MECHANICS AND CONTROL
Vol. 30 No. 4 2011

Radosław GÓRSKI*

ELASTIC PROPERTIES OF COMPOSITES REINFORCED BY WAVY CARBON NANOTUBES

SUMMARY

In the paper the prediction of the elastic Young modulus of single-walled carbon nanotubes (CNTs) and the elastic properties of composites reinforced by straight or wavy CNTs is presented. The properties are evaluated by numerical methods. Nanotubes are modeled and analyzed by the finite element method (FEM). The specific atomistic nature of CNTs is taken into account by using a linkage between molecular and continuum mechanics. The methodology consists in replacing the discrete molecular structure of a CNT with a space-frame FE model by equating the molecular potential energy and the elastic strain energy of both models subjected to small elastic deformations. A three-dimensional frame is further substituted with a one-dimensional beam which represents the reinforcement in a representative volume element (RVE) of the considered composite. The properties of the nanocomposite are determined by modeling and analyzing RVEs using the coupled boundary and finite element method (BEM/FEM). A two-dimensional matrix is modeled by the BEM and CNTs by the FEM using beam elements. The waviness and shape of a single fiber or multiple aligned nanotubes on the properties of the nanocomposite are investigated. Sinusoidal or arbitrary shapes of the reinforcement are considered. The influence of volume fraction of the reinforcement and the fiber/matrix Young's modulus ratio on the elastic properties of the composite is also studied.

***Keywords**: carbon nanotubes, nanocomposites, elastic properties, boundary element method, finite element method*

WŁASNOŚCI SPRĘŻYSTE KOMPOZYTÓW WZMACNIANYCH KRZYWOLINIOWYMI NANORURKAMI WĘGLOWYMI

Artykuł dotyczy wyznaczania modułu Younga jednościennych nanorurek węglowych oraz własności sprężystych kompozytów wzmacnianych prostymi nanorurkami lub o dowolnym kształcie. Własności są wyznaczone metodami numerycznymi. Nanorurki modelowane i analizowane są metodą elementów skończonych (MES). By uwzględnić specyficzną budowę atomową nanorurek, zastosowano połączenie mechaniki molekularnej i kontynualnej. Metoda polega na zastąpieniu dyskretnej struktury nanorurki przez model MES w postaci ramy przestrzennej przez porównanie potencjalnej energii molekularnej i sprężystej energii odkształcenia obu modeli, podlegających małym odkształceniom sprężystym. Trójwymiarowy model ramy jest następnie zastąpiony jednowymiarową belką, która reprezentuje wzmocnienie w reprezentatywnym elemencie objętościowym (RVE) rozważanego kompozytu. Własności nanokompozytu wyznacza się, modelując i analizując RVE połączoną metodą elementów brzegowych i skończonych (MEB/MES). Osnowa modelowana jest MEB jako ciało dwuwymiarowe, natomiast nanorurki MES za pomocą elementów belkowych. Badano wpływ falistości oraz kształtu pojedynczych lub wielu podobnie zorientowanych nanorurek na własności kompozytu. Rozważano sinusoidalne lub dowolne kształty wzmocnienia. Badano także wpływ udziału objętościowego wzmocnienia oraz stosunku modułów Younga osnowy i nanorurek na własności sprężyste kompozytu.

***Słowa kluczowe**: nanorurki węglowe, nanokompozyty, własności sprężyste, metoda elementów brzegowych, metoda elementów skończonych*

1. INTRODUCTION

The continuum models can be useful in analysis of different nanostructures if they are appropriately tailored for a particular molecular structure and loading conditions. Such models are very attractive in terms of data reduction and analysis of structure-property relationships. However, the application of models based on continuum mechanics requires a careful analysis of continuum approximations used in macro models and possible limitations. An excellent review paper on the properties, experimental techniques, simulation methods and applications of carbon nanotubes (CNTs) is presented by Qian *et al.* (2002). The authors discuss several continuum-based methods, especially numerical ones, which are extensively used for modeling of different nanostructures. A method, which links computational chemistry and solid mechanics by substituting a discrete molecular structure with an equivalent-continuum model, is shown by Odegard *et al.* (2002). This substitution is accomplished by equating the molecular potential energy of a nanostructure with the elastic strain energy of a representative continuum model. The authors applied the method for the analysis of graphene sheets and CNTs and determined the effective thickness of models. A similar methodology is

* Department of Strength of Materials and Computational Mechanics, Silesian University of Technology, Konarskiego 18A, 44-100 Gliwice, Poland; Radoslaw.Gorski@polsl.pl

used by Li and Chou (2003) who have presented a stiffness matrix approach for the analysis of CNTs. The analysis of CNTs of different chirality is also shown by Tserpes and Papanikos (2005) who have used the FEM to model the nanostructure.

The combination of polymers with CNTs, acting as a matrix and filler, respectively, results in a new class of materials, called carbon nanotube-reinforced polymers (NRPs). These materials can have extraordinary functional and enhanced mechanical properties, due to unique physical and mechanical properties of CNTs (Saito *et al.* 1998). The unusual properties of CNTs, including for instance small size, low density, excellent electronic and thermal properties and extremely high stiffness and strength, can be utilized practically to produce new nanocomposites of required properties. However, in order to expose these properties influencing the reinforcing effectiveness in NRPs, several issues should be examined and well understood. They include for instance dispersion and orientation of CNTs within a polymer or bonding and interaction between them. In the latest studies, the waviness of CNTs as the additional important issue influencing the effective mechanical properties of NRPs is investigated.

Despite of a substantial increase in computational power, simulation of large systems, including for instance RVEs of nanocomposites, is still nowadays a very demanding task and often performed by continuum methods. In the literature many continuum-based models are presented, for example equivalent-continuum or multiscale models, which try to take into account the physical aspects of the nanoscale, atomic interactions, the length-scale effects, etc. However, the results of many researchers show that continuum models give a useful insight into behavior of different nanomaterials, despite of their discrete atomistic nature, provided that appropriate models are used. The continuum methods, ranging from closed-form expressions to complex micromechanical models and numerical methods, were successfully applied in predicting the effective properties of different composites, including nanocomposites. The solutions are more or less consistent with different analytical models or experiments. It is believed, that for the purpose of the elastic moduli prediction, the continuum assumption is an acceptable simplification. Among the numerical methods, the finite element method (FEM) and the boundary element method (BEM) (Brebbia and Dominguez 1992) are the most frequently used.

Many authors have studied NRPs by using numerical or micromechanics methods but most of papers deal with straight CNTs. The evaluation of the effective properties of carbon nanotube-based composites with straight CNTs by the FEM and the BEM is presented for instance by Chen and Liu (2003, 2004). Fisher *et al.* (2003) have developed a hybrid model that allows the effect of CNTs waviness to be incorporated into a micromechanical method. The model combines the finite element results and a micromechanical model for predicting the effective reinforcing modulus (ERM) of a wavy nanotube. The ERM is then used in the Mori-Tanaka method (Mori and Tanaka 1973) to predict the effective modulus of NRPs. The same authors have presented a similar approach, in which the finite element model of a wavy CNT is used to numerically evaluate the dilute strain concentration tensor (Bradshaw *et al.* 2003). It is then utilized in the Mori-Tanaka method to predict the effective modulus of NRPs with aligned or randomly oriented CNTs. A closed-form analytical model, incorporating the nanotube curvature, length and orientation, for estimating the effective elastic modulus of NRPs, is developed by Anumandla and Gibson (2006). The above models, although accurate and efficient, assume a perfect bonding between a matrix and nanotubes, which are treated as solid elements not hollow. Pantano *et al.* (2008a, 2008b) have developed the FEM models, in which the curvature of CNTs and their interaction with a matrix are taken into account. The nanotubes are modeled as hollow cylinders and the perfect or weak bonding between a matrix and CNTs is analyzed. Shao *et al.* (2009) have presented an analytical model to investigate the influence of CNTs waviness and debonding. Recently, Omidi *et al.* (2010) have proposed a new form of the rule of mixtures, which includes many important factors influencing the reinforcing efficiency, for instance waviness and orientation of inclusions. The method allows for more accurate prediction of mechanical properties of NRPs. Generally, in the papers discussed above, a significant influence of the CNTs waviness (and other aspects) on the effective elastic modulus of carbon nanotube-reinforced composites, has been observed.

In this paper, the continuum methods are used to analyze and determine the elastic properties of CNTs and CNT-reinforced composites with wavy nanotubes. A three-dimensional FEM model of a single-walled CNT is analyzed. It is then substituted with an equivalent one-dimensional beam model in analysis of a two-dimensional RVE of the nanocomposite by the coupled BEM/FEM. The presented approach allows exploiting the advantages of both numerical methods, which have been usually used separately or in a combination with micromechanical methods to analyze such composites. The waviness and shape of nanotubes, the CNT/matrix Young's modulus ratio and the volume fraction of the reinforcement on the elastic properties of the composite are investigated.

2. ANALYSIS OF CNTS BY THE FEM

The analysis of CNTs under external loadings can be performed by using continuum mechanics and a frame-like model due to a similar geometry and behavior in comparison with real CNTs. In the present study, to simulate the deformation and determine the elastic properties of a single-walled carbon nanotube (SWCNT), the method presented by Tserpes and Papanikos (2005) is used. It is based on the methodology shown by Odegard *et al.* (2002) and later by Li and Chou (2003). The methodology is described below in brief for the clarity of the paper.

A SWCNT is modeled as a space-frame structure by the FEM. The very strong covalent bonds, which bind the neighboring atoms, are modeled using three-dimensional elastic beam elements, each of the length l. Nodes of these elements (each having six degrees of freedom) are placed at the locations of carbon atoms. The characteristic bond length $\alpha_{C\text{–}C}$ in the CNT is equal to the finite element length l ($\alpha_{C\text{–}C} = l$). A circular cross-section of the element is assumed thus the wall thickness t of the CNT corresponds to the element diameter d. The above FE model requires the definition of specific values of elastic material and geometrical properties of the connecting beams. A linkage between molecular and continuum mechanics is used in order to obtain these values.

Omitting the electrostatic and non-bonded van der Waals interaction, the main contribution to the total potential energy for covalent systems comes from the following terms:

$$U_{total} = \sum U_r + \sum U_\theta + \sum U_\tau \tag{1}$$

where U_r, U_θ and U_τ are respectively the energies due to bond stretch interaction, bond angle variation (bending) and torsions (dihedral angle torsion U_Φ and out-of-plane torsion U_ω are merged into a single term, i.e. $U_\tau = U_\Phi + U_\omega$).

Under the assumption of small deformations, the simplest harmonic expressions for describing the energies are adequate and adopted, and for the considered energies they take the form:

$$U_r = \frac{1}{2} k_r (\Delta r)^2 \tag{2}$$

$$U_\theta = \frac{1}{2} k_\theta (\Delta\theta)^2 \tag{3}$$

$$U_\tau = \frac{1}{2} k_\tau (\Delta\phi)^2 \tag{4}$$

where k_r, k_θ and k_τ represent the bond stretching, bond bending and torsional resistance force constants (stiffnesses), respectively, while Δr, $\Delta\theta$ and $\Delta\phi$ are the corresponding deviations from the equilibrium positions.

According to continuum mechanics, the corresponding strain energies U_A, U_M and U_T of a uniform structural beam element of the length l under axial force N, pure bending moment M and pure torsion T are respectively:

$$U_A = \frac{1}{2}\int_0^l \frac{N^2}{EA} dL = \frac{1}{2}\frac{EA}{l}(\Delta l)^2 \tag{5}$$

$$U_M = \frac{1}{2}\int_0^l \frac{M^2}{EI} dL = \frac{1}{2}\frac{EI}{l}(2\alpha)^2 \tag{6}$$

$$U_T = \frac{1}{2}\int_0^l \frac{T^2}{GJ} dL = \frac{1}{2}\frac{GJ}{l}(\Delta\beta)^2 \tag{7}$$

where A, I and J are the cross-section area and the area moments of inertia about an axis and polar, respectively, Δl, α and $\Delta\beta$ denotes the length variation, the rotational angle at the ends of the beam and the relative rotation between the ends of the beam, respectively. The Young modulus E and the shear modulus G of the beam are the properties that need to be determined.

By comparing Eqs (2)–(4) with Eqs (5)–(7), representing the energies in two systems, the relationships between structural and molecular mechanics parameters are obtained:

$$\frac{EA}{l} = k_r, \quad \frac{EI}{l} = k_\theta, \quad \frac{GJ}{l} = k_\tau \tag{8}$$

Assuming a circular cross-section of the beam with diameter d and substituting $A = \pi d^2/4$, $I = \pi d^4/64$ and $J = \pi d^4/32$ in Eqs (8), the following beam parameters in terms of the force field constants are derived:

$$d = 4\sqrt{\frac{k_\theta}{k_r}}, \quad E = \frac{k_r^2 l}{4\pi k_\theta}, \quad G = \frac{k_r^2 k_\tau l}{8\pi k_\theta^2} \tag{9}$$

Knowing the force constants k_r, k_θ and k_τ (e.g. from an experiment), the bond diameter d and the elastic constants E and G of all beam elements representing the covalent bonds in the hexagonal lattice can be readily obtained. Using this approach, an arbitrary carbon-related nanostructure can be modeled and simulated.

3. ANALYSIS OF CNT-REINFORCED COMPOSITES BY THE BEM/FEM

In order to compute the elastic properties, the RVE of the CNT-reinforced composite is analyzed by the coupled BEM/FEM. A portion of the considered composite with wavy fibers (nanotubes in the present case) representing the RVE, subjected to known displacements u and static tractions t, is shown in Figure 1.

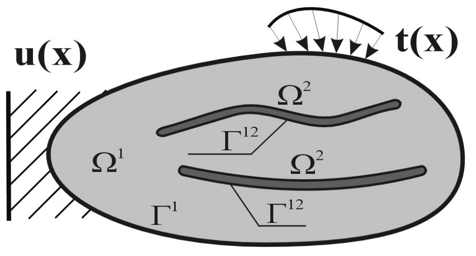

Fig. 1. Matrix reinforced by carbon nanotubes

Because a two-dimensional problem is considered the reinforcement is modeled in a plane. It can be however arbitrary orientated in that plane. The matrix (Ω^1) is modeled by the BEM and its material can be in a plane stress or strain state. Each beam (Ω^2) in Figure 1, modeled by the finite elements, is equivalent to a space-frame FEM model of a SWCNT.

The material of the matrix and CNTs is linear elastic and isotropic. For the BEM region, the mechanical fields satisfy the boundary integral equation, which contains the domain term related to the application of body forces b (Brebbia and Dominguez 1992):

$$c_{ij}(x')u_j(x') = \int_{\Gamma^1} U_{ij}(x',x)t_j(x)d\Gamma(x) - \int_{\Gamma^1} T_{ij}(x',x)u_j(x)d\Gamma(x) + \int_{\Omega^2} U_{ij}(x',X)b_j(X)d\Omega(X) \tag{10}$$

where:

c_{ij} – a constant, which depends on the position of a point,
U_{ij} and T_{ij} – fundamental solutions of elastostatics,
x, x' and X – coordinates of a boundary, collocation and domain point, respectively. Repeated indices denote the summation convention ($i, j = 1, 2$ for a two-dimensional problem).

In order to model CNTs, additional lines inside the BEM region and along the reinforcements (the Γ^{12} boundaries) are introduced. When the RVE is subjected to boundary tractions, the deformed particles act on the matrix along the lines of attachment. In this case, the body forces are unknown interaction forces between the matrix and the nanotubes. These forces are distributed along the interfaces Γ^{12} and they are treated as additional unknown tractions. Numerical solution is obtained after discretization. The outer boundary Γ^1 is discretized into boundary elements and the attachment lines into boundary and beam finite elements. Thus, the total number of degrees of freedom is much smaller than in methods requiring discretization of the whole interior of the plate, e.g. the FEM. Generation of mesh for new RVEs is much easier in the present method than in other domain-based methods. The boundary integral equation is applied for all collocation points, which are nodes along the outer boundary and the interfaces. A perfect bonding between the matrix and the reinforcement at the connected nodes is assumed. The BEM/FEM equations are coupled by assuming conditions of compatibility of displacements and equilibrium of forces between the matrix and reinforcement.

The resulting BEM/FEM equations and other BEM formulations for modeling and analysis of composites are presented by Fedeliński *et al.* (2011). In one of numerical examples, the authors successfully applied the method for the prediction of the effective Young modulus of polymer/clay nanocomposites with aligned straight nanoclay sheets. The results show good accuracy and efficiency of the method in comparison with other approaches.

4. NUMERICAL EXAMPLES

To demonstrate possible applications of the considered methods in analysis of carbon-related nanostructures and different composites with reinforcement of arbitrary shapes, three numerical examples are presented. In the first, a zigzag SWCNT is analyzed and the longitudinal Young modulus is computed. In the second, a single wavy fibre embedded in a matrix is studied, in order to investigate the influence of the waviness on the effective reinforcement. In the third, the properties of a CNT-reinforced composite are computed by analyzing RVEs with multiple wavy nanotubes.

4.1. A single-walled carbon nanotube

The method described in Section 2 is applied to determine the bond properties of an arbitrary single-walled CNT, i.e zigzag, armchair or chiral. The following force constants are used (Tserpes and Papanikos 2005): k_r = 938 kcal mole^{-1} Å^{-2}, k_θ = 126 kcal mole^{-1} rad^{-2} and k_τ = 40 kcal mole^{-1} rad^{-2}. Using these constants and the bond length l = 0.1421 nm in Eqs (9), the following results are obtained: d = 0.147 nm, E = 5490 GPa and G = 871 GPa (the same results are given by Tserpes and Papanikos). The procedure provides a unique value of the bond diameter and the wall thickness ($d = t$).

However, in order to examine different wall thickness of a CNT, the bond's properties will be recalculated. In this paper the following wall thickness of a CNT is assumed: t = 0.34 nm. This is a value used in majority of studies and equals the interlayer spacing of graphene sheets in a graphite. In this case, in order to satisfy the energy equivalence between the molecular and structural approaches, Eqs (8) are used instead of Eqs (9) to compute the elastic properties E and G and the area moment of inertia I. Assuming d = 0.34 nm, the material properties of the bonds for the same values of force constants k_r, k_θ and k_τ are: E = 1020 GPa and G = 162 GPa.

Having determined the bond's properties, a single-walled zigzag (13,0) carbon nanotube is modeled by the FEM and the elastic properties are analyzed. The length of the CNT is L = 50.136 nm, the mean diameter is D = 1.018 nm and the wall thickness is t = 0.34 nm. A three-dimensional frame FE model of the considered SWCNT is presented in Figure 2. The bonds are modeled using three-dimensional elastic beam elements (a 3D elastic BEAM4 in ANSYS system). One beam element per bond is used.

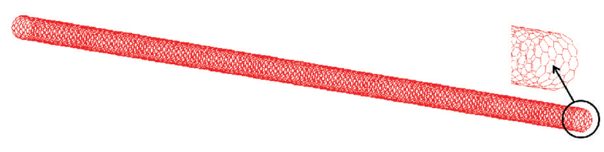

Fig. 2. FE model of a single-walled zigzag CNT

Because the frame FE model will be further substituted with an equivalent one-dimensional beam FE model, the required parameters of the latter are (for a two-dimensional model of the RVE): the Young modulus E_{CNT}, the area moment of inertia I_{CNT} and the area of the cross-section A_{CNT}. The latter parameter can be easily computed:

$A_{CNT} = \pi Dt$ = 1.087 nm^2. The first two parameters are obtained by performing two numerical tests, i.e. the uniaxial tension test and the pure bending test, respectively, using the frame model of the CNT in Figure 2. An illustration of both tests is presented in Figure 3.

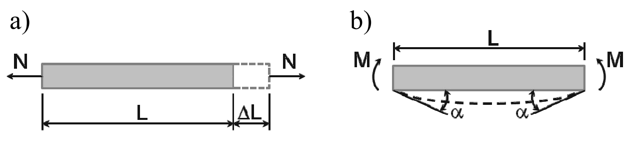

Fig. 3. CNT subjected to: a) uniaxial tension; b) pure bending

In the first test, all nodes at one endpoint of the model are fixed and the CNT is subjected to the axial strain 0.01% (known axial displacements at second endpoint). The Young modulus E_{CNT} of the CNT is thus computed as

$$E_{CNT} = \frac{N\ L}{\Delta L\ A_{CNT}} \tag{11}$$

where N is a total axial force (the sum of all reactions acting at the nodes at one end of the CNT) and ΔL is an elongation of the CNT. Putting the FEM results and the remaining data into Eq. (11), the computed Young modulus of the CNT is E_{CNT} = 1030 GPa. The value is consistent with the commonly accepted value of the in-plane modulus of a graphite. Chang and Gao (2003) have presented an analytical model based on molecular mechanics to predict the properties of CNTs. Using the closed-form expressions derived by the authors, a similar result for the same parameters of CNT is obtained (1044 GPa).

In the second test, all nodes at one endpoint of the model are fixed and the known rotational angle 2α is applied at nodes at second endpoint (α = 0.001 rad). The area moment of inertia I_{CNT} is thus computed as

$$I_{CNT} = \frac{M\ L}{2\alpha\ E_{CNT}} \tag{12}$$

where M is a total bending moment (the sum of all reactions acting at the nodes at one end of the CNT). Putting the FEM results and the remaining data into Eq. (12), the computed area moment of inertia is I_{CNT} = 0.1226 nm^4. Using the formula for a cylindrical cross-section $I = \pi/64[\ (D+t)^4 - (D-t)^4\ ]$, the area moment of inertia is I = 0.1566 nm^4. Because the difference between the FEM prediction and the value obtained by the above formula is small, the area moment of inertia can be computed using standard analytical formula for the continuum cross-section. However, the value obtained numerically will be used in the subsequent section of the paper.

4.2. A single wavy fibre in a matrix

A square plate with a single straight fibre of length L is subjected to the uniform parallel loading t_1 or to the perpendicular loading t_2, as shown in Figure 4a. The cross-section of the fibre is a solid circle of unit diameter D. The length L and the dimensions of the plate are respectively fifty and sixty times larger than the diameter D. The volume fraction of the fibre in the matrix is 1%. The material of the matrix is in plane stress with Poisson's ratio ν_m = 0.3 and the unit Young modulus E_m. The ratio of the phase moduli is E_f/E_m = 1000, where E_f is the Young modulus of the fibre (the order of the ratio is typical for NRPs). The outer boundary of the matrix is divided into 80 boundary elements and the fibre into 20 boundary and 40 finite elements. The BE/FE discretization is shown in Figure 4b.

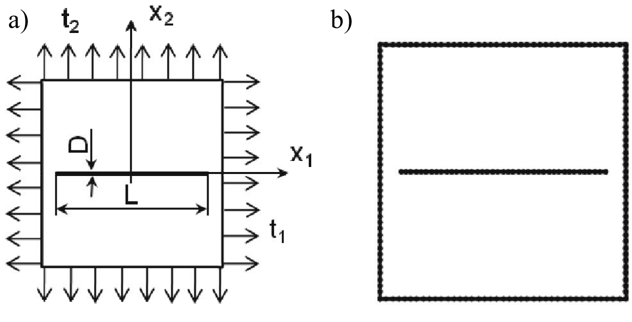

Fig. 4. A single straight fibre: a) geometry and loadings; b) discretization

In order to investigate the fibre's curvature on the results, three shapes shown in Figure 5 are considered: two with the whole wavelength L of a sinus function but different phases (called the 'sine' and the 'cosine', respectively) and one with the half wavelength L (called the 'half sine'). The parameters defining the shape of the fibre are: the waviness ratio $w = a/L$ and the wavelength ratio L/D, where a is an amplitude of a sinus function. During the waviness increase, the position of the dashed line in Figure 5, along which the fibre is orientated, is not changed and it runs across the middle of the square plate. Notice that the total 'height' of the first two wavy shapes is two times the amplitude a in comparison with the third shape.

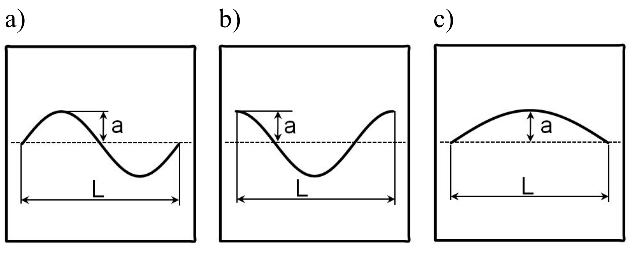

Fig. 5. Shapes of a wavy fibre: a) sine; b) cosine; c) half sine

Four homogenized elastic constants of the considered inhomogeneous material are analyzed by performing two independent tension tests. The following equations are used in order to compute the constants:

– tension along x_1 axis

$$E_{11} = \frac{\bar{\sigma}_{11}}{\bar{\varepsilon}_{11}}, \quad \nu_{12} = -\frac{\bar{\varepsilon}_{22}}{\bar{\varepsilon}_{11}} \tag{13}$$

– tension along x_2 axis

$$E_{22} = \frac{\bar{\sigma}_{22}}{\bar{\varepsilon}_{22}}, \quad \nu_{21} = -\frac{\bar{\varepsilon}_{11}}{\bar{\varepsilon}_{22}} \tag{14}$$

where:

E_{11} and E_{22} – the longitudinal and transverse Young modulus, respectively,
ν_{12} and ν_{21} – the major and minor Poisson's ratios,
$\bar{\varepsilon}_{ii}$ and $\bar{\sigma}_{ii}$ (i = 1 or 2) – the components of the averaged strain and stress, which are obtained on the basis of computed displacements u_i and the applied tractions t_i, respectively.

The normalized longitudinal (E_{11}/E_m) and transverse (E_{22}/E_m) Young modulus is presented in Figure 6a and 6b, respectively. For the 'sine' and the 'cosine' shape and $w < 0.3$, a significant influence of the waviness on the E_{11}/E_m is observed. For $w > 0.3$ the ratio approaches the modulus for the pure matrix. This indicates a considerable reduction of the reinforcing efficiency along the x_1 axis which is about 28% in comparison with a straight fiber (w = 0). The reduction is less for the 'half sine' shape but it is attributed to the smaller total 'height' of the fiber. The opposite tendency is observed for the E_{22}/E_m ratio where the increasing waviness stiffen the material along the x_2 axis. The highest increase is about 60% for the 'cosine' shape in comparison with a straight fiber and it is insignificant for the 'half sine' shape.

The major and minor Poisson's ratios are presented in Figure 7a and 7b, respectively. In both cases, a considerable influence of the waviness on the ratios is observed. Generally, similar responses for the 'sine' and the 'cosine' shape are obtained. The major Poisson's ratio increases for the smaller waviness and then it starts to decrease for all three shapes. The minor Poisson's ratio increases for the whole range of the considered waviness.

The dependence of the normalized longitudinal Young modulus E_{11}/E_m on the ratio of the phase moduli E_f/E_m for different shapes and waviness is presented in Figure 8. The nonlinear dependence is observed especially for smaller values of the E_f/E_m ratio. Generally, the higher the E_f/E_m ratio, the smaller change of the E_{11}/E_m for the considered waviness and shape. The E_{11}/E_m ratio is higher for the 'half sine' fiber than for two other shapes but the highest ratio is for a straight fiber (w = 0).

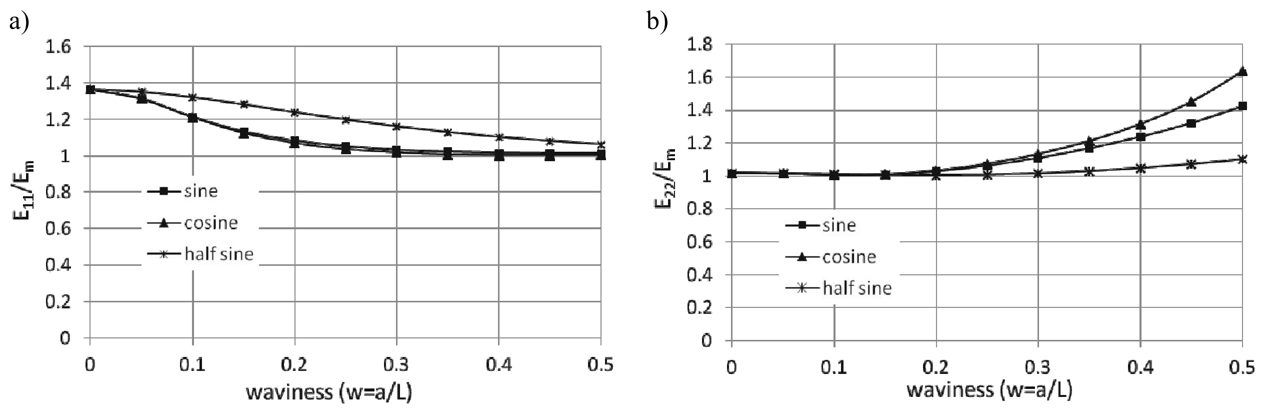

Fig. 6. The normalized Young modulus: a) longitudinal; b) transverse

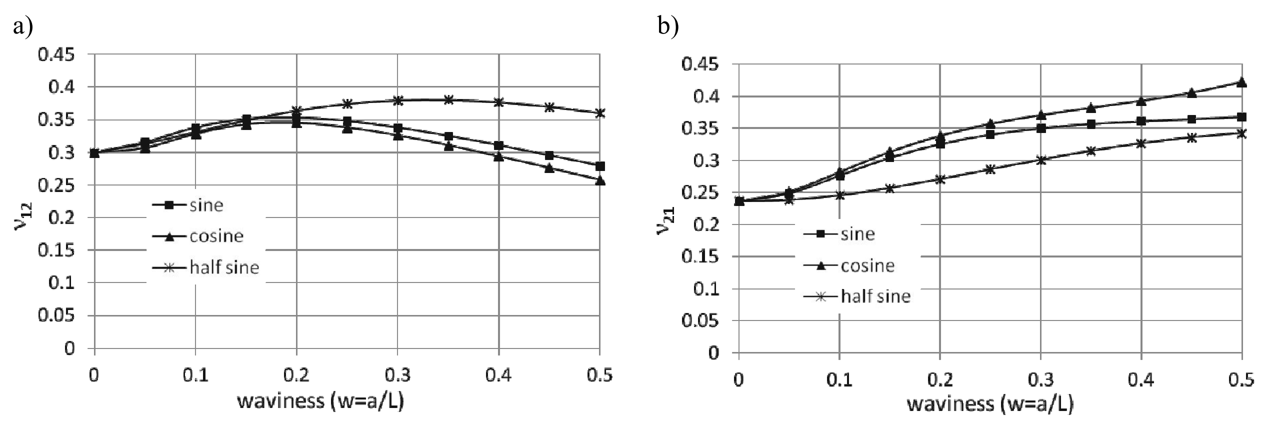

Fig. 7. The Poisson's ratio: a) major; b) minor

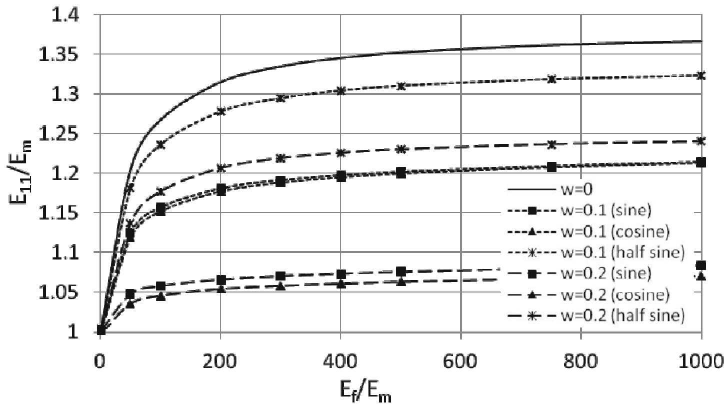

Fig. 8. The normalized longitudinal Young modulus for different ratios of the phase moduli

4.3. Multiple wavy CNTs in a polymer matrix

Square RVE of the carbon nanotube-reinforced polymer (NRP) is subjected to the uniform parallel loading t_1 or to the perpendicular loading t_2, similar as in the previous example. Each zigzag single-walled (13,0) CNT embedded in the RVE is modeled as a hollow tube by beam finite elements. In order to take into account the specific discrete nature of the CNT, the bond properties of the SWCNT and its Young modulus are computed as shown in Example 4.1. Then, the FEM frame model is substituted with an equivalent one-dimensional beam in the analysis of composite's properties by using the RVE concept. Thus, the values for the equivalent beam are (see Example 4.1): D = 1.018 nm, t = 0.34 nm, A_{CNT} = 1.087 nm^2, I_{CNT} = 0.1226 nm^4. The side length of the RVE is 329 nm to preserve the same volume fraction of the reinforcement in a matrix (1%) as in the previous example. The material of the polymer matrix is in plane stress with Poisson's ratio ν_m = 0.3 and the Young modulus E_m. The ratio of the phase moduli is E_{CNT}/E_m = 539, where E_{CNT} = 1030 GPa is the Young modulus of the CNT.

The same shapes as in the previous example are considered, i.e. the 'sine', the 'cosine', the 'half sine' and additionally an arbitrary shape modelled by the NURBS curve. All considered shapes and exemplary RVEs including 30 wavy CNTs are presented in Figure 9.

The parameters defining the shapes are: the waviness ratio $w = a/L$ and the wavelength ratio L/D, where L = 50 nm is the wavelength L for the corresponding first three shapes (compare Fig. 5) or it is a distance L in the x_1-axis direction between the endpoints of the 'nurbs' shape. The latter shape is modeled by four control points. The randomly generated coordinate of each control point in the x_2-axis direction is such that $w \leq w_o$ is satisfied for that point, where w_o is a considered waviness which changes from 0 to 0.3.

The CNTs cannot intersect themselves and the outer boundary of the RVE. The minimal distance between the CNTs and also between them and the outer boundary is assumed. For each waviness and shape ten RVEs with random distributions of CNTs are analyzed and then the results are averaged. The outer boundary of the RVE is divided into 80 boundary elements and each CNT into 8 boundary and 16 finite elements in the coupled BEM/FEM analysis. The same four elastic constants are analyzed as in the previous example. The influence of the volume fraction f_{CNT} of CNTs on the longitudinal Young modulus E_{11} is also studied.

The normalized longitudinal (E_{11}/E_m) and transverse (E_{22}/E_m) Young modulus is presented in Figure 10a and 10b, respectively. For the 'sine' and the 'cosine' shape a significant decrease of the E_{11}/E_m is observed and the responses are similar. For the 'half sine' and the 'nurbs' shape the decrease of the longitudinal modulus is about

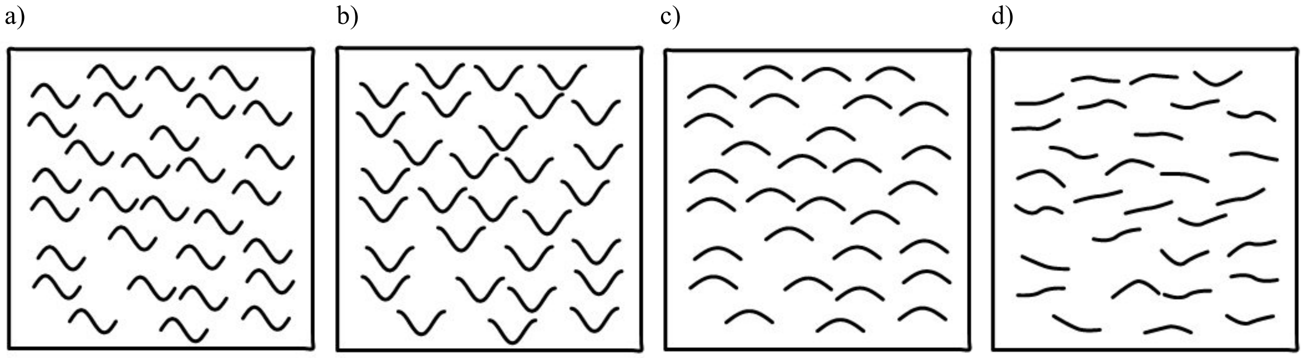

Fig. 9. RVEs containing CNTs of different shapes:
a) sine; b) cosine; c) half sine; d) nurbs

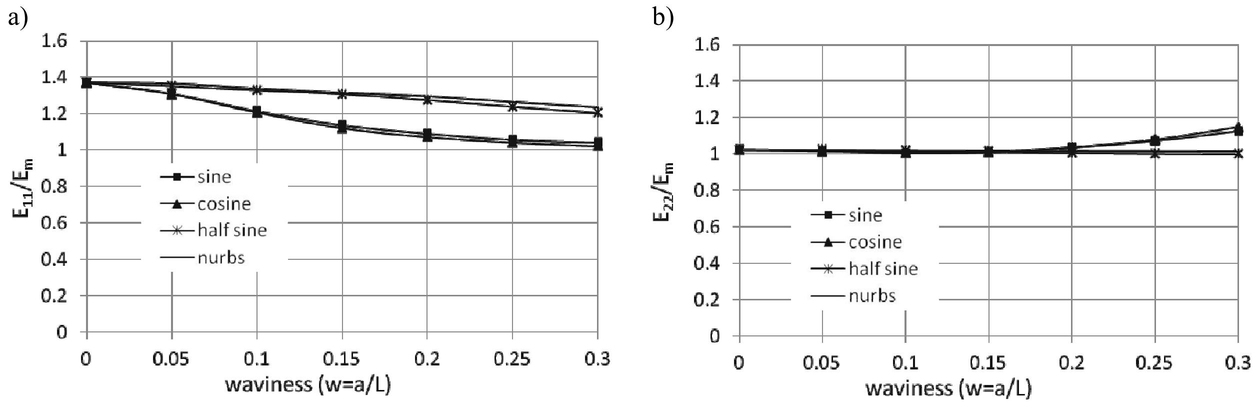

Fig. 10. The normalized Young modulus: a) longitudinal; b) transverse

14% in comparison with straight CNTs (w = 0). The transverse modulus ratio slightly increases for the 'sine' and the 'cosine' shape and it is not sensitive for the two remaining shapes. Similar results are obtained in the present case in comparison with a single fiber from the previous example in the considered range of the waviness ($w \le 0.3$).

The major and minor Poisson's ratios are presented in Figure 11a and 11b, respectively. In both cases, a considerable influence of the waviness on the ratios is observed. Generally, as in prediction of the Young's moduli, the responses for the corresponding shapes (the 'sine' and 'cosine' or the 'half sine' and 'nurbs') are similar. Additionally, the results are similar to predictions for a single fiber for the considered range of the waviness.

The longitudinal Young modulus E_{11} for different volume fractions of nanotubes and for the considered shapes is presented in Figure 12. The largest stiffness of the composite is for the case with straight nanotubes. For the volume fraction of the reinforcement equal 5%, the maximum and minimum increase of the E_{11} in comparison with the pure matrix is about 80% and 47%, respectively for the straight and the sine-shaped nanotubes. It shows that the shape of nanotubes significantly influences the modulus, especially for higher volume fractions.

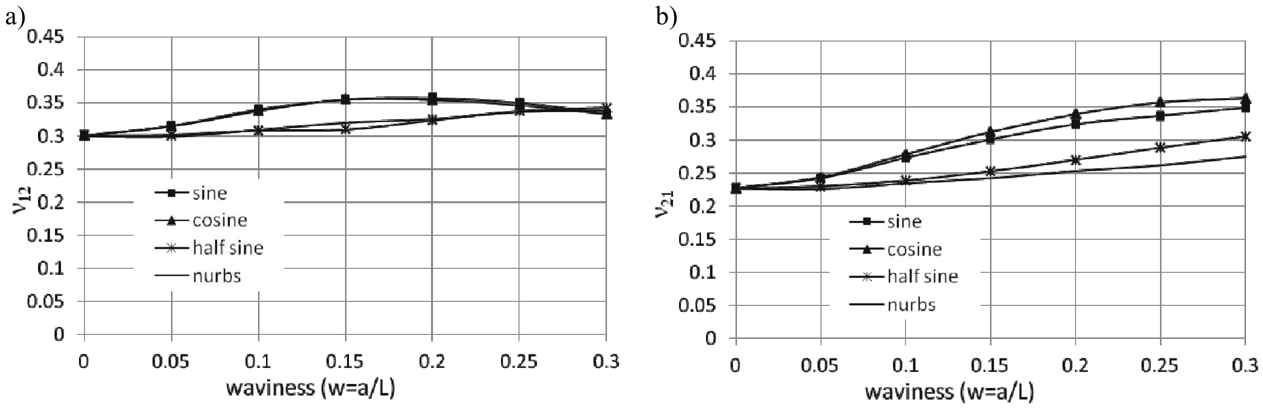

Fig. 11. The Poisson's ratio: a) major; b) minor

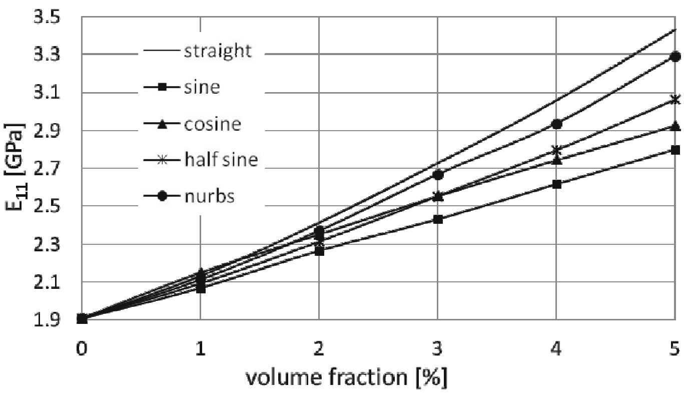

Fig. 12. The longitudinal Young modulus for different volume fractions

5. CONCLUSIONS

In the paper, the continuum methods are used to predict the elastic modulus of carbon nanotubes (CNTs) and the elastic properties of CNT-reinforced composites. The finite element method (FEM) is used to analyze three-dimensional model of a zigzag single-walled CNT (SWCNT) and to determine the elastic Young modulus. In order to model the reinforcement in the representative volume elements (RVEs) of the material, the FEM space-frame structure is substituted by an equivalent one-dimensional beam. A single and multiple straight or wavy nanotubes in a matrix are considered as the RVEs. The coupled boundary and finite element method (BEM/FEM) is used to analyze the nanocomposite. The influence of the shape, waviness, volume fraction and the ratio of CNT/matrix Young's modulus on the elastic properties of the composite are studied.

A linkage between molecular and continuum mechanics is used in order to replace a discrete molecular structure of a CNT with a continuum FEM space-frame model. The FEM model is subjected to small elastic deformations. The method can be applied to analyze SWCNTs of different chirality. The calculated Young modulus of a zigzag SWCNT is 1030 GPa and it is very close to the commonly accepted value of the Young's modulus of a graphite (about 1000 GPa). It is also close to other predictions found in the literature and obtained by applying different methods and models (e.g. analytical expressions or molecular dynamics simulations).

The numerical examples show that the increase of the waviness of a single fiber reduces the longitudinal and increases the transverse Young modulus in comparison with a straight fiber. A significant influence of the waviness on the Poisson's ratios is also observed. Different curvatures of multiple CNTs in RVEs were investigated. Generally, similar results are obtained for the case with multiple CNTs and the corresponding shapes in comparison with a single fiber (for the same volume fraction of a filler, similar material properties and different cross-sections, i.e. solid or hollow). It suggests that the unit cell of the considered materials can be used to analyze the properties instead of more involved RVEs. The results show that the waviness and shape are important mechanisms influencing the reinforcing efficiency in CNT-based composites.

The main advantage of the present method is a possibility of modeling of composites with different types, shapes and orientation of reinforcement. By using the equivalent-beam concept to model the reinforcement in the RVE, one can easily consider different fibers, e.g. nanotubes, nanorods, platelets or other, by changing cross-section parameters of beams. The advantage of the concept, based on a linkage between molecular and continuum mechanics, is its simplicity and the computational efficiency. The shape of the reinforcement, i.e. straight or wavy, can be easily modeled by changing the shape of a one-dimensional line along the attachment. The total number of degrees of freedom is significantly reduced in comparison with the FEM, because the outer boundary of the RVE and the lines along CNTs are only discretized. Another important advantage is a natural modeling the effect of the straightening of wavy CNTs due to the applied load to the RVE.

Because a two-dimensional problem is considered, the present formulation is limited to composites with parallel orientation of the reinforcement (modeled in a plane). The formulation neglects an interaction between a matrix and the reinforcement, which has an atomistic nature, and the perfect bonding is assumed. Another simplification is that the molecular structure of nanotubes is not taken into account directly in the RVE. Instead, the equivalent-beam concept to model the reinforcement is used. Despite of above limitations, the formulation gives a useful information about a behavior of nanocomposites reinforced by wavy CNTs, which would be difficult to obtain using for instance only atomistic simulations. The presented preliminary results show possible applications of the method in analysis of elastic properties of composites with wavy reinforcements. The formulation may be further developed in order to take into account all important physical aspects during the modeling of nanomaterials. This can be a subject of ongoing research and may include for instance modeling of reinforcements of arbitrary shapes, orientation and different lengths in a single RVE, interaction effects between matrix and CNTs, multiscale modeling, etc.

Acknowledgments

The scientific research is financed by the Ministry of Science and Higher Education of Poland in years 2010–2012.

References

Anumandla V., Gibson R.F. 2006, *A comprehensive closed form micromechanics model for estimating the elastic modulus of nanotube-reinforced composites*. Composites: Part A, 37, pp. 2178–2185.

Bradshaw R.D., Fisher F.T., Brinson L.C 2003, *Fiber waviness in nanotube-reinforced polymer composites – II: modeling via numerical approximation of the dilute strain concentration tensor*. Compos. Sci. Technol., 63, pp. 1705–1722.

Brebbia C.A., Dominguez J. 1992, *Boundary Elements. An Introductory Course*. Computational Mechanics Publications, Southampton.

Chang T., Gao H. 2003, *Size-dependent elastic properties of a single-walled carbon nanotube via a molecular mechanics model*. J. Mech. Phys Solids, 51, pp. 1059–1074.

Chen X.L., Liu Y.J. 2004, *Square representative volume elements for evaluating the effective material properties of carbon nanotube-based composites*. Comp. Mater. Sci., 29, pp. 1–11.

Fedeliński P., Górski R. 2006, *Analysis and optimization of dynamically loaded reinforced plates by the coupled boundary and finite element method*. Comput. Model. Eng Sci., vol. 15, No. 1, pp. 31–40.

Fedeliński P., Górski R., Dziatkiewicz G., Ptaszny J. 2011, *Computer modelling and analysis of effective properties of composites*. Comp. Methods Mater. Sci., vol. 11, No. 1, pp. 3–8.

Fisher F.T., Bradshaw R.D., Brinson L.C 2003, *Fiber waviness in nanotube-reinforced polymer composites – I: modulus predictions using effective nanotube properties*. Compos. Sci. Technol., 63, pp. 1689–1703.

Li Ch., Chou T-W. 2003, *A structural mechanics approach for the analysis of carbon nanotubes*. Int. J. Solids Struct., 40, pp. 2487–2499.

Liu Y.J., Chen X.L. 2003, *Continuum models of carbon nanotube-based composites using the boundary element method*. Electron. J. Bound. Elem., vol. 1, No. 2, pp. 316–335.

Mori T., Tanaka K. 1973, *Average stress in matrix and average elastic energy of materials with misfitting inclusions*. Acta Metall., 21, pp. 571–574.

Odegard G., Gates T.S., Nicholson L.M., Wise K.E. 2002, *Equivalent-Continuum Modeling of Nano-Structured Materials*. Compos. Sci. Technol., vol. 62, No. 14, pp. 1869–1880.

Omidi M., Hossein Rokni D.T., Milani A.S., Seethaler R.J., Arasteh R. 2010, *Prediction of the mechanical characteristics of multi-walled carbon nanotube/epoxy composites using a new form of the rule of mixtures*. Carbon, 48, pp. 3218–3228.

Pantano A., Capello F. 2008a, *Numerical model for composite material with polymer matrix reinforced by carbon nanotubes*. Meccanica, 43, pp. 263–270.

Pantano A., Modica G., Capello F. 2008b, *Multiwalled carbon nanotube reinforced polymer composites*. Mater. Sci. Eng. A, 486, pp. 222–227.

Saito R., Dresselhaus G., Dresselhaus M.S. 1998, *Physical Properties of Carbon Nanotubes*. Imperial College Press, London.

Shao L.H., Luo R.Y., Bai S.L., Wang J. 2009, *Prediction of effective moduli of carbon nanotube-reinforced composites with waviness and debonding*. Compos. Struct., 87, pp. 274–281.

Tserpes K.I., Papanikos P. 2005, *Finite element modeling of single-walled carbon nanotubes*. Composites: Part B, 36, pp. 468–477.

Qian D., Wagner G.J., Liu W.K., Yu M-F., Ruoff R.S. 2002, *Mechanics of carbon nanotubes*. Appl. Mech. Rev., vol. 55, No. 6.