RESEARCH ARTICLE

NEMD SIMULATION TO STUDY VISCOSITY OF GRAPHENE FILLED POLYSTYRENE NANOCOMPOSITES

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ABSTRACT

In the present work, nonequilibrium molecular dynamics (NEMD) simulation was carried out to get an insight into the atomistic scale viscosity of graphene–polystyrene nanocomposite. The open access software Packmol was used to create amorphous PS and graphene+PS systems. The initial distribution of atoms in the two systems were created using cubic cells with periodic boundary conditions. Four pieces of graphene with side length of 5 nm x 5 nm and 400 polymeric chains consisting of three monomers per chain were randomly placed in the cubic cells to achieve a low concentration of graphene. The simulation box containing only PS was also created to provide a control. The simulations were conducted using LAMMPS with AIREBO potential and time step length of 1 fs. A Nose–Hoover style was selected to retain the system temperature. The SLLOD equations of motion were then applied to allow the system to undergo the flow under the NVT condition and mean square displacement (MSD), diffusion coefficient (D) and shear viscosity () were calculated.

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INTRODUCTION

Polystyrene (PS) is a long chain vinyl polymer formed by the polymerisation of styrene monomers. Various nanocomposites are developed using this polymer as the base matrix and nanofillers as reinforcement for numerous commercial applications. Hence, a fundamental understanding of the viscoelastic properties of polystyrene based nanocomposites assumes significance. The interaction between a single chain and a nanofiller at atomic level can provide an insight into the rheological properties of these nanocomposites. Molecular dynamics (MD) simulation is a powerful tool to study such viscoelastic mechanisms. Figure 1 (inset) shows a single chain of polystyrene consisting of three styrene monomers. The polymerisation of styrene monomers results in polystyrene which has a molecular formula of $-(CH_2-CH(C_6H_5))-_n$. This polymer is amorphous because the phenyl groups are randomly arranged. In the present work, amorphous polystyrene was generated that consisted of 400 single chains randomly arranged in a rectangular box. The open access *Packmol* software was used to pack these 400 chains in a rectangular box of dimension 85 x 45 x 85 Angstrom in X, Y and Z direction, respectively (Martínez et al., 2009).

The monomer model and polymer chain were developed using open access *Avagadro* software (Marcus, 2012). The initial configurations of monomers were aligned and their geometry was optimized using Gaussian force field and the protein database (pdb) file of atomic coordinates were then used to create input files for *Packmol* software. This software was applied to pack the box with polymer chains without overlapping of the initial distribution of atoms. Four pieces of graphene sheet (5 nm x 5 nm) and a thickness of 0.34 nm were randomly placed in a rectangular box to form nanocomposite containing low percentage of graphene. Figure 1shows the graphene filled polystyrene system created through *Packmol* and visualised through *Vega ZZ* open access software.

Simulation protocol

Potential: Adaptive intermolecular reactive bond order (AIREBO) potential has been used in the present work to describe the bonded and non-bonded atomic interactions of polystyrene chains and graphene nanofiller (Stuart, 2000). The AIREBO potential is best suited to simulate hydrocarbon systems such as graphene because it accurately evaluates both covalent (bonded) and non-bonded interactions between atoms (Zhao, 2010; Grantab, 2010).

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AIREBO potential is an extension of the reactive empirical bond order (REBO) potential and consists of three sub-potentials as given below (Brenner, 1990).

$$E^{AIREBO} = (1/2) [E^{REBO}+E^{LJ}+E^{tors}]$$

where, E^{AIREBO} is the total potential energy of a system of atoms, E^{REBO} is the REBO potential, which represents the energy stored in a bond between atoms; 5^{LJ} is the Lennard-Jones potential that gives the energy due to non-bonded interactions between atoms; and E^{tors} is the from torsional interactions between atoms. A periodic boundary condition has been adopted to simulate this large system.

In order to integrate the Newton's equation of motion a time step of 0.5 fs was used together with the AIREBO potential. The metal unit system was used in AIREBO potential field wherein the units of distance, time, and energy are Angstroms, picoseconds, and electron-volts, respectively. All the molecular dynamics simulations have been performed using the open access large-scale atomic/molecular massively parallel simulator (LAMMPS) (Plimpton, 1995). The VMD (Humphrey, 1996) and Vega ZZ software have been utilised to visualise the polymer structure and configuration.

Relaxation: The *as-created* atomic configuration of the two systems were not in its equilibrium configuration due to the existence of atom overlap and associated local high potential energy. Hence, the potential energies of atoms were relaxed to their local minimum values at specified temperature of interest. The system was run for 30 ps at the temperature and pressure of interest for the N (number of molecules), P (pressure) and T (temperature) ensemble to reach further equilibrium, and which provided the initial point for all simulations. A Nose–Hoover style was selected to retain the system temperature.

Deformation: The SLLOD equations of motion were then applied to allow the system to undergo the planar Couette flow under the NVT condition, where the mean square displacement (MSD), diffusion coefficient (D) and shear viscosity (η) were calculated using the following equations (Alder, 1970; Kubo, 1957).

$$MSD(t) = (N)^{-1} \sum_{i=1}^{n} | ri(t) - ri(t0)|^2$$

$$D= 1/6 \lim_{t \to \infty} d/dt((MSD(t))$$

where N is the total number of atoms, ri(t) is the position of atom i at time t and ri(t0) represents the original location of atom.

$$\eta = (V/k_BT) \int_0^\infty < \sigma xy(t)\, \sigma xy(0) > dt$$

is the viscosity, V is volume and k_B is Boltzmann constant, T is temperature in K and the σxy component of the pressure tensor.

RESULTS AND DISCUSSION

As mentioned in the previous section, for carrying out simulation on graphene+PS system, firstly the atomic configuration was allowed to relax for 30ps and then deformation was performed using a strain rate and time-step of 0.0001 ps^{-1} and 0.5 fs, respectively.
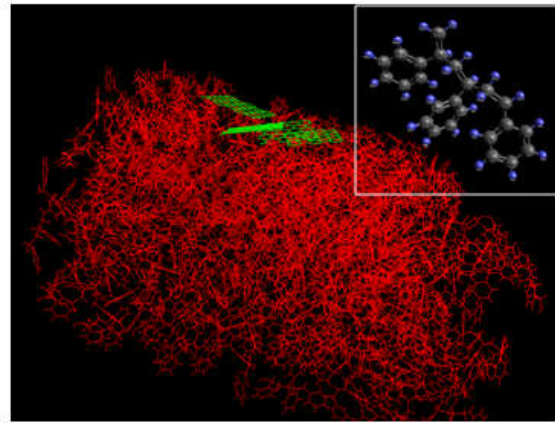

Figure 1. Graphene filled polystyrene system (*Vega ZZ*) (inset shows PS monomer)
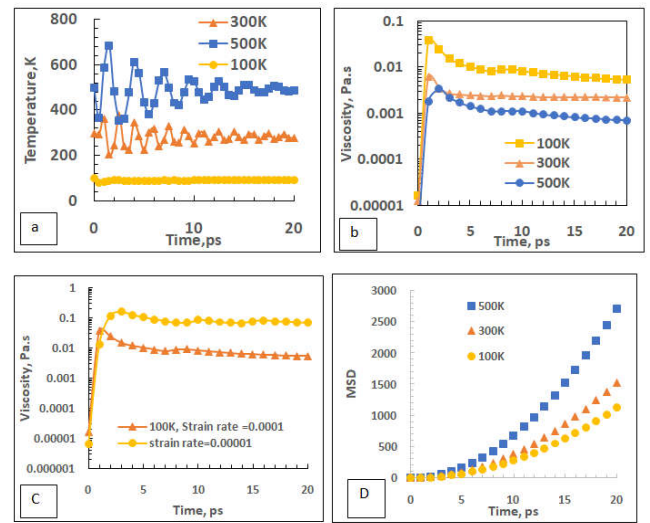

Figure 2 (a) Stabilisation of temperature (b) Temperature dependent viscosity (c) strain rate dependence of viscosity and (d) MSD of graphene+polystyrene system

Figure 2(a) shows the variations of temperaturein the course of relaxation for 30 ps. It is seen from Figure 2(a) that after initial fluctuations, the temperature stabilised between 15 to 30 ps. After relaxation the PS single chains become energetically favourable. These figures demonstrated that the PS systems reached its equilibrium configuration through the relaxation process between 15 to 30 ps. The viscosity of the composite calculated using simulation data has been used to characterize the rheological properties. In LAMMPS simulation the*erate*stylechangesadimensionoftheboxataconstantengineerin gstrainrate. The units of the specifiedstra in rate are 1/time. The box length L as a function of time will change as

$$L(t) = L_0 (1 + erate \text{x dt})$$

where dt is the elapsed time (in time units). For engineering strain rate, the change is based on the original box length wherein the box length is expanded by a factor which is different than that induced by a true strain rate i.e *trate*. In the present case, *erate* was used to change the box length. The no equilibrium MD calculations of shear viscosity, diffusion coefficient and density of graphene– PS nanocomposite containing four pieces of graphene were conducted under three different temperature of 100K, 300K and 500K at a constant strain rate of 0.0001/ps and 0.00001 /ps.

As shown in Fig. 2(b), the shear viscosity gradually reached a constant value as the computation time increases, which indicated that the simulation time of 20 ps was a suitable time period. The last 20 ps of the calculations was used to obtain the average shear viscosity, since the former 10 ns had larger fluctuations. Figure 2(b) also shows the viscosity versus time curves at three different temperatures. With increase in temperature, viscosity decreased significantly. Fig.2(c) shows that with increase in strain rate the viscosity decreased. MSD was another critical factor to describe the microscopic dynamics of nanoparticles, which reflects the rheological properties of nanocomposite. Figure 2(d) shows the MSD versus time curves at three different temperatures.

CONCLUSION

Nonequilibrium MD simulations were performed to investigate the rheological properties of polystyrene with addition of graphene sheets. The simulation results showed that the viscosity of pure PS increased by adding graphene nanoparticles.

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