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The role of hydrogen bonding in interaction energy at the interface of conductive polymers and modified graphene-based nanosheets: A reactive molecular dynamics study



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ABSTRACT

Keywords: Reactive molecular dynamics Interaction energy Graphene-based polymer nanocomposites Hydrogen bonding Interaction energy between conductive polymers and modified graphene-based nanosheets was evaluated using reactive force-field (ReaxFF) molecular dynamics (MD) with considering the molecular orientation of polymers with respect to contact surface. The studied systems consist of conductive polymers, e.g., poly(3-(4-n-octyl)-phenylthiophene) (POPT), poly(3-phenylhydrazone thiophene) (PPHT) as well as modified graphene-based nanosheets by hydroxyl, epoxy, carboxyl, methyl, and carbonyl functional groups. According to the MD results, the highest interaction energy was obtained at the interface of PPHT and carboxylated graphene due to forming hydrogen bonds. Also, PPHT polymer revealed more interaction with reduced graphene oxide (rGO) in comparison with POPT. The main sites of interaction and structural properties of polymers were studied by radial distribution function (RDF) and radius of gyration (R_g). The degree of reinforcement of polymers are in good agreement with experimental data. The obtained results can be used to produce more effective reinforced nanocomposites for solar cell applications.

1. Introduction

The modification of surface is necessary method to enhance the feature of graphene sheet which is a two-dimensional nanomaterial with a layer thickness of one atom [1]. Graphene sheet has showed many outstanding properties [2] and aroused intensive research enthusiasm. Its large aspect ratio, high surface area, high electric conductivity [3] and supernatural properties [4] make it an ideal material for fabricating polymer-based extraordinary nanocomposites for energy storage [5], sensors [6], organic electronics and so on. Recent studies showed that graphene as nanofiller may be preferred over other conventional nanofillers such as carbon nanotubes (CNTs), exfoliated or expanded graphite (EG), etc. due to its unique properties. Carbon nanotubes, as nanofiller, can improve the mechanical and electrical properties of the composite; but, the production cost of CNTs is very high [7]. Graphene has higher surface-to-volume ratio in comparison with CNTs; because of the inaccessibility of the CNT's inner tube surface to polymer molecules [8]. This makes graphene potentially more favorable for improving the properties of polymer matrices, such as electrical properties [9]. The resulting material by fully functionalization of graphene sheet is known as graphene oxide (GO), with remarkably hydrophilic and more reactive [10]. GO is a desirable derivation of pristine graphene which consists of covalently-attached oxygen containing hydroxyl (OH) and epoxy (EP) on the surface of graphene as well as carbonyl (C=O) and carboxyl (COOH) groups on the edge of graphene sheet [10,11]. However, further modifications has been performed with various components for more improving the properties of surface of graphene depending on application of nanocomposites [12]. So, the properties of graphene nanosheets can be tuned by functionalizing their surfaces with electron-accepting or electron-withdrawing groups [13]. Understanding the physics and chemistry of interfacial interactions between graphene sheet and chemicals plays an important role in application of graphene sheet [14,15]. Along with covalently attachment, the non-covalent interactions of polymer/GO can be important for homogeneous distribution of nanofillers in polymeric matrix. In addition to non-covalent interactions such as π - π stacking [1] in graphene/polymer composite, other van der Waals interactions are another driving forces for effective adhesion. Nanocomposites of conducive polymer/graphene sheet or functionalized graphene (FG) sheet can be used as active layer of polymer solar cells in which the polymer as donor material and carbon nanostructure as acceptor material can be tailored by further modification [14]. For

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weak interactions between graphene sheet and polymers, the graphene nanosheets tend to aggregate and decrease the interfacial energy resulting in a deterioration of the final performance of nanocomposites [16]. Therefore, interfaces between graphene nanosheets and polymer matrices should be well-designed through functionalization of graphene in an effective way [17]. The low-cost of conjugated polymers offers their applicability in a large-area devices [18] such as organic solar cell, but the desirability of the solar cells will be low if the active layer which consists of conjugated polymers as donor, does not have a proper nanomorphology; even if the other properties of the active layer are superior [19]. Because of necessity of the suitable charge transfer at the interface of conjugated polymer (donor) and nanoscale carbon materials (acceptor), the interfacial interaction energy in nanocomposites plays a key role in polymer solar cells [20,21]. Alternatively, the reduced graphene oxide (rGO), that can act as a current collector, makes easier the separation of electron-hole pairs in some photovoltaic devices [22]. Generally, the reinforcement of polymer nanocomposites is important factor in their applications.

The maximum π - π interactions is as a result of self-assembly of polymer on graphene sheet and FGs due to regioregularity of polymer [23]. The planar skeleton contributes to charge transport in molecular electronic devices through the π -conjugated backbone; so, the structural evaluation of materials is important [24] for enhancing the efficiency of photovoltaic cells [25]. Wang et al. [26] calculated the atomistic interactions between graphene/polyethylene (PE) using ab initio polymer consistent force field (PCFF). They found that the oxygenfunctionalized graphene has greater amount of interfacial shear force than pristine and hydrogen-functionalized ones during pull-out simulations at different oxygen coverage. Skountzos et al. [27] calculated the degree of mechanical reinforcement in GO/poly(methyl methacrylate) (PMMA) by molecular dynamics simulations using DREIDING allatom force-field. They indicated that the Young's modulus is improved by loading 5.67 wt% of GO. Wan and Chen [17] examined the reinforcement of GO/polymers nanocomposites containing poly(L-lactic acid) (PLLA), poly(3-caprolactone) (PCL), polystyrene (PS), and highdensity polyethylene (HDPE) polymers by micromechanical method. They used the Halpin-Tsai model, Laminate theory and Mori-Tanaka model to study the theoretical elastic moduli of nanocomposites. Nikkhah et al. [28] investigated the interfacial interaction energy between polyethylene and functionalized graphene using molecular dynamics simulation with PCFF force-field. Most molecular dynamics simulation studies have been performed based on DREIDING, PCFF or universal force-field (UFF) as conventional force-fields for estimation of interfacial interaction energy. Raymand et al. [29] carried out molecular dynamics simulations for adsorption of water on ZnO surface using ReaxFF reactive force-field and found the good agreement between MD and quantum mechanics (QM) results. They simulated the adsorption of water on stepped ZnO surface and concluded that the structures that form hydrogen bonding (H-bonding) are favored. Also, steps on the surface promotes an increased level of hydroxylation in the water monolayers. Compton et al. [30] studied on the tuning the mechanical properties of GO/polyvinyl alcohol (PVA) nanocomposite by controlling cooperative intersheet H-bonding. They elucidated the role of Hbonding between GO and PVA in water medium based on ReaxFF forcefield. Their simulation indicated the maximum amount (wt%) of water that can be removed by dehydration reaction from nanocomposites. The work of evaluation of noncovalent and covalent interaction between aromatic structures and GO carried out by Coluci et al. [31] using reactive MD with ReaxFF force-field. Their simulation results are in good agreement with experimental results [32,33]. Thus, the study on chemical reactions (H-bonding, π - π or other types of interactions) can be done using ReaxFF force-field. Also, the calculation of atomic charges is performed via electronegativity equalization method (EEM) [34]. Therefore, ReaxFF uses a bond-order formalism in combination with polarizable charge descriptions to explain both reactive and nonreactive interactions between atoms. This enables ReaxFF to accurately

model both covalent/noncovalent and electrostatic interactions for a wide range of materials and its results are close to the *ab inito* results [35]. In this study, the reactive molecular dynamics with ReaxFF force-field provides the way to study the interaction energy between graphene or FG and two conjugated polymers including poly(3-(4-n-octyl)-phenylthiophene) (POPT) and poly(3-phenylhydrazone thiophene) (PPHT) at the interface. The considered polymers have thiophene ring as a π -bridge rich of electron that make the structure with the planar skeleton. PPHT belongs to the class of such π -conjugated polymers that consist of an hydrazone segment (containing azomethine double bond (-NH-N=CH-)) as a good hole transporting material [36]. POPT with alkyl side chain of 8 carbon atoms was selected as another polymer.

In generally, the effect of hydrazone segment (in PPHT polymer) on the interfacial energy of nanocomposites is studied through its interaction with different functional groups of methyl (CH_3), hydroxyl (OH), epoxy (EP), carbonyl (C=O), and carboxyl (COOH) on the graphenebased nanosheets which is compared with POPT without hydrazone containing azomethine double bond. Also, the effect of different orientation of polymer chain on the interaction energy is studied from microscopic point of view. Therefore, the interaction energy of two polymers (POPT and PPHT) and graphene-based nanosheets is studied. All simulations are performed at experimental and upper temperatures.

2. Systems and simulation method

2.1. The conformation of polymers

All MD simulations were performed using LAMMPS package which is the Sandia National Laboratories' molecular dynamics code [37]. PPHT and POPT polymers (Fig. 1(a, c) and (b, d), respectively) were placed at a distance of 6 Å from graphene-based nanosheets. The structures of polymers/graphene sheet and polymer/FG were sketched, and then imported into the LAMMPS code as data file. For precise comparison; the simulated models of polymers were selected with comparable numbers of atom in order to make a suitable evaluation of the interaction energy between polymers and graphene or FG nanosheet.

The number of atoms in POPT and PPHT polymers was considered 125 and 134, respectively which is small and so the results demonstrate the behavior of small part of the whole polymer chains. However, the term of "polymer" was employed for simplicity throughout the manuscript.

2.2. Molecular structure of modified graphene-based nanosheets

The dimension of graphene and FG sheets in all simulations is (95.1×54.1) Å². To evaluate the effect of oxygenated functional groups of graphene surface on the interaction energy, the structure of GO was selected. The elementary evaluation was based on different oxidation percentages. The amount of interaction energy between polymers and GO sheets was studied at different C:O ratios of GO sheets. For this purpose, the GO sheets were sketched based on model of Boukhvalov et al. [38] that presented the way for functionalizing graphene surface with epoxy (EP) and hydroxyl (OH) functional groups. This model presents the most stable configurations of functionalized graphene with epoxy and hydroxyl groups. The structures of GO sheets were created with considering that the carboxyl (COOH) and carbonyl (C=O) groups are on the edge of graphene sheet by randomly distribution. The different ratios of C:O on the surface of graphene sheets were designed as 2.5 [39] (according to experimental data), 5, 10, 15, 20 as given in Table 1.

In elementary investigations, the position of polymer was mostly set in the vicinity of the surface and edge of GO sheets at C:O ratio of 5. The main factor for evaluating the interaction energy of polymers on the GO surface is studying the interaction energy based on percentage coverage of each functional group. It is essential to remember the one hydroxy Download English Version:

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