# EFFECT OF ALIPHATIC SEGMENT LENGTH ON NYLON-SWCNT INTERACTIONS VIA MOLECULAR DYNAMICS SIMULATIONS

*Syamal S. Tallury and Melissa A. Pasquinelli*

Fiber and Polymer Science/TECS, North Carolina State University 2401 Research Drive, Campus Box 8301 Raleigh, N.C. 27695-8301
Melissa_Pasquinelli@ncsu.edu

## Introduction

Carbon nanotubes have emerged as one of the most interesting materials since their discovery by Ijima[1]. The high aspect ratio and excellent mechanical and electrical properties exhibited by CNTs make them materials of choice as toughening reinforcements in polyamide based nanocomposites[2]. However poor dispersion of nanotubes[3] and the severe dependence of properties on the orientation of fillers[4] in the bulk material require proper engineering of the interface between the CNTs and the polymer matrix. Several studies report the property enhancement of nylon-nanotube nanocomposites[5,6] but fail to understand the nucleation and polymer conformational behavior in the vicinity of the nanoparticle interface. Due to the size and timescale of these interfacial interactions, it is challenging to observe the molecular phenomenon experimentally. Computational approaches such as molecular dynamics[7] and Monte Carlo[8] techniques have been proven useful for studying these interfacial characteristics.

This work aims to explore the interface between single-walled carbon nanotubes (SWCNTs) and a range of polyamides via molecular dynamics (MD) simulations. The goal is to explore the effect of the length of the aliphatic chain on their interaction with the SWCNT. These results could greatly enhance the understanding of polymer-nanotube interfaces and the dependence of the interaction on the chemical structure of the polymers.
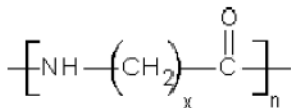


**Figure 1:** Chemical structure of polyamides. In this study, x ranges from 3 to 20.

**Computational Details. Generation of Polymer Models.** The range of polyamides included in this study is listed in Table 1. The models have been constructed in reference to the chemical formula given in **Figure 1**. We chose molecular weights and chain lengths that are significantly larger than those used in previous computational studies[9]. The molecular weights for each polymer chain were standardized; the molecular weight of 15 repeats of PA-20 was set as the reference. The molecular structures were built with the DL_POLY graphical user interface and then relaxed for a few MD steps.

**Table 1: Series of polyamide species included in the study, with the molecular weight (MW) and number or repeat units (RU) in the structure. Refer to Figure 1 for the polyamide notation.**

| Polyamide PA-x | MW (a.m.u.) | RU | Polyamide PA-x | MW (a.m.u.) | RU |
|---|---|---|---|---|---|
| PA-3 | 4615 | 65 | PA-12 | 4728 | 24 |
| PA-4 | 4590 | 54 | PA-13 | 4624 | 22 |
| PA-5 | 4653 | 47 | PA-14 | 4725 | 21 |
| PA-6 | 4633 | 41 | PA-15 | 4541 | 19 |
| PA-7 | 4699 | 37 | PA-16 | 4554 | 18 |
| PA-8 | 4653 | 33 | PA-17 | 4539 | 17 |
| PA-9 | 4650 | 30 | PA-18 | 4777 | 17 |
| PA-10 | 4563 | 27 | PA-19 | 4720 | 16 |
| PA-11 | 4575 | 25 | PA-20 | 4635 | 15 |

**Generation of SWCNT Structures.** A SWCNT of type (10,0) zig-zag was built with the DL_POLY graphical user interface with the built-in nanotube builder. The SWCNT was built 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[10] indicated that SWCNTs with smaller diameters exhibit stronger Van der Waals interactions than those with larger diameters.

**Simulation Details.** All simulations were run using the DL_POLY2.19[11] software package. Molecular dynamics with an NVT ensemble at 300 K was performed with no applied pressure, using the Evans Gaussian temperature constraints and the DREIDING[12] force field. The simulations had a timestep of 1 fs, an equilibration time of 0.5 ns, and a simulation time of 3 ns. 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.
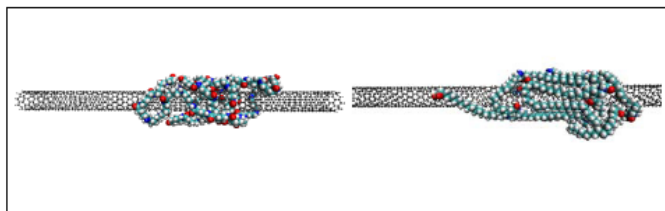


**Figure 2:** PA-5 (left) and PA-20 (right) wrapping a SWCNT at a later time step in the simulations. Blue is nitrogen, red is oxygen, aqua is carbon, white is hydrogen, and black is the SWCNT carbons.

## Results and Discussion

**Polymer conformations.** MD snapshots for two of the representative polymers, PA-5 and PA-20, are given in **Figure 2**. These snapshots depict that for polymers with shorter aliphatic portions like PA-5, the polymer chain prefers localized coiling, whereas for polymers with the longer aliphatic segments like PA-20, the chain tend to exhibit more extended chain configurations where the aliphatic portions align with one another in a fold-like fashion. This behavior can be attributed to the affinity between the long lipophilic portions within the polymeric chains. This phenomenon is in agreement with the folded chain crystal morphology studies conducted by Atkins and coworkers[13]. The polymers from PA-10 onwards showed a clear preference of extended chain conformations over the localized wrapping with the SWCNT.

Another important observation is depicted in Error! Reference source not found. Shorter chains such as PA-5 wrap along the entire diameter of the SWCNT, whereas chains with longer aliphatic portions such as PA-10 and PA-20 do not. This phenomenon is observed to be true for all the polymers in the range PA-10 to PA-20 and the higher aliphatic lengths show more preference for this behavior. It can also be observed that PA-10 onwards the polymers prefer to wrap in an extended-folded chain conformation, unlike the PA-3 to PA-8 that form localized random coils.
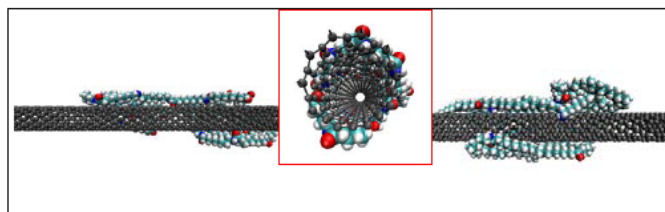


**Figure 3:** PA-10 (left) and PA-20 (right) tend to partially wrap around the diameter of the SWCNT, whereas shorter chains like PA-5 (middle) wrapped the circumference completely.

**Orientation of chemical groups.** The orientation and positions of the functional groups such as the carbonyl carbon and amide group with respect to the SWCNT surface can provide information about the preferential orientation of the polymers at the interface, which could dictate desired properties. **Figure 4** is a snapshot of PA-18, which wraps the SWCNT while persisting lengthwise with two repeat units. The functional groups tend to stack next to each other, facilitating strong intrachain interactions. This behavior is also reported by Cojazzi and coworkers[14] from the study of the chain folding in lamellae. These studies can be very useful to understand the nucleation[15]

behavior of polyamides in the vicinity of nanotubes as reported by Brosse and coworkers[16].

**Statistical mechanics analysis.** The entropic gain due to the interaction of the polyamide chains with the SWCNT are explored by evaluating statistical properties of the chains such as persistence length and the characteristic ratios. The results of this analysis indicate that polymer chains with longer aliphatic portions have a significant increase in the persistence of segment lengths about the SWCNT as compared to polymers PA-3 to PA-8. Results show interesting increase in the segmental length for the chain folding which is in agreement with the previous studies on nylon lamellar crystallites[17]. The entropic contribution of the polymer-SWCNT interactions could be estimated by studying the polymer chain packing and folding in the vicinity of the SWCNT.
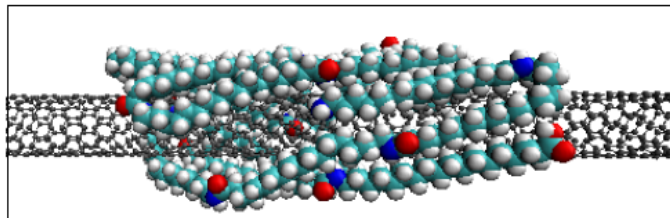


**Figure 4:** PA-18 exhibits a regular folded chain conformation in the vicinity of SWCNT.

## Conclusions

These MD simulations indicate strong dependence of the polyamide-SWCNT interactions on the aliphatic portion length of the polymer. For polyamides with an aliphatic portion with at least 10 carbons prefer to conform to extended, folded chain structures, whereas the chains PA-3 to PA-9 have a more random coil arrangement. The polyamides up to PA-9 tend to wrap completely around the diameter of the SWCNT, unlike those with longer aliphatic portions. These interactions can greatly enhance the nucleation and interfacial behavior of polyamides with carbon nanotubes.

## References

(1)  S Ijima, Nature, 1991, 354: 56—58.
(2)  N Sheng, MC Boyce, DM Parks, GC Rutledge, JI Abes, and RE Cohen, Polymer, 2004, 45(2): 487-506.
(3)  MJ O'Connell, P Boul, LM Ericson, C Huffman, Y Wang, E Haroz, C Kuper, J Tour, KD Ausman, and RE Smalley. Chemical Physics Letters, 2001, 342(3-4):265 – 271.
(4)  SJV Frankland, VM Harik, GM Odegard, DW Brenner, and TS Gates, Composites Science and Technology, 2003, 63: 1655–1661.
(5)  TD Fornes, and DR Paul, Polymer, 2003, 44(14): 3945-3961.
(6)  B Krause, P Potschke, and L Haussler, Composites Science and Technology, 2009, 69(10): 1505-1515.
(7)  Q Zheng, Q Xue, K Yan, L Hao, Q Li, and X Gao. Journal of Physical Chemistry C, 2007, 111(12): 4628–4635.
(8)  C Wei. Nano Letters, 2006, 6(8): 1627–1631.
(9)  M Yang, V Koutsos, and M Zaiser. Journal of Physical Chemistry B, 2005, 109(20): 10009–10014.
(10) LY Jiang, Y Huang, H Jiang, G Ravichandran, H Gao, KC Hwang, and B Liu, J. Mech. Phys. Solids 2006, 54: 2436-2452.
(11) W Smith (ed.). Molecular Simulation, 2006, 32: 933-1121.
(12) SL Mayo, BD Olafson, and WA Goddard. Journal of Physical Chemistry, 1990, 94(26): 8897–8909.
(13) EDT Atkins, MJ Hill, and K Veluraja, Polymer, 1995, 36(1): 35-42.
(14) G Cojazzi, A Fichera, V Malta, and R Zannetti, Die Makromolekulare Chemie, 1978, 179(2): 509-518.
(15) K Saeed and SY Park, Journal of Applied Polymer Science, 2007, 106(6): 3729-3735.
(16) AC Brosse, ST Girault, PM Piccione, and L Leibler, Polymer, 2008, 49(21): 4680-4686.
(17) NA Jones, EDT Atkins, MJ Hill, SJ Cooper, and L Franco, Polymer, 1997, 38(11): 2689-2699.