Dynamics of Graphene Based Polymer Nanocomposites through Detailed Atomistic Simulations

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Graphene based polymer nanocomposites are hybrid materials with a very broad range of technological applications. Furthermore, recent experimental studies revealed that a substantial enhancement of the polymer dynamical and rheological properties can be achieved even with a very low loading of the graphene-based fillers. Graphene oxide is a common precursor for the preparation of these composite fillers and during its reduction graphene sheets with different percentage of oxygen are produced. The improvement in material properties correlates strongly with the nanocomposite microstructure and therefore the study of structure-properties relations is an intense research area

Simulation approaches are valuable tools for the study of molecule/graphene hybrid nanostructured systems at the molecular level. Our study is focused on the effect of the graphene layers on the structural and dynamical properties of polymer systems. Our work concerns the study of three hybrid polymer/graphene interfacial systems: (a) polystyrene/graphene, (b) poly(methyl methacrylate)/graphene and (c)polyethylene/graphene, through detailed atomistic molecular dynamics (MD) simulations [1,2]. In more detail, we present results from atomistic simulations of the above polymer nanocomposites with three types of dispersed graphene: (a) the pure non-functionalized sheet, (b) graphene with hydrogens grafted on the edges and (c) carboxyl-functionalized graphene. The graphene sheets were dispersed in the polar (polyethylene oxide, PEO) and non-polar (polyethylene, PE) polymer matrices in order to study the role of the polymer/graphene intermolecular interactions on the dynamical behavior of the hybrid material. We examine in detail the structural and dynamic properties of the polymer chains and observe the differences in the behaviour of graphene sheets with different functionalization. The relaxation of the polymer chains in the segmental and in the terminal (end-to-end vector) level is examined. In addition, diffusion coefficients of both polymer chain and of the graphene sheets are calculated.

Various properties are being studied related to:

(a) Density profile: The time-averaged molecular density profiles, $\rho(z)$, as a function of the distance from the graphene surfaces of the model films are calculated.

(b) Structural characteristics: Molecular orientation tendencies induced by the confinement are being studied by calculating the second rank order parameter and the polymer chain's conformation tensor.

(c) Mobility aspects: We study the dynamics of polymer chains, both in the level of the monomer and the chain center-of-mass, by monitoring the evolution of the mean square

displacements, as well as through time auto-correlation functions of a vector along the molecule.

All above properties are examined, as a function of the distance from the substrate for a series of film widths, ranging from (2.85-14) nm [2-3].

Furthermore, we study the linear viscoelastic behavior of the polymer/graphene hybrid systems. Zero-shear rate viscosity, η_0, and the shear relaxation modulus, G(t), are directly calculated from the atomistic simulations and compared to experimental data and to theoretical predictions [4]. This work is a part of the complex project oriented on the polymer/graphene systems and contributes to the full understanding of the molecular processes occurring in hybrid nanostructured materials.

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