Mechanical Properties and Reinforcement Mechanisms of Carbon Nanotube Composites with Amine Functional Groups Based on Molecular Dynamics

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Abstract. This study successfully used the concept of molecular dynamics to explore multi-walled carbon nanotubes (MWNTs) with amine functional groups and subsequently applied these to macromolecular materials to construct a novel MWCNT-reinforced macromolecular composite. Nanoscale tensile simulations were performed to examine the reinforcing phenomena of the nanocomposite composed of functional group–based MWNTs and subsequently explore the reinforcement mechanisms involved. The reinforcement mechanism of a nanocomposite made only of MWNTs and macromolecular materials stems from the interfacial energy between the MWNTs and macromolecular material. The interfacial energy is supplied by the Van der Waals force between the MWNTs and macromolecules and is considered a physical bond. By contrast, the interfacial energy between the novel macromolecular composite with amine functional groups was supplied by the chemical bond between the functional groups on the surface of the MWNTs and macromolecular materials. The interfacial binding force of a chemical bond is stronger than that of a physical bond. Therefore, a nanocomposite composed of functional group–based MWNTs can provide greater strength.

1. Introduction
To enhance mechanical properties, a reinforcing agent is added to the polymer. The combined with a matrix and a reinforcing material is added the composite. Due to advances in nanotechnology, the enhanced size has been reduced from microns to nanometers. Nanocomposites are widely used for practical commercialization.

More than 20 years have passed since the discovery of carbon nanotubes (CNTs) [1]. Carbon nanotubes (CNTs) are considered to be the most promising reinforcing materials due to their high strength, flexibility, aspect ratio and low density.

Polymers are characterized by low cost, light weight, and ease of manufacture, but lacking mechanical properties. To enhance mechanical properties, a reinforcing agent is added to the polymer.

Carbon nanotubes (CNTs) with excellent electrical, mechanical and thermal properties and chemical inertness are considered to be ideal for enhancing high performance structures. Since then, one of the main applications of CNTs has been the reinforcement of polymers in processing
composites, as experiments have found that CNTs have excellent mechanical properties. The use of CNTs on nanocomposites has become more promising and successful over the past few decades.

The interfacial stress between the CNT and the surrounding matrix strictly controls the mechanical properties of the CNT-reinforced nanocomposite. A number of methods have been proposed, such as experimental measurements and molecular dynamics (MD), to study stress transfer across the CNT/matrix interface. Experimental testing is both difficult and expensive.

Vaudreuil et al. [2] conducted research on the preparation, characterization, and properties of PMMA/multiwalled carbon nanotubes (MWCNTs) nanocomposites. They found that the elastic behavior of PMMA increased and the mechanical properties were significantly improved. After the nanocomposites were prepared from modified and unmodified MWCNTs, the tensile properties of pure PMMA were moderately improved.

Ray et al. [3] reported the research results of biodegradable poly(butylene succinate) (PBS)/MWCNT nanocomposites prepared by melt blending in a batch mixer. After preparing nanocomposites with 3wt% MWCNTs, it was found that the tensile modulus and thermal stability of PBS were moderately improved, and the mechanical properties of PBS were significantly improved, and the value of elastic modulus was increased by about 88%.

Hartmann et al. [4] describes a carbon nanotube (CNT) palladium embedded experimental and numerical pull-out test. They used molecular dynamics to compare the pull-out force obtained from the experiment with the value of the numerical study and to give an explanation of the deviation based on the material impurity or defect and its effect on the pull-out data. They found that the force data for the simulations and experiments were very consistent.

Huang and Chiu [5] used molecular dynamics (MD) simulation the single-walled nanotube (SWNT) reinforced epoxy composites to study the Young's modules and interfacial binding energy. They also calculated the ability of the interface between the epoxy and the binding energy of SWNT, and explain the influence SWNT reinforced composite material.

Despite considerable efforts committed to strengthening mechanisms CNT/polymer, but functional studies on the impact of CNT-CNT reinforced nanocomposites strengthening mechanisms of very little.

In order to understand the strengthening mechanism of functionalized MWNTs of MWNTs-reinforced nanocomposites, the molecular dynamics was employed to construct the Amine (~NH₂) functional group of MWNTs-reinforced nanocomposites in this study. Using the nanotensile simulation test to explore the strengthening mechanism of functional groups of MWNTs-reinforced nanocomposites was also presented in this paper.

2. Simulation methodology
In this paper, molecular dynamics (MD) was used to create functional group of MWNTs with Amine (~NH₂), and further to establish the analysis mode of the Amine functional groups of MWNTs reinforced nanocomposites. And using nanotensile test and atomic level stress calculation model to investigate the effects of Amine functional groups at MWNTs reinforced nanocomposites. MWNT along transverse axis and periodic boundary conditions on the application model.

2.1. Physical Model and Molecular Dynamics Simulation
The Amine functional groups will be introduced to the surface of MWNT. And the Amine functional group of MWNTs was constructed by Materials Studio® (Accelrys Software Inc., San Diego, CA, USA) which were shown in Figure 1. The structural type of MWNT is the armchair(6,6) with diameters of 8.136Å.

The formation structure of a cross-link between curing agent and epoxy resin is shown in Figure 2. The length of cured epoxy resin chain was tripled to show the polymer characteristics. The supercell model size of nanocomposite was 50Å×50Å×40 Å.
2.2. Potential Energy Simulation and Construction of Nanocomposite

The potential function is COMPASS potential function [5] in this study, MD simulation by the MaterialsStudio® (Accelrys Software Inc., San Diego, CA, USA) Forcite module. In order to develop reasonable and low energy adsorption sites nanocomposite model, the present study used the Monte Carlo method and the simulated annealing method of generating a more reasonable MWNT / epoxy nanocomposites amine functional model [5].

The model is placed in a set of specifications (<NVT> set) simulation, the temperature was gradually increased to 600 K from 300 K, 15 ps duration with no external stress and gradually decreases from 600 K to 300 K, duration 15 ps (use COMPASS force field, time step is 0.1 fs). The initial amorphous matrix was shown in Figure 3 [5].

The simulated tension is minimized by constant strain, and the strain is changed from 0% to 4% in the discontinuous step; the tension phase is completed in 30 ps by using the <NVT> overall control set temperature.

![Figure 1. Appearance of Amine functional group of MWNT (a) top view (b) front](image)

![Figure 2. The molecular model of cured epoxy resin.](image)

![Figure 3. The nanocomposites with Amine functional group of MWNTs/cured epoxy resin.](image)
3. Calculation of the functional group of MWNT/epoxy interfacial bonding energy, atomistic Stress and Young’s modulus

Interface bonding can be provided by van der Waals forces and electrostatic forces in the molecule to evaluate the bonding energy in the composite system. The measurement method of the interaction energy in the composite system was shown in Ref.[6].

This study uses BDT stress, a method of calculating atomic stress to evaluate stress[7]. The Young's modulus E of the functional group of the MWNT/epoxy nanocomposite can be calculated by dividing the tensile stress by the tensile strain on the loading plane in the loading direction within the elastic deformation range of the material. Moreover, based on the slope of the inelastic deformation range of the stress-strain curve, the Young's modulus of the MWNT/epoxy nanocomposite functional group was obtained.

4. Result and discussions

In order to understand the effect of the Amine functional group on the MWNTs, the number of the Amine groups were simulated as 5, and the system temperature was 300 K.

4.1. The analysis on Young’s modulus (E) of pure epoxy

This study first conducted an analysis of the z-axis E value on epoxy to investigate whether adding nanocomposites composed of MWNTs with different functional groups into epoxy yields a reinforcement effect.

To investigate the added functionalized MWNTs in the epoxy resin truly strengthen the material. Firstly, a pure epoxy substrate was carried out simulated tensile test in this study. After the simulation, the E value of pure epoxy is 0.469 GPa. Generally, the strength of epoxy is 40 to 60 MPa. Therefore, the simulated were approximately 10 times the actual values. This considerable discrepancy was attributed to the perfect molecular bond in the epoxy model constructed by this study. In practice, when epoxy solidifies, molecules are not perfectly cross-linked, and the actual hardening process tends to create small pores that result in a considerable difference between the actual and theoretical strength.

4.2. The effect of Amine functional group on Young’s modulus(E)

The Young’s modulus (E) of nanocomposites composed of MWNTs with amine (–NH2) functional groups added in an epoxy substrate was further analyzed. Fig. 4 show the exterior of the nanocomposite following a nanoscale tensile simulation (elongated to a strain of 0.04), and Fig. 5 presents the stress-strain curve.

The Amine functionalized MWNTs were added in epoxy substrate furtherly in this study, and constituted the carboxyl functionalized MWNT/epoxy nanocomposites. After the nanotensile simulation (the total strain is set 0.04), the appearances of nanocomposite in different strain value were shown in Fig. 5, and the stress-strain curve was shown in Figure 6.

Figs. 4 and 5 reveal that the nanocomposite model constructed in this study was reasonable. Fig. 5 shows that the z-axis E value of the MWNT-reinforced composite with an amine (–NH2) functional group was 50.46 GPa.

The E value of a pure-MWNT (without surface functional group) and epoxy-made nanocomposite was subsequently simulated using the same settings. Table 1 shows the results.

In summary, the E value of a nanocomposite composed of MWNTs with an amine (–NH2) functional group was increased, indicating that the functional group positively influenced the strength of epoxy.
Figure 4. Simulated exterior of elongation of MWNT-reinforced composite with amine (–NH₂) functional group: (a) strain: 0 (b) strain: 0.02 (c) strain: 0.04

Figure 5. Stress–strain curve of MWNT-reinforced composite with amine functional group

Table 1. Comparison of Young’s modulus ($E$) value following addition of different MWNTs

| Composition                     | Young’s modulus ($E$) (GPa) |
|---------------------------------|-----------------------------|
| MWNT 6,6 + Epoxy                | 45.32                       |
| Amine-based (~NH₂) MWNT 6,6 + Epoxy | 50.46                       |

4.3. The effect of Amine functional group on interfacial energy

This study analyzed the interfacial energy of nanocomposites composed of CNTs with an amine functional group in epoxy. The interfacial energy equation in Chapter 3 can be used to obtain the interfacial energy of nanocomposites composed of CNTs with different functional groups, as shown in Table 2.

Table 2 reveals that the nanocomposite composed of CNTs with amine functional groups exhibited greater interfacial energy. Combined with increased reinforcement, the nanocomposite could resist greater external forces, which also explains the increase in interfacial energy after the addition of an amine functional group.

Table 2. Comparison of interfacial energy following addition of different CNTs

| Composition                     | Interfacial energy (kcal/mol) |
|---------------------------------|------------------------------|
| MWCNT 6,6 + Epoxy               | -397.219                     |
| Amine-based (~NH₂) MWCNT 6,6 + Epoxy | -418.134                    |
5. Conclusions

This study successfully used the concept of MD to explore MWCNTs with amine (–NH₂) functional groups and subsequently applied it to construct a novel macromolecular CNT-reinforced composite using macromolecular materials. Nanoscale tensile simulations were used to examine the reinforcing phenomena of the nanocomposite composed of functional group–based CNTs and subsequently explore the reinforcement mechanisms involved.

The simulation result showed that a macromolecular composite made of CNTs with amine (–NH₂) functional groups and macromolecular materials demonstrated greater Young’s modulus and interfacial energy (binding force) than a nanocomposite comprising purely CNTs and macromolecular materials.

The results of this study revealed that the reinforcement mechanism of a nanocomposite made of CNTs and macromolecular materials stems from the interfacial energy between CNTs and macromolecular material. The interfacial energy between a nanocomposite made purely of CNTs and macromolecular materials is supplied by the Van der Waals force between CNTs and macromolecules and is considered a physical bond. By contrast, the interfacial energy between the novel macromolecular composite made of CNTs with amine (–NH₂) functional groups and macromolecular materials was supplied by the chemical bond between the functional groups on the surface of the CNTs and macromolecular materials. The interfacial binding force of a chemical bond is stronger than that of a physical bond. Therefore, a nanocomposite composed of functional group–based CNTs can provide greater strength.

References

[1] S. Iijima, Nature, 354 (1991) 56-58.
[2] Vaudreuil S, Labzour A, Sinha-Ray S, El Mabrouk K and Bousmina M, Dispersion characteristics and properties of poly(methyl methacrylate)/multi-walled carbon nanotubes nanocomposites, Journal of nanoscience and nanotechnology, J Nanosci Nanotechnol. 2007 Jul;7(7):2349-55.
[3] Ray SS, Vaudreuil S, Maazouz A and Bousmina M, Dispersion of multi-walled carbon nanotubes in biodegradable poly(butylene succinate) matrix, Journal of nanoscience and nanotechnology, J Nanosci Nanotechnol. 2006 Jul;6(7):2191-5.
[4] Hartmann S, Blaudeck T, Holck O, Hermann S, Schulz SE, Gessner T and Wunderle B, Quantitative in-situ scanning electron microscope pull-out experiments and molecular dynamics simulations of carbon nanotubes embedded in palladium, Journal of Applied Physics, vol.115, no.14, 14 April 2014, 144301 (8 pp.)
[5] Jen-Ching Huang, Cheng-Yi Chiu, 2011, “The Study of Single-walled Nanotube Reinforced Epoxy Composites by Molecular Dynamics”, Polymers & Polymer Composites, Vol. 19, Nos. 4&5, pp. 377–382.
[6] Jihua Gou , Bob Minaie , Ben Wang , Zhiyong Liang and Chuck Zhang, “Computational and experimental study of interfacial bonding of single-walled nanotube composites”,Computational Materials Science 31,2004 225-236
[7] Basinski, Z. S., Duesbery, M. S. and Taylor, R. “Influence of shear stress on screw dislocations in a model sodium lattice,” Canadian Journal of Physics, Vol.49, 2160(1971).