Graphene based Polymer Nanostructured Materials through Molecular Simulations

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ABSTRACT - SUMMARY:

In the present work detailed atomistic molecular dynamics simulations of several graphene based polymer nanocomposite systems have been performed. Systems with graphene sheets of different sizes have been simulated at the same graphene concentration (*~3%*). Pristine graphene and two types of functionalized graphene have been simulated in two different polymer matrices. The aim of our work is to examine spatial and dynamical heterogeneities of such systems and to provide information about the effects of the edge group functionalization of graphene sheets on the properties of hybrid graphene-based materials. Moreover the final properties of the material are examined as a function the complex effect of the graphene's sheet size, mobility and fluctuations.

INTRODUCTION:

Polymer/graphene nanostructured systems are hybrid materials which have attracted great attention the last years both for scientific and technological reasons. The benefits which have been reported, for the hybrid system, are the improvement of the electrical, thermal, mechanical and gas barrier properties of graphene-polymer composites.[1,2]

A main challenge in the study of graphene based polymer nanocomposites is to predict their properties at the molecular level. In the current work the effect of the weight fraction of graphene in a polymer matrix, as well as the size of the graphene sheet, on the properties of polymer chains are examined. Moreover effects of the edge group functionalization of graphene sheets on the properties of hybrid graphene-based materials are demonstrated. We present results of polymer nanocomposites with three types of dispersed graphene: (a) the pure non-functionalized sheet (pristine), (b) graphene with hydrogens grafted on the edges and (c) carboxyl-functionalized graphene. A characteristic snapshot of the simulation is presented in Figure 1.
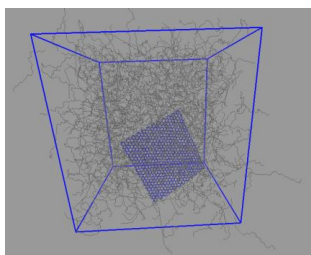

Fig. 1: *Snapshot of polymer/graphene model systems.*

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 behavior of the hybrid material.

SIMULATION METHOD:

We performed detailed atomistic MD simulations of polymer/graphene nanocomposite systems. Details about the all-atom force field which has been used, the MD simulations as well as a description of the analysis methods are given elsewhere [3,4].

RESULTS AND DISCUSSION:

Average density profiles, which have been calculated for the center of mass of the monomers, $\rho(r)$, are presented in Figures 2b for three systems of pristine graphene in PE matrix, with graphene flakes of different areas G_{20}/PE, G_{50}/PE and G_{80}/PE together with the corresponding bulk system. Density is presented as a function of the radial distance from the central atom of graphene. Graphene flakes that have been used in the simulations are almost quadratic with side equal to *20Å*, *50Å* and *80Å* respectively.
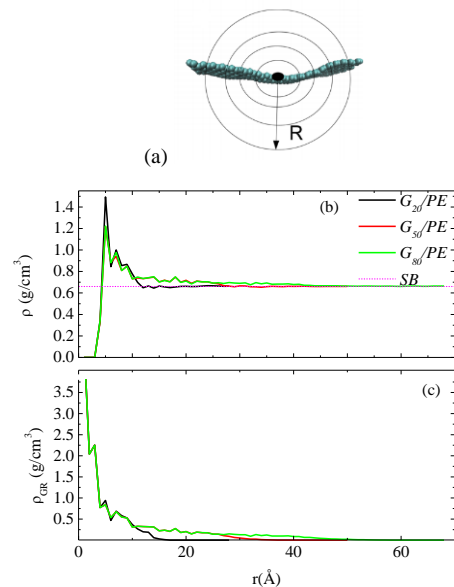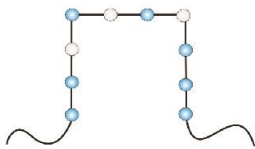

Fig. 2: *(a) Analysis scheme in spherical shells. (b) Mass monomer density profiles of polyethylene as a function of r (distance from the center of the graphene layer) (c) Mass density profiles of graphene layer as a function of r; (Figure from ref. 3)*

A peak of rather similar height (larger than the bulk value) is observed for all systems at a distance/radius of about 0.5 nm, which denotes the attraction of the polymer from the graphene at short distances, while at longer distances the bulk density is attained. In Figure 2c the density of the amount of the graphene in each spherical shell (radial distance – Figure 2a) is presented for all systems. Similar are the results of density profiles for the nanocomposites with functionalized graphene sheets.

An analysis of the PE chain conformations, which is based on the calculation of the distribution of the torsional (dihedral) angles, P_{dih}, in different distances from graphene, follows. Analysis of results has been performed dividing the space around the sheet into two regions, one parallel to the surface and one around the edges. In Figure 3 results for graphene/PEO systems are presented, for the dihedral angle O−C−C−O at various distances from the parallel region of the sheet. Data for bulk polymer are also plotted with black dashed line. An interesting feature in Figure 3 is the change of the ratio between trans and gauche population as we approach the graphene sheet in direction perpendicular to the surface (i.e., parallel layers), for both hydrogenated and carboxylated sheets. An increase of trans population with a corresponding decrease of gauche one is obvious close to the surface.
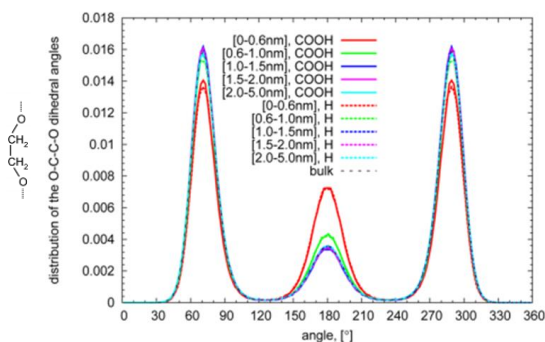

Fig. 3: *Distributions of dihedral angles for graphene/PEO nanocomposites in the parallel region for O−C−C−O plane (Figure from ref. 4).*

Next we present results for the local dynamic properties in nanocomposites by calculating the time evolution of the mean-square displacement (MSD) of segments belonging to different layers (i.e., different distances from graphene sheet in the parallel region). Results for systems with hydrogenated and carboxylated sheets in PEO matrix are presented in Figure 4.

Analysis is restrained on the segments that persist in the same layer during the time of measurement. In both systems we see a dispersion of the curves which reveals strong dynamical heterogeneities in the direction parallel to the graphene sheet. The dispersion is more marked in the system with the carboxylated sheet. The same behavior was found in PE nanocomposites.
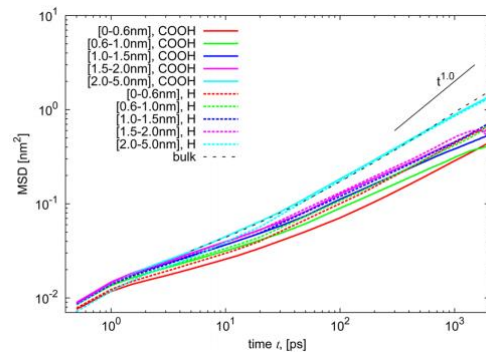

Fig. 4: *Segmental mean-square displacement in parallel layers of PEO nanocomposites. Black solid line serves as a guide to the eye and represents the expected scaling of the mean-square displacement in diffusive regime, i.e., MSD ∼ t^1. (Figure from ref. 4).*

However, comparisons with systems of identical PE short polymers chains interacting with an immobile periodic graphene, [5] reveal more limited dynamical heterogeneities. In the latter case the absence of graphene fluctuations leads to a more well-ordered chain configuration at the interface, as well as to slower chain dynamics in the vicinity of the polymer/graphene interface.
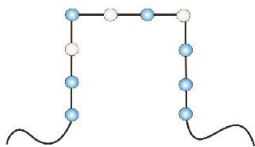
CONCLUSIONS:

The properties of polymer/graphene nanocomposites were explored through detailed atomistic molecular dynamics simulations. Their overall behavior is strongly affected by the spatial heterogeneities induced by the presence of polymer/graphene interfaces. Local structural, conformational and dynamical features were analyzed at the level of both individual segments (atoms or bonds) and entire chains.

Pristine graphene sheets of different sizes were modeled in order to study the effect of the graphene size. Moreover edge-functionalized graphene, was studied as potential nanofiller in PEO and PE matrices of low molecular weight.

Our main findings are as follows: The density of the polymer around the graphene sheet depends on the distance from the surface. In the adsorbed interfacial region, the chains preferably adopt more extended, trans-enriched configurations, in comparison to the bulk polymers. Dynamical heterogeneities in the nanocomposite material are induced by the interactions of the graphene sheet with the polymer matrix.

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