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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). © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4790169>]

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 Ruess,⁷ Scholz and Boehm,^{8,9} and Nakajima¹⁰ until the generally accepted structures of Lerf and Klinowski^{11,12} or Szabó.¹³ Concerning **GO**, as the base for intercalation compounds, it has been recently reported that **GO** can accommodate water¹⁴ and other differ-

ent solvent molecules,¹⁵ cationic surfactants,¹⁶ alkylamines,¹⁷ and alkylchlorosilanes¹⁸ as well as macromolecules^{19–21} 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 7_2 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 relies 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

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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 $\cdots$ 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 $\cdots$ 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 $\times$,^{40,41} M06-2 $\times$,^{40,42} M06-HF,^{40,43} and M06-L^{40,44}) 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 (M06^{40,41} 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). 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 $\cdots$ substrate interactions, the MP2 results were compared with five DFT methods developed by Truhlar and Zhao (M05,³⁹ M05-2 $\times$,^{40,41} M06-2 $\times$,^{40,42} M06-HF,^{40,43} and M06-L^{40,44}).

DFT methods traditionally present several limitations^{28–31,40} 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 Zhao^{41–47,55} 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 (E_i) between **PEO** and **GO** was calculated by the supermolecule approach with basis set superposition error (BSSE) correction using the Counterpoise method.⁶³ The interaction energy was calculated using the following equation: $E_i = E_{PEO/GO}^{PEO/GO} - E_{PEO}^{PEO/GO} - E_{GO}^{PEO/GO}$, where $E_{PEO/GO}^{PEO/GO}$ is the total energy of the polymer/substrate model, $E_{PEO}^{PEO/GO}$ is the total energy of the polymer model with the entire basis set and $E_{GO}^{PEO/GO}$ 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 AIMPACK 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 ($\rho(r_c)$) and its Laplacian ($\nabla^2\rho(r_c)$) 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 $\rho(r_c)$ value is in the order of 10^{-3} and the $\nabla^2\rho(r_c)$ is positive indicating depletion of electron density at the point.⁶⁴

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.

FIG. 1. PEO polymer.

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 **DME** shows the two main interacting parts of the polymer: hydrogen and oxygen. It can be arguable that the model can properly reproduce the hydrogen environment for not presenting two neighboring carbons, but the charges of the hydrogens in **DME** are similar to those of the polymer hydrogens (≈ 0.07 for both cases).

Concerning **GO**, in this work we have considered as a starting point of view a simplified version of the generally accepted **GO** structure of Lerf and Klinowski^{11,12} (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 carbonyl groups included in the model of Lerf and Klinowski,^{11,12} 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 central position of the substituents is not the most favoured from an energetic point of view, but allow to reproduce the environment around the group in a straightforward way. The **PAH** structures will be referred according to their symmetry point group: **D_{2h}** for the pyrene, **D_{3h}** for the triangulene, **D_{6h}** for the coronene and, for the sake of simplicity, the **PAH** derivatives will be referred to as **D_{2h}(O)** for the epoxypyrene

FIG. 2. Scheme of the **GO** structure.

FIG. 3. Structural formulas of the studied models for the simulation of the (a) **PEO**: dimethylether (**DME**) and **GO**: (b) pyrene (**D_{2h}**), (c) epoxypyrene (**D_{2h}(O)**), (d) triangulene (**D_{3h}**), (e) hydroxytriangulene (**D_{3h}(OH)**) and (f) coronene (**D_{6h}**).

and **D_{3h}(OH)** for the hydroxytriangulene. These five models have been chosen in order to reproduce the five main possibilities of interaction of a **GO** surface in their central part: **D_{2h}**, **D_{3h}**, and **D_{6h}** reproduce the interaction with the different parts of the carbon skeleton, a bond, a carbon, and the center of a cycle, respectively. **D_{2h}(O)** reproduces the interaction with an epoxy group and **D_{3h}(OH)** with a hydroxyl group. From an electronic point of view, four of the studied structures (**DME**, **D_{2h}**, **D_{2h}(O)**, and **D_{6h}**) are neutral closed-shell singlets and the other two (**D_{3h}** and **D_{3h}(OH)**) are neutral open-shell structures: **D_{3h}** is a triplet^{67,68} (26.7 kcal/mol more stable at ROMP2/6-31+G(d) level than singlet and far more stable than superior multiplicities) and **D_{3h}(OH)** is a quadruplet (3 kcal/mol more stable than doublet at ROMP2/6-31+G(d)).

The Merz-Singh-Kollman (**MSK**) atomic charges^{69,70} 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 I. **MSK** atomic charges for the studied models at MP2/6-31+G(d) level in e^- units.

	DME	D_{2h}	D_{2h}(O)	D_{3h}	D_{3h}(OH)	D_{6h}
C¹	−0.02	−0.08	0.07	−0.01	0.85	0.00
C²		0.34	0.27	−0.10	−0.40	0.20
C³		−0.42	−0.31	0.30	0.50	0.30
C⁴		−0.33	−0.36	−0.20	−0.50	
C⁵		0.01	0.13	−0.40	−0.40	
C⁶				−0.10	0.00	
O	−0.37		−0.27		−0.67	
H	0.07				0.37

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 O1, O2, O3... O12: O1 and O2 curves represent a [DME][D_{2h}] dimer (35 atoms) with two possible interactions ($O(DME) \cdots \text{bond}(D_{2h})$ and $H(DME) \cdots \text{bond}(D_{2h})$, respectively); O3 and O4 show two possible interactions for a [DME][$D_{2h}(O)$] dimer (36 atoms)

FIG. 5. Orientations for the potential curves of the [DME][D_{2h}] dimer ((a) O1 and (b) O2), [DME][$D_{2h}(O)$] dimer ((c) O3 and (d) O4), [DME][D_{3h}] dimer ((e) O5 and (f) O6), [DME][$D_{3h}(OH)$] dimer ((g) O7, (h) O8, (i) O9 and (j) O10) and [DME][D_{6h}] dimer ((k) O11 and (l) O12).

FIG. 6. Potential energy curves for the closed-shell orientations (**O1**, **O2**, **O3**, **O4**, **O11** and **O12**) at RMP2/6-31+G(d) level.

(O(DME)···O(D_{2h}(O))) and H(DME)···O(D_{2h}(O)); **O5** and **O6** display the two interactions for [DME][D_{3h}] (43 atoms) (O(DME)···C(D_{3h}) and H(DME)···C(D_{3h})); **O7**, **O8**, **O9**, and **O10** exemplify four interactions for [DME][D_{3h}(OH)] (45 atoms) (O(DME)···H(D_{3h}(OH))), H(DME)···H(D_{3h}(OH)), O(DME)···O(D_{3h}(OH)), and H(DME)···O(D_{3h}(OH))); and, finally, **O11** and **O12** illustrate two [DME][D_{6h}] interactions (45 atoms) (O(DME)···cycle(D_{6h}) and H(DME)···cycle(D_{6h})). The MP2 formalism depends on the multiplicity of the system, consequently, the closed-shell systems ([DME][D_{2h}], [DME][D_{2h}(O)], and [DME][D_{6h}]) are described using the RMP2 and the open-shell systems ([DME][D_{3h}] and [DME][D_{3h}(OH)]) with the ROMP2 because of the fact that the UMP2 presents spin contamination problems ($\langle S^2 \rangle^{UMP2} = 4.0$ instead of 3 for [DME][D_{3h}] and $\langle S^2 \rangle^{UMP2} = 5.5$ instead of 3.75 for [DME][D_{3h}(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

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.

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.

	Number of atoms	R(O)MP2/ 6-31+G(d) ^a	UMP2/ 6-31+G(d)		
		d [Å]	E_i [Kcal/mol]	d [Å]	E_i [Kcal/mol]
O1	35	3.000	−2.56		
O2	35	2.750	−1.54		
O3	36	Repulsive			
O4	36	2.375	−1.37		
O5	43	3.125	−2.99	3.125	−1.91
O6	43	2.750	−1.82	2.750	−1.42
O7	45	2.000	−5.71	2.000	−5.38
O8	45	2.750	−0.43	2.875	−0.28
O9	45	Repulsive		Repulsive	
O10	45	3.750	−1.06	4.000	−0.76
O11	45	2.875	−3.56		
O12	45	2.625	−1.99		

^aRMP2 for **O1**, **O2**, **O3**, **O4**, **O11** and **O12** and ROMP2 for **O5**, **O6**, **O7**, **O8**, **O9**, **O10**.

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) $\text{O1} \rightarrow \text{M1}$, (b) $\text{O2} \rightarrow \text{M2}$, (c) $\text{O4} \rightarrow \text{M3}$, (d) $\text{O5} \rightarrow \text{O6} \rightarrow \text{M4}$, (e) $\text{O7} \rightarrow \text{O8} \rightarrow \text{M5}$, (f) $\text{O10} \rightarrow \text{M6}$, (g) $\text{O11} \rightarrow \text{M7}$, (h) $\text{O12} \rightarrow \text{M8}$. The atoms involved in the bond are connected with dotted lines.

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 $\text{H} \cdots \pi$ interactions (**O2**, **O6**, and **O12**) evolve to a structure with a close contact between the C atom and the PAH, those with $\text{O} \cdots \pi$ interactions (**O1**, **O5**, and **O11**) lead to a structure that also presents $\text{H} \cdots \pi$ interactions. However, the structure with $\text{H} \cdots \text{H}$ 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, Laplacian of the 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 ($3.49 \times 10^{-2} \text{ a.u.}$) and its Laplacian (1.31×10^{-1}), the shorter intermolecular bond distance ($1.779 \text{ \AA}$, 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**

TABLE III. Properties of the optimized structures and their intermolecular bonds: (a) interaction energy at R(O)MP2/6-31+G(d) ($E_i^{R(O)MP2}$, 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.

	$E_i^{R(O)MP2} [\text{kcal/mol}]^a$	Involved atoms	$d [\text{\AA}]$	$\rho(r_c) [10^3 (\text{e/a}_0^3)]$	$\nabla^2 \rho(r_c) [10^2 (\text{e/a}_0^5)]$	$\rho(q)_1 [\text{e}^-]$	$\rho(q)_2 [\text{e}^-]$
M1	−3.29	$\text{C} \cdots \text{C}$	3.12	6.85	2.51	0.17	−0.08
		$\text{C} \cdots \text{O}$	3.22	8.36	3.01	0.06	−0.28
M2	−2.08	$\text{C} \cdots \text{C}$	3.28	6.99	2.23	0.00	−0.07
M3	−2.11	$\text{C} \cdots \text{C}$	3.14	6.69	2.67	−0.03	−0.05
M4	−3.89	$\text{C} \cdots \text{H}$	2.91	5.34	1.71	0.07	0.07
		$\text{C} \cdots \text{H}$	2.92	5.25	1.68	0.07	0.06
M5	−7.06	$\text{H} \cdots \text{O}$	1.78	34.90	13.10	0.33	−0.12
M6	−2.88	$\text{O} \cdots \text{C}$	3.11	5.90	2.83	−0.74	−0.12
M7	−3.47	$\text{C} \cdots \text{O}$	2.97	10.70	3.91	−0.12	−0.22
		$\text{C} \cdots \text{H}$	2.79	6.78	5.20	−0.13	0.10
		$\text{C} \cdots \text{H}$	3.23	5.20	2.31	0.34	0.11
M8	−2.84	$\text{C} \cdots \text{C}$	3.19	7.05	2.72	0.18	−0.03

^aRMP2 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 $\cdots$ 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 S2⁷¹ of the supplementary material) such as the interaction energy (E_i), the bond distance for the intermolecular interactions (d), the charge density of the atoms involved in an intermolecular interaction ($\rho(q)$), the electronic density at the intermolecular bond critical points ($\rho(r_c)$), and the Laplacian at these points ($\nabla^2\rho(r_c)$). 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

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**).

		MP2	M05	M05-2X	M06-2X	M06-HF	M06-L
O1	E_i [kcal/mol]	-2.56	-0.81	-1.72	-2.77	-2.66	-2.69
	d [Å]	3.00	3.125	2.875	2.875	2.875	3.125
O2	E_i [kcal/mol]	-1.54	-0.41	-0.81	1.00	-0.95	-1.13
	d [Å]	2.75	3.00	2.75	2.625	2.625	2.625
O3	E_i [kcal/mol]						
	d [Å]						
O4	E_i [kcal/mol]	-1.37	-0.84	-0.82	-0.78	-0.59	-0.40
	d [Å]	2.375	2.50	2.50	2.375	2.50	2.75
O5	E_i [kcal/mol]	-2.99	-0.66	-1.37	-2.27	-2.21	-2.38
	d [Å]	3.00	3.125	3.00	2.875	2.875	3.125
O6	E_i [kcal/mol]	-1.83	-0.37	-0.74	-0.92	-0.87	-0.97
	d [Å]	2.75	3.00	2.75	2.625	2.75	2.625
O7	E_i [kcal/mol]	-5.71	-4.42	-6.71	-8.30	-8.88	-7.04
	d [Å]	2.00	2.125	1.875	1.875	1.875	1.875
O8	E_i [kcal/mol]	-0.43	-0.09	-0.35	-0.57	-0.51	-0.80
	d [Å]	2.75	2.625	2.50	2.375	2.625	2.50
O9	E_i [kcal/mol]			0.47	-0.95	-0.10	-0.69
	d [Å]			4.00	3.625	3.75	2.875
O10	E_i [kcal/mol]	-1.03	-0.78	-1.55	-2.17	-1.71	-1.75
	d [Å]	3.625	3.875	3.50	3.25	3.375	3.375
O11	E_i [kcal/mol]	-3.56	-1.05	-2.06	-3.47	-3.33	-2.93
	d [Å]	2.875	3.125	2.875	2.75	2.75	2.875
O12	E_i [kcal/mol]	-1.99	-0.34	-0.80	-1.13	-0.66	-1.11
	d [Å]	2.625	3.00	2.625	2.50	2.625	2.375

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 V. Average deviation of the properties for the potential energy curves (interaction energy $E_i(\mathbf{Ox})$ and minimum distance $d(\mathbf{Ox})$) and optimized minima (interaction energy $E_i(\mathbf{Mx})$, intermolecular distance $d(\mathbf{Mx})$, 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.

	M05	M05-2X	M06-2X	M06-HF	M06-L
$\Delta E_i(\mathbf{Ox})$ [kcal/mol]	1.32	0.91	0.78	0.87	0.69
$\Delta d(\mathbf{Ox})$ [Å]	0.2	0.08	0.16	0.11	0.18
$\Delta E_i(\mathbf{Mx})$ [kcal/mol]	0.93	0.38	1.72	1.42	1.18
$\Delta d(\mathbf{Mx})$ [Å]	0.34	0.13	0.11	0.34	0.62
$\Delta(\rho(r_c))$ [10^3 (e/a ₀ ³)]	3.75	1.25	1.24	2.46	2.61
$\Delta(\nabla^2\rho(r_c))$ [10^2 (e/a ₀ ⁵)]	1.32	0.67	0.48	0.72	1.15
$\Delta\rho(q)$ [e ⁻]	0.06	0.06	0.06	0.08	0.08

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 $C \cdots O$ 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 $\rho(r_c)$ and $\nabla^2\rho(r_c)$ 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 tend to overestimate the MP2 interaction energy.

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