx structures are very similar to M06-HF structures with the same deviation for M3 and M7 structures.

### Table IV. Interaction energies ($E_i$) and distances ($d$) for the potential energy curves minima using MP2, M05, M05-2X, M06-2X, M06-HF and M06-L methods (6-31+G(d) basis set, BSSE corrected, restricted formalism for O1, O2, O3, O4, O11 and O12 and unrestricted for O5, O6, O7, O8, O9, O10).

<table>
<thead>
<tr>
<th></th>
<th>MP2</th>
<th>M05</th>
<th>M05-2X</th>
<th>M06-2X</th>
<th>M06-HF</th>
<th>M06-L</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>$E_i$ [kcal/mol]</td>
<td>-2.56</td>
<td>-0.81</td>
<td>-1.72</td>
<td>-2.77</td>
<td>-2.66</td>
</tr>
<tr>
<td></td>
<td>$d$ [Å]</td>
<td>3.00</td>
<td>3.125</td>
<td>2.875</td>
<td>2.875</td>
<td>2.875</td>
</tr>
<tr>
<td>O2</td>
<td>$E_i$ [kcal/mol]</td>
<td>-1.54</td>
<td>-0.41</td>
<td>-0.81</td>
<td>1.00</td>
<td>-0.95</td>
</tr>
<tr>
<td></td>
<td>$d$ [Å]</td>
<td>2.75</td>
<td>3.00</td>
<td>2.75</td>
<td>2.625</td>
<td>2.625</td>
</tr>
<tr>
<td>O3</td>
<td>$E_i$ [kcal/mol]</td>
<td>-0.43</td>
<td>-0.09</td>
<td>-0.35</td>
<td>-0.57</td>
<td>-0.51</td>
</tr>
<tr>
<td></td>
<td>$d$ [Å]</td>
<td>2.75</td>
<td>2.625</td>
<td>2.50</td>
<td>2.375</td>
<td>2.625</td>
</tr>
<tr>
<td>O4</td>
<td>$E_i$ [kcal/mol]</td>
<td>-1.99</td>
<td>-0.34</td>
<td>-0.80</td>
<td>-1.13</td>
<td>-0.66</td>
</tr>
<tr>
<td></td>
<td>$d$ [Å]</td>
<td>2.625</td>
<td>3.00</td>
<td>2.625</td>
<td>2.625</td>
<td>2.625</td>
</tr>
</tbody>
</table>

### Table V. Average deviation of the properties for the potential energy curves (interaction energy $E_i(Ox)$ and minimum distance $d(Ox)$) and optimized minima (interaction energy $E_i(Mx)$, intermolecular distance $d(Mx)$, electronic density at the intermolecular bond critical points $\rho(r_c)$, Laplacian of the electronic density at the intermolecular bond critical points $\nabla^2 \rho(r_c)$ and charge densities $\rho(q)$) depending on the method.

<table>
<thead>
<tr>
<th></th>
<th>M05</th>
<th>M05-2X</th>
<th>M06-2X</th>
<th>M06-HF</th>
<th>M06-L</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_i(Ox)$ [kcal/mol]</td>
<td>1.32</td>
<td>0.91</td>
<td>0.78</td>
<td>0.87</td>
<td>0.69</td>
</tr>
<tr>
<td>$\Delta d(Ox)$ [Å]</td>
<td>0.2</td>
<td>0.08</td>
<td>0.16</td>
<td>0.11</td>
<td>0.18</td>
</tr>
<tr>
<td>$\Delta E_i(Mx)$ [kcal/mol]</td>
<td>0.93</td>
<td>0.38</td>
<td>1.72</td>
<td>1.42</td>
<td>1.18</td>
</tr>
<tr>
<td>$\Delta d(Mx)$ [Å]</td>
<td>0.34</td>
<td>0.13</td>
<td>0.11</td>
<td>0.34</td>
<td>0.62</td>
</tr>
<tr>
<td>$\Delta \rho(r_c)$ [10^4 (e/Å^3)]</td>
<td>3.75</td>
<td>1.25</td>
<td>1.24</td>
<td>2.46</td>
<td>2.61</td>
</tr>
<tr>
<td>$\Delta (\nabla^2 \rho(r_c))$ [10^2 (e/Å^5)]</td>
<td>1.32</td>
<td>0.67</td>
<td>0.48</td>
<td>0.72</td>
<td>1.15</td>
</tr>
<tr>
<td>$\Delta \rho(q)$ [e^-]</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
<td>0.08</td>
<td>0.08</td>
</tr>
</tbody>
</table>
IV. SUMMARY AND CONCLUSIONS

In this work, we have carried out a systematic study of the possible interactions between PEO and a substrate of GO by means of different computational methods. To do that, PEO and the GO substrate have been represented by simplified discrete models, which we believe they capture the main ingredients of the problem. In particular, the simple DME molecule has replaced PEO.

As conclusion of this study, we can propose several possible interactions between the confined PEO polymer and the GO substrate that could be classified in three groups: (a) π-like interactions between C, H or O of the polymer and C of the substrate, (b) weak C···O interactions between C of the PEO and O of the hydroxyl groups in GO, and (c) hydrogen bond like interactions between H of the hydroxyl groups in GO and the O of the PEO. All these interactions are weak but stable and intermolecular bond critical points can be found using electron density analysis with values of ρ(r_c) and ∇²ρ(r_c) close to the characteristic ones for weak interactions. The (c) interaction is the strongest by stability and bond critical points analysis, consequently (c) interaction should be the most relevant, specially in GO substrates with a big number of defaults.

The comparison between MP2 method and DFT functionals reveals some differences in stability, interaction distances, and bond critical points properties. Nevertheless, the potential energy curves present similar shapes and the optimized minima properties are comparable. MP2 method is expected to overestimate the interaction energy, but some of the DFT functionals present even bigger interaction energies. The M05-2X is the method that produces more realistic interaction energies, M05 method tends to underestimate the interaction energy, and the M06 style functionals to overestimate the MP2 interaction energy.

ACKNOWLEDGMENTS

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See supplementary material at http://dx.doi.org/10.1063/1.4790169 for Figure S1 and Table S2.