

The Effect of Interface Chemical Bonds on the Behaviour of Nanotube-Polyethylene Composites Under Nano-particle Impacts

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This paper uses the molecular dynamics method to investigate the influence of chemical bonds on the mechanical behaviour of nanotube–polyethylene composites subjected to nano-particle impacts. In the analysis, carbon nanotubes (CNTs) were incorporated into the polyethylene (PE) matrix in two ways, with and without radical centres, so that the resulting nano-composites had two corresponding properties, i.e., with and without chemical bonds at the CNT–PE interfaces. A spherical diamond nano-particle was used to impact and penetrate into the composites with a high velocity. It was found that the interface chemical bonds play an important role in the composite reinforcement.

Keywords: Carbon Nanotubes, Polyethylene, Particle Impact, Molecular Dynamics.

1. INTRODUCTION

The outstanding properties of single walled nanotubes (SWNTs) have raised the possibility of making strong polymer composites with carbon nanotubes (CNTs) as reinforcements. To achieve this, a good dispersion and alignment of SWNTs in polymer matrix and strong bonding between the nanotubes and polymer matrix are required. SWNTs often aggregate into bundles by van der Waals attractions between the tubes. As such homogeneous dispersion is not easily obtained. Researchers have used various techniques such as ultrasonication,¹ high shear mixing,² the aid of surfactants,³ functionalization,⁴ viscous shear flow,⁵ etc., to overcome this barrier. Significant progress has already been made in the dispersion and alignment of SWNTs. However, the interfacial bonding strength and load transferring mechanisms are not yet fully understood.

Several methods such as solution casting with ultrasonication, direct mixing, melt processing, and *in-situ* polymerization have been developed to incorporate CNTs into a polymer matrix. Except direct mixing, which applies only to thermosetting polymers, all the other methods can be used to make CNT–polyethylene composite. In their paper, Tang et al.⁶ have discussed the suitability and difficulty of these methods and used melt processing method to make MWNT/HDPE composite films with various percentage of nanotube content by weight. Evaluating the mechanical properties of the composite films by a small

punch test, they find that the stiffness, the yield strength and the fracture toughness all increased with the increasing percentage of CNTs. Various studies^{7–9} on the nano-mechanical properties of CNT–polymer composites with varying weight percentage of nanotubes also showed an increase in the mechanical properties with increasing weight percentage of nanotubes. In the above experimental studies, the composite with 0% of CNTs gave very low mechanical properties. This demonstrates the immense potential of CNTs in mechanically strengthening polymers. In this work we examine the influence of the CNT–polymer interface properties in reinforcing polymers.

The previous quantum mechanical studies by the authors^{10–12} have demonstrated two possible ways of forming chemical bonds with CNTs; (i) functionalizing the CNTs either with an oxy radical or with an anion followed by reaction with monomer units,¹¹ and (ii) generating radical centers on the polymer chains followed by the addition of CNTs.¹⁰ Recently the authors have presented,¹³ a theoretical rationale for chemical bonding by integrating a CNT into PE matrix using radical initiators and characterizing the interfacial properties by pulling out the CNT from one end. It was further found that the mechanical deformation of CNTs in composite preparation can promote the CNT–PE chemical bonding.¹² Frankland and co-workers^{14–16} have also presented some work on the influence of chemical bonds between CNT and a PE matrix using molecular dynamics simulation. However, they did not demonstrate how chemical bonds between the CNT and PE matrix would be formed; they created chemical bonds by introducing a couple of methylene cross-linked

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units. Hu and Sinnott¹⁷ investigated chemical modification of CNT-polystyrene composites via low energy polyatomic ion beam deposition using molecular dynamics simulation. They demonstrated that when the CNTs are embedded close to the surface, cross-links can be introduced between the nanotube and polymer matrix.

In this work we integrate a CNT into PE matrix with radical centres, and study the effect of chemical bonds between the CNTs and the polymer matrix upon high velocity impact and penetration of a spherical diamond nano-particle.

2. COMPUTATIONAL METHODOLOGY

The models used in this work contain a 75.3 Å long (17,0) single-walled nanotube in polyethylene matrix ($76 \times 46 \times 60 \text{ \AA}^3$) with and without chemical bonds between the nanotube and PE chains. First, twelve PE chains were placed around a (17,0) CNT as shown in Figure 1(a). For the model with chemical bond, five hydrogen atoms along each PE chain were removed to create radical centers. The energy of the system was minimized by conjugate gradient method (Fig. 1(b)). Then a crystalline PE matrix was placed around and the energy was again minimized by conjugate gradient method. The CNT-PE model without chemical bonds was generated in the same way but without removing hydrogen atoms on the surrounding PE chains (Fig. 1(c)). In order to show the interface bonds clearly, the H atoms on the PE chains are not shown in Figures 1(b) and (c). A spherical diamond nano-particle having incident energy of 3.6 eV and a radius of 14.27 Å was projected about 5 Å above the surface as shown in Figure 1(d). Its penetration and bouncing back simulations were studied at 300 K with a time step of 0.5 fs and a step size of 0.001 Å; (i.e., the speed of the particle was 200 m/s).

As in most simulation studies, boundary atoms (atoms from CNT and PE matrix on both sides where the CNT ends and the PE matrix at the bottom) are used to restrict the motion of the specimen and all the other atoms are taken as thermostat atoms to ensure heat conduction. For comparison purposes, simulations are done on polyethylene matrix of the same size and on a single nanotube under the same conditions. The inter-atomic interactions were described by a three-body Tersoff-Brenner potential^{18,19} which allows the formation of chemical bonds with appropriate atomic rehybridization. The non-bonded interactions within the PE matrix and between the polymer matrix and the nanotube were modeled with the Lennard-Jones potential.²⁰

In a typical process, when the particle penetrates into the composite the speed would decrease. However, since our major aim here is to study the effect of chemical bonds at the interface during particle penetration, we make the particle penetration at a constant speed to avoid unnecessary complications. For simplicity, we call the penetration of the particle as loading and its bouncing back as unloading.

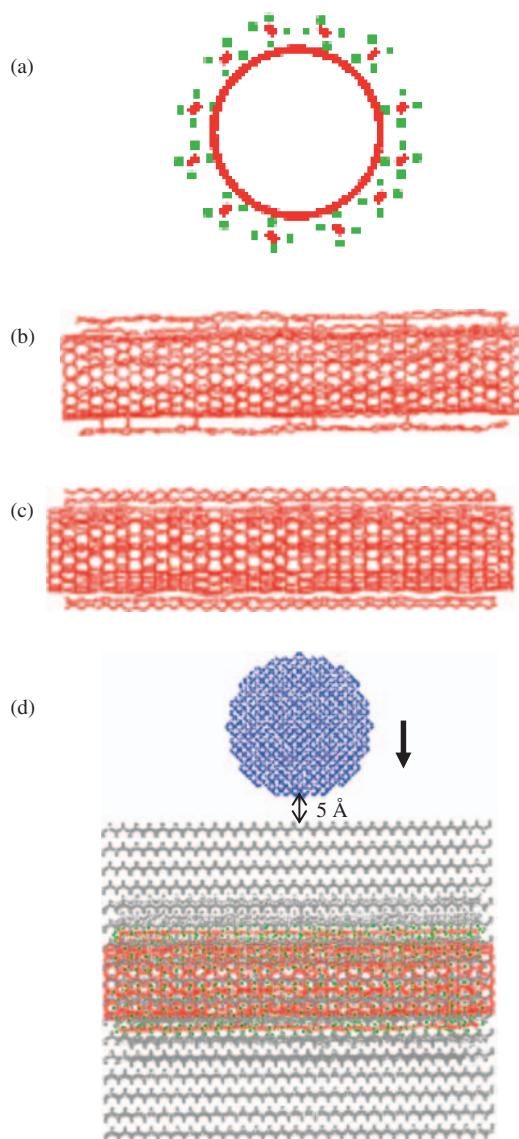


Fig. 1. (a) Initial model (cross-sectional view) of CNT with 12 PE chains, (b) CNT with 12 PE chains with chemical bonds, (c) CNT with 12 PE chains without chemical bonds, and (d) side view of CNT-PE composite nano-particle impact model.

So, in our discussions below we shall use the terms loading and unloading to indicate the penetration and bouncing of the particle in its impact cycle.

3. RESULTS AND DISCUSSION

The chemical bonds formed (Fig. 1(b)) on minimizing the energy of the model shown in Figure 1(a) and their characterization by pull out technique, has been demonstrated and explained elsewhere.¹³

3.1. The PE-CNT Model with and Without Chemical Bonds Under Particle Impact

On loading, there was an initial attraction between the nano-particle and polymer matrix, and as a result,

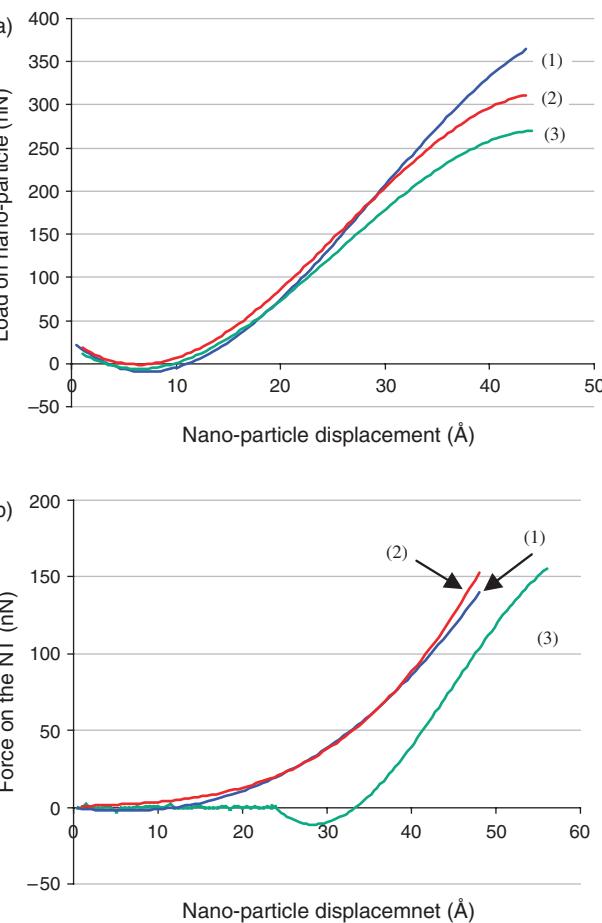


Fig. 2. (a) The nano-particle load–displacement curves (1) CNT is chemically bonded to the polymer chains, (2) CNT not chemically bonded to the polymer chains, and (3) polymer alone. (b) The CNT load–displacement curves (1) CNT is chemically bonded to the polymer chains, (2) CNT not chemically bonded to the polymer chains, and (3) CNT alone.

the polymer chains near the nano-particle moved up. The initial portion of the loading curve (Fig. 2(a)) shows this behaviour where the force has the opposite sign as observed in various indentation simulations.^{21,22} As loading continues, the force on the nano-particle started to increase and kept on increasing until the nanotube fails near the fixed ends.

Once the nano-particle moved by about 15 Å the nanotube inside the polymer matrix started to flatten and by

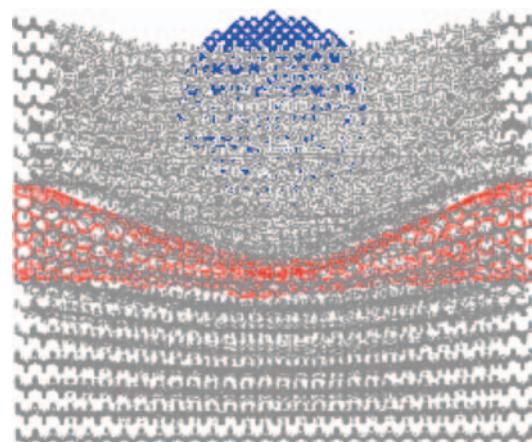


Fig. 3. A side view of the CNT–PE composite on displacing the nano-particle by 32 Å.

about 32 Å the flattened nanotube started to bend. Thereafter flattening and bending of the nanotube continued and when the nano-particle moved by about 48 Å the nanotube failed near the fixed ends. Side view of the CNT–PE composite during loading is shown in Figure 3. In the simulation with the CNT and PE chemically bonded, the bonds do not allow the CNT to bend freely. Unlike a free nanotube, here even when the tube bends, the centre portion of the tube is flat and this can be observed in Figure 4(a).

When there are no chemical bonds between the CNT and PE chains, once the CNT started bending, the nano-particle loading curve started to deviate from that with chemical bonds. The load on the nano-particle became low as seen in Figure 2(a), where curve (2) lies below curve (1) when the particle displacement is greater than 32 Å. This clearly shows that the interface chemical bonds play an important role in strengthening polyethylene. Figure 2(b) shows the force on the CNT. Up to 15 Å particle displacements, the force on the nanotube is almost zero i.e., until then the PE matrix bears the applied load. The influence of the nanotube became significant at a particle displacement of about 15 Å. At higher nano-particle displacements, the load on the CNT is little higher when there are no chemical bonds at the CNT–PE interface.

On releasing the load from a point little before the failure of the CNT, the nanotube unbent and almost recovered

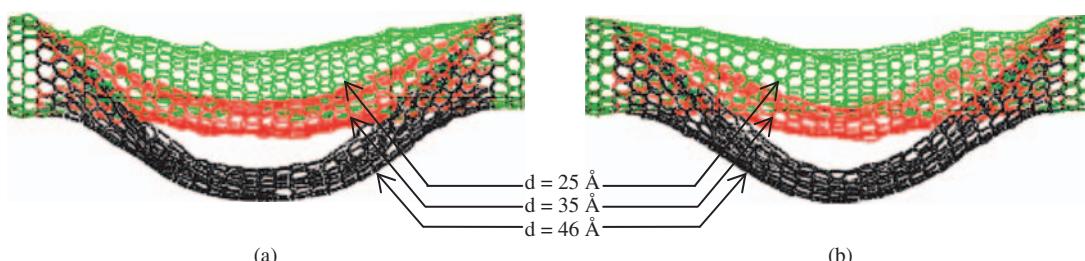


Fig. 4. CNT inside the PE matrix on unloading (at three different particle depths, d) (a) with chemical bonds (b) without chemical bonds.

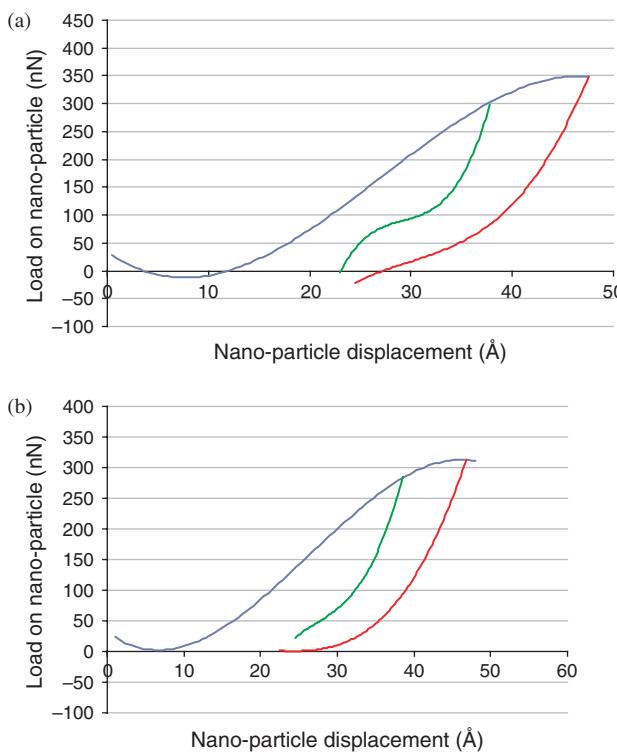


Fig. 5. Load–displacement curves of CNT–PE composite showing loading and two unloading curves (a) with CNT–PE chemical bond (b) without CNT–PE chemical bond.

its cylindrical shape (Fig. 4) but the unloading curve took a different path to the loading curve (Fig. 5), due to the deformation of the polymer. This shows that the deformation of the CNT is almost elastic whereas the PE is inelastic. Unloading from a lower load also followed the same pattern. Figure 4 shows the recovery of the CNT inside the polymer matrix on releasing the load from a depth of about 46 Å.

3.2. PE Alone Under Particle Impact

On loading, again the initial attraction of the PE chains is observed (Fig. 2(a)–curve (3)). The applied load is much lower than the cases where a nanotube was present. In Figure 2(a), curves (2) and (3) overlap up to 15 Å of particle displacement and then they deviate from each other. It was observed that at this point the nanotube inside the PE matrix started to flatten.

3.3. CNT Alone Under Particle Impact

The load on the CNT during the nano-particle impact of a CNT alone under the same simulation conditions is shown in Figure 2(b)–curve (3). In this case the CNT experiences the applied load only after the nano-particle moves by about 24 Å as there is no polymer matrix in between the nano-particle and the CNT.

The comparison of the composites with and without chemical bonds along with the pure PE shows that a higher

nano-particle load is required for composite. An additional load is needed when the nanotube is chemically bonded to the PE chains. In our present study, the CNT–PE composite contains only a single nanotube with about $20 C_{NT} \cdot C_{PE}$ chemical bonds. Even though, the difference in the load–displacement curves has been remarkable. In a real composite, a small percentage of CNTs, 5% by weight say, will involve numerous CNTs. In addition, the actual CNTs are much longer. It is therefore reasonable to expect that much more chemical bonds will be formed in a CNT–PE composite and hence an excellent reinforcement will occur. With this, a high stress transfer ability theoretically predicted by Xiao and Zhang²³ will become possible.

4. CONCLUSION

This study shows that a higher load is required for a nano-particle impact on a CNT–PE composite compare to PE. Presence of chemical bonds at the CNT–PE interface requires even higher loads, demonstrating that high performance composites based on polyethylene and CNTs can be made in the presence of free-radical initiators. Further, it was found that in the composite the bending deformation of CNT is nearly elastic whereas the deformation of PE is inelastic.

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