We study the effects of covalent functionalization of single wall carbon nanotubes (CNTs) on their elastic properties. We consider simple organic molecules -NH, -NH₂, -CH₂, -CH₃, -OH attached to CNTs’ surface at various densities. The studies are based on the first principles calculations in the framework of density functional theory. We have determined the changes in the geometry and the elastic moduli of the functionalized CNTs as a function of the density of adsorbed molecules. It turns out that elastic moduli diminish with increasing concentration of adsorbents, however, the functionalized CNTs remain strong enough to be suitable for reinforcement of composites. The strongest effect is observed for CNTs functionalized with -CH₂ radical, where the Young’s modulus of the functionalized system is by 30% smaller than in the pristine CNTs.

The paper is organized as follows. In Section 2, we present calculation details. The results of the calculations are described and discussed in the third section - 'Results and discussion'. Here we present: (i) how the functionalization procedure changes the equilibrium geometry of the functionalized systems, (ii) how the elastic moduli of the covalently functionalized CNTs deviate from the elastic moduli of the pristine ones, and (iii) how these deviations depend on the concentration of the functionalizing molecules. Finally, the paper is concluded in section 'Conclusions'. We consider three types of CNTs: nominally metallic (9,0), and semiconducting (10,0) and (11,0). All of the CNTs have been covalently functionalized by attaching to their lateral surface simple organic groups, such as -NH, -NH₂, -CH₂, -CH₃, and -OH. We examine those systems at various concentrations reaching up to 4.6·10¹⁴ adsorbed molecules per cm² of CNT’s surface (see Fig. 1). However, in the present paper, we follow the convention of the other authors and measure the concentration of the adsorbents as the number of attached molecules nₐ per doubled unit cell of pristine CNTs, i.e., nₐ = A/2πR², where A is the area of the unit cell, nₐ is the number of carbon atoms in the doubled unit cell, nₐcell is the number of carbon atoms in the doubled unit cell, and R is the radius of the CNT. To facilitate comparison between different CNTs, we express also the concentration of the adsorbents as nₐ/nₐcell·100%. We have considered all possible positions of the adsorbed fragments and determined these positions that lead to the minimum of the total energy of the functionalized CNTs 11, i.e., the equilibrium geometry. Only these positions are depicted in Fig. 1.
The total energies and components of stress tensor are obtained from the ab initio calculations in the framework of the density functional theory\textsuperscript{13,14,16,20,21,41} employing the following realization. We use the generalized gradient approximation (GGA) for the exchange-correlation density functional\textsuperscript{42} and supercell geometry within the numerical package SIESTA\textsuperscript{35,36}. Since in many cases we have to do with system with odd number of electrons, we employ spin-polarized version of the GGA functional. A kinetic energy cut-off (parameter MeshCutoff in the SIESTA code) of 300 Ry and split double zeta basis set with spin polarization have been used in all calculations. Each supercell contains two primitive unit cells along the CNT symmetry axis. The lateral separation (i.e., lateral lattice constants in the direction perpendicular to the symmetry axis) has been set to 30 Å, just to eliminate completely the spurious interaction between neighboring cells. We use the self-consistency mixing rate of 0.1, the convergence criterion for the density matrix of 10\textsuperscript{-5}, the basis set superposition error (BSSE) correction following the well established procedure\textsuperscript{38–40}.

Having determined equilibrium geometry of the functionalized CNTs, we are in the position to calculate their elastic moduli. To do so, we strain (usually we apply tensile strain) the functionalized CNTs along the symmetry axis by \( \Delta l \) and calculate the response. The most interesting quantity, Young’s modulus, has been determined in two ways:

(i) - by comparing the total energy of unstrained (\( E_l \)) and strained (\( E_{l+\Delta l} \)) systems

\[
Y = \frac{V_o}{l} \frac{\partial^2 E_{\text{strain}}}{\partial \varepsilon_{ii}^2}, \quad E_{\text{strain}} = E_{l+\Delta l} - E_l, \quad \varepsilon_{ii} = \frac{\Delta l}{l},
\]

where \( l \) is a lattice constant along the axis of the functionalized tube, \( \Delta l \) is elongation in the chosen direction, and \( V_o \) is volume of the unstressed system, and (ii) from components (\( \sigma_{ii} \)) of the stress tensor \( Y = \sigma_{ii}/\varepsilon_{ii} \). Volume of the pure CNT has been calculated using following relation \( V_o = 2 \cdot \pi \cdot r \cdot l \cdot t \), where thickness \( t \) has been chosen as double Van der Waals radius of C atom (equal to 0.34 nm)\textsuperscript{13,14,16,20,21,41}. In the case of functionalized CNT, we neglect volume of the attached molecules.
Bulk modulus and Shear modulus have been also calculated according to the formulas:

\[
K = \frac{Y}{3(1-2\nu)}, \quad G = \frac{Y}{2(1+\nu)}, \quad (3)
\]

We have also calculated the BBSE corrections to the elastic moduli. These corrections modify the values of Young’s moduli by maximally 10% and do not change the conclusion presented in this article.

At the end, we can compute the Poisson ratio values as follows \( \nu = -((\Delta r/r)/(\Delta l)) \), where \( \Delta r \) describes the change of the average radius of the functionalized CNT that has been caused by the applied strain \( \Delta l \).

II. RESULTS AND DISCUSSION

A. Influence of functionalization on the structure

We have studied the stability and electronic structure of covalently functionalized CNTs in previous works\(^8\)–\(^11\). We have also shown there how the functionalization induces changes in morphology of the functionalized systems and leads to the redistribution of electronic charge. All of the functionalizing fragments considered in the present study induce rehybridization from \( \text{sp}^2 \) to \( \text{sp}^3 \) of C-C bonds in neighborhood of the attachment, but in many cases we have found out that some of the adsorbed molecules also cause stronger deformation of CNT backbone structure. These pronounced changes in the morphology of the functionalized CNTs we observed motivated us to study the global strength of the functionalized CNTs expressed by the elastic moduli. Before we turn to the discussion of the elastic properties, we would like to present shortly the stability of the functionalized CNTs, and the change of geometry (lattice constant and radius) caused by the functionalization.

The adsorption energy (per adsorbed molecule) for all considered functionalizing molecules is shown in Fig. 2 for the prototypical metallic (9,0) CNT. It is seen that all the considered molecules bind to the surface of the (9,0) CNT (i.e., the adsorption energy is negative). However, the strength of the bonding is larger for typical radicals (-NH and -\( \text{CH}_2 \)) than for the non-radicals (-NH\(_2\), -CH\(_3\), and -OH). This we would like to correlate with the induced changes of geometry and elastic moduli later on. As can be seen in Fig. 2, generally, the adsorption energy per molecule remains nearly constant with increasing number of attached molecules. Only for the strong radical -NH, the adsorption energy per molecule gets less negative (indicating that the bonding weakens) with increasing number of attached fragments. This trend obeys also for semiconducting (10,0) and (11,0) CNTs, as it has been illustrated for -\( \text{CH}_2 \) and -OH adsorbents in Fig. 3. At least for these rather similar in diameter CNTs and considered concentration of the adsorbed molecules, the adsorption energy depends rather weakly on the metallic or semiconducting character of the functionalized CNTs and their radius. The functionalization changes the parameters characterizing the backbone of the functionalized CNTs, the longitudinal lattice constant \( l \) and radius \( r \). Longitudinal lattice constants and radii of the functionalized CNTs are larger than of pristine ones and change rather strongly with the number of attached molecules. It is depicted for the (9,0) CNT in Figs. 4 and 5. For example, radius and lattice constant of pure (9,0) CNT equals to 3.592 Å and 8.590 Å, respectively. For (9,0) CNT functionalized with 9 -\( \text{CH}_2 \) molecules per unit cell, the radius increases to 3.715 Å (by 3.31%) and the lattice constant reaches 8.726 Å (increase by 1.58%).

Generally, one can say that functionalization of (9,0) CNT acts as an effective tensile strain, which blows up pristine CNT. The effect is more pronounced for molecules that built strong covalent bonds to the CNT walls. The largest changes of the lattice constant \( l \) and...
FIG. 4. (color online) The equilibrium lattice constant (l) along symmetry axis of the functionalized nanotubes as a function of the number of covalently bound fragments to the sidewall of (9,0) CNTs for -NH, -NH$_2$, -CH$_2$, -CH$_3$, and -OH functionalizing molecules. Top axis gives the concentrations of adsorbed molecules in %.

radius r have been observed for CNT functionalized with -CH$_2$ radicals. For maximal considered concentration of 12.5%, the relative changes of l and r in comparison to the length and radius of the pristine CNTs are equal to 1.56% and 3.31%, respectively. This effect is much weaker for -CH$_3$ functionalized CNT, where percentage change of l is equal to 0.34%, whereas the change of r equals 0.92%.

The relative changes in the l and r parameters induced by functionalization depend rather slowly on metallic-semiconducting character of CNTs and their diameter. The radius of (9,0), (10,0), and (11,0) CNTs functionalized with -CH$_2$ and -OH molecules as a function of number of covalently bound fragments to sidewall of the tube. Top axis gives the concentrations of adsorbed molecules in %.

FIG. 6. (color online) Radius of (9,0), (10,0), and (11,0) CNTs functionalized with -CH$_2$ and -OH as a function of the number of attached fragments per supercell. Since (9,0), (10,0), and (11,0) CNTs contain different number of atoms in the supercell, the percentage concentrations of the attached fragments are also depicted above top axes of each panel for better comparison.

tions can lead to some local structural defects (so-called 5-7 defects). On the other hand, the functionalization with -OH groups slightly changes the cross-section of CNT—from circle to ellipse. Therefore, we have decided to compare (see Fig. 4) both types of attachments for all of the CNTs studied: (9,0), (10,0) and (11,0).

We have noticed, for the biggest considered concentration of 12.5%, that (9,0) CNT functionalized with -CH$_2$ shows the biggest percentage change (3.31%) of radius in comparison to (10,0) and (11,0) CNTs (where percentage changes are equal to 2.83% and 1.81%, respectively). The -OH groups follow the similar trend, however, the functionalization induced changes of the radius are weaker. The relative changes of the radius are 0.64%, 0.43% and 0.39%, for (9,0), (10,0) and (11,0) CNT, respectively. Therefore, one can say that the functionalization of the nanotubes with larger original radius has less influence on its structure than functionalization of CNTs with smaller diameter.

Having described the equilibrium geometry of the functionalized CNTs, we are now in the position to discuss their elastic properties.

B. Elastic properties of pure CNT

Before we turn to the elastic moduli of the functionalized CNTs, we would like to present our results for pristine (9,0), (10,0), and (11,0) ones. This allows for comparison with previous works and provides the reference to the case with functionalization.

Young’s, Shear, and Bulk moduli, and also Poisson’s ratios for (9,0), (10,0) and (11,0) pristine CNTs are gathered in Tab. 1. The calculated Young’s moduli of the pure CNT compare excellently to experimental findings (0.32-
TABLE I. Elastic moduli and Poisson’s ratio of (9,0), (10,0), and (11,0) pristine CNTs.

| Property | (9,0) | (10,0) | (11,0) |
|----------|-------|-------|-------|
| Y (TPa)  | 1.02  | 1.03  | 1.02  |
| K (TPa)  | 0.61  | 0.57  | 0.54  |
| G (TPa)  | 0.41  | 0.43  | 0.43  |
| ν        | 0.22  | 0.20  | 0.18  |

1.80 TPa and previous theoretical works (0.8-1.5 TPa). Calculated Poisson’s ratios are identical to the experimental ones and also very close to previous theoretical predictions (0.19-0.34). Also calculated values of the Shear and Bulk moduli agree fairly well with previously obtained theoretical and experimental values, lying in the range of 0.45-0.58 TPa and 0.50-0.78 TPa, respectively.

We have also calculated the elastic properties for wider range of zigzag pristine CNTs. Only for small CNTs, like (4,0) and (5,0) all the values of elastic moduli are smaller. For larger in diameter CNTs, up to (20,0), the values are very similar to those shown in Tab. I. Starting from (6,0) CNT, all of the elastic moduli seem to be rather weakly dependent on the diameter of CNT. Such behavior of Young’s as well as Shear modulus has been noticed in previous studies for Young’s and Shear moduli.

C. Elastic properties of functionalized CNT

Let us now present theoretical predictions for elastic moduli of the functionalized CNTs. We start the presentation of our results with Young’s modulus of the (9,0) CNT functionalized with -NH, -NH₂, -CH₂, -CH₃, and -OH groups (Fig. 7). For all considered groups, the Young’s modulus decreases with increasing density of the attachments. However, for the radicals, -CH₂ and -NH, the trend is much more pronounced than for other groups. For CNTs functionalized with 9 -CH₂ (i.e., concentration of 12.5%), the Young’s modulus decreases by 28.41%, whereas CNT with 9 functionalizing -CH₃ groups exhibits reduction in the Young’s modulus equal to 13.52%. It confirms the already described tendency that the molecules with stronger binding to the CNT’s surface modify the properties of the functionalized CNTs in a stronger manner.

For the purpose of comparison how the Young’s modulus depends on diameter of the tubes, we have chosen -OH groups and -CH₂ fragments as examples. In Fig. 8, we plot the dependence of Young’s modulus for (9,0), (10,0) and (11,0) CNTs functionalized with -OH and -CH₂ fragments as a function of the density of attached molecules. One can only weakly differentiate between the types of the functionalized nanotubes.

Our calculations show that Poisson ratio for structures functionalized by all considered fragments always oscillates between values 0.17 and 0.24. This quantity, for the studied range of the adsorbent concentrations, neither exhibits clear dependencies on the type of functionalizing molecules nor allows for resolution between (9,0), (10,0), and (11,0) CNTs.

We complete the discussion of the elastic moduli for functionalized CNTs with the presentation of results for Shear and Bulk moduli, the magnitude of which can be easily calculated from Young’s modulus and Poisson ratio employing formulas.

The Shear modulus as a function of the concentration...
of attached molecules is depicted in Fig. 9. Generally, the Shear modulus drops with the increasing density of the attached molecules. This decrease is stronger for \(-\text{CH}_2\) radical than for non-radical groups such as \(-\text{OH}\). For the highest considered concentration of the \(-\text{CH}_2\) radicals, the Shear modulus is smaller by roughly 25\%, and even for the non-radical functionalizing groups the decrease is of the order of 10\%. Therefore, our studies do not corroborate Frankland’s\(^{42}\) suggestion that functionalization has tiny influence on Shear modulus (less than 4.63 \%).

The Bulk modulus as a function of the concentration of attached molecules is shown in Fig. 10. The Bulk modulus behaves similarly to other elastic moduli and decreases with the growing concentration of functionalizing molecules, with the strongest effect observed for functionalization with \(-\text{CH}_2\) radical.

Generally, our studies provide theoretical predictions for the elastic moduli of the covalently functionalized CNTs. These moduli diminish with the concentration of the functionalizing molecules. In the situation of the lack of experimental data, the obtained values should facilitate the understanding and design of the composite materials. First of all, the decrease of elastic moduli is quite modest, particularly for non-radical \(-\text{OH}\), \(-\text{NH}_2\), \(-\text{CH}_3\) groups. Therefore, the functionalized CNTs should still be good reinforcement in composites employing polymers or metals as matrices. On the other hand, the functionalization of CNTs is necessary to bind CNTs to polymer matrix and significantly improves homogeneous dispersion and integration of CNTs into polymers, simultaneously reducing the tendency of pristine CNTs to re-agglomeration. This feature substantially enhances elastic strength of polymer matrices with incorporated CNTs. This effect has been confirmed in a series of experiments studying the Young’s modulus of composites with

III. CONCLUSIONS

We have performed extensive and systematic \textit{ab initio} studies of the elastic properties of the (9,0), (10,0), and (11,0) CNTs functionalized with \(-\text{NH}\), \(-\text{NH}_2\), \(-\text{CH}_2\), \(-\text{CH}_3\), \(-\text{OH}\) molecules covalently bound to the CNT walls at concentrations reaching up to \(4.6\times10^{14}\) molecules per cm\(^2\). Our studies provide valuable theoretical quantitative predictions for elastic moduli (Young’s, Shear, Bulk moduli, and Poisson ratio) of functionalized CNTs, demonstrate clear chemical trends in the elastic moduli, and shed light on physical mechanisms governing these trends. These results are of importance for design of composite materials employing carbon nanotubes.

We have shown that considered molecules form covalent bonds to the CNT surfaces and cause local and global changes in the morphology of the CNT that are generally proportional to the density of the attached molecules. The local deformations include rehybridization of the C-C bonds and defects that influence strength of the functionalized systems. Functionalization of CNTs causes expansion of the functionalized CNTs, i.e., increase of longitudinal lattice constant and radius in comparison to the pristine CNTs. This expansion is proportional to...
the density of the adsorbed molecules. We observe general trend that the molecules forming the stronger bonds to CNTs cause larger deformations of the functionalized systems (i.e., the larger changes of the lattice constants \(l\) and radii \(r\)) and larger reduction of the elastic moduli (Young’s, Shear, and Bulk). All moduli decrease with concentration of the adsorbed molecules. As far as the Young’s, Shear, and Bulk moduli reflect changes in the CNT morphology caused by functionalization, the Poisson’s ratio remains almost unchanged. In a few cases when comparison with experimental or other theoretical studies is possible, we observe reasonable agreement with results of our calculations. In spite of the fact that the functionalization diminishes elastic moduli of CNTs and this effect generally cannot be neglected, the elastic moduli remain large enough to guarantee successful employment of functionalized CNTs for reinforcement of composite materials.

IV. ACKNOWLEDGEMENT

The authors gratefully acknowledge financial support of the Polish Council for Science through the Development Grants for the years 2008-2011 (NR. 15-0011-04/2008, NR. KB/72/13447/TT1-B/U/08) and the SiCMAT Project financed under the European Founds for Regional Development (Contract No.UDA-POIG.01.03.01-14-155/09). We thank also PL-Grid Infrastructure and Interdisciplinary Centre for Mathematical and Computational Modeling of University of Warsaw (Grant No. G47-5) for providing computer facilities.

1. S. Iijima, Nature 354, 56 (1991).
2. M. Terrones, Annu. Rev. Mater. Res. 33, 419 (2003).
3. W. A. Goddard, III, D. W. Brenner, S. E. Lyshchinski, and G. J. Iafrate, *Handbook of Nanoscience, Engineering, and Technology (Electrical Engineering Handbook)* (RC Press LLC, 2003).
4. I. T. Amr, A. Al-Amr, S. T. P, M. Al-Harthti, S. A. Girei, R. Sougrat, and M. A. Ateh, Composites: Part B 42, 1554 (2011).
5. S. Steiner, S. Busato, and P. Ermanni, Carbon 50 (2012).
6. N. Lachman and H. D. Wagner, Composites: Part A 41, 1093 (2010).
7. F. H. Gojny, M. H. G. Wichmann, B. Fiedler, and K. Schulte, Composites Science and Technology 65, 2300 (2005).
8. K. Z. Milowska, M. Birowska, and J. A. Majewski, Acta Physica Polonica A 116, 841 (2009).
9. K. Z. Milowska, M. Birowska, and J. A. Majewski, AIP Conf. Proc. 1399, 827 (2011).
10. K. Z. Milowska, M. Birowska, and J. A. Majewski, Diamond and Related Materials 23, 167 (2012).
11. K. Z. Milowska and J. A. Majewski, J. Chem. Phys. 138, 194704 (2013).
12. G. V. Lier, C. V. Alseno, V. V. Doren, and P. Geerlings, Chem. Phys. Lett. 326, 181 (2000).
13. C. Li and T.-W. Chou, International Journal of Solids and Structures 40, 1517 (2003).
14. E. Hernandez, C. Goze, P. Bernier, and A. Rubio, Phys. Rev. Lett. 80, 4502 (1998).
15. S. Govindjee and J. L. Sackman, Solid State Communications 110, 227 (1999).
16. T. Chang, J. Geng, and X. Guo, Proc. R. Soc A 462, 2523 (2006).
17. N. Yao and V. Lordi, J. App. Phys. 84, 1939 (1998).
18. Z. Xin, Z. Jianjun, and O.-Y. Zhong-can, Phys. Rev B 62, 13692 (2000).
19. K. N. Kudin and G. E. Scuseria, Phys. Rev B 64, 235406 (2001).
20. D. Sanchez-Portal, E. Artacho, and J. M. Soler, Phys. Rev B 59, 12678 (1999).
21. J. P. Lu, Phys. Rev. Lett. 79, 1297 (1997).
22. V. N. Popov, V. E. V. Doren, and M. Balkanski, Phys. Rev. B 61, 3078 (2000).
23. A. Krishnan, E. Dujardin, T. W. Ebbesen, P. N. Yianilos, and M. M. J. Treacy, Phys. Rev. B 58, 14013 (1998).
24. M. M. Shokrieh and R. Rafiee, Materials and Design. 31, 790 (2010).
25. F. Li, Y. Xia, M. Zhao, X. Liu, B. Huang, Z. Tan, and Y. Ji, Phys. Rev. B 69, 165415 (2004).
26. O. V. Pupysheva, A. A. Farajian, H. Nejo, H. Mizuseki, and Y. Kawazoe, Thin Solid Films 499, 256 (2006).
27. M. M. Shokrieh and R. Rafiee, Materials and Design. 31, 790 (2010).
28. B. B. Shirvani, J. Behesti, R. N. A. A. S. Filho, J. M. Filho, S. B. Fagan, and R. Mota, Chem. Phys. Lett. 430, 71 (2006).
29. S. Wang, Z. Liang, T. Liu, B. Wang, and C. Zhang, Nanotechnology 17, 1551 (2006).
30. M. S. Strano, C. A. Dyke, M. L. Usrey, P. W. Barone, M. J. Allen, H. Shan, C. Kittrell, R. H. Hauge, J. M. Tour, and R. E. Smalley, Science 301, 1519 (2003).
31. P. Hohenberg and W. Kohn, Phys. Rev. 136, 864 (1964).
32. W. Kohn and L. J. Sham, Phys. Rev. 140, 1133 (1965).
33. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
34. P. Ordejon, E. Artacho, and J. M. Soler, Phys. Rev. B 53, R10441 (1996).
35. J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejon, and D. Sanchez-Portal, J. Phys.: Condens. Matter 14, 2745 (2002).
36. B. Coto, I. Antia, M. Blanco, I. M. de Arenaza, E. Meaurio, B. Griebel, J. Phys. Chem. B 106, 3046 (2002).
C. Wang, X. Chen, H. Xie, and R. Cheng, Composites: Part A 42, 1620 (2011).