

## A Cross-scale Characterization of Interface Properties between Carbon Nanotubes and Polymer Matrix

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**Abstract.** This paper discusses the methods of promoting covalent bonds between polymer and carbon nanotubes to make high performance composites. Such methods involve attachment of chemical moieties (i.e. functional groups) to the sidewalls of carbon nanotubes, introduction of mechanical deformation on nanotubes, or generation of radicals on the polymer chains using free radical generators. The implementation of the latter method is demonstrated at both quantum mechanics and molecular dynamics levels.

### Introduction

The unique properties of carbon nanotubes (CNTs) have not been realized in nanotube-polymer composites due to the difficulties in processing and the limitation on load transfer. CNTs are held together as bundles and ropes due to the van der Waals attraction 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] etc. to overcome this barrier. Most methods either shorten the nanotubes or disrupt their original structure. For example, in the carboxylic acid group functionalization of nanotubes and the preparation of composites[5], the acid treatment improves the processability and performance of nanocomposites. However, the acid also attacks the defect sites of the CNTs and cut them into many short tubes. Furthermore, excessive functionalization of the CNTs can ruin the tubular framework.

In order to have high stress transfer, strong bonding between the CNTs and polymer chains is necessary. This can be achieved via functionalizing the CNTs [4,6-8], introducing deformations on CNTs, or using radical initiators. One of the successful ways of functionalizing the nanotubes is via the introduction of anions. Once the CNT is functionalized with an anion, it not only serves as an initiator for further reactions that lead to the formation of grafted polymers but also help to disperse the nanotubes. For example, when the nanotubes are functionalized with butyl lithium, they serve as initiators for the in-situ polymerization process leading to polymer grafted CNT composites [4] and at the same time the anion introduced on the CNT surface serves to disperse the nanotubes due to mutual electrostatic repulsion between the charged tubes. In a quantum mechanical work on nanotube functionalization and polymer grafting [9], the authors showed that the polymer grafted CNT can be produced by in-situ free-radical and anionic polymerization methods. Free-radical polymerization method is demonstrated using methoxy radical and ethylene monomer. In this way it was discovered that it is possible to functionalize the CNT with the oxy radical and the newly formed nanotube-oxy radical can function as an initiator for the polymerization of ethylene leading to polyethylene chain grafted nanotube. Anionic polymerization method is demonstrated using secondary butyl lithium and propylene oxide monomer. It was also found that the CNT can be functionalized with sec-butyllithium and the resulting CNT anion can react with propylene oxide and the reaction can propagate.

On the other hand deformation of CNTs is often introduced during the processing of composites. For example, in mechanical blending, deformation and the resultant curvature changes of CNTs are significant and unavoidable. It is known that the small diameter nanotubes are more reactive [10] and it is explained by the high curvature in which the CNT carbon atoms have more sp<sup>3</sup> character.

Based on this, the authors examined the reactivity of hydrogen and alkyl radicals with nanotubes under some deformation modes via molecular dynamics cum quantum mechanics methods [11]. It was found that the deformation-induced ridges have high binding energies with radicals but deformation-flattened surfaces have lower binding energies compared to the non-deformed CNTs.

Radicals can be generated on the polymer chain using peroxides. Patil and Brois [12] had grafted ethylene-butylene copolymer onto fullerene by heating them to 150° C and adding *tert*-butyl peroxide. Carbon nanotubes are fullerene related structures and peroxides are capable of abstracting hydrogen atoms from polymer chains. On the basis of the above idea, the authors studied the possible chemical bond formation between the CNT and PE chain radicals using model compounds in the quantum mechanical calculations.

This paper will present a theoretical rationale for chemical bonding by integrating the CNTs into PE matrix using radical initiators and characterizing the interfacial properties between the nanotubes and the matrix.

### Computational Technique

Nanotube–polyethylene chain models were generated and investigated by Quantum mechanics and molecular dynamics methods. In the quantum mechanics calculations, segment of a (17,0) nanotube with hydrogen atoms added to the dangling bonds of the perimeter carbons was used. Alkyl radicals were used to represent the polyethylene chain. The geometrical parameters were fully optimized using density functional theory (DFT) with a hybrid functional B3LYP [13-16] and a 3-21G basis set [17]. For open-shell molecular radicals, the unrestricted formalism was used. The computations were carried out on a super computer using the *ab initio* quantum chemistry package Gaussian 03 [18].

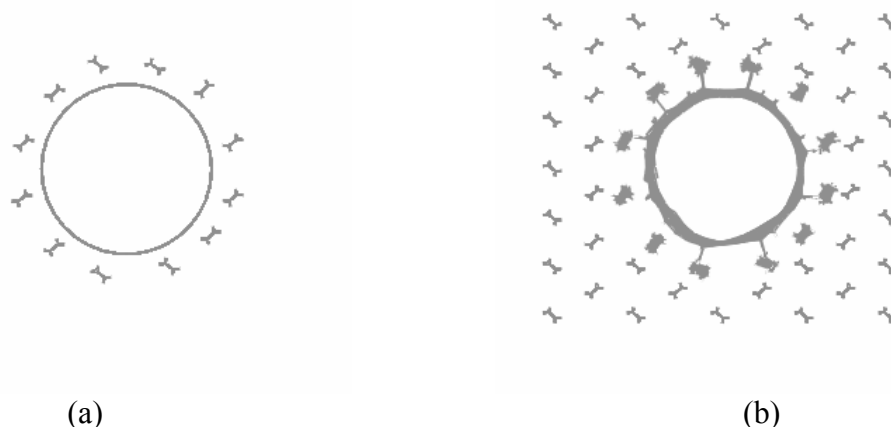


Fig. 1. Cross-sectional views of (a) the initial model of CNT surrounded by 12 PE chains with 60 radicals uniformly distributed along the chains, and (b) an energy minimized structure of CNT-PE chains together with the crystalline PE matrix.

In the molecular dynamics method, the inter atomic interactions were described by a three-body Tersoff-Brenner potential [19, 20]. The non-bonded interactions within the PE matrix and between the polymer matrix and the nanotube were modeled with the Lennard-Jones potential [21]. To demonstrate the strong interfacial interactions between the CNTs and PE chains, first twelve polyethylene (PE) chains, with each having 56 methylene groups, were placed around a (17,0) CNT of about 75 Å long. Five hydrogen atoms at equal distances along each PE chain were removed. This initial model is shown in Fig. 1(a). The energy of the system was minimized by conjugate gradient method. Then a crystalline PE matrix was placed around this as shown in Fig. 1(b) and the energy was minimized by conjugate gradient method. Another CNT-PE model was generated in the same way but without removing hydrogens on the surrounding PE chains.

The NT was pulled out from one end in both cases. The simulations were carried out at 300 K with Berendsen thermostat for the reasons pointed out in Ref. [22]. The time step for integration was 0.5 fs.

### Results and Discussions

The DFT/B3LYP(3-21G) optimized geometry of the segment of a nanotube-alkyl radical ( $C_{136}H_{34}-C_5H_{11}$  radical) is shown in Fig. 2, where  $C_{136}H_{34}$  represents a segment of a (17,0) nanotube with 34 hydrogen atoms added to the dangling bonds of the perimeter carbons and the alkyl radical  $C_5H_{11}$  represents a section of a polymer chain with hydrogens added to the dangling bonds of the carbons at its ends. A new C-C bond was formed between the section of the nanotube sidewall and the alkyl radical with a bond length of 1.644 Å and the bonding at the attachment carbon become tetrahedral with elongated C-C bonds from the attachment site to neighboring carbon atoms. This shows that the alkyl radical forms covalent bond with the CNT. Thus the results demonstrate the possible covalent bonds formation between the CNT and the PE chains.

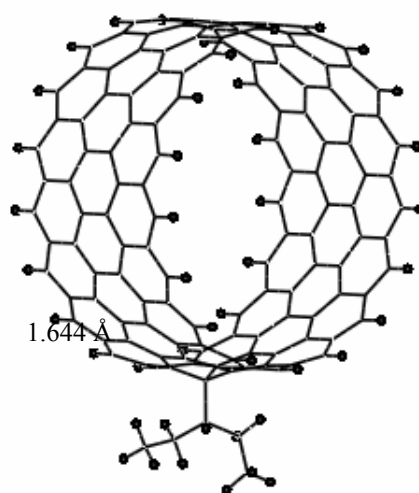


Fig. 2. DFT/B3LYP(3-21G) optimized structure of the (17,0) CNT segment and the  $C_5H_{11}$  radical.

On minimizing the energy of the model shown in Fig. 1(a) using Tersoff-Brenner potential, 22 PE carbon atoms were within 1.7 Å and 37 hydrogen atoms were within 1.2 Å of the NT carbon atoms, indicating the newly formed chemical bonds. The inner portion of Fig. 1(b) shows some of these chemical bonds. The addition of more PE chains around this model did not form new chemical bonds on energy minimization (Fig. 3(a)). The model generated without radicals on the PE chain did not form any  $C_{NT}-C_{PE}$  bonds. However, about 80 hydrogen atoms of the PE chains were within 1.2 Å of the NT carbon atoms and the resulted structure is shown in Fig. 3(b).

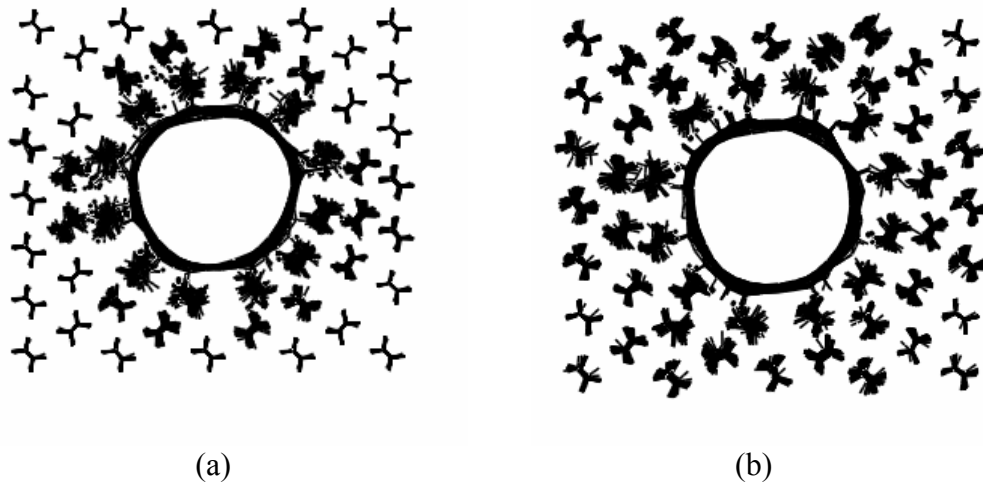


Fig. 3. Cross sectional views of the energy minimized structures of CNT-PE composite (a) with and (b) without  $C_{NT-C_{PE}}$  chemical bonds.

Thus both the calculations at the molecular dynamics and quantum mechanics scales demonstrate that it is possible to form chemical bonds between the PE chains and the CNT by introducing radicals on the PE chains. In principle, radicals can be generated on PE chains by chemical or radiation attack. For example, an oxy radical formed by the pyrolysis of peroxide is capable of abstracting a hydrogen atom on the polymer chain.

In order to characterize the interface properties the CNT was pulled out of the PE matrix in both cases (i.e. with and without chemical bonds between CNT and PE matrix) and the resulted structures are shown in Figs. 4(a) and (b). It is clearly seen from Fig. 4(a) that the PE chains which are chemically bonded to the CNT are dragged with the nanotube. Some of these chains also drag portions of the PE matrix with them due to the weak van der Waals forces present between the chains. On the other hand, when there are no chemical bonds between CNT and PE matrix, as shown in Fig. 4(b), the PE chains are dragged only partially due to the adhesion effect. As the adhesion forces are weak compared to the chemical interactions, the PE chains are dropped out after some time. Thus, the comparison clearly demonstrates the strength of the bonds formed with the radicals on the PE chains.

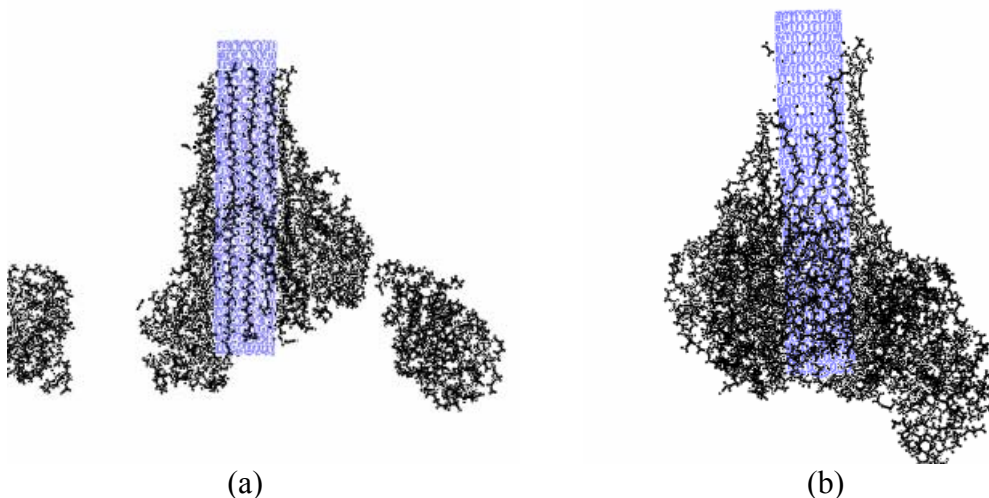


Fig. 4. (a) NT pullout when there are C-C bonds between the NT and PE chains, (b) NT pullout when there are no C-C bonds between the NT and PE chains.

As PE is one of the simplest and well studied polymers with known crystalline structures, the PE-NT composites have been studied theoretically to a certain extent using molecular dynamics

simulation [23,24]. For example, according to the molecular dynamics simulation work of Wei et al. [23] polyethylene form chemical bonds with a (10,0) CNT with C-C bond length of 1.54 Å. This is much shorter compared to our quantum mechanics results. In the work of Frankland et al. that discussed the effect of chemical bonds [24], the bonds between NT and PE chains were artificially created by introducing a couple of methylene cross-linked units. Thus those studies fail to explain how chemical bonds can be formed in the first instance.

## Conclusions

This study demonstrated the ways of integrating CNTs into a polymer matrix using the cross-scale results obtained by quantum mechanics and molecular dynamics analysis. The interfacial properties characterized by the pull out of the nanotube in the models generated with and without chemical bonds demonstrates the strength of the bonds formed with the radicals on the PE chains. The investigation suggests that high performance PE based carbon nanotube composites can be made in the presence of free-radical generators such as peroxides.

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