

## A MOLECULAR DYNAMICS STUDY OF POLYMER/GRAPHENE NANOCOMPOSITES

Anastassia N. Rissanou<sup>b,c\*</sup>, Vagelis Harmandaris<sup>a,b,c\*</sup>

<sup>a</sup>Department of Applied Mathematics, University of Crete, GR-71409, Heraklion, Crete, Greece.

<sup>b</sup>Archimedes Center for Analysis, Modeling & Computation, University of Crete, P.O. Box 2208, GR-71003, Heraklion, Greece.

<sup>c</sup>Institute of Applied and Computational Mathematics (IACM), Foundation for Research and Technology Hellas (FORTH), GR-71110 Heraklion, Crete, Greece.

[\\*rissanou@tem.uoc.gr](mailto:rissanou@tem.uoc.gr), [vagelis@tem.uoc.gr](mailto:vagelis@tem.uoc.gr)

**Keywords:** Graphene/Polymer Nanocomposites, Molecular Dynamics.

### Abstract

*In this work, we study three hybrid polymer/graphene interfacial systems (polystyrene/graphene, poly(methyl-methacrylate)/graphene and polyethylene/graphene) through detailed atomistic molecular dynamics (MD) simulations. Density profiles, structural characteristics and mobility aspects are being examined at the molecular level for all model systems. In addition, we compare the properties of the hybrid systems to the properties of the corresponding bulk ones, as well as to theoretical predictions. Qualitative and quantitative differences in density profiles, in structure and dynamic properties of the polymer chains in particular at the polymer/graphene interface are established.*

### 1. Introduction

Graphene based polymer nanocomposites are hybrid materials with a very broad range of technological applications. [1,2] Graphene polymer nanocomposites are based on the incorporation of graphene in polymer matrices. 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. [3] Due to the above properties the study of graphene based polymer composite materials is a very intense research area.

The current work [4,5,6] refers to a detailed multi-scale hierarchical simulation study on hybrid polymer/graphene interfacial systems. This approach consists of two stages. In the first one, which has been accomplished up to now, we perform detailed atomistic molecular dynamics (MD) simulations of polymer/graphene interfacial systems. We explore the effect of graphene on various properties of polymers, by studying three well known and widely used polymers, polyethylene (PE), polystyrene (PS) and poly(methyl-methacrylate) (PMMA). Density profiles, structural characteristics and mobility aspects are being examined at the molecular level for all model systems. [4,5]

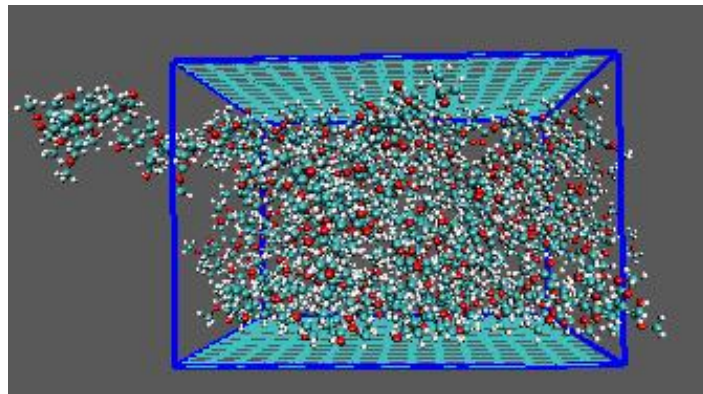
The second stage of our work involves the extension of the proposed methodology to mesoscopic description using proper coarse-grained (CG) models. To achieve this, a methodology to develop CG models from the atomistic description, proper for bulk polymeric systems, will be extended to hybrid nanocomposite mater. [7,8,9] Therefore, hierarchical

multi scale methodologies, which involve systematic linking between simulation methods from different levels of description, are necessary. [10] The overall methodology will allow us to provide a fundamental study of the coupling between microstructure at the interface and macroscopic properties (structural, mechanical, elastic and dynamical-rheological) of graphene/polymer nanocomposite systems.

## 2. Simulation Method

The systems studied in this work are the following polymer/graphene composites: (a) PS/Graphene, (b) PMMA/Graphene and (c) PE/Graphene. The corresponding bulk polymer systems are studied as well. For PS and PMMA polymer chains were 10-mers, while PE chains consist of 22-mers, (i.e. 22 CH<sub>2</sub> groups). Note that the molecular backbone length of all systems is very similar, since PS and PMMA chains have 20 (CH<sub>2</sub> or CH) groups in the backbone. The reference bulk systems consist of 56 10-mer chains for PS, 54 10-mer chains for PMMA and 420 22-mer chains for PE.

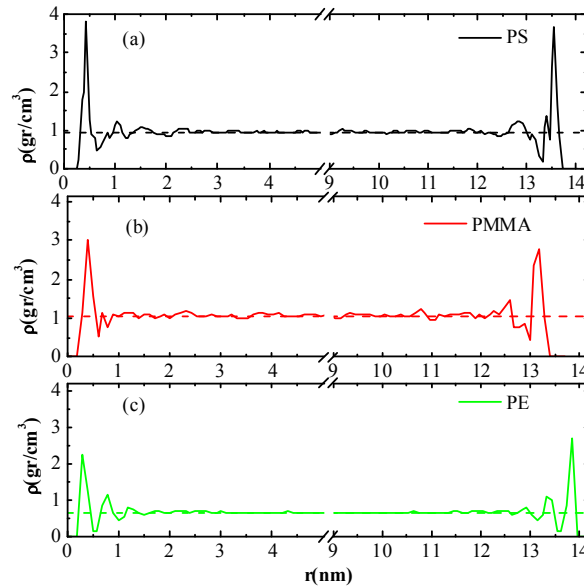
We performed atomistic NPT and NVT Molecular Dynamics (MD) simulations using the GROMACS code. [11] All simulations were carried out at constant temperature equal to T=500K for PS and PMMA and T=450K for PE, and pressure P=1atm. An all atom representation model has been used. Graphene has been represented as a set of LJ carbon atoms, centered at their crystallographic positions. Details about the all-atom force fields, as well as the MD simulations are given elsewhere. [4,6] A snapshot from an equilibrated conformation of a PMMA film between two graphene layers, which contains 27 PMMA chains is depicted in Figure 1.



**Figure 1.** Snapshot of a poly(methyl methacrylate) system, which contains 27 polymer chains, confined between two graphene layers. Periodic boundary conditions have been applied on the center of mass of the molecule. (Figure from ref. 4)

## 3. Results and Discussion

The polymer arrangement, with respect to the surface, is presented through the calculation of the density profiles as a function of the distance from the graphene layer,  $\rho(r)$ . In Figure 2 three density profiles are depicted for the three hybrid polymer/graphene systems. Density profiles are based on the monomer center of mass and are averaged over time. The bulk density value is presented with a dashed horizontal line in each system.



**Figure 2.** Monomer density profiles as a function of distance from graphene layers for a) PS, b) PMMA and c) PE, hybrid polymer/graphene systems. Bulk system's density is represented by a dashed horizontal line in all cases. (Figure from ref. 5)

Although the qualitative picture is almost the same, for the three hybrid systems, a more careful observation brings out quantitative differences. The highest attraction from the surface is exerted on PS, PMMA follows, while the lowest is the one on PE, as it is obvious from the values of the peaks in the density profiles. This can be attributed to: (a) the existence of a side group in the first two polymers (i.e., a phenyl ring in PS, a carboxyl and a methyl side group in PMMA), and (b): the fact that the polymer/graphene dispersion (van der Waals) forces are larger for PS and PMMA than for PE, because of their larger bulk density, i.e. there are more polymer atoms per unit volume. Moreover, graphene layer seems to prefer the phenyl ring more than the side groups of PMMA, which is reflected in the higher first peak of  $\rho(r)$  for PS compared to PMMA. Another interesting observation is that PE, due to the absence of a side group, appears a more well-ordered layered structure close to the surface, as it is evident from the second and the third peak in the density profile. The peaks become gradually lower as the distance from the surface increases (i.e. the attraction is smaller). A very small second peak is rather detectable in PS density profile, whereas the curve is structureless after the first peak in PMMA.

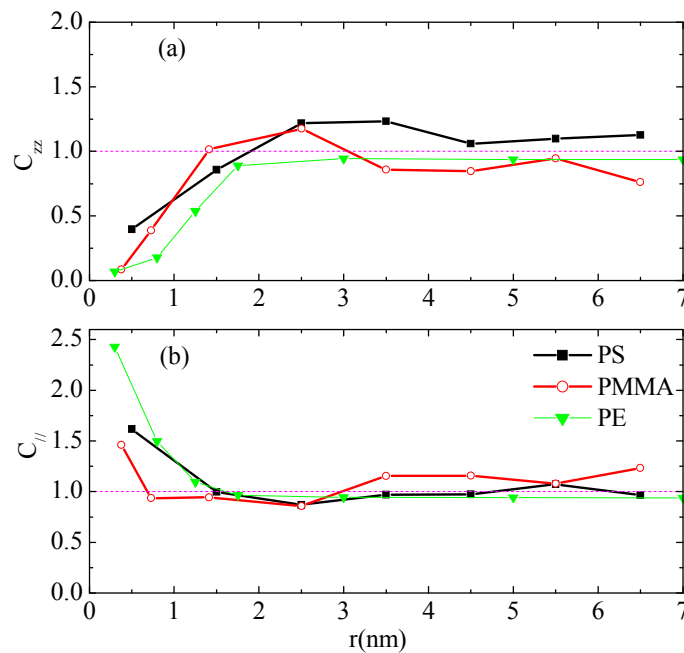
In the following, the conformation tensor, given by the following formula:

$$C_{ab} = 3 \left\langle \frac{R_{ee\alpha} R_{ee\beta}}{\langle R_{ee}^2 \rangle_0} \right\rangle, \text{ provides information for the conformations of the polymers on the entire}$$

chain level.  $\langle R_{ee}^2 \rangle_0$  is the mean end-to-end distance of an unperturbed chain (i.e. bulk polymer system) and  $\alpha, \beta$  are the x,y,z components. The deviation of this tensor from the equilibrium value  $C=I$  (i.e., unit tensor) provide information for the orientation and the extension of the whole polymer chain. In Figure 3 we present the perpendicular ( $C_{zz}$ ) and the parallel ( $C_{//}$ ) to the surface components of the conformation tensor as a function of the distance from the graphene layer for the three systems. The distance is measured from the chain's center of

mass. The parallel components have been calculated as the mean value of the two in-plane components (in  $x$  and  $y$  directions), i.e.  $C_{//} = (C_{xx} + C_{yy})/2$ .

In Figure 3 the data show that all systems tend to the behavior of the corresponding bulk system beyond  $1.5\text{nm}$ . At distances closer to the graphene layer, conformations are elongated in the  $xy$  direction and compressed in the  $z$  direction as it is realized from the values of  $C_{zz}$  and  $C_{//}$  which are lower and higher than 1 respectively. This length scale corresponds to about 2-3 times the average bulk radius of gyration,  $R_g$ . Error bars are ranged between  $[0.1-0.2]$  for all systems.



**Figure 3.** Conformation tensor as a function of distance from graphene layers for PS PMMA and PE systems. (a) The perpendicular to the surface component,  $C_{zz}$  and (b) the average of the two parallel to the surface components,  $C_{//}$ .

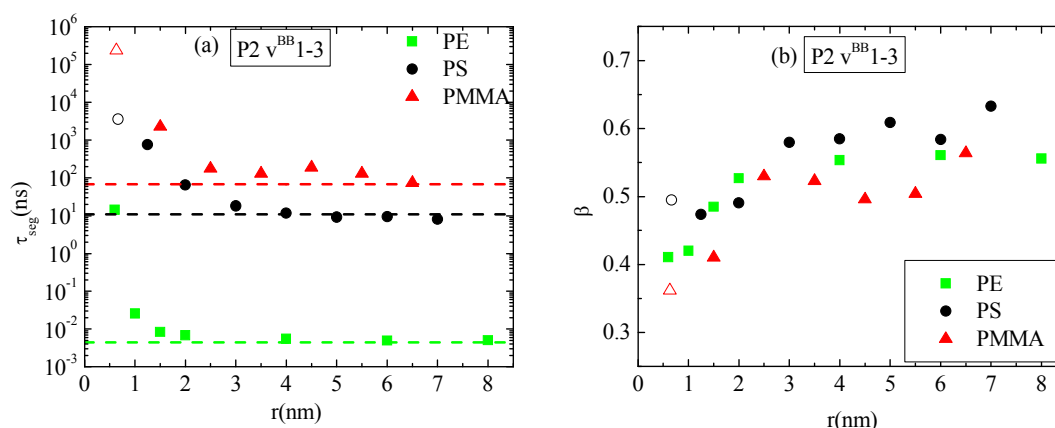
Finally a brief discussion for the dynamics of the hybrid interfacial systems is presented. Dynamics in the segmental level can be studied through the calculation of the second-order

bond order parameter as a function of time:  $P_2(t) = \frac{3}{2} \langle \cos^2 \theta(t) \rangle - \frac{1}{2}$  for a characteristic

vector, arbitrary defined along the molecule.  $\theta$  is the angle between the arbitrary vector, which is defined along the molecule and one Cartesian axis. In this work, we define a characteristic vector along the backbone of the polymer chain ( $v^{bb}$ ), for each polymer, which connects one carbon atom to the next not consecutive carbon atom (1-3) and  $\theta(t)$  is the angle of the vector under consideration ( $v^{bb}$ ) at time  $t$  relative to its position at  $t=0$ . We examine the dynamics as a function of the distance from graphene (i.e., at different adsorption layers). A quantitative comparison among the three systems is based on a fit of  $P_2(t)$  with KWW stretch exponential functions. The segmental relaxation time, which is calculated as the integral of the

KWW curves through the relation:  $\tau_{seg} = \frac{\tau_{KWW}}{\beta} \Gamma\left(\frac{1}{\beta}\right)$  where  $\Gamma()$  is the gamma function, is

presented in Figure 4a for the three polymers. Polymer segments (vectors) close to graphene relax much slower than segments far away from it, with the differences gradually decaying. The segments far enough from the graphene layer exhibiting a “bulk-like” behavior. However, there are also clear (quantitative and qualitative) differences between the relaxation of the backbone vector for the different polymers. In more detail, for PS the slower dynamics of the segments close to the graphene decays within the first 3-4 adsorption layers gradually approaching the bulk behavior at longer distances. For PMMA the relaxation of the backbone vector is gradual only for the first two adsorption layers and then there is jump to a faster relaxation rate. Finally, PE chains show a slightly different behavior; the relaxation rate in the first adsorption layer is considerably slower than the rest layers. The well-ordered structure of PE in this layer is responsible for this diversification.



**Figure 4.** (a) Segmental relaxation time of the backbone characteristic vector  $\mathbf{v}^{BB}$ , based on  $P_2(t)$  time autocorrelation function, for PS, PMMA and PE hybrid polymer/graphene systems as a function of the distance from graphene. Dashed lines represent the values for the segmental relaxation times of the corresponding bulk systems. (b) The stretch exponent  $\beta$ , as extracted from the fit with KWW functions for the three systems. (Figure from ref. 6)

The values of  $\beta$  exponents are depicted in Figure 4b. For all systems  $\beta$  values increase with the distance from the surface. This observation indicates that the existence of the graphene layer leads systems to larger deviations from the ideal Debye behavior (i.e., wider distribution of relaxation times). Furthermore,  $\beta$  exponents for all three polymers, reach their distance-independent “bulk-like” values, beyond the same range of distances about  $\sim 2-4$  nm, given the statistical uncertainty.

#### 4. Conclusions

A comparative study of three different polymer/graphene nanocomposites through detailed atomistic molecular dynamics simulations has been presented here. We studied polystyrene (PS)/graphene, poly(methyl methacrylate) (PMMA)/graphene and polyethylene (PE)/graphene interfacial systems. Our work shows clearly that the structural, conformational and dynamical properties of the polymer chains diversify from their corresponding bulk behavior, as a function of the distance from the graphene layer.

The density profiles of all three polymers highlight the attraction between the graphene layer and the polymer chains. The bulk density value is attained away from the surface, for each

polymer respectively. Furthermore, quantitative differences are observed among the three polymers. The highest attraction from the graphene layer is observed for PS, then for PMMA and finally for PE polymer chains. Moreover, the calculation of the conformation tensor showed that all systems tend to bulk behavior beyond distances which correspond to 2-3 times the average bulk radius of gyration.

Qualitative and quantitative differences in the dynamics of the polymer chains in particular at the polymer/graphene interface are also detected. Results concerning the segmental dynamics render PE much faster than the other two polymers, PS follows, while PMMA is the slowest one. Clear spatial dynamic heterogeneity has been observed for all model systems, with different dynamical behavior of the adsorbed polymer segments. The segmental relaxation time of polymer ( $\tau_{seg}$ ) as a function of the distance from graphene shows an abrupt decrease beyond the first adsorption layer for PE, as a result of its the well-ordered layered structure close to graphene, though a more gradual decay for PS and PMMA. The distribution of the relaxation times of adsorbed segments was also found to be broader than the bulk ones for all three polymer/graphene systems.

The current work is a part of a general computational approach for the study of realistic polymer/graphene systems, with main goal the quantitative prediction of the macroscopic properties of realistic nanocomposite systems, especially at the interface. To achieve this, polymer/graphene hybrid systems are required to be examined at various length and time scales. Therefore, hierarchical multi scale methodologies [9,10,12] which involve systematic linking between simulation methods from different levels of description, are necessary.

## References

- 
- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jing, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov. Electric field effect in atomically thin carbon films. *Science*, 306 (5696): 666-669, 2004.
  - [2] Z. Stitalsky, D. Tasis, K. Papagelis and C. Galiotis. Carbon nanotube-polymer composites: Chemistry, processing, mechanical and electrical properties. *Prog. Pol. Sci.*, 35: 357-401, 2010.
  - [3] H. Kim, A. A. Abdala and C. W. Macosko. Graphene/polymer nanocomposites. *Macromolecules*, 43: 6515-6530, 2010.
  - [4] A. N. Rissanou and V. Harmandaris. Structure and dynamics of poly(methyl methacrylate)/graphene systems through atomistic molecular dynamics simulations. *J. Nanopart. Res.*, 15(1589): 2-14, 2013.
  - [5] A. N. Rissanou and V. Harmandaris. A Molecular Dynamics Study of Polymer/Graphene Nanocomposites. *Macromoleculal Symposia*, 331-332:43-49, 2013.
  - [6] A. N. Rissanou and V. Harmandaris. Dynamics of various polymer-graphene interfacial systems through atomistic molecular dynamics simulations. *Soft Matter*, 10: 2876-2888, 2014.
  - [7] V. Harmandaris, N. P. Adhikari, N. F. A. van der Vegt and K. Kremer. Hierarchical Modeling of Polystyrene: From Atomistic to Coarse-Grained Simulations. *Macromolecules* 39: 6708-6719, 2006
  - [8] V. Harmandaris, N. P. Adhikari, N. F. A. Van der Vegt, K. Kremer, B. A. Mann, R. Voelkel, H. Weiss, CheeChin Liew. Ethylbenzene diffusion in polystyrene: United atom atomistic/coarse grained simulations and experiments. *Macromolecules*, 40: 7026-7035, 2007.
  - [9] V. A. Harmandaris and K. Kremer. Predicting polymer dynamics at multiple length and time scales. *Soft Matter*, 5: 3920-3926, 2009.

- [10] C. Baig and V. Harmandaris. Quantitative Analysis on the Validity of a Coarse-Grained Model for Nonequilibrium Polymeric Liquids under Flow. *Macromolecules* 43: 3156-3160, 2010.
- [11] B. Hess, C. Kutzner, D. van der Spoel and E. Lindahl. GROMACS 4: Algorithms for Highly Efficient, Load-Balanced, and Scalable Molecular Simulation. *Journal of Chemical Theory and Computation*, 4: 435-447, 2008.
- [12] V. Harmandaris and K. Kremer. Dynamics of polystyrene melts through hierarchical multiscale simulations. *Macromolecules*, 42: 791-802, 2009.