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Influence of imperfections on carbon nanotube properties

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ABSTRACT

Theoretical and experimental research of polymer and other composites, up to now, have shown that carbon nanotubes as a reinforcement significantly improve the mechanical properties of aforementioned composites (Tserpes et al, 2008, Li & Chou, 2006), thanks to its extremely high tensile strength and modulus of elasticity. However, different defects within nanotube structure such as vacancy defects, or waved shape of the nanotube, can greatly influence the mechanical properties of carbon nanotube and thus, decrease the final mechanical properties of carbon nanotube reinforced composites (Motamedi et al, 2012, Farsadi et al, 2013). In this paper, the properties of straight and waved carbon nanotubes are investigated and compared using finite element method. Also, different vacancy defects are considered and presented on straight and waved carbon nanotubes, armchair and zig-zag pattern.

Keywords: carbon nanotube, waviness, vacancy defect

1. INTRODUCTION

After the paper presented by (Iijima, 1991), carbon nanotubes (CNTs) have attracted a lot of attention in many theoretical and experimental researches, with main goal primarily to find out their properties and characteristics. So far, common conclusion is that CNTs possess extraordinary mechanical, as well as thermal and electric properties. Because of that, they are, among other, a logical choice as a reinforcement in composite materials, either to improve mechanical properties of composite, due to their extremely high tensile strength and elasticity modulus (Tserpes et al, 2008), or to improve electrical conductivity (Murarescu et al, 2011). Due to their nano size, it is very difficult to conduct experimental studies, therefore the computer multiscale modelling and numerical methods emerges as a logical solution in investigating the properties of CNTs and nanocomposites. When considering numerical approaches, nanotubes have been modelled separately in two different systems of mechanics, molecular dynamics (Yakobson et al, 1997, Iijima et al, 1996, Chang & Gao, 2003, Liew et al, 2006, Zhang & Huang, 2008) and structural mechanics. Modelling in latter system is based on the substitution of covalent bonds between the atoms with nodes and beam finite elements (Brcic et al, 2009, Brcic et al., 2013, Brcic, Canadija & Brnic, 2013).

Initially, the researches of CNTs properties were conducted on ideal model of nanotube (Fisher et al, 2002, Fisher et al, 2003, Bradshaw et al, 2003, Charlier, 2002). But more detailed studies of CNTs revealed that CNTs rarely come in ideal form and without any defects. They are usually waved, regardless of the manner of production control Ebbesen & Takada, 1995, Shokrieh & Rafiee, 2010). Studies have shown that the waviness of the nanotube has an influence on the final mechanical properties of nanocomposite materials (Jiang et al, 2006, Tan et al, 2007, Qian et al, 2002).. Also, a common problem in nanotube structure is appearance of various vacancy defects (Shaffer & Windle, 1999, Vigolo et al, 2000), which can occur either naturally or artificially. Thus, it is very interesting to study the impact of defects and waviness of CNTs on their mechanical properties, specifically on the elastic modulus, since it eventually leads to decrease of final mechanical properties of nanocomposites. Change of elastic moduli of the CNTs is given in this paper, shown on straight and several waved CNTs, armchair and zig-zag pattern, with different vacancy defects.

2. IMPEREFECTIONS

2.1. Waviness

CNTs are basically a large molecule consisting of a carbon atoms, arranged in hexagonal mesh and rolled up to form a tube. Depending by the number of those tube-like structures, CNTs can be classified as single, double or multi walled CNTs, with length in order of micrometers and diameter in order of nanometers. Thus, CNTs aspect ratio (diameter/length ratio) is very high. Several experiments have shown that CNTS within nanocomposite are mainly waved (Shaffer & Windle, 1999, Vigolo et al, 2000). This can be explained with the already mentioned high aspect ratio of CNTs, which leads to very small bending stiffness, and waved shape of CNTs. In literature, the waviness of nanotubes is defined with the waviness ratio *w* (Farsadi et al, 2012):

$$w = \frac{a}{l}, \qquad (1)$$

where *a* represents wave amplitude and *l* wavelength, as shown in Figure 1.

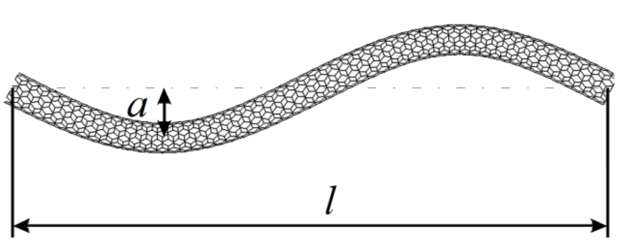

Figure 1 *Definition of the CNT waviness.*

2.2. Vacancies and 5-7-7-5 defects

Apart of waviness, the mechanical properties of CNTs are influenced by various defects within nanotube structure, which can occur either naturally or artificially. The defects can be classified in four different groups (Charlier, 2002, Ebbesen & Takada, 1995): topological, rehybridization (carbon atoms hybridizing between sp^2 and sp^3 hybrid orbitals), incomplete bonding defects (vacancies and dislocations) and doping with other atoms than carbon. Topological defects imply that instead of hexagons in nanotube structure, other mesh form like heptagons, pentagons can occur, or sometimes even triangles, octagons and similar. In this paper, focus will be on topological and incomplete bonding defects. As stated above, defects can occur naturally, but can also be introduced artificially. Some authors report that bending stiffness can increase due to presence of defects (Hou & Xiao, 2007), or can help to create interlayer bonds between carbon sheets (Banhart, 2004).

Experimental results (Ebbesen & Takada, 1995) have shown that topological 5-7-7-5 defects, or Stone – Wales (SW) defects, are commonly present in CNTs and randomly distributed, thus altering the elastic properties of CNTs. (Chandra et al., 2004) report that 5-7-7-5 defects significantly reduce the Elastic moduli of single walled CNT. 5-7-7-5 defects are composed from two pentagons and two heptagons, and are formed by rotating one carbon bond by 90°, Figure 2. The rotation of the bond leads to the elongation of the tube along the axis connecting the pentagons and shrinking of the tube in perpendicular direction, according to atomistic simulations. This defect is not thermodynamically stable at lower strains, so it rarely occurs naturally.

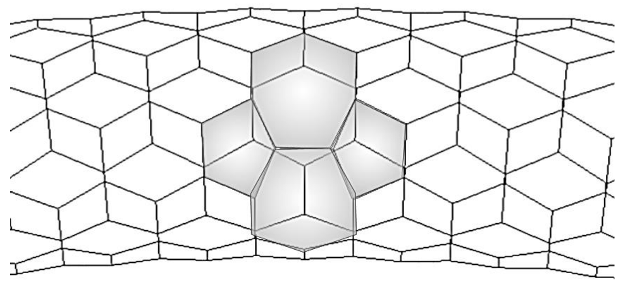

Figure 2 *Stone – Wales (5-7-7-5) defect in CNT structure.*

Incomplete bonding defects, or vacancies can appear, for example during a purification process or by irradiation. In ionic radiation, carbon atoms in CNT structure are “knocked out” from the hexagonal mesh, and thus leaving a dangling bonds and carbon atoms that are bonded to only two neighboring atoms, instead of three. This kind of configuration is known as unrelaxed configuration, and is not energetically stable, so often new bonds tend to appear and create pentagons in CNT structure (relaxed configuration). Authors (Sammalkorpi et al, 2004) report that relaxed CNT configuration obtains much higher tensile strength than an unrelaxed CNT configuration, supporting the fact that vacancy defect also affect the mechanical properties of CNTs.

3. CNT EXAMPLES

Influence of imperfections, i.e. waviness, 5-7-7-5 and vacancy defects, on elastic modulus of CNTs in this paper is shown on finite element model of single walled CNT, armchair (5,5) and zig-zag (9,0) pattern. The selected sizes of CNTs have similar diameter; armchair (5, 5) = 0,678 nm, zig-zag (9, 0) = 0,695 nm, and aspect ratio (length/diameter) around 20,2. The CNTs are modelled as a space frame structure, where the atoms are replaced by nodes, and covalent bonds with the beam finite elements (Brcic et al, 2009, Brcic et al., 2013, Brcic, Canadija & Brnic, 2013). There are

1130 nodes and 1685 beam elements in defect free armchair nanotube model, and 1188 nodes and 1773 beam finite elements in defect free zig-zag nanotube model. To determine the elastic modulus, an axially loaded nanotube model was used, with 1 nN axial force used in all examples. The longitudinal elastic modulus was obtained using classical term:

$$E = \frac{F \cdot l}{A \cdot \Delta l}, \qquad (2)$$

where l represents nanotube length (13,77 – 13,93 nm for armchair; 13,92 – 14 nm for zig-zag pattern), Δl the elongation calculated by finite element method.

Five models of CNTs have been prepared for each nanotube pattern, with different waviness ratio, according to (1), i.e. four waved nanotubes and one straight, as shown in Figure 3. To prepare the waved shape of the nanotube, eigenvalue analysis of a CNT was performed, with different eigenvalue parameters.

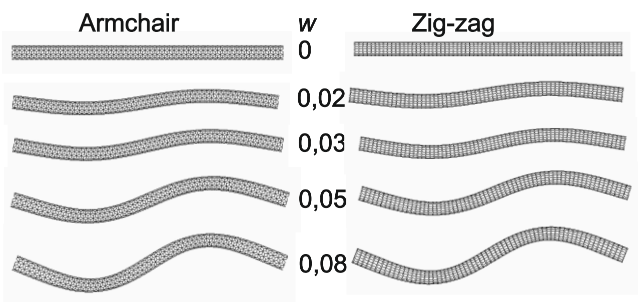

Figure 3 *Examples of waved CNTs.*

The first case studied in this paper was example with randomly selected percentage of missing atoms/nodes in CNTs, i.e. given percentage of nodes (0,1%, 0,5%, 1%, 2%, 5% and 10%) were removed from the nanotube structure. Vacancies are obtained by deleting one node and corresponding three beam elements from CNT structure. This was done for both patterns of CNTs, and for all waved shapes.

Since vacancies are one of the reason for CNT waviness, the second vacancy defects case was prepared and presented, in which 1 to 8 atoms were removed from the position with the maximum curvature at the internal side of the CNT, Figure 4. The remaining part of the CNT is defect free. This defect case was implemented only on armchair and zig-zag CNT with the waviness ratio 0,02.

The last vacancy defect case was 5-7-7-5 defects, which were created by rotating the corresponding beam element by 90° and scaled down to 75%, as suggested in the literature. The beam elements were redefined with the nodes at the new positions. The latter defect case was implemented on armchair and zig-zag nanotube with the waviness ratio 0,05, with 2, 4, 6, 8 and 10 of those 5-7-7-5 defect per each CNT, respectively.

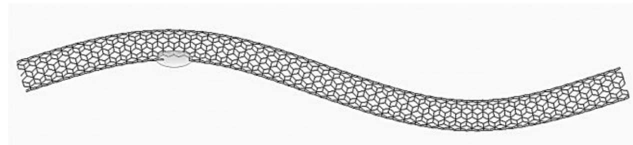

Figure 4 *Marked position of 1 to 8 vacancy defects in waved nanotube.*

4. RESULTS

Obtained results for longitudinal elastic modulus are given in following tables and figures, for corresponding vacancy case. As expected, there is a noticeable drop of longitudinal elastic modulus with the increase of the waviness ratio of the nanotube, regardless of the CNT pattern. Also, within the same waviness ratio of the CNT, the value of elastic modulus also decreases with the increase of the vacancies (from 0,1% to 10%), but is practically unaffected when percentage of defects is less than 1%. Obtained results for elastic modulus of defect free CNT, both armchair and zig-zag pattern, 1048 GPa and 1030 GPa respectively, coincide well with the result given in the literature (Chandra et al., 2004, Kalamkarov et al, 2006).

Results for second vacancy case, when 1 to 8 nodes were removed from the position with the maximum curvature at the internal side of CNT, are depicted in Figure 5. Decrease of the elastic modulus with the increase of the number of removed nodes is noticeable. Similar trend, i.e. elastic modulus decrease with the increase of the defects number, is visible for third vacancy (5-7-7-5) case, Figure 6.

Table 1 Results for first vacancy case, armchair nanotube

Longitudinal elastic modulus *E*, GPa (Armchair nanotube)					
	Waviness ratio, *w*:				
Vacancy %:	0	0,02	0,03	0,05	0,08
No defects	1048,76	526,22	341,58	135,09	74,27
0,1%	1008,82	526,38	335,58	132,74	72,96
0,5%	979,79	511,43	316,59	127,16	71,98
1%	667,74	456,06	313,61	126,50	69,89
2%	796,56	434,06	285,31	117,67	60,25
5%	662,10	331,67	219,99	76,94	47,99
10%	146,87	57,89	74,42	59,98	13,91

Table 2 Results for first vacancy case, zig-zag nanotube

Longitudinal elastic modulus *E*, GPa (Zig-zag nanotube)					
	Waviness ratio, *w*:				
Vacancy %:	0	0,02	0,03	0,05	0,08
No defects	1030,99	533,16	349,11	139,97	77,45
0,1%	987,36	533,14	342,38	138,77	73,05
0,5%	918,42	523,70	328,33	129,49	74,78
1%	848,07	516,36	310,91	124,27	73,59
2%	818,34	421,74	299,12	97,38	56,66
5%	446,47	246,32	87,64	103,91	47,93
10%	282,99	88,98	60,26	36,85	18,77

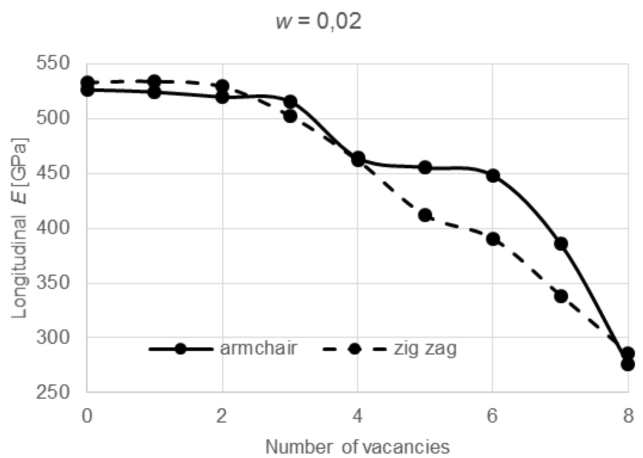

Figure 5 *Results for second vacancy case, for 1 to 8 vacancies.*

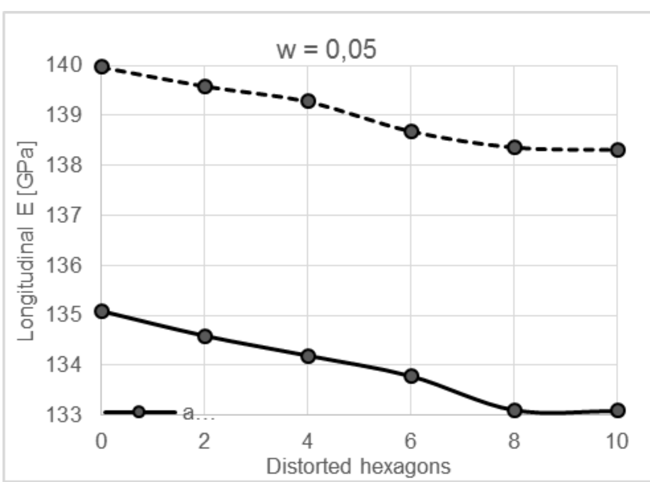

Figure 6 *The dependence of longitudinal modulus on 5-7-7-5 type of defects.*

5. CONCLUSIONS

The influence of the various imperfections of the carbon nanotubes on basic mechanical properties, i.e. longitudinal elastic modulus, is shown and analysed in this paper, on finite element model of armchair and zig-zag CNTs, with different waviness ratio and various vacancy defects. Common conclusion is that CNTs are quality choice as a reinforcement in the nanocomposite materials, due to their excellent mechanical properties, but as it is shown, various defects and geometrical characteristics can affect their mechanical properties. The longitudinal elastic modulus of carbon nanotube decreases with the increase of the waviness ratio, which is most pronounced in the nanotubes without defects (armchair from 1048 GPa to 74 GPa, 93%; zig-zag from 1030 GPa to 77 GPa, 92,5%). Decrease of the elastic modulus is noticeable from Tables 1 and 2, with the increase of the vacancies in the nanotubes with the same waviness ratio. That decrease is more pronounced as the waviness ratio increases. Some irregularities in values of elastic modulus in Tables 1 and 2 can be attributed to randomly positioned vacancies in each particular analysis.

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