Imperfections in carbon nanotubes structure and their impact on the basic mechanical properties

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Abstract. Theoretical and experimental research of nanocomposite materials have shown that usage of carbon nanotubes as a reinforcement, significantly improves the mechanical properties of aforementioned composites. Carbon nanotubes rarely appear in ideal form. 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. The paper at hand investigates degradation of basic mechanical properties of single and double walled carbon nanotubes, straight and waved, with different vacancy and topological defects. Also, various nanotube patterns are considered.

1. Introduction
Very soon after the landmark paper of Iijima in 1991 [1], carbon nanotubes (CNTs) attracted considerable research attention in many theoretical and experimental researches, with main goal to find out their properties and characteristics. Common conclusion, so far, is that CNTs possess extraordinary mechanical, thermal and electrical properties. Those facts make them a logical choice as a reinforcement in composite material, either to improve mechanical properties of composites [2], or to improve electrical conductivity [3]. Due to their size, computer modelling and numerical methods are logical solution for investigating the mechanical properties of CNTs and nanocomposite materials. One of the numerical approaches is based on structural mechanics, where covalent bonds between atoms in nanotube structure are replaced with finite elements and nodes [4, 5, 6]. Initially, research on CNTs was directed toward determination of mechanical properties of ideally shaped CNTs [7, 8, 9], but more careful research detected that single walled (SWNT) and multiwalled (MWNT) carbon nanotubes rarely come in ideal form and without defects. Regardless of the manner of production control and methods, CNTs are usually waved [10, 11], and studies have shown that the waviness of the nanotube has an influence on the final mechanical properties of CNTs and, thus, nanocomposite materials [12, 13, 14]. Another common problem in nanotube structure is appearance of various defects [15, 16, 17], which can occur either naturally or artificially. All of the aforementioned leads to the necessity for detailed study of the impact of defects and waviness of CNTs on their mechanical properties, specifically on basic mechanical properties like elastic modulus, since it eventually leads to the decrease of final mechanical properties of the nanocomposites. The paper at hand investigates the change of longitudinal elastic moduli of SWNT and DWNT, both straight and waved, with different defects. Different pattern of CNTs are considered, i.e. armchair, zig-zag and combined chiral pattern.
2. Imperfections (waviness, vacancies and defects)

CNTs can be classified as SWNT, double (DWNT) or MWNTs. Their aspect ratio (diameter/length ratio) is very high, with diameter in order of nanometers and length in micrometers. High aspect ratio leads to waved shape of CNTs, which is experimentally proved [15, 16], and to small bending stiffness. Waviness of CNTs is in literature defined with the waviness ratio \( w = a / l \) [18], where \( a \) represents wave amplitude and \( l \) wavelength. Mechanical properties of CNTs are influenced not only by waviness but also by various defects within nanotube structure. Those defects can occur either naturally or artificially. Mainly, defects can be classified in four different groups [10, 19]: topological, rehybridization, incomplete bonding defects and doping with other atoms than carbon. Topological defects imply that instead of hexagons in CNT structure, other mesh form can occur (heptagons, pentagons and similar). Focus in this paper will be on topological and incomplete bonding defects (vacancies or “missing” atoms). Research, experimental and theoretical [10, 17], have shown that topological Stone-Wales (SW) or 5-7-7-5 defects, are commonly present in CNTs and randomly distributed, thus altering the elastic properties of CNTs. SW defects are composed from two pentagons and two heptagons. This defect is formed by rotating one carbon bond by 90°. Defects classified as incomplete bonding defects, vacancies, can occur in CNTs structure for example during a purification process or by irradiation.

3. Nanotube examples

Several different CNT models, single and double walled, have been prepared in this paper. Influence of imperfections is shown on FEM model of following nanotube models: SWNT, armchair (5, 5) and zig-zag (9, 0) pattern; DWNT, armchair (4,4/9,9), zig-zag (7,0/16,0), chiral A (4,4/16,0), chiral B (7,0/9,9) patterns. Chiral A pattern denotes a DWNT with inner armchair tube and outer zig-zag, and accordingly, chiral B denotes a DWNT with inner zig-zag tube, and outer armchair. The selected SWNTs have similar diameter (0,678nm – 0,695nm) and aspect ratio (20,2). The same goes for DWNTs, similar inner (0,535nm – 0,54nm) and outer (1,20nm – 1,23nm) diameter and aspect ratio (20,1). All CNTs are modelled as a space frame structure, where atoms are replaced by nodes, and covalent bonds with the beam finite elements [4, 5, 6]. In DWNTs, van der Waals (VDW) interactions are formed between atoms in inner and outer tube. Those VDW interactions between two different DWNT layers were modelled with rod finite elements, with properties adjusted to match the forces which originate from Lennard – Jones potential. 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 \( E = (F/l/A \Delta l) \), where \( l \) represents nanotube length and \( \Delta l \) the elongation obtained from FEM analysis. The number of finite elements rises from around 2350 elements in single SWNT model to 355000 elements in DWNT model, due to the VDW interactions. Five models have been prepared for each SWNT pattern, with different waviness ratio, i.e. four waved and one straight, and three models for each DWNT pattern (one straight and two waved), as shown in figure 1.

![Figure 1. Examples of waved SWNTs (a) and DWNTs (b).](image-url)
In the first defect case studied in this paper, randomly selected percentage of missing atoms (0.1%, 0.5%, 1%, 2%, 5%, 10%) were removed from CNTs structure. Vacancies are obtained by deleting one node and corresponding three beam elements from CNT structure. That was done for both, SWNTs and DWNTs, for each shape. In the second studied case, 5-7-7-5 (SW) defects were implemented into CNTs structure, with 2, 4, 6, 8 and 10 of those defects in each SWNT and the same amount of SW defects in DWNT, but in inner and outer layer altogether. The second case was implemented on armchair and zig-zag SWNT, with waviness ratio 0.05, and on all patterns of DWNT, with waviness ratio 0.029.

4. Results

Results for longitudinal elastic modulus obtained from aforementioned examples are given in following tables and figures. Tables 1 to 3 show the results for the first vacancy case, for armchair and zig-zag SWNT, armchair and zig-zag DWNT, chiral A and chiral B DWNT, respectively. 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 type and pattern. The value of elastic modulus also decreases with the increase of the vacancies within the same waviness ratio of the CNT, but is practically unaffected when percentage of defects is less than 1%. Results for elastic modulus of defect free SWNT, both patterns, table 1, as well as for DWNT, table 2, coincide well with the results given in the literature [20, 21, 22]. When it comes to SW defects, a decrease of elastic modulus values can be noticed for both, SWNTs and DWNTs, but that decrease is not as drastic as in vacancy case, figure 2.

Table 1. Results for first vacancy case, armchair and zig-zag SWNT

| Vacancy %: | Waviness ratio, w (armchair): | Waviness ratio, w (zig-zag): |
|------------|-------------------------------|-------------------------------|
|            | 0,02 | 0,03 | 0,05 | 0,08 | 0     | 0,02 | 0,03 | 0,05 | 0,08 |
| No defects | 1048,76 | 526,22 | 341,58 | 135,09 | 74,27 | 1030,99 | 533,16 | 349,11 | 139,97 | 77,45 |
| 0,1%       | 1008,82 | 526,38 | 335,58 | 132,74 | 72,96 | 987,36 | 533,14 | 342,38 | 138,77 | 73,05 |
| 0,5%       | 979,79 | 511,43 | 316,59 | 127,16 | 71,98 | 918,42 | 523,70 | 328,33 | 129,49 | 74,78 |
| 1%         | 667,74 | 456,06 | 313,61 | 126,50 | 69,89 | 848,07 | 516,36 | 310,91 | 124,27 | 73,59 |
| 2%         | 796,56 | 434,06 | 285,31 | 117,67 | 60,25 | 818,34 | 421,74 | 299,12 | 97,38 | 56,66 |
| 5%         | 662,10 | 331,67 | 219,99 | 76,94 | 47,99 | 446,47 | 246,32 | 87,64 | 103,91 | 47,93 |
| 10%        | 146,87 | 57,89 | 74,42 | 59,98 | 13,91 | 282,99 | 88,98 | 60,26 | 36,85 | 18,77 |

Table 2. Results for first vacancy case, armchair and zig-zag DWNT

| Vacancy %: | Waviness ratio, w (armchair): | Waviness ratio, w (zig-zag): |
|------------|-------------------------------|-------------------------------|
|            | 0,02 | 0,03 | 0,05 | 0,08 | 0,02 | 0,03 | 0,05 | 0,08 |
| No defects | 1111,82 | 355,06 | 55,57 | 1104,17 | 381,76 | 58,93 |
| 0,1%       | 1098,17 | 348,81 | 54,70 | 1080,36 | 373,29 | 58,75 |
| 0,5%       | 1067,27 | 344,32 | 53,43 | 1047,19 | 374,03 | 57,57 |
| 1%         | 982,84 | 335,69 | 49,47 | 1007,07 | 381,49 | 51,64 |
| 2%         | 856,31 | 314,64 | 47,48 | 886,28 | 341,62 | 47,95 |
| 5%         | 599,24 | 209,10 | 33,94 | 676,09 | 259,06 | 40,57 |
| 10%        | 404,66 | 140,67 | 22,98 | 377,76 | 185,33 | 21,15 |
Table 3. Results for first vacancy case, Chiral A and Chiral B DWNT

| Vacancy %:          | Longitudinal elastic modulus $E$, GPa | Waviness ratio, $w$ (Chiral A): | Waviness ratio, $w$ (Chiral B): |
|---------------------|---------------------------------------|---------------------------------|---------------------------------|
|                     |                                       | 0                               | 0.029                           | 0.086                           |
| No defects          |                                       | 1150.27                         | 362.87                          | 60.69                           |
| 0.1%                |                                       | 1100.68                         | 360.06                          | 60.54                           |
| 0.5%                |                                       | 1065.38                         | 351.03                          | 58.46                           |
| 1%                  |                                       | 1059.48                         | 325.77                          | 57.03                           |
| 2%                  |                                       | 893.37                          | 279.15                          | 56.43                           |
| 5%                  |                                       | 667.07                          | 257.85                          | 45.19                           |
| 10%                 |                                       | 393.66                          | 156.01                          | 22.96                           |

Figure 2. The dependence of longitudinal modulus on SW defects, SWNTs(a) and DWNTs (b).

5. Conclusions
The impact of the various imperfections within carbon nanotube structure on the basic mechanical properties of CNTs is shown and analysed in this paper, on FEM model of armchair and zig-zag SWNT and four patterns of DWNT. Also, this was done on CNTs with different waviness ratio. Final conclusion is that CNTs possess excellent mechanical properties, and are quality choice as a reinforcement in the nanocomposite materials, but as it is shown, various defects and geometrical characteristics can affect their properties, and thus decrease the final mechanical properties of nanocomposite. The effect of SW defects is lesser when compared to vacancies. Future research will be focused on theoretical modelling of nanocomposite materials, reinforced with SWNTs and DWNTs, based on FEM, to study the impact of nanotubes imperfections on nanocomposite mechanical properties. Also, the experimental research of nanocomposite materials is planned, to confirm the theoretical results and conclusions.

6. Acknowledgments
This work has been financially supported by the University of Rijeka under the project no. 16.09.2.1.03 and by Croatian Science Foundation under the project no. 6876. This support is gratefully acknowledged.

7. References
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