ATOMISTIC MOLECULAR DYNAMICS SIMULATIONS OF MULTIPHASE POLYMER/GRAPHENE NANOSTRUCTURED SYSTEMS

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ABSTRACT

In this work structural, conformational and dynamical properties of polymer/graphene nanostructured systems are investigated through all-atom Molecular Dynamics (MD) simulations. Three hybrid polymer/graphene interfacial systems (polystyrene (PS)/graphene, poly(methyl methacrylate) (PMMA)/graphene and polyethylene (PE)/graphene) are studied and their behavior is compared to the corresponding bulk polymers. A strong effect of graphene layers on both structure and dynamics of polymer chains is observed. Furthermore, we examine spatial and dynamical heterogeneities of graphene based polymer nanocomposite systems and provide information about their properties for various edge-group functionalized graphene sheets.

INTRODUCTION

Polymer/graphene nanostructured systems are hybrid materials, which have attracted great attention the last years both for scientific and technological reasons and are very promising candidates for a broad range of possible applications.[1] From the scientific point of view the main challenge is to study such nanostructured systems at the molecular level and predict their structure-properties relations. A particular important question concerns the way that the polymer/graphene interface affects the properties of the polymer chains, as well as the estimation of the width of the interphase, based on the specific property under study.[2]

The first part of this work constitutes a study of confined polymer films. Three hybrid polymer/graphene interfacial systems (polystyrene (PS)/graphene, poly(methyl methacrylate) (PMMA)/graphene and polyethylene (PE)/graphene) are investigated. Various properties are calculated related to: density profile and structural – conformational characteristics in the atomic and the monomeric level. All properties are examined, as a function of the distance from the substrate. The properties of the macromolecular chains are being compared to the properties of the corresponding bulk systems at the same temperature.[3,4]

In the second part, graphene based polymer nanocomposite systems are studied.[5,6] Systems with graphene sheets of different sizes have been simulated at the same graphene concentration (~*3%*). Pristine graphene and two types of edge group functionalized graphene (hydrogenated and carboxylated) have been simulated in two different polymer matrices, a non-polar, polyethylene (PE) and a polar one, polyethylene oxide (PEO). Spatial and dynamical heterogeneities of graphene based polymer nanocomposite systems are detected. Different functionalization of the graphene sheet determines a different width for the interphase of the various properties of polymer, highlighting the effect of the edge functional groups.

MODELS AND SIMULATION METHOD

In the current study we present results from all-atom (AA) molecular dynamics simulations. Two types of systems are examined a) Different polymers (PE, PS and PMMA) confined between periodic graphene sheets and b) graphene based polymer nanocomposites which are consisted of graphene sheets and polymer chains. For PS, PMMA and PEO polymer chains are *10*-mers, while PE chains consist of *22*-mers. Number of monomers was chosen in such a way that the backbone consists of almost the same number of CH2, and/or CH, groups for all systems. Periodic boundary conditions, which have been applied in all three directions of the simulation box, ensure infinite

graphene layers with no edges for the first case. The graphene is initially modeled as a set of Lennard-Jones carbon atoms, centered at their crystallographic positions (lattice constant is *2.462Å* at *T = 300K*) in the *xy*-plane. For the second case, graphene flakes are almost quadratic with dimensions *20x20Å* ^{2} (G_{20}), *50x50Å* ^{2} (G_{50}) and *80x80Å* ^{2} (G_{80}). All simulations were carried out at constant temperature equal to *T = 500K* for PS and PMMA, *T = 450K* for PE and *T = 318K* for PEO. Simulation details, as well as information about the force fields which were used in each case are given in our corresponding publications.[3,4,7,5,6]

RESULTS AND DISCUSSION

a) Confined polymer films

One important property of the hybrid systems is the molecular density of the polymer chains at the polymer/graphene interface. We have analyzed the density of the polymer chains, as a function of the distance from the graphene layer. Density profiles, based on the monomer center of mass, *ρ(z)*, for the three hybrid polymer/graphene systems are presented in Figure 1. For all polymer/graphene systems the average density profiles show a high peak in *ρ(z)*, around *0.4nm* from the graphene layer, whereas at long distances density attains the corresponding bulk value.[3,7] This maximum is due to dispersion van der Waals forces between polymer atoms and graphene carbons which induce "physically" adsorption of chains on the graphene layers. Slight quantitative differences among the three density profiles exist related to the value of the first peak of *ρ(z)*, which reveals the weakest attraction from the graphene layer on PE, while PMMA and PS feel a stronger attraction. Furthermore, more extended structure (i.e., two additional lower peaks) is observed in the density profile curve of PE which can be attributed to the well-ordered layered structure of PE close to graphene.

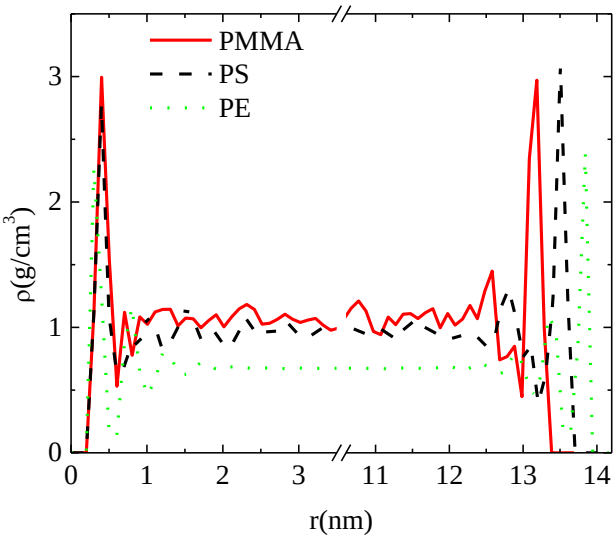


***Figure 1**. Monomer density profiles as a function of distance from graphene layers for PS, PMMA and PE hybrid polymer/graphene systems. (Figure from ref. 4)*

The orientation of polymer chains close to graphene can be described through the second rank bond order parameter, $P_2(\cos\vartheta) = \frac{3}{2}\langle\cos^2\vartheta\rangle - \frac{1}{2}$, where, where, ϑ is the angle between an arbitrary vector and one Cartesian axis (*z*- in our case , in order to characterize chain structure as a function of distance from the graphene layers.) The vector that we have chosen is along the molecule's backbone (v^{bb}). Data for the z-component of the bond order parameter $P_2(\cos\vartheta)$, as a function of distance from graphene, start from the origin (i.e., position of the graphene layer) and end to the middle of the simulation box are presented in Figure 2 for all three polymers (PE, PS, PMMA).

Dashed normal lines indicate an area up to *0.5nm* from graphene surface (i.e., the first adsorption layer).

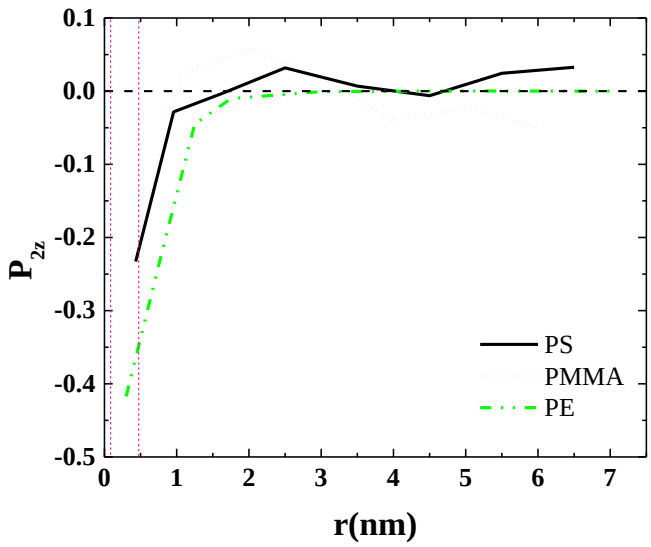


Figure 2 *. Bond order parameter $P_2(\cos\vartheta)$ along z-axis as a function of distance from graphene layer for a vector defined along the backbone for the three polymers. (Figure from ref. 7)*

In this layer, $P_2(\cos\vartheta)$ values of v^{bb} are negative, in the range of (*-0.45*) to (*-0.25*), which indicate that backbone tends to an almost parallel to the surface orientation ($P_2 = -0.5$ corresponds to $\vartheta = 90^o$). At longer distances $P_2(\cos\vartheta)$ has values close to zero and consequently suggests a random orientation of the polymer chain.

b) ***Nanocomposite Systems***

The way that the structural and dynamical properties of polymer chains are affected by pristine and/or functionalized graphene sheets, in graphene/polymer nanocomposites is presented in the following. The components of the model simulated systems are depicted in Figure 3.

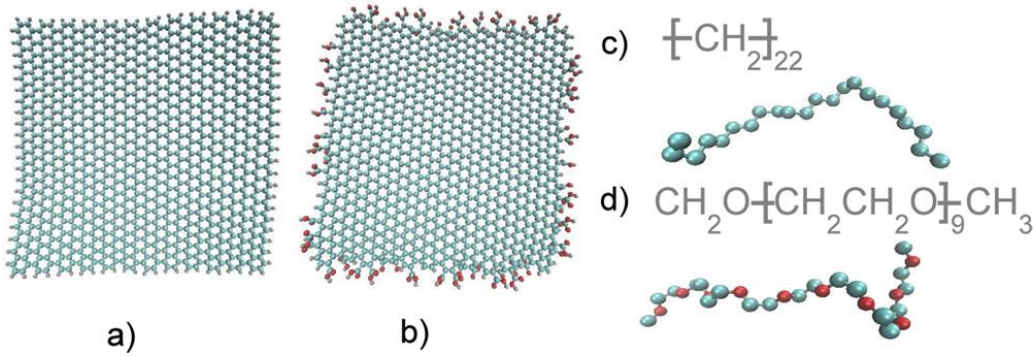


Figure 3*. Components of the model simulated systems : (a) hydrogenated graphene sheet, (b) carboxylated graphene sheet, (c) polyethylene, and (d) poly(ethylene oxide). (Figure from ref. 6)*

Density profiles, calculated for the center of mass of the monomers, *ρ(r)*, as a function of the radial distance from the central atom of graphene, are presented in Figure 4 for PE/graphene nanocomposite systems. Graphene flakes that have been used in the simulations are almost quadratic with side equal to *20Å*, *50Å* and *80Å* respectively. The corresponding bulk system is also included (SB).

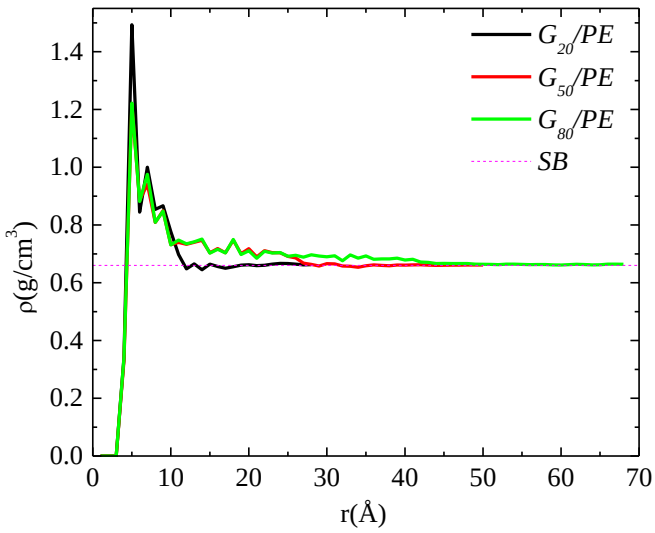
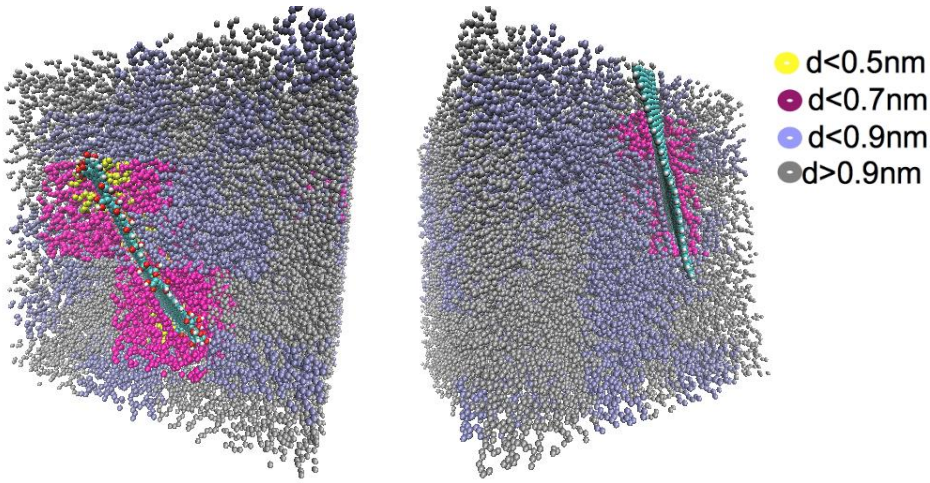


Figure 4. *Mass monomer density profiles of polyethylene as a function of r (distance from the center of the graphene layer).*

A peak of rather similar height is observed for all systems at a distance 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.

The effect of the terminal groups on the dynamics of the polymer chains as a function of the distance from the graphene layer is presented in Figure 5 for nanocomposites of PEO with carboxylated and hydrogenated graphene flakes.



a) COOH **b) H**

Figure 5*. Configurations of systems of Poly(ethylene oxide) (PEO)/graphene (a) functionalized graphene with carboxyl groups. (b) functionalized graphene with hydrogen atoms. d: is the displacement of the PEO monomers from the closest to them atom of graphene. (Figure from ref. 6)*

A qualitative different behavior of the dynamics of the monomers is observed between the two systems. For the case of graphene sheets functionalized with hydrogen atoms the slower monomers (those with the shortest displacement (*d*) from the closest to them atom of graphene) are observed to be above and below the graphene layer in parallel to the graphene planes.

Moreover there is a gradual increase of their dynamics with the increasing distance from the graphene. This behavior is qualitative similar with the one of the confined polymer films as well as with the nanocomposites with pristine graphene flakes. For the systems with carboxylated graphene flakes the slowest monomers are observed around the edges of the graphene due to their electrostatic interactions with the carboxyl groups.

CONCLUSIONS

In the current study we present results concerning the way that graphene affects the structural, conformational and dynamical properties of various hybrid polymer/graphene nanostructured systems using detailed atomistic Molecular Dynamics simulations. The systems under investigation are: a) confined polymer films (PE, PS, PMMA) with periodic graphene sheets and b) Nanocomposites where graphene flakes of finite size move freely in a polymer matrix (PE, PEO). In the second case both pristine and functionalized graphene sheets are examined. Moreover two types of edge-functionalization are used a) with hydrogens and b) with carboxyl groups.

In all cases heterogeneity is induced to the properties of the polymer due to the presence of the graphene flake. The higher density close to the graphene surface indicates the attraction of the polymer from graphene. Polymer chain orientation is affected by the graphene flake resulting in an almost parallel orientation at distances very close to the surface. At close to the graphene distances a retardation of the dynamics of the polymer chains is observed whereas at longer distances polymer dynamics approaches the one of the corresponding bulk system. The effect of the terminal groups at the edges of the functionalized graphene flakes is also significant. For the case of a hybrid PEO/graphene nanocomposites with carboxylated graphene sheets the slowest monomers are those which are close to the edges of graphene due to the electrostatic interactions of polymer with the carboxyl groups. For the rest of the systems the slowest monomers are above and below the graphene sheet in parallel planes.

The current analysis, at the molecular level, allows us to shed light on the relation between the local structure and final properties of the desired material.

AKNOWLEDGEMENTS

Authors would like to acknowledge the Goodyear project: “High Fidelity Coarse-Graining of Rubber Systems”.

REFERENCES

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jing, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov. Science 306 (2004) 666-669.

[2] H. J. Butt, H. Duran, W. Egger, F. Faupel, V. Harmandaris, S. Harms, K. Johnston, K. Kremer, F. Y. Lin, L. Lue, C. Ohrt, K. Raetzke, L. Ravelli, W. Steffen and S. D. B. Vianna. Macromolecules 47 (23) (2014), 8459-8465.

[3] A. N. Rissanou, V. Harmandaris. J. Nanopart. Res. 15:1589 (2013) 1-14.

[4] A. N. Rissanou, V. Harmandaris. Soft Matter 10 (2014) 2876-2888.

[5] A. N. Rissanou, A. J. Power, V. Harmandaris. Polymers 7 (2015) 390-417.

[6] P. Bacova, A. N. Rissanou, V. Harmandaris. Macromolecules 48 (2015) 9024–9038.

[7] A. N. Rissanou, V. A. Harmandaris. Macromol. Symp. 331-332 (2013) 43-49.