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THE INFLUENCE OF THICKNESS, DIAMETER, CHIRAL AND BOND ANGLE ON THE VALUE OF YOUNG'S MODULUS FOR CHIRAL SINGLE-WALLED CARBON NANOTUBES

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In the carbon-nanotube study field, Young's modulus is of prime significance, as it needs to be put into all CAE softwares when we like to analyze, design, or even manufacture a device made up of carbon nanotubes. It seems that, however, no authors devoted their efforts to the investigation of the effect of thickness, diameter, chiral angles, and bond angles especially on Young's modulus for chiral carbon nanotubes. This paper, thus, will examine the effects above closely and thoroughly and from the related figures shown can we find distinctly the correlation among them. It should be stressed here that, when the impact of bond angles on Young's moduli is taken into account, the precise values of them can be obtained.

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Keywords: Carbon nanotube, Young's modulus, Thickness, Diameter, Chiral angle, Bond angle.

1. Introduction

Since carbon nanotubes were first found by Iijima in 1991[1], numerous numerical simulations and analytical as well as experimental approaches have been devoted to this promising field; among them, many were focused on how to attain the values for Young's modulus of armchair and zigzag nanotubes. As for chiral configuration, very few were dedicate to it, much less to discussing the effect of thickness, diameter, chiral and bond angles on the value for Young's modulus. The paper, therefore, will go through the contents mentioned above cautiously and completely so as to observe the relationship between them and meanwhile get the more precise values of Young's moduli for carbon nanotubes.

As stressed previously, amid the articles having been published thus far, many were in connection with the computation and simulation of Young's modulus. Popov *et al.*[2], for instance, derived analytical equations to predict Young's modulus and Poisson's ratio for differing

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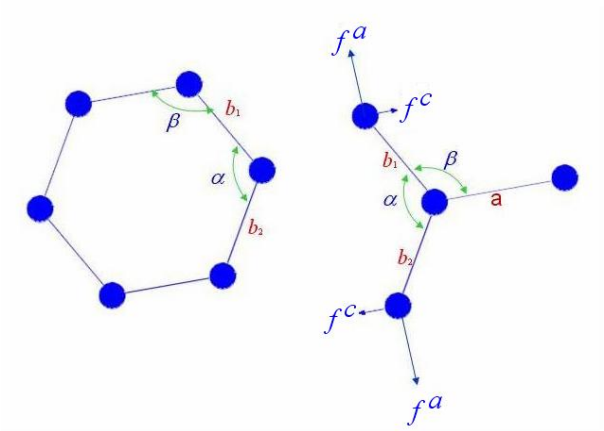
chiral and achiral SWCNTs(the acronym for Single-Walled Carbon NanoTubes). Van *et al.*[3] made use of the so-called first all-electron *ab initio* methodology for Young's moduli of SWCNTs too. In 2003, Chang and Gao[4] proffered a molecular mechanics means in which a 'stick-spiral' pattern relating the elastic properties of a single-walled carbon nanotube to its molecular structure was introduced and then the closed-form expressions for elastic moduli of SWCNTs under axial loading were secured. Bao *et al.*[5] procured an average Young's modulus for a series of chiral SWCNTs with the help of molecular dynamics simulation . Shen *et al.*[6] achieved closed-form expressions for the elastic properties of SWCNTs subjected to diverse loading conditions by using an energy approach. Chang *el al.*[7] gained the axial elastic moduli and Poisson's ratios for chiral carbon nanotubes under the 'stick-spiral' model. Xiao *et al.*[8] expanded the 'stick-spiral' model to torsion loadings and scrutinized the nonlinear stress-strain correlation for defect-free nanotubes. Afterward, Chang *et al.*[9] established the governing equations originated from Chang and Gao smoothly and obtained the closed-form expressions for Young's modulus, Poisson's ratio, and shear modulus of chiral carbon nanotubes. Leung *et al.*[10], meanwhile, proposed an energy-equivalent manner and declared that both diameters and chiral angles can influence the Young's modulus of a single-walled carbon nanotubes. Fang *et al.*[11] presented an innovative way to calculate the value for Young's modulus of chiral nanotubes in 2007. Fan *et al.*[12] studied the elastic properties of MWCNTs(the acronym for Multi-Walled Carbon NanoTubes) via a finite element simulation. Shokrieh *et al.*[13] later investigated the Young's moduli of grapheme sheets and carbon nanotubes simultaneously. Mohammadpour *et al.*[14] also probed into the Young's modulus of SWCNTs with finite element software.

2. Molecular structure mechanics of carbon nanotubes

Viewing the structure and deformation traits of the SWCNT, we can divide chemical carbon-carbon bond into three categories named bonds $\boldsymbol{a}$, $\boldsymbol{b}_1$,$\boldsymbol{b}_2$,and bond angle into two groups called angles $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ as shown in Fig. 1(a).



a b

Fig. 1 Schematic diagrams of a chiral SWCNT: (a)the hexagonal unit and (b) force distribution in bonds b_1 and b_2 .

Then keep in mind that only bond elongation and bond angle variation are decisive in the system potential energy. And now, we may embark on the derivation of a closed-form expression for obtaining the value of Young's modulus.

2.1 The derivation processes for Young's modulus of chiral single-walled CNTs

To illuminate the processes clearly, Fig. 1(b) would be brought forth again. The axial force $\boldsymbol{F}$ acting on a SWCNT can be decomposed to $\boldsymbol{f}^{a}$ perpendicular to bond *a* and $\boldsymbol{f}^{c}$ along bond *a* just like those in Fig. 1(b).The mutual relationships of the forces can be expressed as

$$f^{a}=F\cos(30^{0}-\theta) \tag{1}$$

For a SWCNT under axial forces, however, only bond elongation and bond angle variation are decisive in the total system potential energy as stated before, and the interaction of carbon bonds can be depicted in this way

$$U=U_{\rho}+U_{\theta}=\frac{1}{2}\sum_{i} K_{i}\ (dR_{i})^{2}+\frac{1}{2}\sum_{j} C_{j}\ (d\theta_{j})^{2} \tag{2}$$

the bond elongation and bond angle variation equilibrium equations whereupon are

$$F_{i}=K_{i}\ dR_{i} \qquad M_{j}=C_{j}\ d\theta_{j} \tag{3}$$

As illustrated in Fig.1(b),force equilibrium of bond elongation for a chiral SWCNT takes the form

$$F\cos(30^{0}-\theta)\sin(\frac{\alpha}{2}) =K_{b}\,db_{1} \tag{4}$$

The moment equilibrium caused by bond angle variation in plane $\boldsymbol{b}^{1}$ -$\boldsymbol{b}^{2}$ may be depicted as

$$\frac{F\cos(30^{0}-\theta)\cos\frac{\alpha}{2}b_{1}}{2}=Cd\alpha+Cd\beta\cos\psi \tag{5}$$

ψ ,the torsion angle formed by planes $\boldsymbol{b}_{1}$ -$\boldsymbol{b}_{2}$ and $\boldsymbol{a}$- $\boldsymbol{b}_{1}$, is

$$\cos\psi=\frac{\tan\frac{\alpha}{2}}{\tan\beta} \tag{6}$$

The geometrical relation between angles α and β leads to

$$\cos\beta=-\cos[\frac{\pi}{n+m}]\cos(\frac{\alpha}{2}) \tag{7}$$

When we differentiate both sides of Eq.(7) , the result would be

$$d\beta=-d\alpha\ \frac{\sin(\frac{\alpha}{2})\cos(\frac{\pi}{n+m})}{2\sin\beta} \tag{8}$$

Under the assumption $a = b_1$, which is often the case for chiral SWCNT and substituting Eqs.(6),(8) into Eq.(5),the correlation between $d\alpha$ and $d\,b_1$ can be yielded

$$d\alpha = \frac{db_1}{b_1}\cot\left(\frac{\alpha}{2}\right)\frac{2\Pi K b_1^{\,2}}{C} \tag{9}$$

in Eq.(9)

$$\Pi = \frac{\sin\beta\cot\left(\frac{\alpha}{2}\right)}{4\sin\beta\cot\left(\frac{\alpha}{2}\right) - 2\sin\left(\frac{\alpha}{2}\right)\cot\beta\cos\left(\frac{\pi}{n+m}\right)} \tag{10}$$

The axial strain $\varepsilon_f{}^a$ and circumferential strain $\varepsilon_f{}^{a'}$ of a (n,m) chiral nanotube is defined by

$$\varepsilon_f{}^a = \frac{d\left[b_1\sin\left(\frac{\alpha}{2}\right)\right]}{b_1\sin\left(\frac{\alpha}{2}\right)} \tag{11}$$

And the Young's modulus of a SWCNT is then

$$Y = \frac{2\cos(30^0 - \theta)CK}{\left(2\sin\frac{\alpha}{2} + \sin\alpha\right)\left(a^2\Pi K\cot^2\frac{\alpha}{2} + C\right)t} \tag{12}$$

in which the C and K represent force constants of bond elongation and angle variation respectively; a, the carbon bond-bond distance, is taken to be 0.1421 nm and the area of carbon nanotubes may be described in terms of the thickness t as $2\pi rt$; here, r stands for the radius of a carbon nanotube.

It must be emphasized that, unlike other articles, in which the derivation of closed-form expressions for Young's moduli of single-walled carbon nanotubes is too complicated by which the even the most prominent engineer and scholar are often perplexed, this work uncovers every procedure of the derivation so closely that most people in the relevant fields may understand fully and examine readily into all the smallest possible details to judge their accuracy.

By way of the closed form expression for obtaining the value of Young's modulus concerning carbon nanotubes in which the variables t(connected with thickness), n+m (related to the quantity for diameters and chiral angles), and α as well as β (associated with the bond angles) are included, we are ready to probe deep into the influence of the thickness, diameter, chiral angle, and bond angle on the values for Young's moduli of SWCNTs.

3. Results and discussions

Before the treatment of results and discussions, some fascinating problems need to be addressed: For sp^2 hybrid orbital, the bond angles (denoted by α and β here between carbon bonds as shown in Fig. 1(b)), must be co-planar and have the value of 120^0 respectively. In the process of rolling a graphene sheet into the carbon nanotube, however, the bond angle β is compressed; for an (1,1) armchair nanotube, the β angle is pressed into 90^0 , and the discrepancy between is so huge that an (1,1) armchair tube just can't exist spontaneously. In the case, some scholars adopted a term "bent bonds," but this term is simply used to signify the

p-orbital portion such as sp^4 or sp^5 is increased (which has been evidenced by the electron density diagram obtained from X-ray study), not to indicate the bond lengths are shortened or lengthened because of the curvature or whatever. And so, the statement $a = b_1$ can be applied superbly well to the carbon nanotube with infinitesimal diameters.

Still, some researchers have argued that the values of Young's modulus for carbon nanotubes obtained from the models other than ab-initio method must be compared with those got from ab-initio calculation because the results procured by both kinds of approaches are different. At present, however, no one can find a closed-form expression attained by way of the ab-initio study and thus the contrast is obviously impossible. Furthermore, the difference, if exists, should occur only in the quantities of Young's modulus, but the trend of them must be identical. To clarify the perplexing problem, let's take a carbon nanotube with diameter of 0.3 nm or so (which can exist merely for a very short period of time) as an example, and it can be imagined readily that the Young's modulus of the carbon nanotube mentioned above must be low and meanwhile the Poisson's ratio need be high since a carbon nanotube with diameter 0.3 ought to be exceedingly unstable. The Young's moduli acquired in the present paper are completely compatible with the conclusion; the results secured by ab-initio method, must also comply with the rule, that is, the Young's modulus of a carbon tube with smaller diameter should be lower to that of larger diameter nanotube. If the values gained from ab-initio calculation violate this physical phenomenon, just as some researchers have affirmed that there is a distinction between the results obtained by ab-initio and other models. Then it can be inferred that the ab-initio method is not suitable for the analysis of carbon nanotubes.

Eventually, can a carbon nanotube with diameter of 0.2 nm(a (2,1) chiral configuration perhaps) exist in nature? To most scholars in the related field of carbon nanotube's study, the answer would be negative. Some other day, under proper artificial condition, however, maybe it can be produced in the laboratory. This paper, hence, still includes it for comparison.

The section will be arranged as follows: subsection **3.1** devotes itself to the discussion of the trend of quantities procured by the closed-form expression within this paper for obtaining the values of Young's moduli of carbon nanotubes to show that the tendency secured in present paper is totally the same as those derived in other distinguished articles. **3.2** scrutinizes the effect of thickness on Young's modulus. **3.3** inspects the influence of diameters on Young's moduli of SWCNTs. **3.4** studies the impact of chiral angles on them. And ultimately, **3.5** investigates the results with the use of differing bond angles.

3.1 The thorough discussion of the values earned by the expression in the paper

As the marrow of this paper is dedicated to the chiral SWCNTs, the values of Young's moduli for the subsequent chiral configurations (2n,n), (3n,n), (4n,n), and (5n,n) will be calculated and the trend of them be drawn then to see whether or not they are consistent with the results of other noted articles having been published thus far.

From Fig. 2 can we observe the discrepancy of Young's modulus between various chiral nanotubes and the trend of them which fits in superbly well with the existing results displayed in most articles. It should be stressed here that the thickness is taken to be 0.34 nm-the interlayer space of graphite, when the values for Young's moduli of SWCNTs were reckoned. The reason why the number of thickness for single-walled carbon nanotubes needs to be set to 0.34 nm will be made clear later.

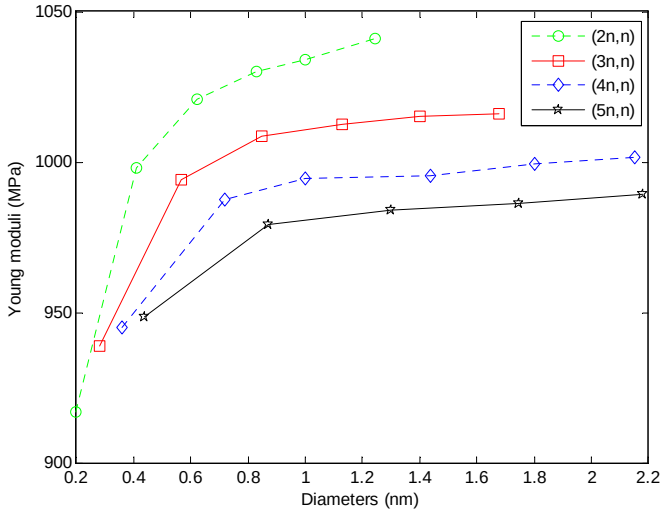


Fig. 2 The scheme of the value for Young's moduli of (2n,n), (3n,n), (4n,n), and (5n,n) chiral configurations.

3.2 The effect of thickness on the Young's modulus

As we shall see, the figure of thickness for carbon nanotubes is crucial in determining the value of Young's modulus, its quantity proposed by a great variety of literature differed so widely from a low of 0.066 nm provided by Yakobson et al. to a high of 0.65 nm suggested by Odegard et al. which obviously would cause tremendous confusion that some people just presented the notion of surface Young's modulus to avoid the problem entirely. But, should we do so? can we find a suitable thickness for the carbon nanotube?

In order to solve the enigma, let's take a close look at Eq. (12) $Y = \dfrac{2\cos(30^0 - \theta)CK}{(2\sin\dfrac{\alpha}{2} + \sin\alpha)(a^2 \Pi K \cot^2\dfrac{\alpha}{2} + C)t}$ and it can be found that the thickness t is in the denominator; now, suppose the chiral angle θ approaches 30^0, that is, $\cos(30^0 - \theta)$ comes near to 1, and α, β approximate 120^0, and then take the extreme value 1.06 TPa of Young's modulus when diameters are very great, we may get the quantity of thickness of nanotubes to be 0.34 nm, which is also the interlayer space of graphite. That's why **3.1** utilized it to compute the value for Young's modulus.

3.3 The influence of diameters on Young's moduli of SWCNTs

From Figs. 3 through 7 can we note that for fixed chiral angles, the values of Young's moduli ascend when diameters grow larger until they reach the maximum 1.06 TPa for armchair tubes.

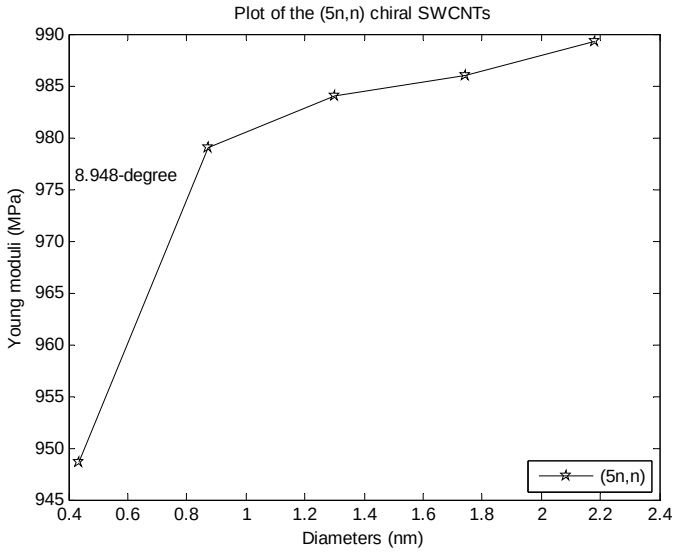


Fig. 3 The variation of Young's moduli with diameters for (5n,n) chiral SWCNTs having fixed angle 8.948

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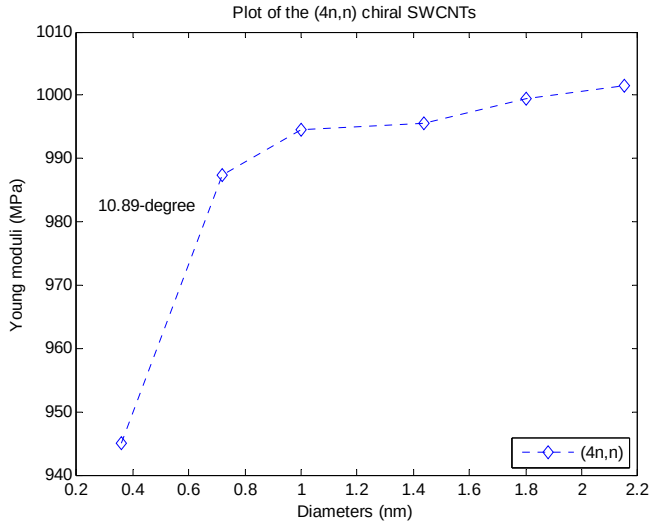

Fig. 4 The variation of Young's moduli with diameters for (4n,n) chiral SWCNTs having fixed angle 10.89

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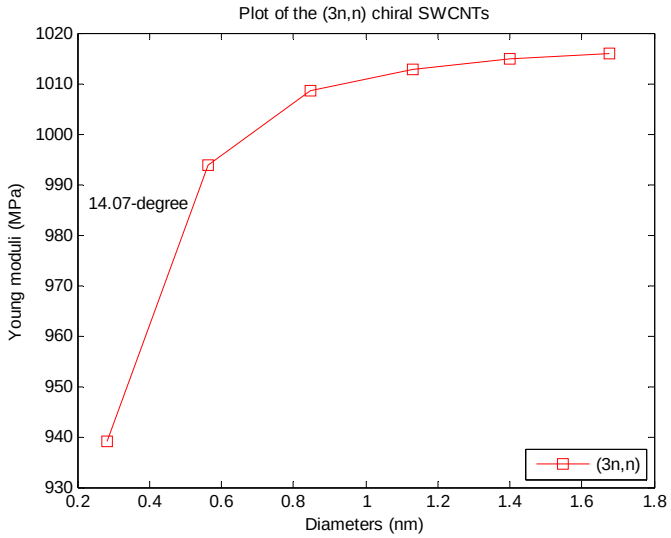

Fig. 5 The variation of Young's moduli with diameters for (3n,n) chiral SWCNTs having fixed angle 14.07

0

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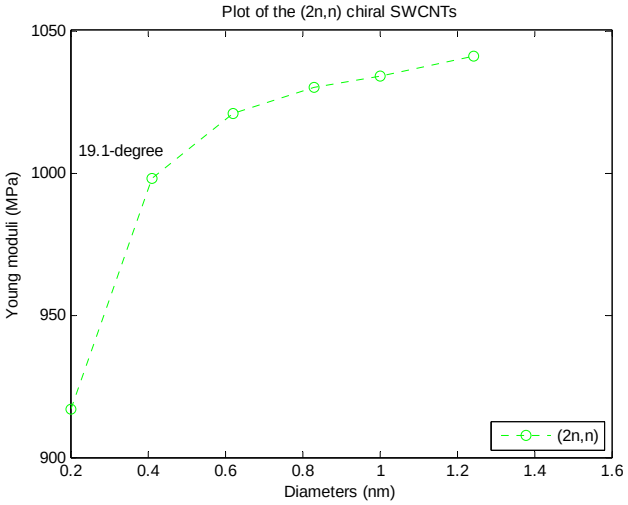

Fig. 6. The variation of Young's moduli with diameters for (2n,n) chiral SWCNTs having fixed angle 19.1

0

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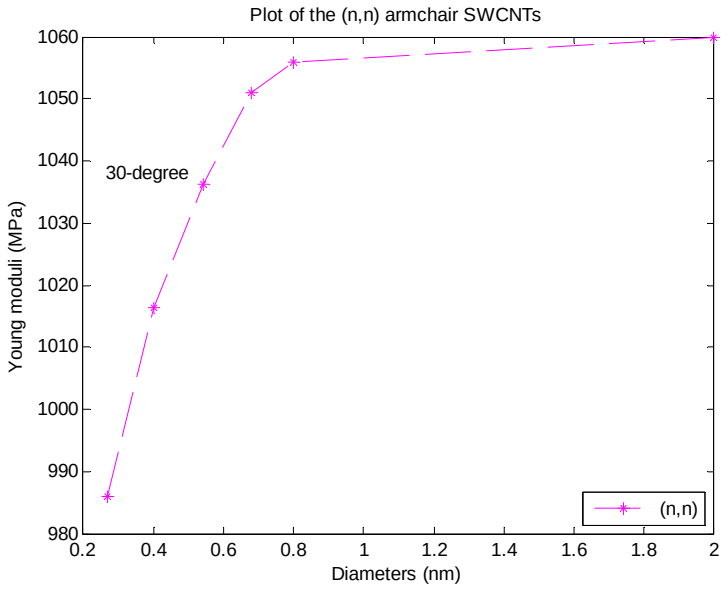

Fig. 7 The variation of Young's moduli with diameters for (n,n) armchair SWCNTs having fixed angle 30^0 *in which the maximum value 1.06 TPa can be reached.*

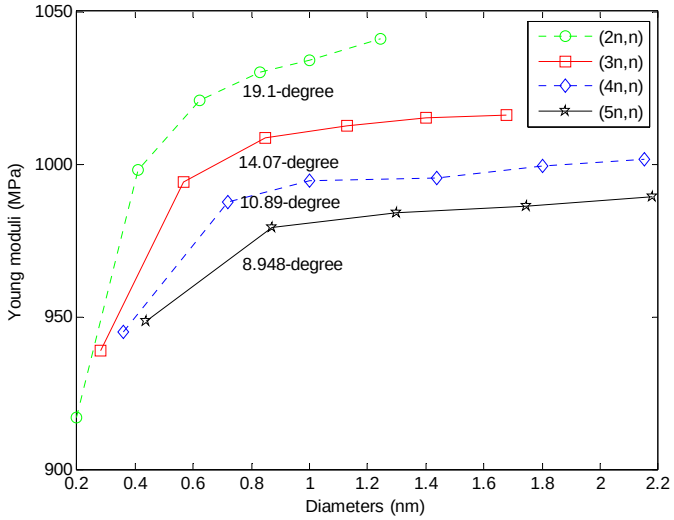

Fig. 8 The correlation of Young's moduli with chiral angles for (2n,n), (3n,n), (4n,n), (5n,n) chiral SWCNTs.

3.4 Impact of chiral angles on the Young's modulus

Similarly, from Fig. 8 can we see while the diameter is constant, the quantities of Young's moduli rise with the greater chiral angles.

3.5 The computational results of Young's moduli by using differing bond angles

This topic is scarcely mentioned in the related study fields of carbon nanotubes. It's

exceedingly important, however, if we like to acquire the precise values for Young's modulus of carbon nanotubes. Here, (2,1), (3,1), (4,1), and (5,1) chiral tubes will be employed as an illustration and bond angles $\alpha \fallingdotseq \frac{2}{3}\pi$ and $\beta \fallingdotseq \pi - \cos^{-1}[\frac{\cos(\frac{\pi}{n+m})}{2}]$ as well as $\alpha = \beta = 120^0$ would be laid in Eq. (12) separately for comparison, that is, for a (2,1) chiral SWCNT, if $\alpha \fallingdotseq \frac{2}{3}\pi$ and $\beta \fallingdotseq \pi - \cos^{-1}[\frac{\cos(\frac{\pi}{n+m})}{2}]$ are utilized, then

$$\alpha \cong \frac{2}{3}\pi,\ \beta \cong \pi - \cos^{-1}[\frac{\cos(\frac{\pi}{n+m})}{2}] \cong 104^0,\ \Pi = 0.22727,\ Y = 916.87\,MPa$$

When $\alpha = \beta = 120^0$ is put into Eq. (12) we obtain

$$\alpha = \beta = 120^0,\ \Pi = 0.2,\ Y = 968.43\,MPa$$

In the same way, for a (3,1) chiral SWCNT, if $\alpha \fallingdotseq \frac{2}{3}\pi$ and $\beta \fallingdotseq \pi - \cos^{-1}[\frac{\cos(\frac{\pi}{n+m})}{2}]$ are uesd, then

$$\alpha \cong \frac{2}{3}\pi,\ \beta \cong \pi - \cos^{-1}[\frac{\cos(\frac{\pi}{n+m})}{2}] \cong 110^0,\ \Pi = 0.205,\ Y = 939\,MPa$$

In contrast, if $\alpha = \beta = 120^0$ is exerted, the result will be

$$\alpha = \beta = 120^0,\ \Pi = 0.185,\ Y = 999\,MPa$$

To a (4,1) chiral tube, when making use of $\alpha \fallingdotseq \frac{2}{3}\pi$ and $\beta \fallingdotseq \pi - \cos^{-1}[\frac{\cos(\frac{\pi}{n+m})}{2}]$ as bond angles, we get

$$\alpha \cong \frac{2}{3}\pi,\ \beta \cong \pi - \cos^{-1}[\frac{\cos(\frac{\pi}{n+m})}{2}] \cong 113.8^0,\ \Pi = 0.19328, Y = 945\,MPa$$

If $\alpha = \beta = 120^0$ is harnessed, however,

$$\alpha = \beta = 120^0, \Pi = 0.17857,\ Y = 1014\,MPa$$

Finally, when a (5,1) chiral SWCNT and $\alpha \fallingdotseq \frac{2}{3}\pi$ and $\beta \fallingdotseq \pi - \cos^{-1}[\frac{\cos(\frac{\pi}{n+m})}{2}]$ are under consideration, then

$$\alpha \cong \frac{2}{3}\pi\,,\quad \beta \cong \pi - \cos^{-1}\left[\frac{\cos(\frac{\pi}{n+m})}{2}\right] \cong 115.6^{0}\,,\quad \Pi = 0.0.1857\,, Y = 948\,MPa$$

But if $\alpha = \beta = 120^{0}$ is put forth as chiral angles, the Young's modulus will be

$$\alpha = \beta = 120^{0}\,, \Pi = 0.0.174\,,\quad Y = 1026.2\,MPa$$

While the values of Young's moduli gained from distinct groups of bond angles are drawn in Fig. 9, it's evident that the differences between are noticeable and therefore can't be ignored.

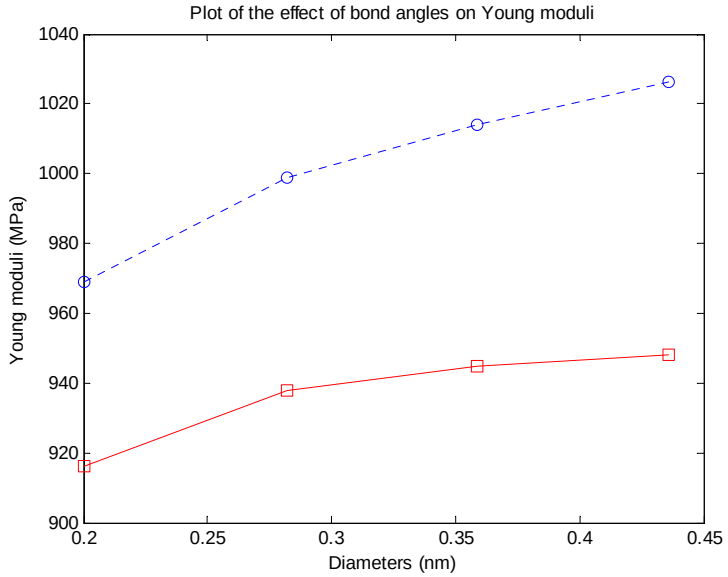

Fig. 9 The scheme of the effect of bond angles on Young's moduli in which blue represents the results calculated by $\alpha = \beta = 120^{0}$ *directly and red symbolizes those reckoned by* $\alpha \doteqdot \frac{2}{3}\pi$ *and* $\beta \doteqdot \pi - \cos^{-1}\left[\frac{\cos(\frac{\pi}{n+m})}{2}\right]$ *instead.*

4. Conclusions

Indeed, there were a large number of articles devoting themselves to the computation of Young's moduli for carbon nanotubes. This paper, nonetheless, is the first in which all the probable influential factors are in and thus the influence of them on the value for Young's modulus of "chiral" carbon nanotubes can be examined closely and stated clearly. Moreover, the closed-form expression derived here can be utilized to count the Young's moduli for carbon nanotubes being extremely small in diameter. Still, although the expression in this paper doesn't have its counterpart in the articles using ab-initio method for calculation to compare, the results reckoned by the expression fit perfectly well with the physical phenomenon, that is, the Young's modulus of

a smaller carbon nanotube should be lower to that of a larger one. Ultimately, when it comes to obtaining the precise quantities of Young's moduli, the bond angles $\alpha \fallingdotseq \frac{2}{3}\pi$ and $\beta \fallingdotseq \pi - \cos^{-1}\left[\frac{\cos(\frac{\pi}{n+m})}{2}\right]$ should be placed into the expression above to assure their accuracy.

Acknowledgments

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