

# MODELING THE INTERFACIAL PHENOMENA OF POLYMER-SWCNT INTERACTIONS VIA MOLECULAR DYNAMICS SIMULATIONS

Syamal S. Tallury<sup>1,2</sup> and Melissa A. Pasquinelli<sup>1</sup>

<sup>1</sup>Fiber and Polymer Science/TECS,

<sup>2</sup>Materials Science and Engineering,

North Carolina State University

2401 Research Drive, Campus Box 8301

Raleigh, N.C. 27695-8301

sstallur@ncsu.edu; Melissa\_Pasquinelli@ncsu.edu

## Introduction

Nanomaterials that have large interfacial areas as a characteristic provide new avenues to multifunctional and extreme performance materials<sup>1</sup>. Carbon nanotubes (CNTs), with inherent high aspect ratios, are very promising contenders as reinforcement for polymer composite materials. CNTs have a very high modulus, ranging up to 1 TPa, and thus can greatly enhance the modulus of nanocomposites to several GPa<sup>2</sup>. CNTs are remarkably flexible and are nearly same size as a typical polymer chain while having versatile electronic properties ranging from nonmetallic to metallic<sup>3</sup>. An important factor of the desired properties of CNT-based nanocomposites is the molecular interactions at the interface between the CNT reinforcement and the polymer matrix.

Single-walled carbon nanotubes (SWCNTs) have been utilized in polymer processing as nucleating agents to increase crystallinity<sup>4</sup>. Although both isothermal and non-isothermal<sup>5</sup> crystallization was observed using SWCNTs in certain polymers, the molecular details of the process are still unknown. This study explores the interfacial molecular conformations via molecular dynamics (MD) simulations. Simulations were performed with various polymeric species at larger chain lengths than previously reported<sup>6,7</sup> to understand the chain conformations in the vicinity of the SWCNT. Our results provide useful insights into molecular phenomenon of polymer chain folding and their non-covalent interaction with CNTs.

## Computational Details

**Single chain adsorption studies.** The polymers included in this study can be categorized based on chemical composition into two broad groups, flexible backbone type and stiff backbone type. The molecular weight of all the chosen polymers is held the same as that of 20 repeat unit long PET chain. The chemical structures were generated using the DL\_POLY<sup>8</sup> graphical user interface.

MD simulations were performed with DL\_POLY 2.19<sup>8</sup>. An NVT (constant number of molecules, temperature, and volume) ensemble at 300 K was done with no applied pressure, using the Evans Gaussian temperature constraints and the Dreiding<sup>9</sup> force field. The simulations had a timestep of 1 fs, an equilibration time of 0.5 ns, and a simulation time of 3 ns for statistical analysis. All cutoff radii were set to 10.0 Å. Initial configurations of the SWCNT and polymer chain were created by aligning the SWCNT along the z-axis and then placing the polymer chain such that the perpendicular distance from the SWCNT is around 40 Å, implying that the polymer chain is well outside the cut off radius of interaction at the initial stage. If the MD simulations at this initial configuration did not result in wrapping, then this distance and orientation was altered to attempt to “induce” wrapping. Analysis was performed with VMD<sup>10</sup>.

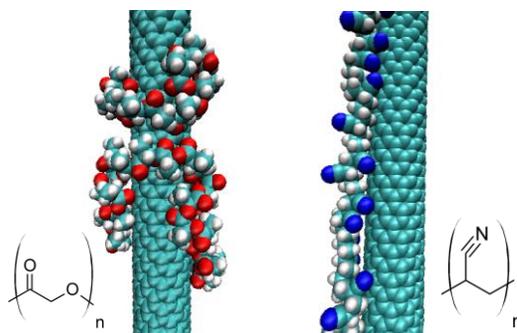
**Nucleation studies.** Polyamide-6 (PA-6) was chosen due to its commercial relevance to study the nucleation due to SWCNT addition. For this purpose, two simulations were conducted: one with the SWCNT and another on a pure polymer system. The structures for this study were built using Materials Studio 5.0 software package<sup>11</sup> with the Discover and Amorphous Cell modules and the simulations were performed on LAMMPS molecular dynamics package<sup>12</sup> employing the second generation force field PCFF<sup>13</sup>. In order to simulate melt compounding technique, the temperature was gradually decreased from 500 K to 300 K for both systems.

**SWCNT Structures.** A SWCNT of type (10,0) zig-zag was used in both studies. The SWCNT was created to have a diameter of 7.7 Å and a length of 125.0 Å. We chose such a small diameter since a recent study<sup>14</sup>

indicated that SWCNT with smaller diameters exhibit stronger Van der Waals interactions than those with larger diameters.

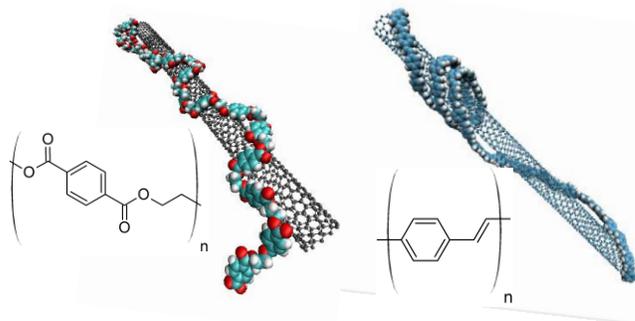
## Results and Discussion

**Single chain adsorption results.** MD snapshots for two flexible backbone chains, polylactic acid (PLA) and polyacrylonitrile (PAN), are given in **Figure 1**. Both polymers are composed of flexible backbones but the presence of carbonyl groups along the chain does not exhibit any orientation relative to the SWCNT surface<sup>15</sup> and thus PLA wraps in a random conformation around the SWCNT. The cyano side groups of the PAN chain interact very well with the SWCNT while letting the aliphatic backbone extend along the SWCNT axis. There is a remarkable difference in the polymer chain conformations between the two species. Comparable results were observed for other flexible backbone polymers in the series<sup>15</sup>. Two polymers, polymethylmethacrylate (PMMA) and polystyrene (PS), preferred intrachain coiling over interactions with the SWCNT. However, preliminary results<sup>16</sup> suggest that these polymers can overcome the intrachain coiling through the inclusion of a good solvent for each polymer, such as dimethyl formamide (DMF), during the MD simulations and produced random conformations comparable to PLA in Figure 1.



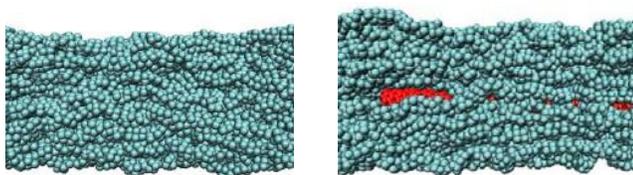
**Figure 1:** MD snapshots of the interaction between a SWCNT and PLA (left) and PAN (right). The atoms are: carbon (cyan), hydrogen (white), oxygen (red), and nitrogen (blue). Images were created with VMD<sup>10</sup>.

MD snapshots for a polymer with a semi-rigid backbone, polyethylene terephthalate (PET), and a rigid backbone, polyparaphenylene vinylene (PPV), are given in **Figure 2**. The polymers with a semi-rigid backbone tend to form an S-shaped conformation but never fully wrap completely around the circumference of the SWCNT. The rigid backbone polymers, however, do completely wrap around the SWCNT in distinct conformational patterns; PPV exhibits a distorted helical conformation. Comparable results were observed for other rigid and semi-rigid backbone polymers in the series<sup>17</sup>. Analysis using visual-analytic tools suggests that for PPV, two distinct spiral structures persist as a function of time that differ only in the orientation of the plane of spiral<sup>18</sup>, suggesting that the  $\pi$ - $\pi$  interactions drive the helical conformations.

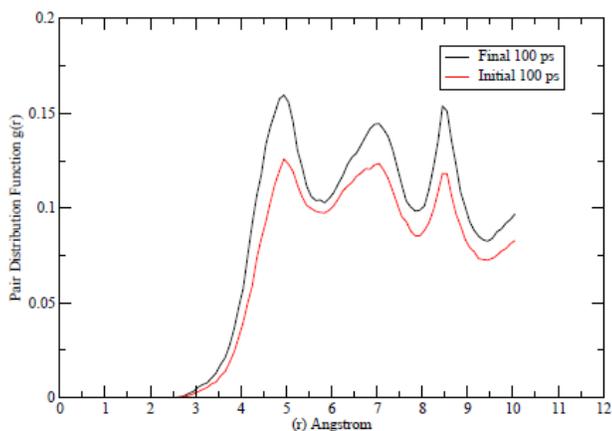


**Figure 2:** MD snapshots of the interaction between the SWCNT and PET (left) and PPV (right). The atoms are: carbon (cyan/black, left; blue, right), oxygen (red), and hydrogen (white). Images were created with VMD<sup>10</sup>.

**Nucleation studies.** The polyamide-6 (PA-6) system with 36 chains of 50 repeat units was run with and without the SWCNT to observe the chain folding and nucleation behavior. **Figure 3** depicts the snapshots of the two systems, which provides evidence of a remarkable change in the ordering of chains as the simulations progressed. In order to further understand the ordering in the systems, the radial distribution functions (RDF) between nitrogen atoms were calculated, which are time averages across portions of the MD trajectory. From the RDF between the amino nitrogen atoms in **Figure 4**, it was observed that the hydrogen bonding increased significantly as the simulation progressed, as indicated by the peak around 5 Å. The ordering in the system and hydrogen bond formation was dramatically more pronounced when the SWCNT was included in the simulation.



**Figure 3: MD snapshots of the polyamide-6 system pure (left) and with SWCNT (right). The SWCNT is shown in red. Images were created with VMD<sup>10</sup>.**



**Figure 4: RDF plot between amino nitrogen atoms in polyamide-6/SWCNT system. The black (final steps) curve shows remarkable ordering over the red (initial steps) curve.**

## Conclusions

MD simulations of the interface between a SWCNT and various polymers indicate that polymers with both flexible and rigid backbones tend to wrap around the SWCNT, although in different conformations. Flexible backbones like nylons wrap in a random conformation, whereas semi-rigid backbones like PET partially wrap in more ordered helices. Results show that pi electron cloud in the backbones increases the interaction with the SWCNT. Nucleation studies hint at non-isothermal crystallization behavior by SWCNT due to heterogeneous nucleation. Ordering in the polyamide-6 systems was predicted from these MD simulations to be enhanced due to the presence of SWCNT. Other trends and the correlation of these features to the properties of nanocomposites are currently being explored. We are also developing visual analytical tools<sup>18</sup> that will enable these complex systems to be further analyzed for salient features that connect the molecular details to bulk phenomena.

## Acknowledgements

This project was funded through start-up funds awarded to M.A.P. by North Carolina State University. The authors thank Russell Gorga, Alan Tonelli and Tim Fornes for their guidance in this work. The authors would also like to acknowledge Steve Plimpton at Sandia National Labs for providing the LAMMPS software package as open source software, the Klaus Schulten laboratory at UIUC for providing a free copy of VMD, and also EPSRC's Collaborative Computational Project for the Computer Simulation of Condensed Phases (CCP5) and the Computational Science and Engineering Department at Daresbury Laboratory for providing a free copy of the DL\_POLY package.

## References

- Coleman, J.N.; Khan, U.; Blau, W.J.; and Gun'ko, Y.K. *Carbon* **2006**, *44*, 1624.
- Frankland, S.J.V.; Harik, V.M.; Odegard, G.M.; Brenner, D.W.; and Gates, T.S. *Composite Sci. and Tech.* **2003**, *23*, 1655-1661.
- Andrews, R.; Weisenberger, M.C. *Curr. Opin. Solid State and Mat. Sci.* **2004**, *8*, 1, 31-37.
- Brosse et. al, *Polymer*, **2008**, *49*, 4680-4686.
- Mitchell, C. A.; Krishnamoorti, R. *Polymer* **2005**, *46*, 8796-8804.
- Liu, W.; Yang, C.-L.; Zhu, Y.-T.; Wang, M. *J. Phys. Chem. C*, **2008**, *112*, 1803-1811.
- Zheng, Q.; Xue, Q.; Yan, K.; Hao, L.; Li, Q.; Gao, X. *J. Phys. Chem. C*, **2007**, *111*, 4628-4635.
- Smith, W (ed.). *Molecular Simulation* **2006**, *32*, 933-1121. [http://www.ccp5.ac.uk/DL\\_POLY/](http://www.ccp5.ac.uk/DL_POLY/).
- Mayo; Olafson; Goddard, *The Journal of physical chemistry* **1990**, *94*, 8897-8909.
- Humphrey, W.; Dalke, A.; and Schulten, K., *J. Molec. Graphics*, **1996**, *14*, 33-38. <http://www.ks.uiuc.edu/Research/vmd/>
- Accelrys. Accelrys Software, San Diego, CA (2004).
- S. J. Plimpton, *J Comp Phys*, **1995**, *117*, 1-19. <http://lammps.sandia.gov>
- Sun, H.; Ren, P.; Fried, J. R. *Computational and Theoretical Polymer Science* **1998**, *8*, 229-246.
- Jiang, L. Y.; Huang, Y.; Jiang, H.; Ravichandran, G.; Gao, H.; Hwang, K.C.; and Liu, B. *J. Mech. Phys. Solids* **2006**, *54*, 2436-2452.
- Tallury, S.S.; and Pasquinelli, M.A. *J. Phys. Chem. B* **2010**, *114*(12), 4122-4129.
- Tallury, S.S.; Srivastava, A.; Howell, Z.; and Pasquinelli, M.A. To be submitted.
- Tallury, S.S.; and Pasquinelli, M.A. *J. Phys. Chem. B* **2010**, *114*(29), 9349-9355.
- Thakur, S.; and Pasquinelli, M.A. Submitted to *Macromolecular Theory and Simulations*.