

## Molecular Dynamics Simulation Study on the Carbon Nanotube Interacting with a Polymer<sup>†</sup>

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Received November 30, 2011, Accepted January 5, 2012

Using molecular dynamics simulation method, we studied the carbon nanotube (CNT) non-covalently interacting with a polymer. As the polymer coiled around the CNT, the diameter of CNT deformed by more than 40% of its original value within 50 ps. By considering three different polymers, we conclude that the interaction between the CNT and polymer is governed by the number of repeating units in the polymer, not by the molecular weight of polymer.

**Key Words** : Carbon nanotube, Polymer, Molecular dynamics simulation, Deformation, Binding energy

### Introduction

The non-covalent binding with polymer profoundly affects the properties of carbon nanotubes (CNTs).<sup>1</sup> The CNTs wrapped with polymer can be dispersed in solution and in matrix.<sup>2-4</sup> This type of functionalization of CNT can be also utilized for the self assembly of CNTs into ordered structures.<sup>5</sup> Therefore, it is important to understand the interaction between the CNT and polymer. There have been computational<sup>6-10</sup> and experimental<sup>11-15</sup> studies on this subject: for example, Didenko *et al.*<sup>13</sup> reported the coiling of polymers around CNTs. Numata *et al.*<sup>14</sup> observed that polysaccharides wrap CNTs in a distinct, helical way. Gou *et al.*<sup>16</sup> studied the CNT-reinforced epoxy composites by using molecular dynamics (MD) simulation and experimental methods. MD simulations<sup>17,18</sup> reported that the helical wrapping of CNT with an oligomer is sensitive to the conformation of the repeating units (RUs) within the oligomer. Laio *et al.*<sup>19</sup> studied the interfacial characteristics of a CNT-polystyrene (PS) composite by using molecular mechanics (MM) simulation.

Both experimental and theoretical studies have demonstrated that a CNT deforms transiently or permanently under an external force, such as the van der Waals force field from a surface.<sup>20</sup> A CNT is likely to deform when it is coiled with a polymer, but this type of deformation has not been studied previously. Herein, by using MD simulation, we investigate the binding of CNT with a polymer and the consequent deformation of CNT. Our work is relevant to the interfacial bonding and deformation of CNT in a polymer matrix.<sup>21,22</sup> Specifically, we considered 3 different polymers: PS, poly [2-(dimethylamino) ethyl metacrylate)] (DMAEMA), and the copolymer of PS and DMAEMA, poly (DMAEMA-*co*-St). PS is a cheap and easily accessible polymer consisting of aromatic rings which are known to disperse CNTs.<sup>23,24</sup> Poly(DMAEMA) has also attracted interest as a stabilizer in

dispersing CNTs.<sup>24,25</sup> A poly (DMAEMA-*co*-St) has been chosen for the growing interest in applying copolymers to the non-covalent functionalization of CNT.<sup>26</sup> We found that a CNT can be temporarily deformed in the course of interaction with polymer. The deformation of the CNT lasted nearly 160 ps, and its diameter decreased by more than 40% of its original value within 50 ps. The interaction strength of the CNT with the polymer was dictated by the number of RUs in the polymer.

### Simulation Details

We simulated a single CNT interacting with a single polymer of PS, poly (DMAEMA), or poly (DMAEMA-*co*-St). Our CNT was (18, 18) armchair-type and had a diameter of 24.4 Å and a length of 59 Å. The structures of PS, poly (DMAEMA) and poly (DMAEMA-*co*-St) were built using the graphical user interface of DL\_POLY.<sup>27</sup> Three polymers simulated are shown in Table 1 and depicted in Figure 1. The total molecular weight of each polymer was set to be approximately equal. Before running MD simulation, all the polymers were optimized using the conjugate gradient method for 5000 steps.

MD simulations were performed using DL\_POLY package.<sup>27</sup> We used a constant number, volume, and temperature (NVT) simulation at 300 K using the Nose-Hoover thermostat.<sup>28</sup> We used DREIDING<sup>29</sup> force field for the interatomic interaction and hydrogen atoms are treated implicitly. The cutoff radius of every interaction potential was set to 10.0 Å. We used a cubic simulation box with an edge length of 280.0 Å, and the periodic boundary conditions (PBCs) were imposed.<sup>28</sup> The initial distance between the CNT and polymer was around 20 Å (Figure 2). We used a time step of 1 fs and a production run time of 400 ps. This time scale was long enough to allow the polymers to coil around the CNT.

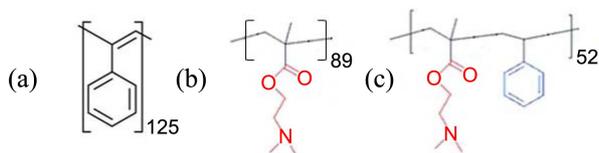
### Results and Discussion

Figure 2 shows the snapshot of the CNT interacting with a

<sup>†</sup>This paper is to commemorate Professor Kook Joe Shin's honourable retirement.

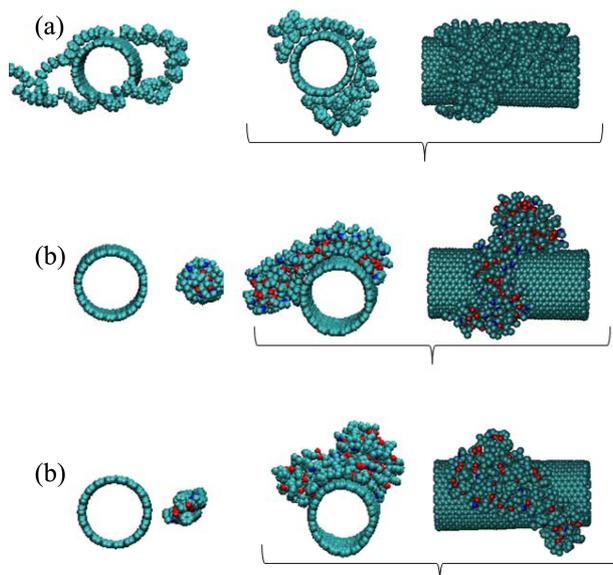
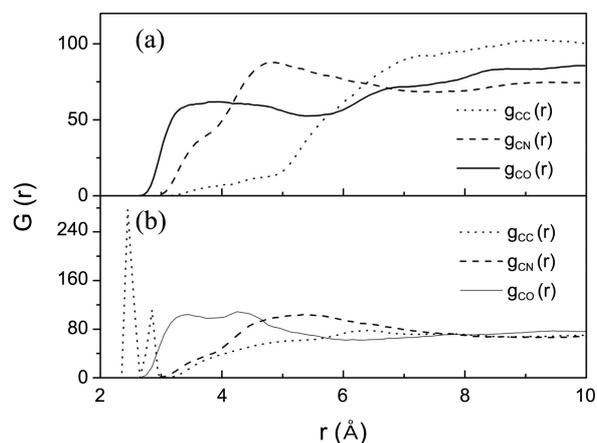
**Table 1.** Three polymers simulated in this work.

Abbreviation	Name	End-to-end length (Å)	Molecular weight (amu)	$N_{RU}$
PS	poly(styrene)	196.2	13021	125
poly(DMAEMA)	poly[2-(dimethylamino) ethyl methacrylate]	113.7	13083	89
poly (DMAEMA-co-St)	poly[2-(dimethylamino) ethyl methacrylate-co-styrene]	170.4	13156	52

**Figure 1.** Three polymers simulated. Drawn in (a), (b) and (c) are the repeating units of PS, poly(DMAEMA), and poly(DMAEMA-co-St), respectively.

polymer taken at different times of simulation. For PS and poly(DMAEMA-co-St) (Figures 2(a) and 2(c)), the plane of the aromatic ring initially tends to be vertical to the wall of the CNT. The planes of rings gradually aligned parallel to the wall of CNT as time goes by. Figure 2 also shows that the PS almost fully coils around the entire diameter of the CNT but poly(DMAEMA) and poly(DMAEMA-co-St) chains are not long enough to loop around the entire diameter.

We calculated the radial distribution functions (RDFs) between the carbon (C) atoms of the CNT and various atoms of polymer.  $g_{CO}(r)$  and  $g_{CN}(r)$ ,  $g_{CC}(r)$ , respectively, are the RDFs for the doubly-bonded oxygen (O) atoms, the nitrogen (N) atoms, and the methyl C atoms of the polymer (Figure 3(a)). In the case of poly(DMAEMA), the first peaks of  $g_{CO}(r)$ ,  $g_{CN}(r)$ , and  $g_{CC}(r)$ , respectively, are located at 3.4 Å, 4.8 Å and 7.0 Å. Therefore, the O atoms of poly(DMAEMA) are

**Figure 2.** Simulation snapshots of the CNT bound with different polymers. Figures (a), (b), and (c) are for PS, poly(DMAEMA), and poly(DMAEMA-co-St), respectively. All the snapshots are taken at 0 ps (left) and 400 ps (right: two different views). Drawn in cyan, blue, and red are carbon, nitrogen, and oxygen atoms, respectively.**Figure 3.** The radial distribution functions (RDFs) for the pairs of the carbon atoms of the CNT and the various atoms of polymer. Drawn are the RDFs between the carbon atoms of the CNT and the doubly-bonded oxygen atoms, the nitrogen atoms, and the carbon atoms of the polymer,  $g_{CO}(r)$ ,  $g_{CN}(r)$ ,  $g_{CC}(r)$ , respectively. Figures (a) and (b) are for poly(DMAEMA) and poly(DMAEMA-co-St), respectively.

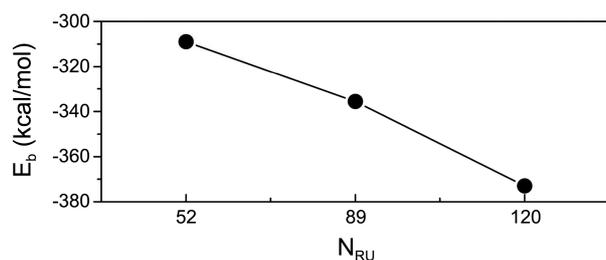
located closer to the CNT than the O and N atoms. In the case of poly(DMAEMA-co-St) (Figure 3(b)), the first peaks of RDFs are located at 2.5 Å, 3.3 Å and 5.0 Å for  $g_{CC}(r)$ ,  $g_{CO}(r)$  and  $g_{CN}(r)$ , respectively. The C atoms of styrene are closer to the CNT than N or O atoms of DMAEMA and therefore should dominate the interaction of the copolymer with the CNT.

We calculated the binding energy between the CNT and each polymer  $E_b$  by using the following relation,

$$E_b = [E_{total} - (E_{CNT} + E_{polymer})], \quad (1)$$

where  $E_{total}$ ,  $E_{CNT}$ , and  $E_{polymer}$ , respectively, are the configuration energies of the CNT bound with polymer, of the isolated CNT, and of the isolated polymer. In Figure 4,  $E_b$  is plotted vs. the number of RUs in the polymer,  $N_{RU}$ . Although all three polymers have nearly identical masses (see Table 1),  $E_b$  clearly decreases with the increase in  $N_{RU}$ . The PS exhibits the strongest interaction with the CNT, followed by poly(DMAEMA-co-St) and poly(DMAEMA). Presumably, the aromatic rings of PS are better in binding to the wall of CNT via the  $\pi$ - $\pi$  stacking interaction.

We inspected the deformation of the CNT by following the time change in the diameter of the CNT. The deformation occurred within 15 ps from the start of simulation and lasted up to 160 ps. After 160 ps, the CNT recovered its original shape (as shown in Figure 2). Figure 5 shows the radial cross section of the CNT at its maximal deformation (polymer not shown). A significant deformation of CNT is evident for every case. The height and width of the radial cross section



**Figure 4.** Binding energy of CNT with polymer vs. the number of repeating units,  $N_{RU}$ , in the polymer. Line is drawn for visual guide.



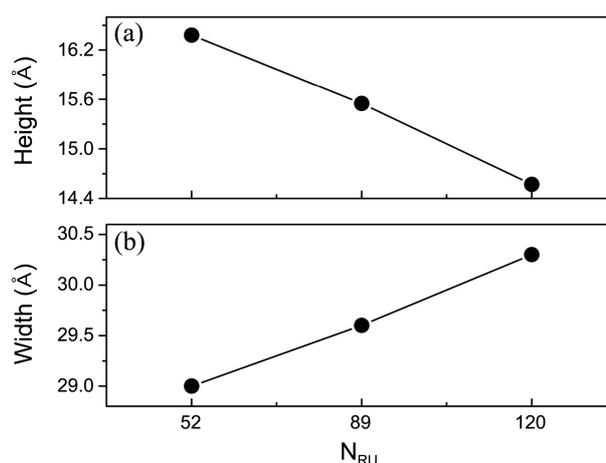
**Figure 5.** Snapshot of the CNT at its maximum deformation. Drawn in (a), (b), and (c) are the CNTs interacting with PS, poly(DMAEMA), and poly(DMAEMA-co-St), respectively. The CNT lies along the Z-axis and polymers are not shown. Drawn in cyan, blue, and red are carbon, nitrogen, and oxygen atoms, respectively.

of CNT are compressed and widened, respectively, from the original diameter of CNT. We calculated the height (Figure 6(a)) and width (Figure 6(b)) of the radial cross section at the maximal deformation of the CNT. To calculate the height, we divided the CNT into 60 segments along its axis (the Z axis). Within each segment, we calculated the difference in the maximal and minimal Y coordinates. This difference is averaged over the segments to give the height plotted in Figure 6(a). The height decreases as the number of RUs increases. The shrinkage in height ranges from 33% to 40% of its original diameter. Experimentally, a radial deformation of up to 60% of its diameter has been reported to be fully reversible.<sup>30,31</sup> Figure 6(b) shows the horizontal width of the CNT vs.  $N_{RU}$ . As in the height calculation, the CNT is divided into 60 segments along the Z direction. The difference between the maximal and minimal X coordinates of each segment is averaged to give the width. As  $N_{RU}$  increases, the width increases. The degree of expansion in width (18-30% of the original diameter) is smaller than that of decrease in height. Figure 6 shows that, as for , the degree of deformation of CNT is governed by  $N_{RU}$ .

In this work, we considered the aromatic ring or a polar group as the monomer unit of polymer. It would be interesting to see if the number of repeating units plays a central role for different kinds of repeating units such as vinyl, ethylene, and ethylene glycol. In the case of copolymer, the sequence of repeating units (whether it is head-to-tail, head-to-head, or random) might affect the interaction of polymer and CNT as well. Such an investigation is left as future work.

### Conclusion

MD simulations were performed to investigate the CNT interacting with a polymer. By considering PS, poly(DMAEMA), and poly(DMAEMA-co-St) with nearly identical molecular weights, we found the strength of



**Figure 6.** Radial deformation of CNT. (a) The height in the radial cross section of CNT vs.  $N_{RU}$ . (b) The width in the radial cross section of the CNT vs.  $N_{RU}$ . Lines serve as visual guide.

interaction between the CNT and the polymer is determined by the number of RUs in the polymer, not by the mass of the polymer. PS had the highest number of RUs and therefore had the strongest binding to the CNT. After the initial contact with the polymer, the CNT transiently deformed for 160 ps and eventually recovered its original shape. During this elastic deformation, the diameter of the CNT decreased by more than 40% within 50 ps. The degree of the deformation was also governed by the number of RUs.

**Acknowledgments.** This work was supported for two years by a Pusan National University Research Grant. JJ thanks Prof. Kook Joe Shin for having been a great teacher and for all the support he has shown over the years.

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