

ATOMISTIC SIMULATION OF PYRENE FUNCTIONALIZED α,ω -PMMA AS DISPERSING AGENT OF GRAPHENE FOR THE FABRICATION OF POLYMER NANOCOMPOSITES

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Abstract. *In the present study, molecular modeling has been used as a design tool for proposing a strategy that can help alleviate the problem of graphene stacking in a polar PMMA matrix. Our idea is to leave graphene sheets (GS) intact and instead to functionalize the PMMA chains with proper end groups such as pyrene end-functional groups; then, the so called py-PMMA-py chains are formed with a strong tendency to adsorb on GS. The simulations showed that the pyrene end-functional groups adsorb strongly on the two faces of GS and, as a result of the intervening polymer mass, GS are kept separate and well-dispersed in the nanocomposite at all conditions studied.*

1 INTRODUCTION

Graphene has attracted increasing attention since its discovery a decade ago because of its extraordinary electronic, thermal, and mechanical properties and its potential for a variety of promising applications. Unfortunately, due to strong π - π stacking interactions, graphene sheets (GS) tend to agglomerate into multilayer graphene structures in a polymer matrix, which can dramatically affect the final properties of the nanocomposite. This observation was made in a recent study [1] where we computed the mechanical properties of syndiotactic poly(methyl methacrylate) and its nanocomposites with GS. Aggregation of GS into the polymer matrix can adversely affect the performance of the fabricated polymer nanocomposite material.

Similar results concerning graphene agglomeration have been published by Park and Aluru [2] who reported that GS tend to aggregate in water environment. Li et al. [3] have also reported the aggregation of GS in a polyethylene matrix. The above results were extracted by applying Molecular Dynamics (MD) simulations.

In the literature, there have been only very few studies of pyrene-graphene interactions, but all of them have demonstrated the excellent adsorption of the pyrene group on GS. The MD simulations of Xu and Yang [4], for example, have provided strong evidence for a very favorable interaction of pyrene-polyethylene glycol (py-PEG) with GS. We should also mention the work of Zhang et al. [5] who quantified this strong adsorption by calculating the interaction between a graphene sheet and pyrene (~55pN) by applying the Single Molecule Force Spectroscopy technique.

2 COMPUTATIONAL PART

2.1 Systems studied and Molecular model

Our simulations were executed with cubic cells subject to three-dimensional periodic boundary conditions. The selected polymer system was atactic poly(methyl methacrylate) (PMMA). The simulations were carried out in the *NPT* statistical ensemble at $T=550\text{K}$ and $P=1\text{atm}$. For the purpose of the current study, four different model systems were simulated, each of which contained 100 PMMA chains (either PMMA or py-PMMA-py, see Fig. 1). Details of all simulated systems are given in Table 1.

System 1: In this system, 6 GS were added to the simulation cell but no pyrene groups were introduced at the ends of the chains (see Fig. 2).

System 2: In this system, again 6 GS were added to the simulation cell; in addition, 40% of its PMMA chains bared pyrene groups at both of their ends. The loading of the resulting nanocomposite in GS was 12.01 wt. %.

System 3: In this system, a smaller number (equal to 4) of GS were added to the simulation cell while the number of PMMA chains that were functionalized by pyrene groups at their ends remained the same (60%).

System 4: Here, the number of GS that were added to the simulation cell was even smaller (equal to 3) but the number of PMMA chains that bare pyrene groups at their ends remained the same (60%).

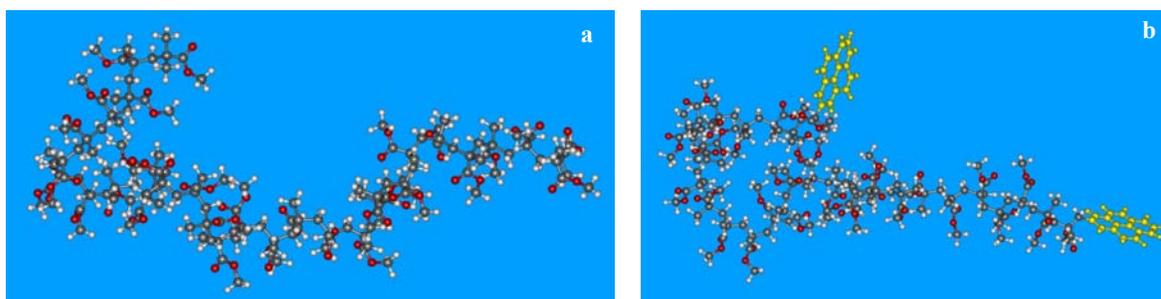


Figure 1: Typical atomistic representation of: (a) a PMMA chain, and (b) a py-PMMA-py chain.

In all cases, strictly monodisperse samples were assumed with each PMMA chain consisting of 30 monomers (methyl methacrylate, MMA). The molecular weight of each chain was equal to $3005.49 \text{ g mol}^{-1}$ for PMMA chains and equal to $3405.96 \text{ g mol}^{-1}$ for py-PMMA-py ones. We also mention that all GS were terminated with hydrogen atoms and had lateral dimensions of $(39 \times 39) \text{ \AA}^2$. The loading of the four systems in GS was: 12.50% wt. for System 1, 12.01% wt. for System 2, 8.34% wt. for System 3, and 6.25% wt. for System 4.

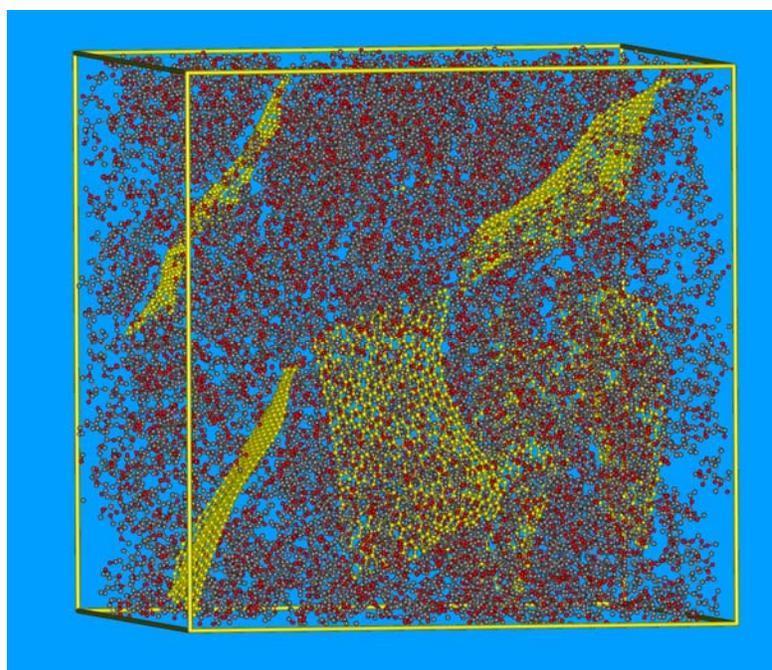


Figure 2: A typical atomistic snapshot of the initial configuration of System 1.

The simulations were carried out with the very accurate explicit-atom Dreiding force-field [6]. For each of the four simulated systems mentioned in Table 1, the initial configuration was created using the MAPS 3.2 [7] software package followed by a minimization energy process using the steepest descend method to remove overlaps. The resulting minimum-energy configurations were then submitted to a classical MD simulation in the *NPT* statistical ensemble at temperature and pressure conditions as they mentioned above, using the Nosé-Hoover thermostat/barostat [8,9]. In the simulations, electrostatic interactions were computed using the accurate PPPM [10] (Particle-Particle-Particle-Mesh) method with a real space cutoff of 12 \AA ; the atomic charges had been calculated using the Gasteiger [11] method of partial equalization of orbital electronegativity through the MAPS 3.2 [7] simulation platform. For the Lennard-Jones (LJ) interactions, the cutoff radius was set equal to 12 \AA .

Å. The equations of motion were integrated with the velocity Verlet [12,13] integrator with a time step equal to 1fs. All MD simulations were performed with the LAMMPS [14] code.

Table 1. Technical details (number of PMMA chains, number of py-PMMA-py chains, number of GS, and % wt. in GS loading) of the PMMA-GS nanocomposite systems simulated in this work.

System	PMMA chains	py-PMMA-py chains	graphene sheets	wt. % graphene loading
1	100	-	6	12.50
2	60	40	6	12.01
3	60	40	4	8.34
4	60	40	3	6.25

3 RESULTS

Our MD simulations for System 1 (where all of chains are non-functionalized ; they contain no pyrene group) showed that after a short simulation time (approximately 3ns) the GS started to self-assemble forming the characteristic π - π stacks of the graphitic structure. The time evolution of the displacement of the GS for System 1 is shown in Figure 3.

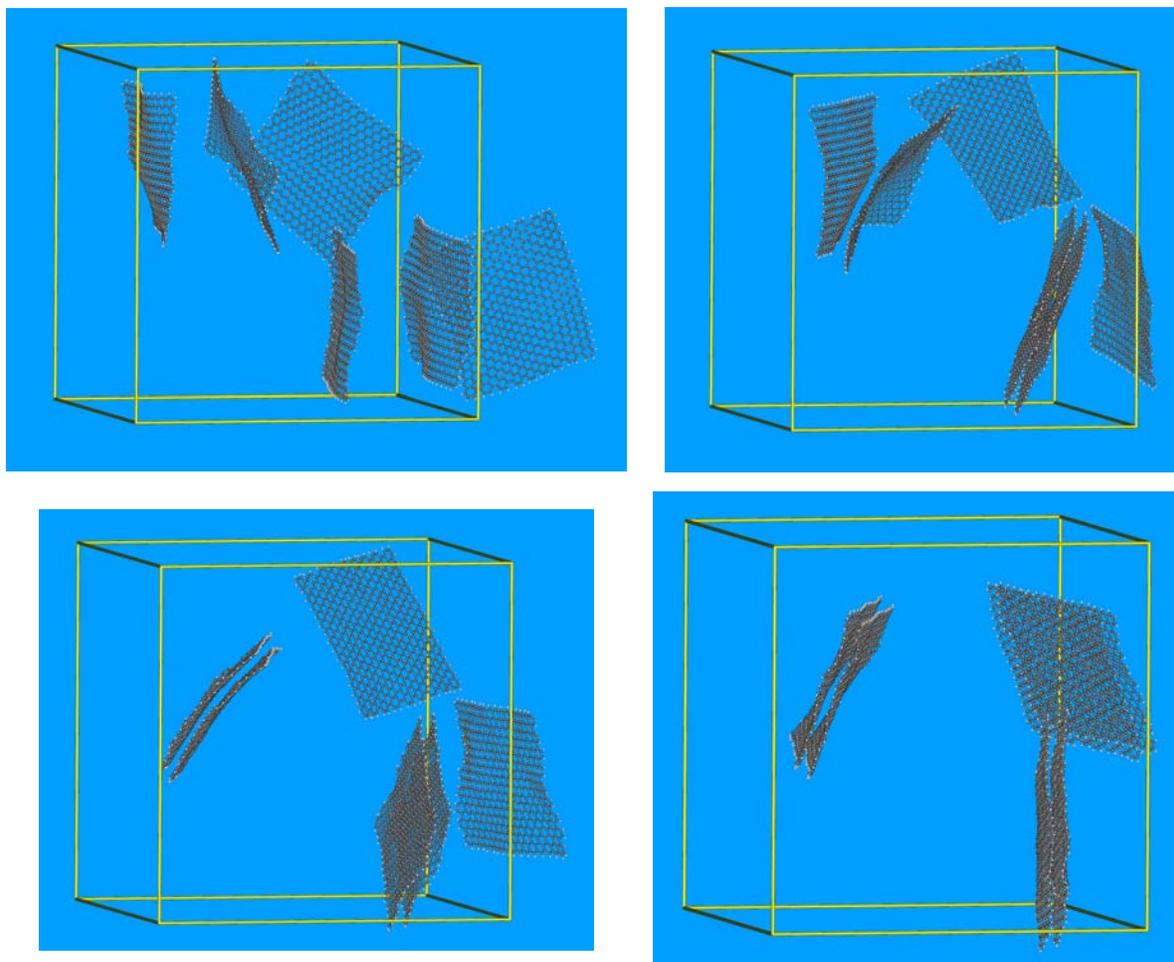


Figure 3: Evolution of GS self-assembly and agglomeration in the course of the MD simulations with System 1.

In contrast, for the rest of the Systems (systems 2, 3 and 4), no GS stacking was observed. Even after a long simulation time (approximately 130 ns), all GS remained well-separated and dispersed in the polymer matrix. In order to quantify this direct observation, we show the time evolution of the distance of the centers-of-mass between all GS pairs in all systems (Figs 4a-d). We see that only for System 1 the distance between some GS pairs (pairs 1-4, 2-3 and 5-6) drops at value 3.4 Å (which is the average distance of graphenes when they form typical graphitic structures). For the rest of the systems (Systems 2, 3 and 4), the distance for all GS pairs remains constantly far away from this value.

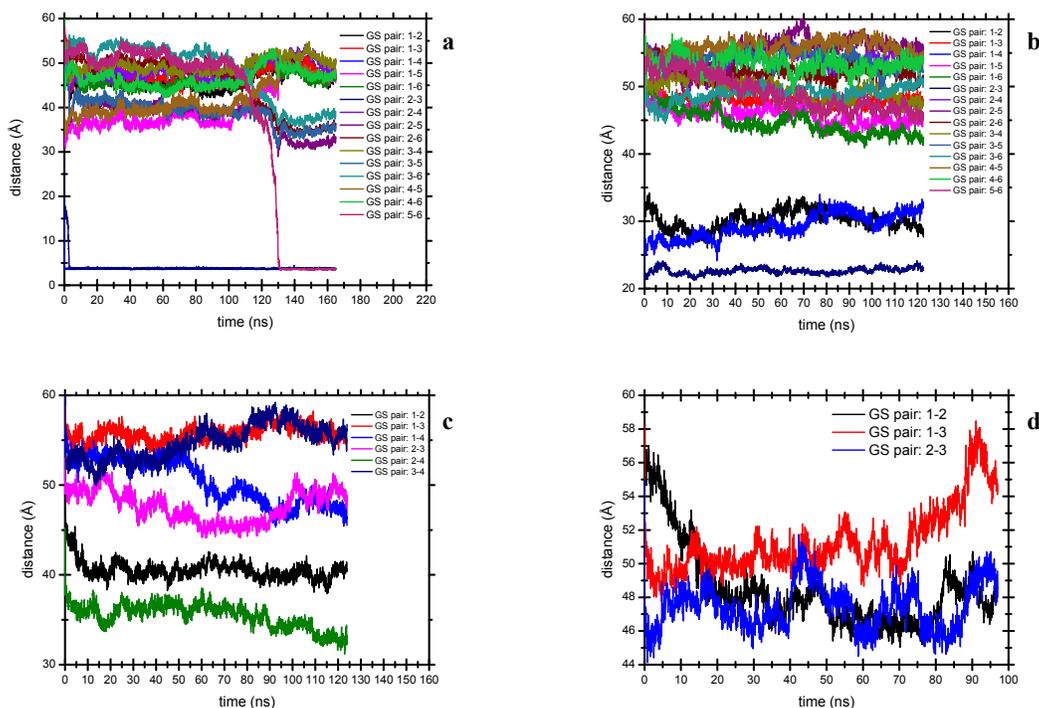


Figure 4: Time evolution of the distances between GS centers-of-mass in the course of the present *NPT* MD simulations for: (a) System 1, (b) System 2, (c) System 3, and (d) System 4.

By inspecting the atomistic snapshots more carefully, we concluded that pyrene groups adsorb on GS in three distinct structures (see Figs. 5a-c):

First structure: A py-PMMA-py chain can be adsorbed on the same face of the same GS by both of their end-pyrene groups. The resulting structure looks like a *loop* (a typical example is shown in Fig. 4a).

Second structure: A py-PMMA-py chain can use the two end-pyrene groups to adsorb on the two different faces of the same GS. This results in a structure which we call an *extended loop* (a typical example is shown in Fig. 4b).

Third structure: A py-PMMA-py chain uses its two end-pyrene groups to adsorb to the surfaces of two different GS. We call the resulting structure a *bridge* (a typical example is shown in Fig. 4c).

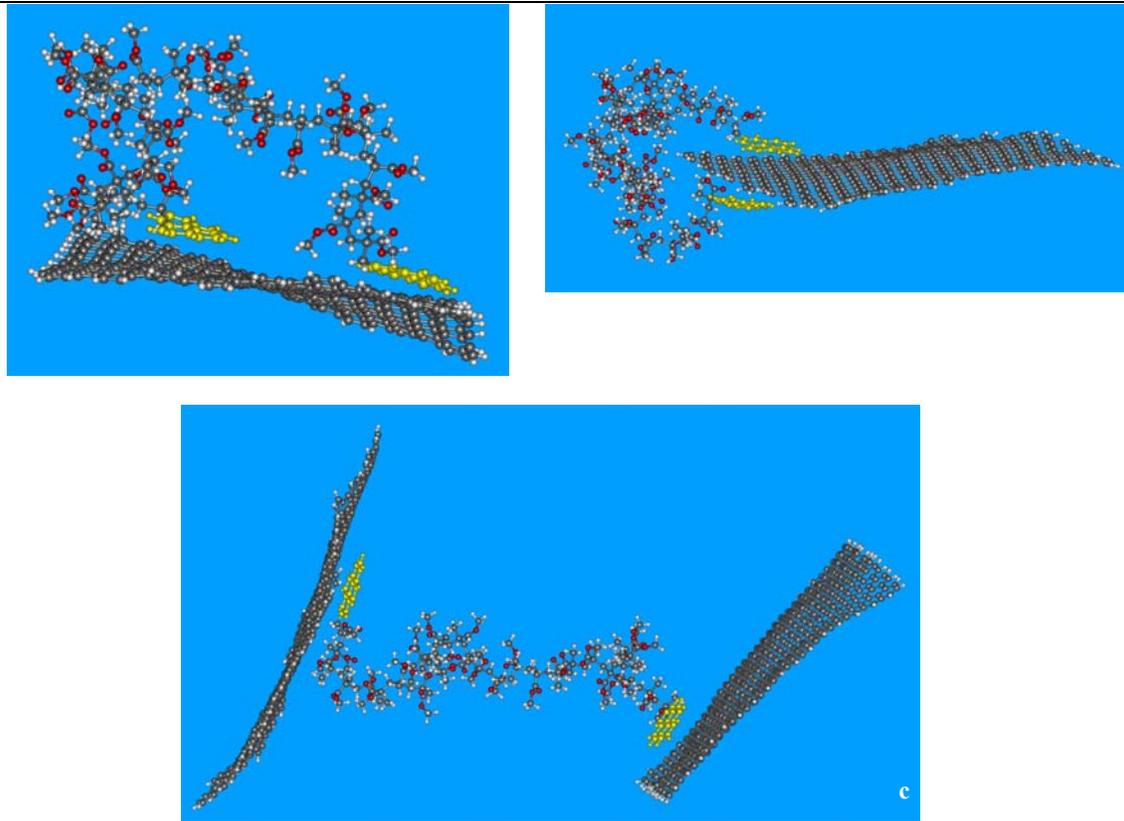
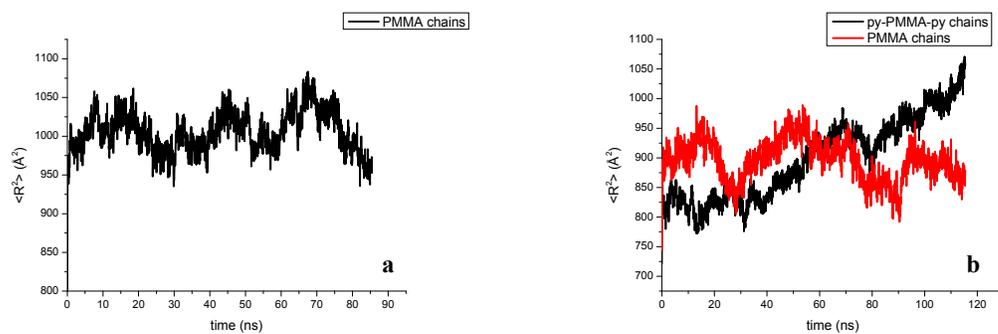
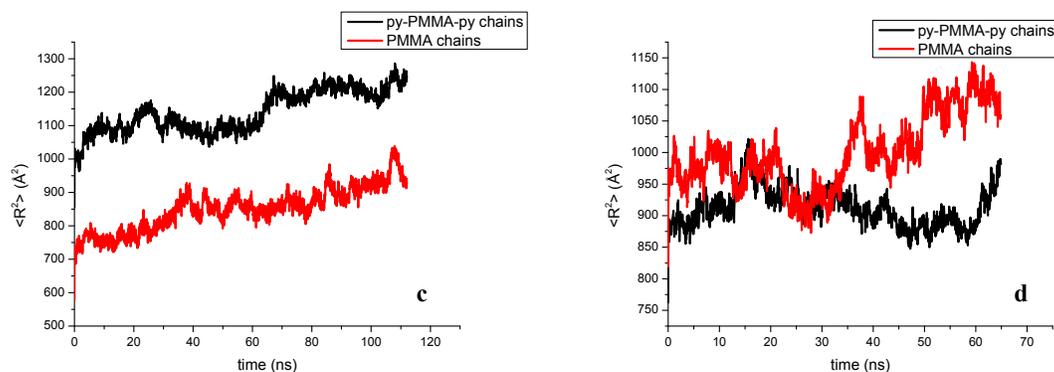


Figure 5: Typical examples of (a) loop, (b) extended loop, and (c) bridge configurations from the *NPT* MD simulations with System 2.

Finally, we have calculated the time evolution of the mean-squared chain end-to-end distance $\langle R^2 \rangle$ separately for PMMA and py-PMMA-py chains. As it is shown in Figure 6, $\langle R^2 \rangle$ is larger for py-PMMA-py chains, something that can be explained by the stretching of this type of chains in order to form the structures described above. As the simulation time evolves, we also observe that the value of $\langle R^2 \rangle$ for py-PMMA-py chains continues to increase; this implies that loops and bridges are continuously formed in the polymer matrix.





Σχήμα 6: Time evolution of the $\langle R^2 \rangle$ for PMMA and py-PMMA-py respectively for: (a) System 1, (b) System 2, (c) System 3 and (d) System 4.

4 CONCLUSIONS

The detailed atomistic MD simulations carried out in the present study showed that by functionalizing a fraction of PMMA chains with pyrene end-functional groups to form py-PMMA-py chains can prevent the self-assembling of GS to π - π stacked structures and thus can help keep GS uniformly dispersed in the polymer matrix. A careful analysis of the MD trajectories revealed that pyrene groups adsorb strongly on the two faces of GS and, as a result of the intervening polymer mass, GS are kept separate in the nanocomposites containing pyrene-functionalized PMMA chains. Several interesting structures were observed in the simulations: a) py-PMMA-py chains adsorbed on the same face of a GS through both of their end pyrene groups thereby forming a *loop*, b) py-PMMA-py chains adsorbed on the two faces of the same graphene sheet thus forming an *extended closed loop*, and c) py-PMMA-py chains adsorbed on two different GS thereby forming a *bridge*. It is through these loop, extended loop and bridge structures that GS remain apart and well dispersed in the matrix, even at very high wt. % loadings of GS.

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