## INTERFACIAL CHARACTERISTICS OF POLYMER NANOCOMPOSITES VIA MOLECULAR DYNAMICS SIMULATIONS

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## ABSTRACT

Composites that have large interfacial areas provide new avenues to engineer multifunctional and extreme performance materials. Polymer nanocomposites have increased surface area at the interface between the reinforcement and the matrix, and thus only a small fraction of reinforcement is sufficient, compared to a microfiller, to achieve a significant enhancement in the mechanical strength. Due to the size scale of reinforcements, the molecular interactions at the interface play a critical role in the overall desired properties. Carbon nanotubes (CNTs) are an attractive option for a reinforcement material due to their high surface areas, high aspect ratios, impressive mechanical strength, and versatile electronic properties. Since an understanding of the molecular level interactions between CNTs and polymers is necessary to engineer polymer nanocomposites with desired properties, we used molecular dynamics (MD) simulations to optimize the interfacial characteristics of this important class of materials. The MD simulations revealed interfacial characteristics of a variety of polymer nanocomposites by providing insights into how polymers prefer to align relative to the reinforcement, how interfacial interactions are affected by properties of both the polymer and reinforcement, and how these interfacial characteristics impact the desired properties of the nanocomposite.

## INTRODUCTION

The superior electrical and mechanical properties of carbon nanotubes (CNTs) can be utilized to develop polymer nanocomposites for applications such as high performance fibers or tissue engineering scaffolds. Non-covalent engineering of the polymer-CNT interface not only preserves the CNT properties but also avoids the brittleness in the composite materials. Because molecular dynamics (MD) simulations solve Newton's equation of motion for each particle (which are commonly atoms or groups of atoms) as a function of time, they are a useful tool for predicting the interfacial characteristics of polymer nanocomposites.[1] Specifically, MD simulations can predict properties such as the density, glass transition temperature, adhesion energy at the interface, or the degree of plasticity. MD simulations can also predict the effects during processing and use, such as the presence of moisture and other substances, the effects of thermodynamics such as temperature or pressure, the application of shear and/or drawing, or the impact of its chemical environment (solvent, moisture, additives, oxygen, etc.) or physical environment (confinement). In addition, MD simulations can provide molecular level details that cannot be obtained easily experimentally, such as the degree of alignment at the interface with a nanofiller, the degree of hydrogen bonding, the amount of entanglements within the polymer matrix, or even how the system may degrade.

We have utilized MD simulations to characterize polymer-CNT interactions.[2-5] Several studies have suggested that polymers adsorb on the CNT surface by either wrapping around the CNT or aligning along the longitudinal axis of the CNT. In the case of conjugated polymer chains, this phenomenon is of critical importance as it gives rise to better orientation of chains and hence can improve the strength as well as the conducting properties of the composite material. In addition, the effect of the volume fraction of CNTs can also impact its mechanical properties. Thus, we have investigated the alignment of a series of polymers with single-walled CNTs with varying degrees of backbone rigidity and, for polythiophenes (PTs), also varying degrees of alkyl chain side groups. In addition, we present the effect of the volume fraction of triple-walled CNTs on the mechanical properties of polyimide nanocomposites. These simulation results reveal how atomistic interactions impact the interfacial characteristics of polymer nanocomposites, and thus lead to the optimization of the desired properties of these materials.

# METHODOLOGY

The simulation details are summarized below; please refer to our other work for more specific details.[2-5]

*Systematic study of polymer alignment with SWCNTs.* A series of MD simulations were performed with polymers of varying degrees of saturation, aromaticity, and aliphaticity on both the backbone and the side chains. Table 1 lists the names of the polymers and their chemical structures are given in the insets of Figures 1 and 2, and the type of CNT used in each simulation is also given in Table 1.

For the first 13 polymers listed in Table 1, MD simulations were performed [2-3] with the NVT ensemble (constant number of molecules, temperature, and volume) at about 27 °C, with a time step of 1 fs, an equilibration time of 0.5 ns, and a simulation time of 3 ns for statistical analysis. The Dreiding[6] force field was used with the DL\_POLY[7] software program. All cutoff radii were set to 10.0 Å. Initial configurations of the SWCNT and polymer chain were created by aligning the (10,10) 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.

For the PTs listed in Table 1,[4] we performed MD simulations on four different polymers with varying degrees of backbone rigidity and side chain length. With the PT placed between 10 to 20 Å away from the longitudinal axis of the (9,9) SWCNT of length 200 Å and diameter of 12 Å, two different starting configurations relative to the SWCNT were built: one where each PT is initially parallel to the SWCNT longitudinal axis, and one that is initially perpendicular. The MD simulations were performed with the LAMMPS[8] software program on Sun Linux computer. With the pcff force field,[9] we used an NVT ensemble with periodic boundary conditions, with a time step of 1 fs for a total time of 0.3 ns. Interaction energies were calculated using a script integrated with the LAMMPS simulation program and were averaged over the final 100,000 simulation steps.

**PI/CNT nanocomposites.** The chemical structure of PI is given in Figure 3; for the TWCNT, we used the (10, 10) (13, 12), (15, 15) type, with an outer diameter of 20.34 Å and a total length of 245.9 Å.[5] Seven molecular models of different volume fractions in the range of 4.48–34.42% for the nanocomposites were built by incorporating various ratios and arrangements of TWCNTs within the PI polymer chains; the arrangements are given in the insets of Figure 3 and other details are given in Table 2. With the pcff force field, we used an isobaric and isothermal (NPT) ensemble was used to reduce local minima of the simulation

box and compact the PI chains. We used a time step of 1fs for a total time of 1ns. Once the system was equilibrated, it was subjected to uniaxial deformation by applying a 5.0% strain along the z direction under an isochoric and isothermal (NVT) ensemble at 0.01 K with the Nose–Hoover thermostat and periodic boundary conditions. The system was stretched with a strain rate of 0.001% every 0.1 ps for 0.5 ps. The elastic modulus and stress-strain curves were obtained for both nanocomposites with different volume fraction and pure PI matrix for further comparison.

|              | Polymer Name   | Molecular<br>Weight<br>(amu) | SWCNT<br>Type | SWCNT<br>Length<br>(Å) | SWCNT<br>Diameter<br>(Å)  | E <sub>inter</sub><br>(kcal/mol)  |
|--------------|--|------------------------------|---------------|------------------------|---|---|
| PPE          | polyaryleneethynylene  | 3735                         | (10,10)       | 120                    | 7   | $-204.2 \pm 8.3$  |
| PA           | polyacetylene  | 3864                         | (10,10)       | 120                    | 7   | $-415.1 \pm 7.4$  |
| PPV          | polyparaphenylene vinylene   | 3876                         | (10,10)       | 120                    | 7   | $-391.7 \pm 5.3$  |
| PPY          | polypyrrole  | 3825                         | (10,10)       | 120                    | 7   | $-375.7 \pm 5.7$  |
| PET          | polyethylene teraphthalate   | 3850                         | (10,10)       | 120                    | 7   | $-288.8 \pm 4.4$  |
| PP           | polypropylene  | 3822                         | (10,10)       | 120                    | 7   | $-267.3 \pm 5.8$  |
| PAN          | polyacrylonitrile  | 3888                         | (10,10)       | 120                    | 7   | $-243.7 \pm 6.0$  |
| PEO          | polyethylene oxide   | 3828                         | (10,10)       | 120                    | 7   | $-258.4 \pm 7.5$  |
| PS           | polystyrene  | 3888                         | (10,10)       | 120                    | 7   | $-106.1 \pm 3.9$  |
| PLA          | polylactic acid  | 3816                         | (10,10)       | 120                    | 7   | $-278.3 \pm 6.8$  |
| PCL          | polycaprolactome   | 3876                         | (10,10)       | 120                    | 7   | $-308.9 \pm 5.4$  |
| N6           | polyamide 6  | 3815                         | (10,10)       | 120                    | 7   | $-286.1 \pm 6.0$  |
| PMMA         | polymethylmethacrylate   | 3800                         | (10,10)       | 120                    | 7   | $-112.5 \pm 2.8$  |
| rr-P3HT      | regioregular<br>poly(hexythiophene)  | 4989                         | (9,9)         | 200                    | 12  | $\begin{array}{c c} \parallel -341.6 \pm 4.4 \\ \bot \ -260.0 \pm 5.3 \end{array}$            |
| PQT-12       | poly(3,3-<br>didodecylquaterthiophene) 5987 (9,9) 2  |                              | 200           | 12                     | $\begin{array}{c c} \parallel & -377.5 \pm 4.8 \\ \hline \bot & -305.2 \pm 4.5 \end{array}$ |   |
| PBTTT-<br>14 | poly(2,5-bis(3-<br>tetradecylthiophen-2-<br>yl)thieno[3,2-b]thiophene                                  | 5562                         | (9,9)         | 200                    | 12  | $\begin{array}{c c} \parallel & -380.0 \pm 5.6 \\ \hline \perp & -329.3 \pm 5.3 \end{array}$  |
| PTzQT-<br>14 | poly(2,5-bis(3-<br>tetradecylthiophen-2-<br>yl)thiophen-2-yl)thiophen-2-<br>ylthiazolo[5,4-d]-thiazole | 7272                         | (9,9)         | 200                    | 12  | $\begin{array}{c c} \parallel & -380.7 \pm 5.4 \\ \hline & \bot & -418.3 \pm 5.8 \end{array}$ |

Table 1 Polymer systems that were part of the systematic study of alignment with SWCNTs, and their average interaction energy ( $E_{inter}$ ) with the SWCNT. Data are adapted from Ref. 2-4.

### **RESULTS AND DISCUSSION**

Systematic study of polymer alignment with SWCNTs. As observed in Figure 1, MD snapshots for polymer-SWCNT interactions indicate that the rigid backbone polymers (PPE, PA, PPV, PPY) interact with the SWCNT in distinct conformational patterns; PPV, for example, exhibits full wrapping along the circumference of the SWCNT in a distorted helical conformation along the longitudinal axis. Polymers with a semi-rigid backbone (PET) tend to form an S-shaped conformation but never fully wrap completely around the circumference of the SWCNT. In contrast, flexible backbone chains (PP, PAN, PEO, PS, PLA, PCL, N6, PMMA) interact and wrap the SWCNT in a random configuration, meaning that the polymers wrap completely around the circumference of the SWCNT but no distinct persistent conformations are observed; for polymers with a flexible background but a bulky side group (PMMA, PS), wrapping along the circumference of the SWCNT. The interaction energies in

Table 1 suggest that chemical functional groups such as carbonyls, esters, and amines within the backbone appear to increase the interaction of the polymer chain with the SWCNT. In addition, aromatic groups both within the backbone and on side-chains exhibit much pi-pi alignment with the SWCNT; 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,[10] suggesting that the pi-pi interactions drive the helical conformations.



Figure 1 Alignment of polymers with (a) rigid or semi-flexible, and (b) flexible backbones with SWCNTs. This figure is adapted from Refs. 2 and 3.

We extended this work to investigate PTs, a class of conjugated polymers, all of which contain thiophenes, a sulphur heterocycle, where the conjugation imparts conductivity to the polymers as well as other electronic properties that make PTs a potential material for many advanced applications, and the aliphatic side chains impact its alignment with CNTs. The results are given in Figure 2 and Table 1; we used two different starting conformations, one where the polymer is initially parallel to the longitudinal axis of the SWCNT, and one where it is initially perpendicular, so we can probe variability in the observed conformations. Among nanocomposites with an initial configuration of the PT parallel with the SWCNT, interaction energies in Table 1 increase in magnitude as the flexibility of the backbone decreases, from -341.6 kcal/mol for rr-P3HT to -380.7 kcal/mol for PTzQT-14. A similar trend was observed for a perpendicular initial configuration, from -260 kcal/mol for rr-P3HT to -418.3 kcal/mol for PTzQT-14. For all initial configurations, the attraction between the PT and SWCNT increased as backbone flexibility decreased.

We calculated the interfacial distances between each sulfur atom in the PT to the SWCNT surface; values were averaged over the entire simulation period and plotted as a function of the PT sulfur atom. Results of the interfacial distances in Figure 2 indicate that the orientations are dependent on the physical conformation of the PT and SWCNT as well as initial configuration (parallel versus perpendicular). Nanocomposites with rr-P3HT, PQT-12, and PTzQT-14 in parallel initial configuration exhibited consistent distances between sulfur atoms and the SWCNT surface of approximately 3 to 4 Å. In contrast, all PTs that initially started perpendicular to the SWCNT longitudinal axis, as well as PBTTT-14 in parallel initial configuration, exhibited greater distances between sulfur atoms and the SWCNT surface. Visual analysis of each MD snapshot of the final conformation from the simulation trajectory from the insets of Figure 2 indicate that certain sulfur atoms were forced away from the

SWCNT surface by either the aliphatic groups inserting between the PT backbones and the SWCNT surface, or the polymer chain folding onto itself.



Figure 2 Alignment of PT polymers with SWCNTs (inset), and the interfacial distance of each sulfur atom to the SWCNT surface. This figure is adapted from Ref. 5.

PI/CNT nanocomposites. The profiles of the PI number density per length unit of each equilibrated composite system with varying volume fractions of TWCNTs is depicted in Figure 3, along with the corresponding cross-sectional arrangement for each system, and a few interesting features are discovered. First, dips appear in the polymer number density profiles where the TWCNTs are located. For the seven models investigated in this work, the number density values are not zero where these dips occur. Thus, PI polymer chains can be observed at the ends of the TWCNTs near the simulation box boundary from snapshots. Secondly, the peaks in the polymer number density for systems with more than one TWCNT indicate that the polymer chains interpenetrate among the TWCNTs to some degree. In addition, the degree of interpenetration differs for the systems that include the same number of TWCNTs but a different geometrical arrangement. Especially in Figure 3(b) and (c), the different spacing between the TWCNTs caused the different chain geometry, highlighting the impact of dispersion on the matrix density. Finally, spikes in the polymer number density occur at the interface of the nanocomposite, suggesting that there could be an increase in the ordering of the polymer chains due to the presence of the TWCNTs. This effect is more prominent as the volume fraction of TWCNTs increases.

The interaction energy and its standard deviation between the TWCNTs and the PI chains for different systems prior to applying the uniaxial strain are given in Table 2. With the increase of the volume fraction of TWCNTs, the interaction energy is observed to increase

significantly, which is due to the increased amount of surface area for the PI chains to interact with the TWCNTs. For the systems with same number of TWCNTs but different geometrical arrangement, V2a and V2b, V4a and V4b, the "b" versions have higher interaction energy values than the "a" versions, resulting from more TWCNT surface area interacting with the polymer.

Through the uniaxial tensile simulation in the direction of TWCNT axis, the elastic modulus  $(Y_c)$  can be obtained for each system, and are given in Table 2. The modulus values increase with an increase of the TWCNT volume fraction. The mild decrease of modulus caused by the geometrical arrangement between "*a*" and "*b*" may result from the ordering of polymer chains that are easily impacted by the arrangement of TWCNTs, as is the number density of the polymer matrix (Fig. 3). By calculating the elastic modulus of a pure PI matrix and a nanocomposite system with different TWCNT volume fractions, the fraction of ordered polymer regions (*a*) can be calculated with the rule of mixture. We observe that *a* increases with an increase of the number of TWCNTs, which indicates that polymer ordering increases when more TWCNTs are added into the nanocomposite system; this finding is consistent with measurements through thermal analysis that indicate that TWCNTs can act as nucleation sites for the crystallization of the polymer within the matrix.[11]



Figure 3 Plots of the polymer number density and snapshots of the morphologies (inset) under the different CNT volume fractions: (a) V1, (b) V2a, (c) V2b, (d) V4a, (e) V4b, (f) V6, and (g) V12. This figure is adapted from Ref. 5. In addition, the chemical structure of the PI is given in the top left.

*Table 2 Details about the different volume fraction systems that were studied in this work. The data are adapted from Ref. 5.* 

| System | No.<br>TWCNTs | $f_{\scriptscriptstyle CNT}(\%)$ | Einter (kJ/kg)       | $Y_c$ (GPa) | а    |
|--------|---------------|----------------------------------|----------------------|-------------|------|
| V1     | 1             | 4.48                             | $-0.0227 \pm 0.0001$ | 75.3        | 4.4  |
| V2a    | 2             | 8.33                             | $-0.0303 \pm 0.0001$ | 121.4       | 9.4  |
| V2b    | 2             | 8.25                             | $-0.0367 \pm 0.0002$ | 133.2       | 32.3 |
| V4a    | 4             | 15.35                            | $-0.0377 \pm 0.0002$ | 215.2       | 42.0 |
| V4b    | 4             | 15.13                            | $-0.0487 \pm 0.0002$ | 231.4       | 79.2 |
| V6     | 6             | 20.93                            | $-0.0583 \pm 0.0002$ | 289.4       | 74.5 |
| V12    | 12            | 34.42                            | $-0.0712 \pm 0.0004$ | 431.5       | 80.0 |

#### CONCLUSIONS

In a systematic MD simulation study of a variety of polymers with varying degrees of backbone rigidity and chemical composition interacting with a SWCNT, we observed that, in contrast to flexible and semi-flexible backbone polymers, rigid backbone polymers preferred distinct conformations relative to the SWCNT, which can also be impacted by long aliphatic side groups. The presence of carbonyls, esters, and amines within the backbone increased the interaction of the polymer chain with the SWCNT, and aromatic groups both within the backbone and on side chains exhibit significant pi-pi interactions with the SWCNT. In addition, for a series of PTs with varying backbone rigidity and aliphatic side chain lengths, alignments relative to the SWCNT surface were observed to be dependent on the initial conformations and energetics.

We also performed MD simulations of nanocomposites comprised of CNTs and PI, a class of polymers that have excellent mechanical strength and high thermal resistance. As a function of the number of CNT walls, we reported molecular details of the pullout process, and predict the critical loading rate required to obtain a complete pullout for each CNT. As a function of increasing volume fraction of CNTs, the strength and modulus are calculated to increase, and are observed to be impacted by both how the CNTs are aligned relative to one another and the degree of PI chain alignment, especially at the interface. These MD simulation results are consistent with experimental observations.

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