Non-linear multi-scale finite element method for prediction of tensile behaviour of carbon nanotube-reinforced polymer composites

Ehsan Mohammadpour[(1)] and **Mokhtar Awang**[(2)]

Mechanical Engineering Department, Universiti Tehnologi PETRONAS, 31750 Seri Iskandar, Perak, MALAYSIA
e-mails: eh.mohammadpour@gmail.com[(1)], mokhtar_awang@petronas.com.my[(2)]

SUMMARY

The ability of using carbon nanotubes as the strongest and stiffest elements in nanoscale composites remains a powerful motivation for research in this area. This paper describes a finite element modelling appropriate for the numerical prediction of the mechanical behaviour of polypropylene which is reinforced with single-walled carbon nanotubes. A multi-scale representative volume element is proposed for modelling the tensile behaviour of carbon nanotube reinforced composites. Within the representative volume element, the reinforcement is modelled according to its atomistic microstructure. A model based on the modified Morse interatomic potential is used for simulating the isolated carbon nanotube. In this work, the matrix is modelled as a medium in a form of a continuum by utilizing solid elements and in order to describe its behaviour, an appropriate non-linear material model is adopted. A cohesive zone model is assumed between the nanotube and the matrix with an ideal bonding until the interfacial shear stress exceeds the corresponding strength. By using the representative volume element, a unidirectional nanotube/polymer composite was modelled and the results were compared to the corresponding rule-of-mixtures predictions. The effect of interfacial shear strength on the tensile behaviour of the nanocomposite was also studied. The influence of adding a single-walled carbon nanotube to the polymer is discussed and the results show that Young's modulus and tensile strength of the polymer significantly increase in the presence of carbon nanotubes.

Key words: *carbon nanotube, reinforced polymer composite, multi-scale, finite element method, Morse interatomic potential.*

1. INTRODUCTION

Among various nanomaterials, carbon nanotubes (CNTs) have gained widespread attention owing to their superior properties, good chemical stability, and large surface areas [1]. CNTs are extremely thin tubes and feature an enviable combination of mechanical, thermal, electrical, and optical properties [2]. Their size, shape, and properties constrain them as prime contenders in exploiting the growth of a potentially revolutionary material for diverse applications. Therefore, in many studies, CNTs have been used as reinforcements in polymer matrix composites [2-5].

Obtainment of the optimum load transfer across the CNT-polymer matrix interface is one of the issues that emerge in CNT reinforced polymers. Many research

studies have been done to measure the interfacial strength between CNT and polymer matrix. Since most of the studies are impeded by the technical difficulties involved in the manipulation of the nanotubes, the use of theoretical and computational approach to predict the load transfer ability of the nanocomposites might be one of the solutions to the problem [6]. Lau et al. [7] studied theoretically the stress transfer properties between single-/multi-walled nanotubes and polymer matrix. They used local density approximation, elastic shells and conventional fiber pullout models. Lordi and Yao [8] used force-field based molecular mechanics to study the binding energies and sliding friction between the nanotubes and different polymer matrices. They found out that helical polymer conformations play significant role in the strength of the interface. They suggested that the strength of the interface may result

from molecular-level entanglement of the two phases and forced long-range ordering of the polymer. Liao and Li [9] studied the interfacial characteristics of the CNT/polystyrene composite system in the absence of atomic bonds between nanotubes and polymer matrix using molecular mechanics. Results showed that the interfacial shear stress of the nanotube/polystyrene composite system is about *160 MPa*, which is significantly higher than most carbon fiber-reinforced polymer composites.

Frankland et al. [10] studied the matrix-nanotube shear strength using molecular dynamics simulations. It was concluded that the shear strength of a polymer/nanotube interface with weak non-bonded interactions could be increased by over an order of magnitude with the introduction of a relatively low density ($<1\%$) of chemical bonds between the nanotube and polymer. Tan et al. [11] studied the effect of van der Waals-based interface forces on the CNT-polymer composite. They incorporated a non-linear cohesive law introduced by Jiang et al. [12] in the micromechanical model of the composite. The results showed that CNTs improve the mechanical behaviour of a composite only at the small strains. Tserpes et al. [13] proposed a multi-scale representative volume element (RVE) for modelling of the tensile behaviour of carbon nanotube-reinforced composites. A perfect bonding was assumed between the nanotube and the matrix until the interfacial shear stress exceeded the corresponding strength which simulated debonding effect. It was found out that the tensile strength significantly increases by increasing interfacial shear strength.

Since computational models usually over-predict the tensile modulus of composites, Bhuiyan et al. [14] built a RVE to investigate the effect of polymer-filler contact properties. While assuming perfect filler–polymer interfacial contact leads to over-predicted tensile modulus of the CNT/PP composites by *85%* for *5 wt%* CNT/PP composites, more accurate data were obtained by assuming imperfect CNT/PP contact, CNT agglomerates and alignment in the composites.

In this paper, a multi-scale RVE for CNT-reinforced composites is proposed to investigate the non-linear behaviour of composite under tension. Finite element simulations were performed to simulate the pullout of a single-walled carbon nanotube (SWCNT) from the polypropylene (PP) matrix. The PP resin model was constructed by incorporating three-dimensional solid elements. In this study, the chemical bonding between SWCNTs and the PP was not considered because SWCNTs have less defects and more chemical stability compared to MWCNTs. Only the influences of non-bonded interactions on interfacial stress transfer were studied. A cohesive law for interfaces between the CNT and polymer was established characterized by the van der Waals' force.

2. FINITE ELEMENT MODELLING

A cylindrical RVE consisting of CNT, PP matrix and contact interface was modelled using ANSYS software. In the FE modeling, CNTs were assumed to be solid structures. A three-dimensional (3D) RVE with the applied boundary conditions was investigated under uniform extension to determine the tensile behaviour of CNT/PP composites. Figure 1 shows the FE model of RVE and CNT. For each model, one end was constrained in all directions and the other end ($z=L$), where L is the length of RVE, was free to move in the z direction. An axial displacement was applied to all the nodes at the edge of the RVE. A higher order 3D structural solid element (SOLID186 element with three degrees of freedom per node) was used for both matrix and SWCNT. A cohesive zone material model was used at the CNT/PP interface. An optimum mesh density that guarantees a fully converged solution with a minimum computational time was determined based on a parametric study. Perfect bonding was assumed between the phases and all the phases were assumed to be homogeneous, isotropic, and linearly elastic. The material properties and dimensions used for the RVE are shown in Table 1. The stress–strain relationship of the composite was calculated as the ratio of the average stress to the applied strain. The average stress generated in the RVE was calculated using the nodal stresses obtained from the FEA by accounting for all phases present in the RVE.
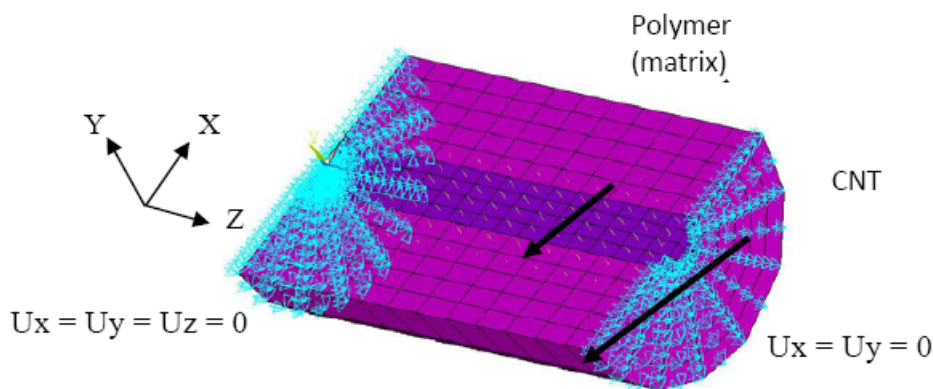

Fig. 1 A 3D RVE with the applied boundary conditions

Table 1   Material properties and geometrical dimensions of the RVE

	Young's modulus (GPa)	Interfacial shear strength (MPa)	Poisson's ratio	Inner diameter (Å)	Outer diameter (Å)	Length (Å)
CNT	880	-	0.3	-	6.78	200
PP	0.751	-	0.3	6.78	30	200
Interface	-	30	-	-	6.78	200

2.1 Carbon nanotube

An armchair SWCNT with chiral index of (5,5) was chosen for the model. The CNT properties were obtained from previous study conducted by present authors based on the Modified Morse potential equations [15]. A correlation between inter-atomic molecular potential energies and strain energies of a beam has been established by using equivalence of energies. Figure 2 shows the non-linear stress–strain curve of armchair (5,5) SWCNT under axial tension.
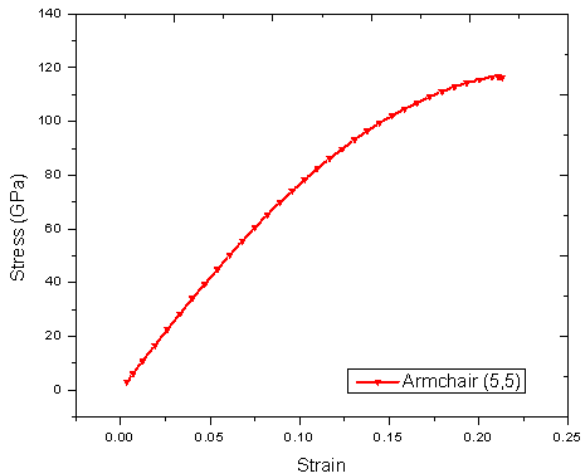

Fig. 2   Stress-strain curve of armchair (5,5) SWCNT under axial tension [15]

2.2 Polymer matrix

Since the volume fraction of CNTs is about *5%* in the RVE, subsequently, the volume of polymer matrix is much higher than that of CNTs at molecular scale. As a reasonable compromise, surrounding polymer is taken into account as a continuum medium and solid elements are used to construct the thick resin. A higher order 3D 20-node solid element, SOLID186, was employed for this purpose. The element has three degrees of freedom per node which are translations in *x*, *y* and *z* directions. This element supports non-linear material behaviour and is well suited to model curved boundaries. The simulated resin was treated as an nonlinear isotropic material with Young's modulus of *0.751 GPa* and *0.3* as Poisson's ratio according to the experimental data.

2.3 Nanotube/matrix interface

Fundamental to the reinforcing effectiveness are the interfacial characteristics between the nanotube and the matrix. Upon this issue, a considerable number of works have been reported previously [11, 14]. Since CNTs usually agglomerate due to the van der Waals' force [17], they are extremely difficult to disperse and align in most of the common polymer matrices [18]. Moreover, carbon nanotubes usually do not bond well to polymers, as a consequence their interaction exhibits the van der Waals' force [19] which is much weaker than covalent bonds. This leads to sliding of CNT in polymer matrix when subjected to loading.

McCarthy et al. [20] studied the interaction between carbon nanotubes and a conjugated polymer to gain a better understanding of the binding. A good wetting between the conjugated polymer and nanotubes has been observed. Wagner et al. [21] reported the stress transfer ability of nanotubes-polymer interfaces of the order of *500 MPa*. Schadler et al. [22] studied mechanical behaviour of multi-walled carbon nanotube (MWCNTs)/epoxy composites in tension and compression. It was found that the compression modulus is higher than the tensile modulus, indicating that load transfer to the nanotubes in the composite is much higher in compression. Later on, Cooper et al. [23] used a scanning probe microscope tip to measure the interfacial strength of an individual SWCNT ropes and MWCNTs bridging across holes in an epoxy matrix. Based on these experiments, the interfacial shear strength between the MWCNTs and the epoxy matrix was calculated to be in the range of *35–376 MPa*, whereas most of SWCNT ropes were fractured instead of being pulled out of the epoxy matrix. Barber et al. [24] also directly measured adhesive interactions between the MWCNT and the polyethylene-butene matrix by performing reproducible nano-pullout experiments using atomic force microscopy. The result showed a relatively high interfacial debonding stress of *47 MPa*. Wagner [25] used a traditional force balance approach which was modified for a hollow tube. He applied an expanded form of Kelly-Tyson model to calculate the interfacial strength between the SWCNT and polymer. It was shown that high values of the interfacial strength are attainable.

As CNTs are represented by solid elements, the interfacial shear stress cannot be computed directly.

To overcome this obstacle, an approach described by Tserpes et al. [13] was considered. Figure 3 shows a free-body diagram of CNT in the RVE. From the FE analysis, the normal stresses σ_1 and σ_2 at nodes 1 and 2, respectively, are computed. If constant shear stress τ along the element is assumed, then the equilibrium formulation can be written as:

$$|\sigma_1 - \sigma_2|A = \tau\pi Dl \qquad (1)$$

where, D is the outer nanotube diameter and l is the CNT length. From Eq. (1) τ will be computed and compared to the interfacial shear strength (ISS) value. If $\tau \leq$ ISS, the interface has failed leading to load-carrying disability of the specific element, which is modelled by a cohesive material model (CZM). The above procedure was repeated at each load step. According to the experimental studies, a very small ISS ($=30$ MPa) was chosen for the present interface model.
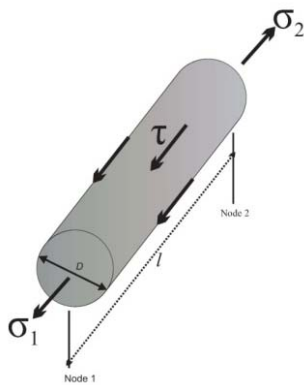

Fig. 3 Schematic diagram of the beam representing the nanotube

In RVE proposed here, simulation of nanotube/ matrix debonding was incorporated. The debonding refers specifically to the separation of bonded contact. Bilinear material behaviour with tractions and separation distances was defined according to Ref. [16]. A cohesive zone material has been defined to simulate the traction separation behaviour of the CNT/polymer interface by adopting augmented Lagrangian method. Figure 4 shows the interface elements.
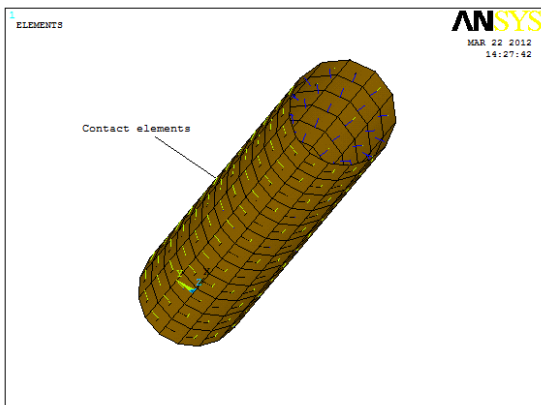

Fig. 4 Contact elements representing CNT/polymer interface

3. RESULTS AND DISCUSSION

A unidirectional nanotube/polymer composite was modelled in the RVE. The armchair (5,5) nanotube spanning the length of the matrix was used as reinforcement. The nanocomposite specimen was subjected to an axial tension by fully constraining the nodes of one end and applying an incremental displacement at the nodes of other end. Figures 5(a) and 5(b) shows the RVE deformation under tensile loading.
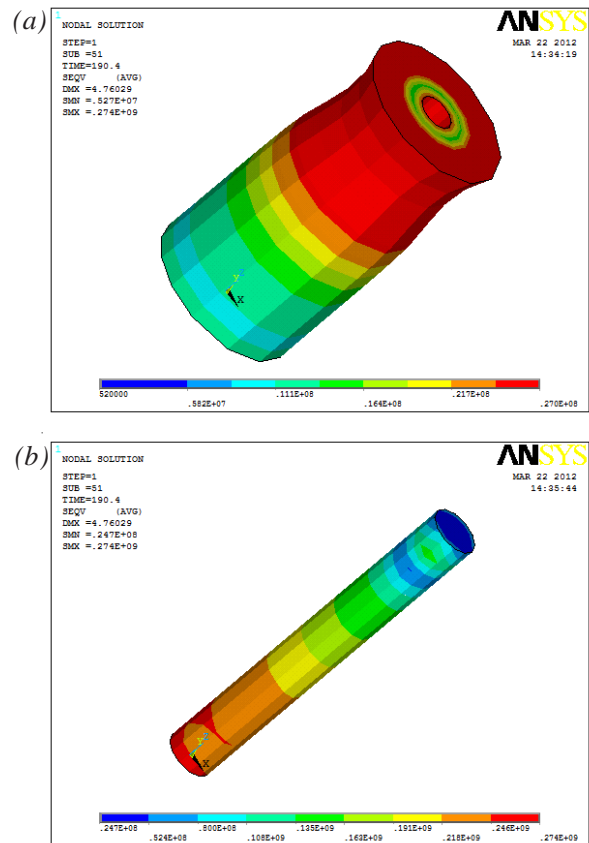

Fig 5. Von Mises stress distribution in: (a) polymer matrix; (b) CNT

For a composite under uniaxial loading, the dependence of elastic modulus on the nanotube volume fraction can be estimated by the rule-of-mixtures. Under constant strain conditions, the longitudinal elastic modulus of the composite E_C is given by:

$$E_c = E_n v_n + E_m v_m \qquad (2)$$

where E_n and E_m are the longitudinal elastic modulus of the nanotube and the matrix, respectively, and v_m is the matrix volume fraction. For $V_n = 5\%$ in (5,5) chiral index, with E_n and E_m values of 0.88 TPa and 0.751 GPa, respectively, the E_C value equals to 44.7 GPa.

Figure 6 compares the tensile stress–strain curves predicted by the multi-scale model with the results from the rule-of-mixtures. In these initial analyses, as can be seen, the stiffness of the matrix was enhanced significantly by the addition of carbon nanotubes. The result of the simulation of pure PP under tension is also added to the graph. While the initial stiffness of pure

PP is almost *0.768 GPa*, by adding the CNT to the RVE, the stiffness increased significantly to *1.35 GPa*. Such an increment, by *75%*, clearly shows the reinforcement effect of CNT on the composites even at an ISS value as low as *30 MPa*. Indeed, at low strains, the predicted stress–strain curve is much closer to linear behaviour given by the rule-of-mixtures. The deviation observed at larger strains is due to the non-linear behaviour of different phases involved in the RVE consisting of CNT, PP, CNT/polymer interface.
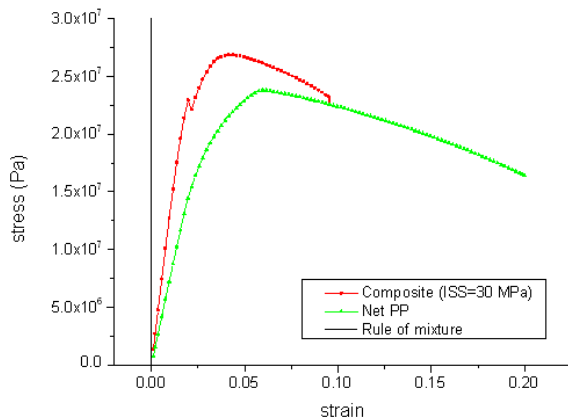

Fig. 6 Stress–strain curves for pure PP, composite and rule-of-mixture

4. CONCLUSIONS

A RVE finite element model for predicting the tensile behaviour of carbon nanotube-reinforced composites has been proposed. The continuum FE method has been employed for building the RVE and performing the analysis while the data regarding the behaviour of the nanotube are drawn from Morse potential, enabling thus the investigation of the impact of interfacial failure on the mechanical properties of the composite.

The simulation results have shown a significant enhancement in the stiffness of the polymer due to the addition of the nanotubes. The prediction of composite's initial stiffness was verified by the rule-of-mixtures and the initial stiffness value was *44.7 GPa*. The result also shows that stiffness has been increased over *75%* when inserting CNT into the RVE. This study of interfacial bonding of CNT/PP indicated that there could be an effective stress transfer from the PP resin to the nanotube even at ISS being as low as *30 MPa*.

5. ACKNOWLEDGEMENT

6. REFERENCES

[1] T. Ogasawara, T. Tsuda and N. Takeda, Stress-strain behaviour of multi-walled carbon nanotube/PEEK composites, *Composites Science and Technology*, Vol. 71, No. 2, pp. 73-78, 2011.

[2] P.-C. Ma, N.A. Siddiqui, G. Marom and J.-K. Kim, Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: A review, *Composites Part A: Applied Science and Manufacturing*, Vol. 41, No. 10, pp. 1345-1367, 2010.

[3] G. Broza, Thermoplastic elastomers with multi-walled carbon nanotubes: Influence of dispersion methods on morphology, *Composites Science and Technology*, Vol. 70, No. 6, pp. 1006-1010, 2010.

[4] D. Bikiaris, Microstructure and properties of polypropylene/carbon nanotube nanocomposites, *Materials*, Vol. 3, No. 4, pp. 2884-2946, 2010.

[5] M. Cadek, J.N. Coleman, K.P. Ryan, V. Nicolosi, G. Bister, A. Fonseca, J.B. Nagy, K. Szostak, F. Bequin and W.J. Blau, Reinforcement of polymers with carbon nanotubes: The role of nanotube surface area, *Nano Letters*, Vol. 4, No. 2, pp. 353-356, 2004.

[6] Ch. Li and T.-W. Chou, Elastic moduli of multi-walled carbon nanotubes and the effect of van der Waals forces, *Composites Science and Technology*, Vol. 63, No. 11, pp. 1517–1524, 2003.

[7] K.-T. Lau, Interfacial bonding characteristics of nanotube/polymer composites, *Chemical Physics Letters*, Vol. 370, No. 3-4, pp. 399-405, 2003.

[8] V. Lordi and N. Yao, Molecular mechanics of binding in carbon-nanotube-polymer composites, *Journal of Materials Research*, Vol. 15, No. 12, pp. 2770-2779, 2000.

[9] K. Liao and S. Li, Interfacial characteristics of a carbon nanotube-polystyrene composite system, *Appl. Phys. Lett.*, Vol. 79, pp. 4225-4228, 2001.

[10] S.J.V. Frankland, A. Caglar, D.W. Brenner and M. Griebel, Molecular simulation of the influence of chemical cross-links on the shear strength of carbon nanotube-polymer interfaces, *J. Phys. Chem. B*, Vol. 106, No. 12, pp. 3046-3048, 2002.

[11] H. Tan, L.Y Jiang, Y. Huang, B. Liu and K.C. Hwang, The effect of van der Waals-based interface cohesive law on carbon nanotube-reinforced composite materials, *Composites Science and Technology*, Vol. 67, No. 14, pp. 2941-2946, 2007.

[12] L.Y. Jiang, Y. Huang, H. Jiang, G. Ravichandran, H. Gao, K.C. Hwang and B. Liu, A cohesive law for carbon nanotube/polymer interfaces based on the van der Waals force, *Journal of the Mechanics and Physics of Solids*, Vol. 54, No. 11, pp. 2436-2452, 2006.

[13] K.I. Tserpes, P. Papanikos, G. Labeas and Sp.G. Pantelakis, Multi-scale modeling of tensile behavior of carbon nanotube-reinforced composites, *Theoretical and Applied Fracture Mechanics*, Vol. 49, No.1, pp. 51-60, 2008.

[14] Md.A. Bhuiyan, R.V. Pucha, M. Karevan and K. Kalaitzidou, Tensile modulus of carbon nanotube/polypropylene composites - A computational study based on experimental characterization. *Computational Materials Science*, Vol. 50, No. 8, pp. 2347-2353, 2011.

[15] E. Mohammadpour and M. Awang, Nonlinear finite-element modeling of graphene and single- and multi-walled carbon nanotubes under axial tension, *Applied Physics A*, Vol. 106, No. 3, pp. 581-588, 2012.

[16] W.B. Lu, J. Wu, J. Song, K.C. Hwang, L.Y. Jiang and Y. Huang, A cohesive law for interfaces between multi-wall carbon nanotubes and polymers due to the van der Waals interactions, *Comp. Meth. App. Mech. Engng.*, Vol. 197, No. 41-42, pp. 3261-3267, 2008.

[17] M. Bystrzejewski, A. Huczko, H. Lange, T. Gemming, B. Buchner and M.H. Rummeli, Dispersion and diameter separation of multi-wall carbon nanotubes in aqueous solutions, *J. Colloid Interface Sci.*, Vol. 345, No. 2, pp. 138-142, 2010.

[18] A.J. Blanch, C.E. Lenehan and J.S. Quinton, Optimizing surfactant concentrations for dispersion of single-walled carbon nanotubes in aqueous solution, *J. Phys. Chem. B*, Vol. 114, No. 3, pp. 9805-9811, 2010.

[19] N.G. Sahoo, S. Rana, J.W. Cho, L. Li and S.H. Chan, Polymer nanocomposites based on functionalized carbon nanotubes, *Progress in Polymer Science*, Vol. 35, No. 7, pp. 837-867, 2010.

[20] B. McCarthy, J.N. Coleman, R. Czerw, A.B. Dalton, M. in het Panhuis, A. Maiti, A. Drury, P. Bernier, J.B. Nagy, H.J. Byrne, D.L. Carroll and W.J. Blau, A microscopic and spectroscopic study of interactions between carbon nanotubes and a conjugated polymer, *J. Phys. Chem. B*, Vol. 106, No. 9, pp. 2210-2216, 2002.

[21] H.D. Wagner, O. Lourie, Y. Feldman and R. Tenne, Stress-induced fragmentation of multiwall carbon nanotubes in a polymer matrix, *Applied Physics Letters*, Vol. 72, No. 2, pp. 188-190, 1998.

[22] L.S. Schadler, S.C. Giannaris and P.M. Ajayan, Load transfer in carbon nanotube epoxy composites, *Applied Physics letters*, Vol. 73, No. 26, pp. 3842-3844, 1998.

[23] C.A. Cooper, S.R. Cohen, A.H. Barber and H.D. Wagner, Detachment of nanotubes from a polymer matrix, *Applied Physics Letters*, Vol. 81, No. 20, pp. 3873-3875, 2002.

[24] A.H. Barber, S.R. Cohen and H.D. Wagner, Measurement of carbon nanotube-polymer interfacial strength, *Applied Physics Letters*, Vol. 82, No. 23, pp. 4140-4142, 2003.

[25] H.D. Wagner, Nanotube–polymer adhesion: A mechanics approach, *Chemical Physics Letters*, Vol. 361, No. 1-2, pp. 57-61, 2002.

NELINEARNA, VIŠESKALNA METODA KONAČNIH ELEMENATA ZA PREDVIĐANJE VLAČNOG PONAŠANJA POLIMERNIH KOMPOZITA OJAČANIH UGLJIČNIM NANOCIJEVIMA

SAŽETAK

Mogućnost korištenja ugljičnih nanocijevi kao najjačih i najkrućih elemenata među kompozitima nano veličina i dalje predstavlja snažnu motivaciju za daljnja istraživanja. U ovome se radu opisuje proces modeliranja primjenom metode konačnih elemenata koji je prikladan za numeričko modeliranje mehaničkog odgovora polipropilena ojačanog ugljičnim nanocijevima s jednostrukom stijenkom. Ponuđen je višeskalni reprezentativni elementarni volumen za modeliranje vlačnog ponašanja kompozita ojačanih ugljičnim nanocijevima. Unutar reprezentativnog elementarnog volumena spomenuto pojačanje je modelirano u skladu sa svojom atomskom mikrostrukturom. Također, model temeljen na modificiranom Morseovom međuatomskom potencijalu korišten je za simuliranje individualne ugljične nanocijevi. Matrica je modelirana kao prostor u formi kontinuuma korištenjem prostornih elementata te je u svrhu opisa ponašanja prostornog elementa korišten pripadajući nelinearni materijalni model. Kohezijska zona je simulirana između nanocijevi i matrice s idealnim spojem sve dok površinsko posmično naprezanje ne prekorači odgovarajuću čvrstoću. Koristeći reprezentativni elementarni volumni element, modeliran je jednosmjerni kompozit koji se sastoji od nanocijevi i polimera, a rezultati su uspoređeni s odgovarajućim predviđanjima zadanima tzv. "pravilom mješavina". Učinak površinske posmične čvrstoće na vlačno ponašanje nano-kompozita je također razmotren. Utjecaj dodavanja ugljične nanocijevi s jednom stijenkom polimeru je raspravljen, a rezultati pokazuju da se vlačna čvrstoća i modul elastičnosti polimera znatno povećavaju u prisutnosti ugljičnih nanocijevi.

Ključne riječi: ugljična nanocijev, ojačani polimerni kompozit, višeskalna metoda, metoda konačnih elemenata, Morseov međuatomski potencijal.