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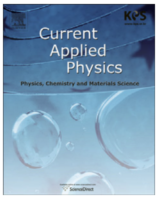

Investigation of the interface between polyethylene and functionalized graphene: A computer simulation study

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ABSTRACT

The effect of surface chemical functionalization of a single graphene layer on its thermodynamic work of adhesion (WA) with polyethylene (PE) chains has been investigated using molecular dynamics (MD) simulation. For this purpose, amine (NH_2), carboxyl (COOH), hydroxyl (OH), and methyl (CH_3) functional groups were distributed randomly throughout the graphene surface using a Monte Carlo (MC) algorithm to achieve graphene functionalized structures with minimized potential energies. The MD simulation results showed that the thermodynamic WA between the PE and the functionalized graphene was larger than that between the PE and the pristine graphene. In fact, the electronegativity of functional groups and Van der Waals forces play influential roles in the thermodynamic WA between the PE and the functionalized graphene. In addition, the amount of thermodynamic WA was increased with increasing the functional group surface density, except for the graphene functionalized with the methyl groups. The segmental density of the PE chains near the single sheet surface was determined based on the density profile calculation. The polymer segments exhibited strong ordering and sharp density variations near the PE/graphene interface. The dynamic of chains was quantitatively characterized by calculating mean square displacement (MSD). Furthermore, the influence of functionality on the glass transition temperature (T_g) of the PE at the PE/graphene interface region was investigated. The results showed that the T_g at the PE/graphene interface was much higher than that of the bulk polymer. In fact, the functionalization of the graphene surface seems to considerably enhance the T_g of the polymer due to lowering the chains mobility.

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1. Introduction

Graphene as one of the strongest materials possessing exceptional properties is used as a reinforcement to improve the properties of polymers [1–3]. Many researchers indicated that the incorporation of only a small amount of exfoliated graphene resulted in considerable enhancement of electrical conductivity, mechanical and thermal properties of polymers [4,5]. The control of interfacial interactions plays a crucial role in designing nanocomposites with desirable physical and mechanical properties.

The adhesion on a molecular level which arises from interfacial interactions between adhesive and adherent can be quantified by calculation of thermodynamic WA. The thermodynamic WA between two dissimilar materials at the interface may consist of weak interactions, polar, and induced polar forces [6]. One of the approaches to measure the WA between the solids is based on the surface free energy data which generally comes from contact angle experimental measurements. Nonetheless, these measurements consist of some complexities including the effect of surface roughness, the necessity to establish equilibrium on the surface, and the difficulty to study some solid surfaces with high surface free energy. Molecular dynamics (MD) simulation is one of the most accepted methods used for atomic-scale characterization of material properties to obtain insight into the interfacial molecular interactions and adhesion [7]. Some researchers have investigated the interfaces between polymers and solids using MD simulations. Minoia et al. [8] applied MD simulation to characterize polymer/carbon nanotube (CNT) interface. They found that regular lamellar-type structures of the polymer were formed on the CNT surface. Their study on the effect of nanotube size and functionalization on interfacial interactions, indicated that the interface stability

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decreased with the curvature of the carbon surface, while the chemical groups attached on the tube wall *sterically* hindered the forming of the lamellar structures. Langeloth et al. [9] used a coarse grained (CG) model of a mixture of bisphenol A diglycidyl ether (DGEBA) and diethylenetriamine (DETA) to perform a reactive MD simulation of the epoxy resin curing reaction in the presence of a generic surface. They observed a strong layering effect for DGEBA in the interphase while it was depleted for DETA. The depletion zone for crosslinks near the surface is a weak point of such systems where failure is likely to happen. Zaminpayma et al. [10] investigated the adhesion between poly (3-hexythiophene) (P3HT), poly(2-methoxy-5-(3-7-dimethyloctyloxy) −1,4 − phenylenevinylene) (MDMO-PPV), and poly((((2ethylhexyl)oxy) methoxy-1,4-phenylene)-1,2-ethenediyl) (MEH-PPV) with single-wall carbon nanotube (SWCNT) using a reactive forcefield. They found that P3HT adheres to SWCNT better than MDMO-PPV and MEH-PPV due to the existence of a sulfur atom in its backbone. Eslami et al. [11] modeled a nanometric polyamide-6,6 film in contact with a graphene surface in a huge simulation box using a long time Coarse-grained molecular dynamics simulation. Their simulation was enabled to cover a broad range of length scales and achieve the long-time relaxation regime of long chains. Then, the interplay between the change in structural and the associated dynamic properties in the interphase was compared with the bulk polymer. The work of adhesion between polyimide and silicon surface was evaluated by Makeev et al. [12]. The observation of a transition between noncontact and contact adhesion regimes as a function of the interfacial bonding strength was attributed to structural relaxation in the organic layer near the interface. Ghanbari et al. [13] simulated silica nanoparticles which were embedded in polystyrene matrix using coarse-grained MD simulation. According to their results, the structure of the polymer chains is strongly affected by the silica nanoparticle. Layering, chains expansion, and orientation of segments were observed at the interface which depended on nanoparticle wetability, grafting density and length of grafted chains on the nanoparticle, and matrix chains characteristics. Li [14] simulated the PE reinforced with different kinds of nanofillers, such as bucky-ball nanoparticles, graphene, SWCNTs, X-shaped and Y-shaped SWCNT junctions. The effects of these filers on the structural and physical properties of PE were investigated using MD simulations. The results indicated that graphene had larger interaction with the PE than the other nanoparticles. The MD simulation results obtained by Cui et al. [15] showed that the adhesion between epoxy molding compound (EMC) and copper oxide (Cu_2O) lattice was greater than the adhesion between EMC and silver oxide (Ag_2O). The molecular concept of interfacial interactions between polymer chains and fillers via MD simulation can provide a deeper insight about molecular interfacial adhesion mechanisms [16,17]. Weak interfacial bonding between inorganic fillers such as graphene and most of polymers leads to poor dispersion of the filler and lower stress transfer at the interface region [18]. Therefore, efforts have been made to functionalize the graphene surface by using different functional groups, which improve the interfacial adhesion and facilitate the dispersion of the graphene sheets in a polymer matrix [1,19,20].

In this research work, the influence of functionalization of the graphene with various functional groups on the PE/graphene interfacial adhesion was investigated using MD simulation. For this purpose, the graphene surface was covered with various types and surface densities of polar and non-polar functional groups. The thermodynamic WA between linear amorphous PE chains and the functionalized graphene was calculated using MD simulation. In addition, the segmental density of the PE chains at the interface between the contacting polymer and the modified single sheet was investigated. The influences of pristine and functionalized graphene on the glass transition temperature (T_g) of the PE were also studied. The T_g of the polymer chains at the interface region was predicted by performing a cooling process. For this purpose, the chain motions in the bulk-like region and polymer–vacuum interface were limited.

The results of current research work can provide a deeper insight about molecular interfacial adhesion mechanisms between polymer chains and fillers to design an interface with proper strength. As well-known, interfacial adhesion has a crucial role on the mechanical properties of polymer composites. It should be mentioned that the simulation results of polymer/graphene interface can be used in modeling mechanical properties of graphene reinforced polymers in future works.

2. Computational details

2.1. Monte Carlo (MC) strategies

Various functional groups, such as amino (NH_2), carboxyl (COOH), hydroxyl (OH), and methyl (CH_3) were used to functionalize the graphene surface. MD simulation was carried out on the graphene surface modified with surface densities of 0, 0.40, 0.81, 1.21, 2.03, 2.84, and 4.06 functional groups per nm^2. The functional groups were supposed to randomly end-graft onto only one surface of the graphene via chemical covalent bonding. As an instance of the created models, Fig. 1(a) shows the randomly grafted graphene with 1.21 OH groups per nm^2. As shown, the surface modification seems to change the geometry of the atoms and causes the bonded graphene atoms to the functional groups to rise out of the graphene plane surface and change their hybridization from sp^2 to sp^3 (Fig. 1(b)).

In the case of random graphene functionalization, we tried to find the most probable positions for the attached groups via MC simulation method. According to our knowledge, less attention has been paid to finding the most probable positions of the functional groups on the graphene sheet [1,2,19,21]. In these research works, functionalization of the graphene were carried out in a random manner. However, there was a question here, which positions of functional groups on the graphene can lead to most probable energetically structure. In another word, the question was that the random manner functionalization method, which was applied in other research works, could result in a stable structure. Therefore, a MC algorithm was utilized to find the most probable positions for the attached functional groups.

The periodic unit cell of the graphene model used in this work consisted of 700 carbon atoms. The carbon sites of the graphene unit cell were labeled with respective values 1, 2, 3 … n−1, n (n = 700). Thereafter, the m functional groups were randomly attached on these carbon sites to construct the first configuration of the functionalized graphene (Figure S-1 in the supplementary data section). The interaction energy between all the attached functional groups was calculated using pairwise additive approximation. The new configuration was generated by randomly selecting of one of the attached groups and moving it to a random unoccupied position (Figure S-2). After calculation of the interaction energy of this new configuration using Metropolis algorithm [22], the stability toward the first configuration was evaluated. It should be mentioned that the energy of the structures in the MC part was calculated based on the same force field which was used in the MD part. In order to select the appropriate number of steps for performing the algorithm, the algorithm with different steps between 10^4 and 10^6 was carried out. It was found that the average and standard deviation values were independent from the number of steps. Then, 10^5 was selected as the number of moves for performing this algorithm for each functionalized graphene.

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