Atomistic Simulation of Pyrene Functionalized α,ω-PMMA as Dispersing Agent of Graphene for the Fabrication of Polymer Nanocomposites

Emmanuel N. Skountzos[a], Vlasis G. Mavrantzas[b], Constantinos Tsitsilianis[a]

[a] Department of Chemical Engineering, University of Patras & FORTH/ICE-HT, Patras GR 26504, Greece

[b] Particle Technology Laboratory, Department of Mechanical & Process Engineering, ETH-Z, CH-8092 Zürich, Switzerland

INTRODUCTION

- Polymer nanocomposites based on carbon black, carbon nanotubes, and layered silicates find extensive applications in the recent years due to their improved mechanical, thermal, electrical, and gas barrier properties compared to the corresponding properties of the pure matrix.
- More recently, the discovery of graphene has opened a new direction in the field through the design of the so called class of graphene-based polymer nanocomposites.
- In the literature,[1,2] significant improvements in the mechanical (but also *electrical*, *thermal* and *barrier*) properties of graphene-based polymer nanocomposites have been reported for many glassy polymers.
- In our recent atomistic simulation study[3] we showed that at just 5.67% wt. loading of a PMMA matrix in GS, the Young's modulus E, was improved by ~74%.
- An important finding of our simulations was also that GS tend to self-assemble in the PMMA matrix and agglomerate into multilayer graphene structures due to strong π-π stacking.
- In the present work we propose a new methodogy in order to prevent graphene stacking by functionalizing not the graphene sheets, but the polymer chains.

MOLECULAR MODEL & SYSTEMS STUDIED

- The selected polymer system is the atactic PMMA (all chains in the simulation box consist of random sequences) (Figure 1a).
- The proposed functionalization focuses on adding at the two free ends of the polymer chains, pyrene groups creating the so called py-PMMA-py chains (Figure 1b).

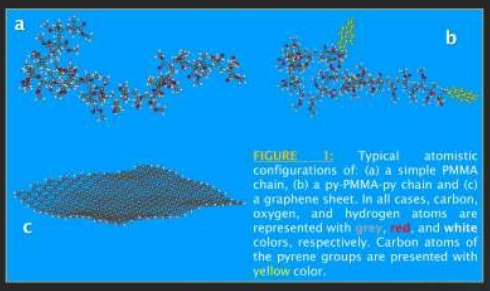

FIGURE 1: Typical atomistic configurations of: (a) a simple PMMA chain, (b) a py-PMMA-py chain and (c) a graphene sheet. In all cases, carbon, oxygen, and hydrogen atoms are represented with grey, red, and white colors, respectively. Carbon atoms of the pyrene groups are presented with yellow color.

- In our simulations, strictly monodisperse samples were assumed, each aPMMA and py-PMMA-py chain consisted of 30 monomers (methyl methacrylate, MMA) implying a molecular weight of 3005.49 gr/mol.
- The graphene sheets had lateral dimensions of (39 × 39) Å² (Figure 1c).
- Four different model systems were simulated (see Table 1), in order to examine the effectiveness of the proposed functionalization on preventing the graphene agglomeration in the polymer matrix.

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

TABLE 1: Details (number of PMMA chains, number of Py-PMMA-py chains, number of graphene sheets, and wt.% graphene sheet loading) of the PMMA-GS nanocomposite systems simulated in this work.

- The simulations have been executed with rectangular parallelepiped simulation cells with all atoms subjected to three-dimensional periodic boundary conditions.
- The simulations were carried out with the very accurate, explicit-atom DREIDING force-field[4] for the calculation of atomistic interactions between PMMA and graphene sheets using the LAMMPS software.
- The simulations were executed at T=550K and P=1atm.

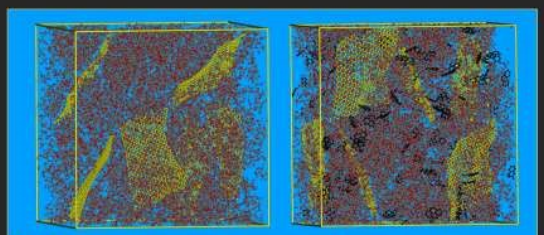

FIGURE 2: Initial configurations of (a) System 1 (no py-PMMA-py addition) and (b) System 2 (40 py-PMMA-py chains) in the simulation cell (Hydrogen atoms have been omitted for clarity). In both cases, carbon, oxygen, and hydrogen atoms are represented with grey, red, and white colors, respectively. Carbon atoms of the graphene sheets are presented with yellow color while the carbon atoms of pyrene groups are presented with black color.

RESULTS

➢ Evolution of self-assembly of System 1

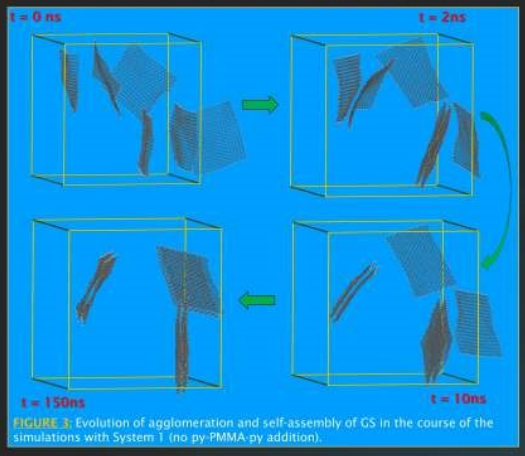

FIGURE 3: Evolution of agglomeration and self-assembly of GS in the course of the simulations with System 1 (no py-PMMA-py addition).

- In our MD simulations with System 1 (all chains of which are non-functionalized; they contain no pyrene groups), and after a very short simulation period (approximately 10 ns), GS started self-assembling giving rise to well-ordered structures characteristic of the π-π stacked configuration of GS in graphite (Figure 3).
- Initially, four (out of the six) GS in the simulation cell came together to form two separate stacks, and later the other two GS joined these two stacks.

➢ Evolution of non self-assembly of System 2

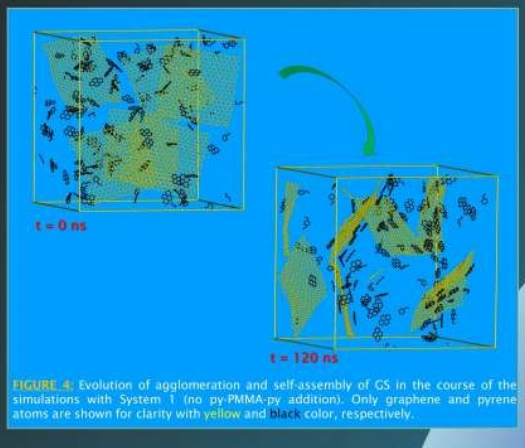

FIGURE 4: Evolution of agglomeration and self-assembly of GS in the course of the simulations with System 1 (no py-PMMA-py addition). Only graphene and pyrene atoms are shown for clarity with yellow and black color, respectively.

- In contrast, for System 2, no GS was observed to come close to another GS and form an agglomerate even after a long simulation time (Figure 4).
- Another direct observation is that at the end of the simulation several pyrene molecules have clearly adsorbed on the graphene sheets.
- Similar behavior exists for the rest of the simulated systems (Systems 3 and 4).

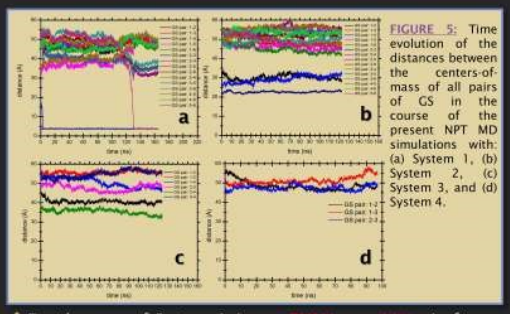

FIGURE 5: Time evolution of the distances between the centers-of-mass of all pairs of GS in the course of the present NPT MD simulations with: (a) System 1, (b) System 2, (c) System 3, and (d) System 4.

- For the case of System 1 (no py-PMMA-py addition) after ~ 120ns of simulation time all graphene sheets have agglomerated.
- For Systems 2-4 all graphenes remained totally separated in the polymer matrix after several nanoseconds of simulation time.

➢ Pyrene adsorbance on graphene sheets

- Several pyrene molecules can adsorb in a single graphene sheet (Figure 6).

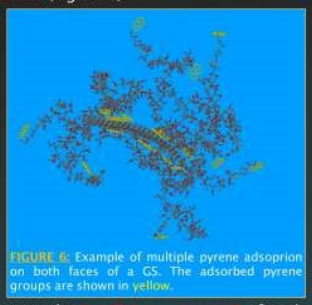

FIGURE 6: Example of multiple pyrene adsoprion on both faces of a GS. The adsorbed pyrene groups are shown in yellow.

- We can observe the parallel arrangement of each pyrene on the graphene surface (π-π stacking) with the rest of the polymer chain extending normal and parallel to the surface of the GS.

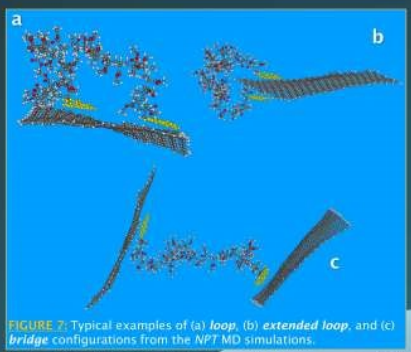

FIGURE 7: Typical examples of (a) ***loop***, (b) ***extended loop***, and (c) ***bridge*** configurations from the *NPT* MD simulations.

- By inspecting the atomistic snapshots more carefully, we concluded that pyrene groups adsorb on GS in three distinct structures:
  - ✓ 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* (Figure 7a).
  - ✓ 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* (Figure 7b).
  - 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* (Figure 7c).

REFERENCES

1. Ramanathan T. et al., *Nature Nanotechnology*, (2008).
2. Li, X. G. et al., *ACS Macro Lett*, (2012).
3. Skountzos E. N. et al., *Macromolecules*, (2014).
4. Mayo, S. L. et al., *Phys. Chem-Usl*, (1990).

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