Local glass transition of polyisoprene induced by graphene planes observed in silico through atomistic molecular dynamics simulations

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Abstract A study on the molecular mechanisms of natural rubber reinforcement due to the addition graphene planes was carried out by molecular dynamics simulations. Simulations of pure natural rubber (Polyisoprene; PI) and Polyisopren-graphene composite (PI-GRA) were performed and analyzed for their glass transition temperatures ($T_g$). In the simulations, simulated annealing technique was used to change the temperature from 100 K to 300 K in order to observe the glass transition from the point where the sudden increase in volume and sudden decrease in density were observed. Glass transition temperature ($T_g$) from the molecular dynamics trajectory of pure PI was 207.9 K, close to the value $T_g = 211$ K obtained from the experiment. Also, we found that glass transition temperature ($T_g$) increased to 220.1 K when adding graphene planes into the PI matrix. In addition, further analysis of MD trajectories showed that the overall density of pure 16-mer cis-1,4-polyisoprene at low temperature (100 K) is higher than the density at high temperature (300 K) and the threshold density for glass transition was 929.4 kg/m$^3$. For PI-GRA at 100 K, density of the whole system was higher than the threshold density, which showed that the whole polymer was in glass phase. However, at 300 K, the network of PI molecules nearby the graphene planes were orderly organized and possessed higher density than the threshold density, showing the properties of glass. In the middle area, PI molecules were arranged disorderly and has a lower density than the threshold, showing the properties of rubber.

1. Introduction

Carbon-based composites have become an immensely active field of research, since the discovery of graphene, a two-dimensional honeycomb carbon layers with distinct electrical, thermal and mechanical properties [1]. Graphene composites are promising for the applications in polymer reinforcements and flexible sensors [1,2]. Glass transition temperature ($T_g$) is an important parameter that characterizes mechanical properties of polymers for practical uses. Polymeric materials at temperatures below $T_g$ are found significantly ‘harder’ and more ‘glassy’ than materials at temperature higher than $T_g$, which are relatively ‘viscous’ and rubbery. Hard plastic materials, such as polystyrene, are used when $T_g >$ room temperature. Meanwhile elastomers, such as polyisoprene, are needed at $T_g <$ room temperature [3]. To alter $T_g$ polymers for industrial applications, nanoparticles are introduced into the polymer matrix. Confinement effect [3] and interfacial interactions between polymer matrices and fillers limit the
mobility and configurational entropy of polymer chains, so that the cooperatively rearranged regions (CRR) formed and the diffusion coefficient of molecules CRR regions become lower according to the Adam-Gibbs (AG) Theory [4–6]. In this work, we investigated the local transition of cis-1,4-polyisoprene (PI) induced by parallel infinite graphene plane. This novel system simplified the problem into 1D. Also, a simple method was proposed to estimate the thickness of cooperatively rearranged region (CRR).

2. Methodology

2.1. Simulation setup

Starting structures of the 16-mer cis-1,4-polyisoprene (PI) model were built by using an in-house PYTHON script. Atomic coordinates of five carbon atoms within each PI monomer were copied and translated to create a 16-mer linear chain. Then, hydrogen atoms were added and OPLS/AA force field parameters [7] were assigned automatically. For the system of pure-PI, 100 PI chains were randomly added into a 12×12×12 nm$^3$ simulation box. Then, the system underwent a 5-ns equilibration in an NPT ensemble at temperature 300 K regulated by velocity-rescale algorithm and pressure 1 atm regulated by the Berendsen barostat [8]. The box was then shrunk until the dimension became about 6×6×6 nm$^3$. After that, the stepwise simulated annealing was performed. A 10-ns constant temperature simulation was performed, follow by a 1-ns annealing simulation in which the temperature was linearly decrease by 20 K, making one cycle. The cycle was then repeated until the temperature was decreased from 300 K to 100 K. For the system of graphene-PI composite. A 6×6 nm$^2$ graphene sheet was frozen on the xy-plane. Periodic boundary condition in all axes was set, so that the graphene sheet become infinite number of parallel infinite planes, separated by the box dimension in z-axis. After that, the same number of PI chains (100 chains) were add and the system underwent the same simulation protocol as for pure-PI. All molecular dynamics simulations were performed by using GROMAC5.1.2 package [9].

2.2. Trajectory analysis

All pieces of 10-ns constant temperature trajectory at T = 300 K, 280 K, 240 K, 220 K, 200 K, 180 K, 160 K, 140 K, 120 K and 100 K were taken for further analysis. Averages and standard deviations of density were extracted from all the trajectory parts, and from the simulations of both pure PI and graphene-PI composites. The evaluation of glass transition temperature (Tg) and the threshold density will be explained later in the result section. To investigate the effects of graphene addition to PI, local density was measured along the z-axis (perpendicular to graphene planes) by counting the average number of carbon atoms within thin slabs of thickness 0.117 nm. The numbers were then rescaled into the density of PI chains.

3. Results

An atomistic molecular dynamics simulation was performed on a simulation box containing 100 molecules of 16-mer cis-(1,4)-polyisoprene under NPT ensemble. Multi-step simulated annealing was used to vary the temperature from 100 K to 300 K. The relationship between the varied temperature and the increased volume is shown in figure 1a. At lower temperatures (100-180K), volume of the simulation box was increased at the rate of 0.079 nm$^3$/K. A higher temperature (220-300 K), volume of the simulation box was increased at higher rate of 0.172 nm$^3$/K. Density was also plotted as a function of temperature as show in figure 1b. At lower temperature (100-160 K), density of the simulation box was decreased at the rate of $-0.400$ nm$^3$/K. At the higher temperatures (240-300 K, density of the simulation box was decreased at higher rate of $-0.752$ nm$^3$/K. Linear regressions of the $\rho$-T relationships were performed for both intervals (100-160 K and 240-300 K). The two linear relationships intercept at the temperature of 207.9 K. Sudden increase in the rate of change in density indicated that transition from glassy state to rubbery state might occur of the glass transition temperature $T_g = 207.9$ K and the threshold density $\rho_0 = 929.4$ kg/m$^3$. The estimated $T_g$ from the simulation is slightly different from the
experimental value (~200 K) [10], as simulated chains were relatively short compared to the real polymer.

Figure 1. Changes in (a) box volume and (b) density as a function of temperature obtained from simulated-annealing molecular dynamics of 16-mer cis-1,4-polyisoprene molecules at temperatures ranged from 100 K to 300 K. Green and red dashed lines lines indicated piecewise linear relationships of volume-temperature and density-temperature at T < T_g (green) and T > T_g (red). The vertical dashed line indicated glass transition temperature (T_g) and the horizontal dashed line indicated density threshold for glass transitions.

Figure 2. Superimposed snapshots of a 2-nm thick slab taken every 2 ns from 10 ns MD trajectory of 16-mer cis-1,4-polyisoprene at (a) 100 K and (b) 300 K.

This was confirmed by a visual inspection of pure 16-mer PI shown in figure 2. At 100 K (figure 2a), low chain mobility was observed as the carbon atoms in PI chains slightly fluctuated. The polymer network was seen as ‘semi-crystal’ as empty spaces were seen though the 2-nm thin slab, suggesting a ‘glassy’ state of PI, in which the density was above \( \rho_0 \). However, at 300 K (figure 2b), high chain mobility was observed as the carbon atoms in PI chains largely fluctuated and the dynamics of polymer chains spanned almost the whole space of the simulation box, suggesting a ‘rubbery’ state of the system, in which the density was below \( \rho_0 \). Effect of graphene to properties of PI were investigated though another system containing 100 molecules of cis-1,4-polyisoprene filling up the space between infinite graphene sheets separated by the distance ranged from 4.68 nm to 5.16 nm, correspond to the temperature range of 100 K to 300 K in the the simulated annealing simulation. Global glass transition temperature (T_g) was obtained by linear regression of \( \rho-T \) relationship with in two intervals, similar to the pure PI. A significant shift in global T_g of the graphene PI composite compared to the pure PI was seen in figure 3a and figure 3b, where the T_g become 220.1 K when graphene sheets were presented.
This increase in $T_g$ at the presence of a carbon-based filler was similar to the increased $T_g$ of polybutadiene filled with fullerenes [3].

![Figure 3](image1.png)

**Figure 3.** Changes in (a) box volume and (b) density as a function of temperature obtained from simulated-annealing molecular dynamics of a graphene-PI composite system containing molecules of 16-mer cis-1,4-polysisoprene placed between two parallel graphene planes at temperatures ranged from 100 K to 300 K. Green and red dashed lines indicated piecewise linear relationships of density-temperature at $T < T_g$ (green) and $T > T_g$ (red). The vertical dashed line indicated glass transition temperature ($T_g$) and the horizontal dashed line indicated the density threshold for glass transitions.

![Figure 4](image2.png)

**Figure 4.** Superimposed snapshots of a 2-nm thick slab taken every 2 ns from 10 ns MD trajectory of the graphene-PI composite system at (a) 100 K and (b) 300 K.

Visual inspection on the chain dynamics was carried out by the VMD program on the graphene-PI novel composite at 100 K to 300 K (figure 4), along with the local density measured along the z-axis perpendicular to the graphene plane. Similar to the pure-PI, five conformational snapshots were taken every 2 ns from the MD trajectory at temperatures 100 K (figure 4a) and 300 K (figure 4b). At 100 K, the superimposed snapshots displayed a semi-crystalline behaviour, as alternating density local minima and maxima were observed in figure 5. This was in agreement with the local distribution profile from the previous simulations of PI on graphite [11]. High-density region was observed near the graphene plane, in which the peak density of $2650 \pm 50$ kg/m$^3$ was measured at the distance 0.41 nm from the graphene plane. Other density peaks become smaller when the distance from graphene increased, but still higher than the threshold density at glass transition state (indicated by horizontal dashed line), suggesting the glassy state at 100 K for the whole region. At 300 K, the density became lower along with increasing volume. The peak density closest to graphene was $2500 \pm 50$ kg/m$^3$. Peak densities at the middle were lower than the threshold density. CRR boundaries at $1.34 \pm 0.01$ nm from graphene
planes were defined by the distance between a graphene plane and the furthest density peak with density higher than the threshold density. PI chains within the distance 1.34 ± 0.01 nm were in ‘glass’ state but PI chains located further than 1.34 ± 0.01 nm were in ‘rubbery’ state, and confirmed that graphene plane can induce local glass transition at temperatures higher than $T_g$. In conclusions, the proposed thickness of cooperatively rearranged regions (CRR) of natural rubber induced by a large graphene plane at 300 K was 1.34 ± 0.01 nm.

4. Conclusions
We investigated glass transition phenomena occurred within natural rubber network and effects introduced by the addition of graphene. The novel composite polymer system consisted of parallel infinite graphene sheet within PI matrix. Glass transition temperature ($T_g$) was found from the piecewise relationship of either $V$-$T$ or $\rho$-$T$. For pure PI, $T_g$ were found from to be 207.9 K at the threshold density of 929.4 kg/m$^3$. Global $T_g$ was found increased when graphene planes are present. Then, local density analysis showed that at $T > T_g$, PI chains in the CRR region within the distance 1.34 ± 0.11 nm from graphene planes become glassy and more ordered. This finding provided an insight for engineering the mechanical properties of composites with carbon-based filler.

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Figure 5. Time averaged local density along the axis perpendicular to graphene planes calculated from the graphene-PI composite simulations at 100 K (light blue) and 300 K (orange). Vertical dashed lines indicated the boundary between CRR and rubbery (shaded in orange) regions. Vertical solid lines indicated the adjacent graphene planes at 300 K.