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2009 J. Phys.: Condens. Matter 21 215301

(http://iopscience.iop.org/0953-8984/21/21/215301)

IOP Publishing Journal of Physics: Condensed Matter

J. Phys.: Condens. Matter **21** (2009) 215301 (6pp) doi:10.1088/0953-8984/21/21/215301

Enhanced mechanical properties of single-walled carbon nanotubes due to chemical functionalization

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Received 1 November 2008, in final form 26 March 2009

Published 30 April 2009

Online at stacks.iop.org/JPhysCM/21/215301

Abstract

Recent studies have shown that the chemical functionalization of carbon nanotubes weakens most of their mechanical properties such as the critical buckling force under compression and the critical buckling moment under torsion. However, the mechanical properties including the critical bending curvature and the critical bending moment of single-walled carbon nanotubes can be improved after functionalization as shown in this paper. The molecular mechanics simulations reveal that there exists an optimum functionalization degree at which the critical curvatures of the functionalized carbon nanotubes reaches its maximum value. The critical curvatures of the carbon nanotubes increase with increasing functionalization degree below the optimum value, while the critical curvatures change little as the functionalization degree is beyond the optimum value. The influences of the bending directions and the aspect ratios of the functionalized carbon nanotubes are also examined via molecular mechanics simulations.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Due to the remarkable electrical, mechanical and thermal properties of carbon nanotubes (CNTs) [1], they have been widely regarded as a promising reinforcing phase for composites [2]. Current studies [3–5] have shown that the van der Waals (vdW) force at the interface between the polymer and CNTs plays a minor role in transferring the external loading to CNTs in composites. The molecular dynamic (MD) simulations by Frankland *et al* [5] showed there is only 2 MPa shear strength when considering only the vdW interactions at the interface. To achieve the strong interface adhesion, one of the efficient ways is the covalent sidewall functionalization of CNTs by different chemical processes [6]. The work by Liao and Li [7] showed that the interface shear strength is up to 160 MPa as strong bonding occurs between the CNT and the surrounding matrix. However, the covalent sidewall functionalization alters the sp^2 hybridization of the tubule wall and the defects of the 'sp^3-hybridized carbon atom' [8] are produced at these points of attachment. Consequently, lots of these defects weaken some of the mechanical properties of CNTs, such as the elastic modulus [9], the fracture strain [9], the tensile strength [9] and the critical buckling force under axial compression [8] as well as the critical buckling moment under torsion [10]. It seems that functionalization only has adverse effects on the mechanical properties of CNTs as shown in the above studies [8–10]. In this work, the results obtained from molecular mechanics simulations show that the functionalization is favorable for single-walled carbon nanotubes (SWCNTs) under bending deformation due to the increase in the critical curvature and the critical moment. The direct advantage from the increments is that SWCNTs and the corresponding composites may bear more external moment and larger deformation, and the potential advantage for the increment of the critical curvature is that the carbon nanorings [11] may be achieved by using SWCNTs having shorter length and smaller diameter.

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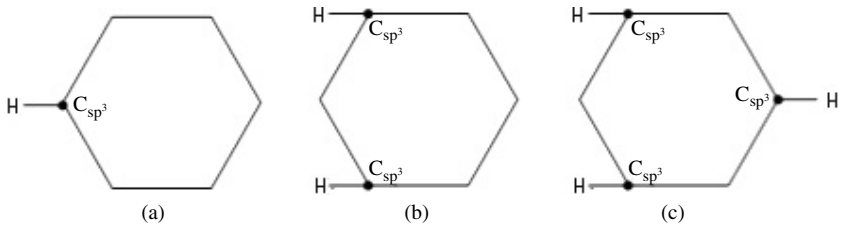

Figure 1. A schematic of the distribution density: (a) sparse distribution: one sp^3-hybridized carbon atom in a single hexagonal carbon ring; (b) moderate distribution: two sp^3-hybridized carbon atoms in a single hexagonal carbon ring; (c) dense distribution: three sp^3-hybridized carbon atoms in a single hexagonal carbon ring.

2. Simulation tools and set-up

Here, the simulation tool is molecular mechanics (MM). MM simulation is different from MD simulation because MM seeks to resolve the equilibrium condition of the system by minimizing the potential energy, while in MD the equation of motion is solved based on certain time integration schemes. The potential-energy minimization is carried out by the conjugate gradient algorithm. In our MM simulations, a COMPASS force field is used. A COMPASS force field is a general all-atom force field for atomistic simulation of common organic molecules, inorganic small molecules and polymers developed by using state-of-the-art *ab initio* and empirical parameterization techniques. It is the first *ab initio* force field that was parameterized and validated using condensed-phase properties. The functional forms [12] used in this force field are as follows:

$$\begin{aligned}
E_{\text{total}} = & \sum_{b} [k_2(b-b_0)^2 + k_3(b-b_0)^3 + k_4(b-b_0)^4] \\
& + \sum_{\alpha} [k_2(\alpha-\alpha_0)^2 + k_3(\alpha-\alpha_0)^3 + k_4(\alpha-\alpha_0)^4] \\
& + \sum_{\phi} [k_1(1-\cos\phi) + k_2(1-\cos 2\phi) + k_3(1-\cos 3\phi)] \\
& + \sum_{\chi} k_2\chi^2 + \sum_{b,b'} k(b-b_0)(b'-b_0') \\
& + \sum_{b,\theta} k(b-b_0)(\alpha-\alpha_0) \\
& + \sum_{b,\phi} (b-b_0)[k_1\cos\phi + k_2\cos 2\phi + k_3\cos 3\phi] \\
& + \sum_{\alpha,\phi} (\alpha-\alpha_0)[k_1\cos\phi + k_2\cos 2\phi + k_3\cos 3\phi] \\
& + \sum_{b,\alpha} k(\alpha'-\alpha_0')(\alpha-\alpha_0) + \sum_{\alpha,\alpha,\phi} k(\alpha-\alpha_0)(\alpha'-\alpha_0')\cos\phi \\
& + \sum_{i,j} \varepsilon_{ij} \left[2\left(\frac{r_{ij}^0}{r_{ij}}\right)^9 - 3\left(\frac{r_{ij}^0}{r_{ij}}\right)^6 \right]. \qquad (1)
\end{aligned}$$

The functions can be divided into two categories—valence terms including diagonal and off-diagonal cross-coupling terms and nonbond interaction terms. The valence terms represent internal coordinates of bond (b), angle (α), torsion angle (ϕ) and out-of-plane angle (χ), and the cross-coupling terms include combinations of two or three internal coordinates. The nonbond interaction is considered by using an LJ-9-6 function for the vdW term.

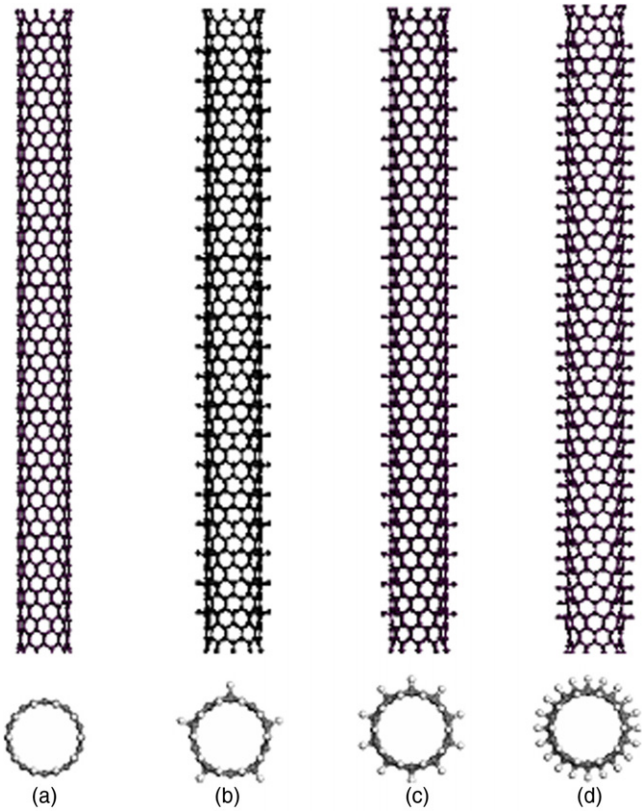

Figure 2. (a) A pristine (10, 0) SWCNT; (b) the corresponding functionalized (10, 0) SWCNT with the sparse distribution of the hydrogen groups; (c) the corresponding functionalized (10, 0) SWCNT with the moderate distribution of the hydrogen groups; (d) the corresponding functionalized (10, 0) SWCNT with the dense distribution of the hydrogen groups. The functionalization degree is about $S = 12\%$, $S = 24\%$ and $S = 48\%$, respectively, for case (b), case (c) and case (d).

No periodic boundary conditions are applied to both the nonfunctionalized SWCNTs and functionalized SWCNTs. Three types of distribution density of the hydrogen groups or the sp^3-hybridized carbon atoms, i.e., 'sparse distribution', 'moderate distribution' and 'dense distribution' are considered and shown in figure 1.

For simplification, these hydrogen groups are regularly distributed throughout the tube wall shown in figure 2, that is to say, the hydrogen groups are distributed at equal intervals along the circumference or the longitudinal direction of the whole tube, and they are either located on the same cross

section of the tube or arrayed in line along the tube axis. Therefore, for any entirely functionalized tube with the sparse distribution, the moderate distribution or the dense distribution, the corresponding functionalization degree defined by S, i.e. the fraction of carbon atoms bearing the hydrogen atom, is about $S = 12\%$, $S = 24\%$ and $S = 48\%$, respectively. These specific parameters of the functionalization degree will be used in the whole paper. They are not beyond the upper limit (50%) of the functionalization degree from the experimental results [13].

3. Results and discussion

Firstly, the present approach is validated by comparing the obtained critical bending curvature κ_{p} of pristine armchair (8, 8), (12, 12) and (16, 16) SWCNTs and pristine zigzag (10, 0), (16, 0) and (22, 0) SWCNTs with the results by other research groups [14, 15]. The aspect ratio l/d, i.e. the ratio of the tube length l to the diameter d, is about 11 for these SWCNTs. To obtain the critical bending curvature, the bending loading is applied to the two end planes of an SWCNT; the loading approach in Cao and Chen [14] is also used here. A series of very small increments $\Delta\theta_i (i = 1, 2, 3, \ldots, n)$ of bending angles are imposed by rotating two end planes of an SWCNT in opposite directions until the SWCNT buckles abruptly, and the corresponding strain energies U_i of the SWCNT is obtained for each loading step. Then, the critical curvature is given as

$$\kappa_{\mathrm{p}} = \sum_{i=1}^{n} \Delta\theta_i / l. \tag{2}$$

The approach is also used to obtain the critical bending curvatures of functionalized SWCNTs. The comparisons of critical curvatures are shown in figure 3. It can be seen from the figure that the obtained results agree well with the results by Cao and Chen [14] and Sun and Liew [15] for different chiralities and diameters of SWCNTs. In the study by Cao and Chen [14], both MD simulations and the finite element method (FEM) are used to investigate the bending buckling of single-walled carbon nanotubes by using a COMPASS force field, while the mesh-free method and the Tersoff–Brenner potential are used to investigate the bending buckling of single-walled carbon nanotubes in the study by Sun and Liew [15].

In what follows, the effect of functionalization on buckling is studied. For pristine SWCNTs, the critical bending curvature κ_{p} and the critical moment M_{p} are independent on the bending direction due to their geometric symmetric feature even though the buckling is determined by the deformation ability of the compressive zone [16]. However, for a functionalized SWCNT, the geometric structures in the compressive zones upon bending are greatly different for different bending directions. Therefore, we first investigate the effect of bending directions on the critical curvature κ_{f} and the critical moment M_{f} of functionalized SWCNTs. The entirely functionalized (10, 0) SWCNT and partially functionalized (8, 8) SWCNT are used with consideration of the sparse distribution of the functional groups, and the corresponding functionalization degree is 12% and 6%, respectively. We define the parameter β

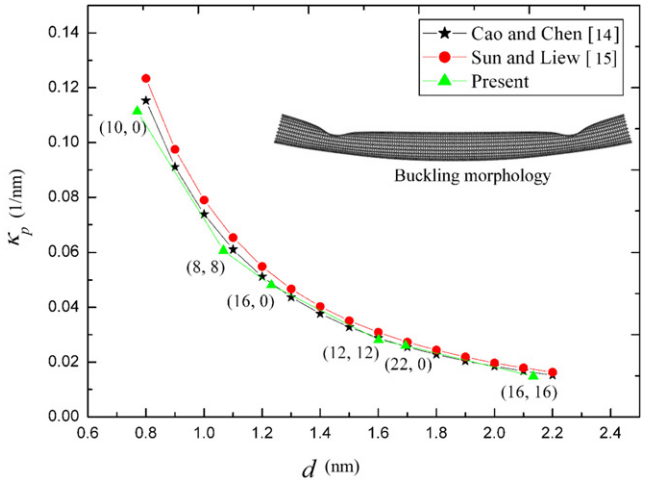

Figure 3. Critical curvatures of pristine SWCNTs with different chiralities and diameters.

to represent the bending direction. According to the structural symmetry of the two functionalized SWCNTs, the range of parameter β is from 0° to 36° for the (10, 0) SWCNT and from 0° to 45° for the (8, 8) SWCNT. The situation $\beta = 0$ denotes that a line of hydrogen atoms along the tube axis are just located at the zone having the maximum compressive strain. The line of hydrogen atoms is gradually away from this zone with the increase of β. Considering the difficulty to precisely calculate the bending rigidity of functionalized SWCNTs, it is unconventional to calculate the critical moment by using the following relation between bending rigidity D and bending curvature κ in the mechanics of materials:

$$M = D\kappa. \tag{3}$$

It is noted that we may roughly estimate that the parameter D of the functionalized SWCNT is smaller than that of the corresponding pristine SWCNT by regarding functionalized SWCNTs as a continuous medium. The estimation is based on both the reduction of Young's modulus E due to functionalization and the following equation describing a continuous medium:

$$D = EI, \tag{4}$$

where I is the moment of inertia for both pristine and functionalized SWCNTs. It should be noted that the functionalized SWCNTs may be regarded as linear elastic bodies similar to the pristine tube under the small deformation [17] and equation (4) may be used for the functionalized SWCNTs. As a result, a direct and efficient way is used to obtain the critical moment of pristine or functionalized SWCNTs, it is

$$M_{\mathrm{f}} = \Delta U_{n-1}/\Delta\theta_{n-1}, \qquad \text{or} \qquad M_{\mathrm{p}} = \Delta U_{n-1}/\Delta\theta_{n-1}, \tag{5}$$

in which ΔU_{n-1} and $\Delta\theta_{n-1}$ denote the increment of strain energy and the increment of the bending angle of the last loading step before buckling. The dimensionless critical curvature $\kappa_{\mathrm{f}}/\kappa_{\mathrm{p}}$ and critical moment $M_{\mathrm{f}}/M_{\mathrm{p}}$ are shown in figure 4(a). It can be seen from figure 4(a) that $\kappa_{\mathrm{f}}/\kappa_{\mathrm{p}}$

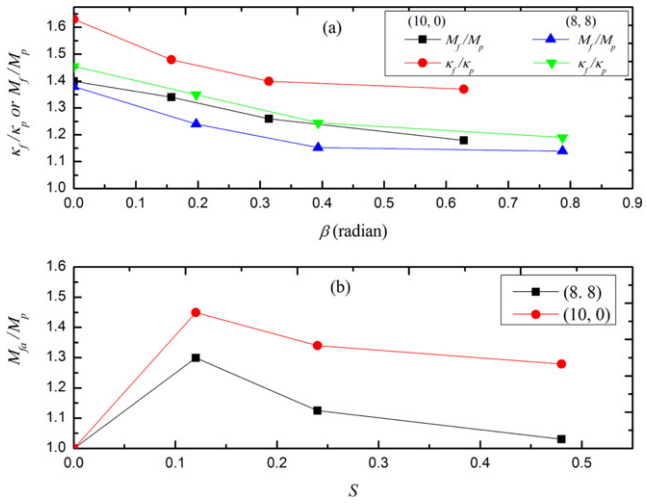

Figure 4. (a) The effect of bending directions on the critical bending curvatures and the critical bending moments of the functionalized (10, 0) and (8, 8) SWCNTs; (b) the effect of the functionalized degree on the critical bending moments of the (10, 0) and (8, 8) SWCNTs.

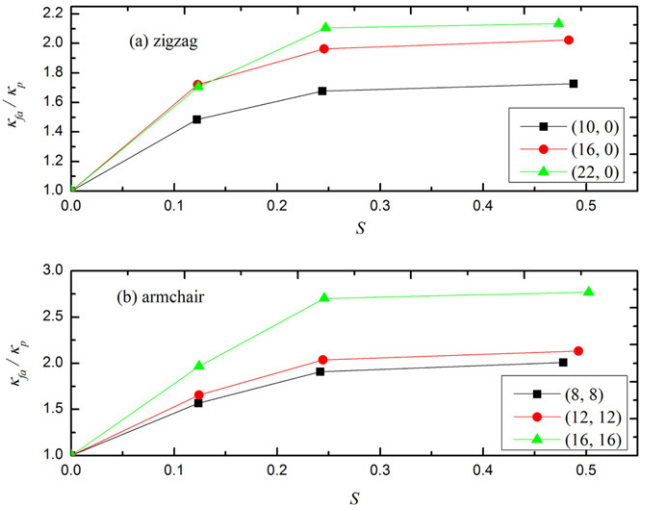

Figure 5. Effect of the functionalization degree on the critical bending curvatures of: (a) zigzag SWCNTs and (b) armchair SWCNTs.

and M_f/M_p are a maximum as $\beta = 0$, i.e. a line of the functional groups are just located in the compressive zone having the maximum compressive stain and the two parameters gradually decrease as the functional groups are gradually away from the maximum compressive strain zone. However, the minimum values of the two parameters are still slightly larger than one. These variations show that the structure in the compressive zone has a dominant effect on the critical curvature and the critical moment. The cause of the increment of the critical curvature or critical moment is that some spatial tetrahedral structures out of the wall of the SWCNT are formed on the tube wall due to sp^3 hybridization; these structures may bear larger compressive deformation compared with the original smooth wall. Moreover, the critical moments M_f under different parameter β are calculated, the average value M_{fa} for these critical moments are obtained for the given functionalization degree, and the dimensionless moments M_{fa}/M_p under different functionalization degree are shown in figure 4(b). We can see from figure 4(b) that the moments of the functionalized (10, 0) and (8, 8) SWCNTs increase with increasing functionalization degree and reach a maximum as the functionalization degree is about 12%; as the functionalization degree increases further, the moments decrease gradually, and the moments are slightly larger than those of the pristine SWCNTs as the functionalization degree reaches the maximum. The cause of the variation is that Young's moduli of SWCNTs change little as the functionalization degree is lower than 12%. The obvious improvement of the critical curvature gives rise to the increase of the moment. As the functionalization degree is beyond 12%, the Young's moduli of SWCNTs decrease with the increase of the functionalization degree, and the decreased amplitude is large due to the larger distribution density of the functional groups and the larger functionalization degree [17]. The obvious reduction of the modulus gives rise to the decrease of the moment though the critical curvature increases due to the functionalization. Our recent studies [17] have revealed that the reduction of Young's modulus may be up to about 37% after the entire functionalization with the dense distribution of the functional groups. However, the increment of the critical curvature may be up to about 200% shown in section 4 of this paper. Therefore, the positive effect of the critical curvature may overcome the negative effect of the Young's modulus due to the functionalization. This point can be seen from figure 4(b) in which the dimensionless moments are still larger than one.

Further, the effect of the functionalization degree on the critical curvature is investigated. The above six types of SWCNTs having aspect ratio $l/d = 11$ are used. The critical curvatures κ_f under different parameters β and the average value κ_{fa} of these critical curvatures are calculated. The simulation results of the dimensionless critical curvatures κ_{fa}/κ_p are shown in figure 5(a) for the zigzag SWCNTs and figure 5(b) for the armchair SWCNTs. It can be seen from figures 5(a) and (b) that the curvatures κ_{fa}/κ_p increase with increasing functionalization degree of these tubes at the start, while they increase little as the functionalization degree is beyond about 24%, regardless of the chirality and the diameter. With the consideration of the reduction of the Young's modulus due to the increases of the functionalization degree and the density of the functional groups, the optimum functionalization degree is about 24% at which the critical bending curvatures of functionalized SWCNTs reach the maximum. We also observe from figure 5 that the critical curvature has the diameter dependence on the armchair or zigzag SWCNTs, namely the larger the tube diameter is, the larger the increased amplitude of the critical curvature. Additionally, our simulations show that the buckling morphologies of SWCNTs with different functionalization degrees are similar to those of the corresponding pristine SWCNTs shown in figure 3, and two symmetric kinks appear near two ends of a functionalized SWCNT.

The average strain energies U of the functionalized zigzag (10, 0) SWCNTs and armchair (12, 12) SWCNTs

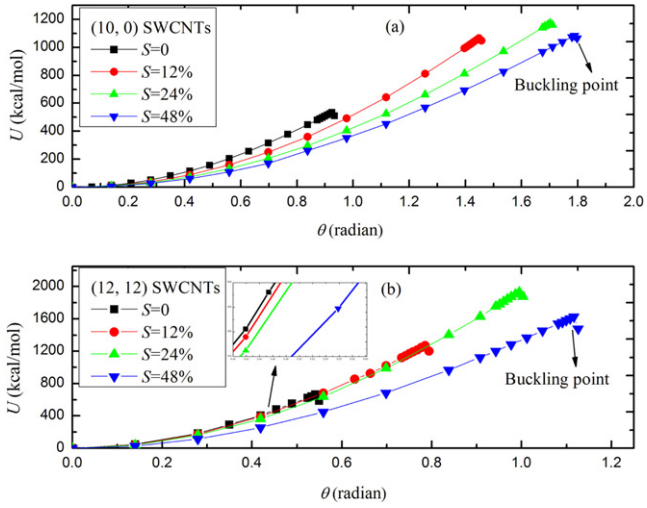

Figure 6. Effect of the functionalization degree on the strain energies of the (10, 0) and (12, 12) SWCNTs.

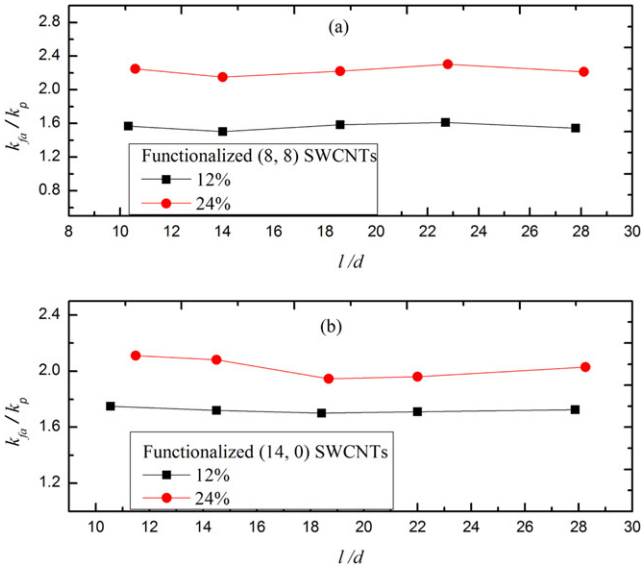

Figure 7. Effect of the aspect ratios l/d of the (8, 8) and (14, 0) SWCNTs on the critical curvatures.

under different bending directions are also calculated for the given functionalization degree. The corresponding average strain energies U versus the bending angles θ are plotted in figures 6(a) and (b). It can be seen from the two figures that the larger the functionalization degree the smaller the increase in strain energy for the same bending angle. In the mechanics of materials, the relation of strain energy U versus bending rigidity D is written as

$$U = D\theta^2/(2l). \tag{6}$$

This equation indicates the strain energy is proportional to the bending rigidity D for the given bending angle. Therefore, figures 6(a) and (b) show that the larger the functionalization degree, the smaller the bending rigidity of the functionalized SWCNTs. In other words, the bending rigidity of the SWCNTs decreases with increasing functionalization degree.

Finally, the effect of aspect ratios l/d on the critical curvatures of functionalized SWCNTs is explored for different functionalization degree. The critical bending curvatures of the armchair (8, 8) SWCNTs and zigzag (14, 0) SWCNTs under different aspect ratios are calculated, and the functionalization degree is taken as $S = 12\%$ and 24% in these simulations. The dependence of the dimensionless critical curvatures κ_{fa}/κ_p on the ratio l/d is shown in figure 7(a) for the (8, 8) SWCNTs and figure 7(b) for the (14, 0) SWCNTs. It can be seen from the two figures that the aspect ratios l/d have little effect on the critical curvature of the armchair or zigzag SWCNTs under the given functionalization degree, which is similar to that of pristine SWCNTs [14, 15]. The results also imply that aspect ratios have little effect on the optimum functionalization degree. The SWCNT with the aspect ratio smaller than 10 is not considered here due to little use for practical purposes.

4. Conclusions

From the point of view of mechanical properties of SWCNTs, the effect of the chemical functionalization on critical bending curvatures and critical bending moments of SWCNTs is investigated by using MM simulations. The results show that functionalized SWCNTs may bear more external bending loading and larger bending deformation than those of pristine SWCNTs. Considering the functional groups of hydrogen atoms, there exists a optimum functionalization degree of about 24% at which the critical curvature reaches the maximum, regardless of the chiralities, diameters and aspect ratios of SWCNTs. The bending rigidity of an SWCNT decreases with increasing functionalization degree. The present study will benefit the design of carbon nanotube reinforced composites.

Acknowledgments

The authors thank Dr Y Sun for helpful discussion. The work is supported by a grant from City University of Hong Kong (project no. 7002237). The comments from these reviewers are highly appreciated.

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