JAST, Vol. 13, No. 2, pp. 1- 6

JAST
Journal of Aerospace Science and Technology

Scientific-Research Article

Multi-scale Modeling for Thermal Conductivity Analysis of Epoxy Nanocomposite - CNT

Ali Vahedi[1]*, Mohammad Homayoune Sadr[2] ,Saeed Shakhesi[3]

1 , 2 - Faculty of Aerospace Engineering, Amirkabir University of Technology -
3- Space Transportation Systems Research Institute, Iran Space Research Institute
* Tehran, Hafez St.

Email: *a.vahedi@aut.ac.ir

Hierarchical multi-scale modeling was used in the paper to investigate the contact area between the nanoparticle component and the surrounding environment. The modeling of the nanoparticle component and the interface region was designed using molecular dynamics. First, the desired thermal properties were obtained at the nanoscale, and then the obtained results were used at a larger longitudinal scale in a numerical solution by finite element method. Finally, by numerical homogenization, the optimal thermal properties were calculated, and the obtained results were compared with the existing experimental results. The effect of other influential parameters such as volume ratio, aspect ratio (length to diameter ratio), particle alignment on the interface region and the optimal thermal properties of the nanocomposite were also investigated. Three-dimensional CNT-Nanocomposite epoxy samples were investigated in this study. The overall thermal conductivity was evaluated by obtaining the interfacial thermal conductivity between the nanoparticle component and the surrounding environment (resin) and then changing the influential parameters. Relevant thermal properties and behavior of RVE and analysis of the results in all scales have been reviewed. Significant cases of curing and simulation of epoxy bonding and related hardener have been considered in the molecular dynamics modeling of nanocomposites.

***Keywords**: Thermal properties, Nanocomposite, Multi-scale modeling, Molecular dynamics, Finite element method, Carbon nanotubes, Epoxy*

Introduction

Designing and manufacturing advanced materials with optimal mechanical, electrical, and thermal properties is one of the continuous needs of technology development in the present era.

One of the main challenges in engineering, especially in aerospace, is the management of

1 Assistant professor (corresponding author)
2 Associate Professor
3 Associate Professor

Received: 9 December 2020
Accepted: 29 December 2020 Print ISSN: 1735-2134

thermal issues. Due to their high thermal conductivity, conventional metals transfer heat efficiently. However, they are not efficient in parts where the lightness of the structure is considered due to their high density and price. On the other hand, polymeric materials have a lower density and price, but their mechanical and thermal properties are low. Carbon nanostructures such as graphene and carbon nanotubes have the most mechanical and thermal properties and are therefore very suitable materials to be added to polymeric materials to enhance these properties. The effects of the atomic scale must be considered to simulate the coefficient of thermal conductivity of epoxy-CNT and to study the potential of CNT nanofiller to increase the coefficient of thermal conductivity of polymer composites. This is because phonons transmit a significant portion of the thermal energy through the vibrations of the atomic lattice in the contact area between the nanofiller and the surrounding matrix. Weak interactions of van der Waals bonds between nanoparticles and the surrounding polymer can reduce the coefficient of thermal conductivity. This indicates the importance of studying the interface using molecular dynamics. Other influential factors such as diameter, aspect ratio (length to diameter ratio), the volume ratio of CNTs, and the alignment and dispersion of CNTs within the matrix substrate should also be considered in the development of CNT composites. This study aims to identify and discuss the parameters mentioned above that affect the thermal properties of CNT polymer composites to simulate the coefficient of thermal conductivity of epoxy-CNT and to study the potential of CNT nanofillers to increase the coefficient of thermal conductivity of polymer composites. Therefore, heat transfer between CNT and epoxy is modeled using molecular dynamics simulation. Then a continuous model of polymer nanocomposite was fabricated using the finite element to evaluate the optimal coefficient of thermal conductivity. Finally, the effect of diameter, length, aspect ratio and volume ratio, alignment, and dispersion of CNTs inside the matrix substrate is systematically studied on the optimal coefficient of thermal conductivity of epoxy nanocomposites. This study aims to identify and discuss the parameters mentioned above that affect the thermal properties of CNT polymer composites.

Multi-scale modeling is developed to simulate heat transfer in CNT epoxy nanocomposite in this research. For this purpose, epoxy polymer and CNT amplifier atomic models were first fabricated using reactive molecular dynamics simulations. This step also involves bonding and curing the relevant epoxy resin and hardener. The most crucial goal of this advanced atomic model is to achieve interfacial-interference thermal conductivity between CNT and epoxy. In the next step, the optimal coefficient of thermal conductivity of the nanocomposite is evaluated using the finite element method. In the finite element analysis, the amount of interfacial-interference thermal conductivity determined by atomic simulation in the previous step determines the heat transfer rate between CNT and epoxy resin.

In this research, the LAMMPS software package [1] has been used to advance molecular dynamics simulation. To define atomic interactions for the CNT component, the optimized Tersoff potential, proposed by Lindsay and Broido [2], was used. It is worth noting that this version of the optimized Tersoff potential is accurate in simulating the thermal properties of graphene and reproducing the scattering curves of graphite phonon [2]. in the following, the construction of epoxy is discussed. Epoxy is a thermosetting polymer (thermoset) formed from two chemical agents: resin and hardener (curing agent). The resin consists of short polymer chains with epoxy groups at both ends, and the hardener contains polyamine monomers. The resin and chemical hardeners are mixed to form amine groups during the curing and bonding process. The epoxy resin contains DGEBA, which is cured with DETA in this research. Five DGEBA molecules react with two DETA molecules to form a 100% bond network structure. The CAMPASS potential function [4,3] was used to describe the atomic reactions of the DETA/DGEBA epoxy system. Optimized Tersoff potential was used for CNT modeling. Also, Lennard-Jones potential (6-9-LJ) was used to introduce van der Waals interactions between epoxy and CNT. DETA/DGEBA epoxy system (DGEBA as Resin and DETA as hardener) were created by repeating the original structure with a ratio of 5 to 2 and 37 repetitions containing 10925 atoms. The simulation time

interval was set to 0.25 femtoseconds. During the curing and bonding process, the chemical reactions were simulated using stepwise methods and the base distance criterion [5–8]. In this study, bonding is formed with a 3% chance if the atom distance between the corresponding groups of amine and epoxide is in the range of up to 6 angstroms, checked once every ten femtoseconds. In this system, the bond formation density reached 68%, and the epoxy density reached 1.13 gr/cm3 at a temperature of 300 K and a pressure of 1 atmosphere. It is noteworthy that in fabricated epoxy samples, the bond formation density is not uniform everywhere in epoxy and that it is not possible to measure the bond formation density locally and generally in practice [9-11]. Epoxy density is a suitable way to estimate the degree of bond formation [12]. As known, as the degree of bond formation increases, so does the epoxy density. For the epoxy mixture, the density was 1.128 gr/cm3, and the degree of bond formation was 68%, which is a perfect match compared to the experimental densities of 1.133 gr/cm3 [13] for DETA/DGEBA epoxy.

Multi-scale modeling

Figure 1 shows the atomic model of a single-layer CNT inside DETA/DGEBA cured epoxy after quenching by the Nose-Hoover method of constant pressure-constant temperature (NPT) at room temperature.

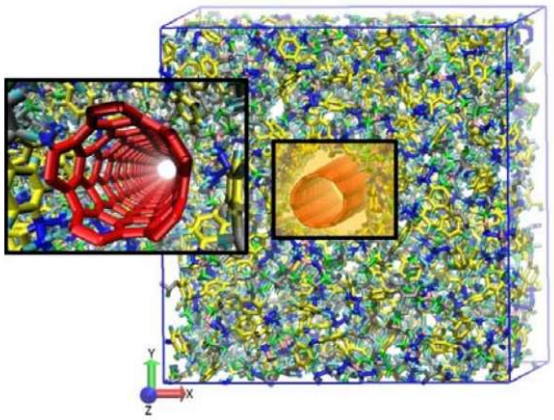

Figure 1: Molecular dynamics model developed to explain interatomic interactions in CNT-DGEBA/DETA epoxy system

After creating a balanced model of a single-layer CNT of cured DETA/DGEBA epoxy system, it is possible to calculate the interfacial-interference thermal conductivity between CNT and epoxy atoms. At this stage, after equilibrating the composite structure by the Nose-Hoover constant temperature (NVT) at room temperature (300 K), an initial temperature difference of 100 K between the CNT component and the matrix Epoxy is applied. After using this method, the temperature of the DETA/DGEBA system and CNT component are fixed at 300 and 400 K for 50 picoseconds, respectively. The NVT is switched off to simulate heat transfer between CNT and epoxy, and the composite structure is allowed to calm down by simulating NVE constant energy without constant temperature mode. CNT temperatures and the DETA/DGEBA epoxy system are calculated as a function of time during the NVE process. Based on the thermal turbulence, the results are for one stage of noise calculations, so six independent simulations with independent initial atomic velocities are performed. At this stage, the CNT and epoxy temperature results as a function of time during the NVE mode are averaged for all independent simulations to have a normal, noise-free curve [14,5–17]. As shown in figure 2, the temperature difference between CNT and epoxy decreases exponentially. Interfacial-interference thermal conductivity of λ is obtained using the following equation [15,14]:

$$\Delta T(t) = \Delta T(0) e^{\left[-\left(1/M_{Ep}C_{p_{Ep}} + 1/M_{CNT}C_{p_{CNT}}\right)\lambda St\right]}$$

Where M and Cp are the mass and heat capacity and S is the outer surface of the CNT, respectively. In this study, the heat capacity of CNT and epoxy is 1.87 j/gK [18] and 1 J/ [15], respectively. It is noteworthy that this method has already been used in several theoretical studies to evaluate the interfacial-interference thermal conductivity of CNT or graphene with other polymer substrates [14, 5–17]. Figure 2 (a) shows the average temperatures obtained from epoxy and CNT. Figure 2 (b) shows $\Delta T(t)/\Delta T(0)$ function, estimated by an exponential function.

Based on the results and equation (1), the interfacial-interference thermal conductivity of CNT and epoxy was calculated to be 5.4 MW/m2K. In the final step, the optimal coefficient of thermal conductivity of CNT-epoxy nanocomposite was evaluated using the finite element. As is common in the finite element

analysis of composite structures, a representative volume element (RVE) is considered with few CNT. Abacus software and coding in a Python environment are used to model CNT epoxy nanocomposite to evaluate the coefficient of thermal conductivity. A common assumption is to consider the geometry of the cylinders for CNTs and to consider the length-to-diameter ratio as the aspect ratio of CNTs.

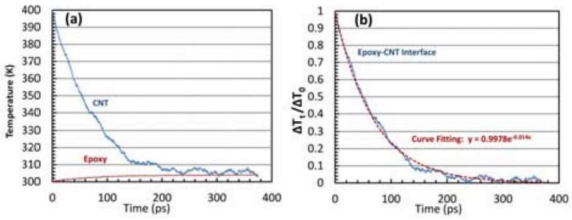

Figure 2 (a): Average temperatures from 6 independent MD simulations in the contact area **(b)** Normalized diagram for the temperature difference between CNT and epoxy as a function of time

Figure 3 (a): Example of a three-dimensional representative volume element with a CNT volume percentage of 2 and an aspect ratio of 40. **(b)** Mesh sample with DC3D4 element**. (c)** Three-dimensional thermal profile

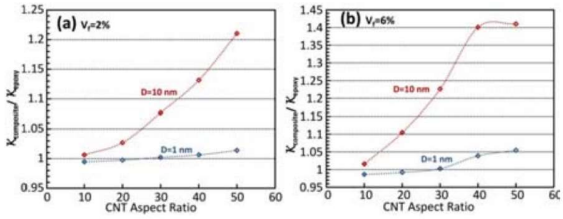

Figure 4: Effect of aspect ratio on the optimal thermal conductivity of CNT epoxy nanocomposites for two diameters of 1 nm and 10 nm and volumetric percentages of CNT: 2% and 6%

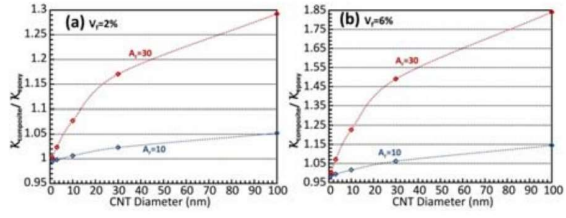

Figure 5: Effect of CNT diameter on the optimal thermal conductivity of CNT epoxy nanocomposites for 10 and 30 aspect ratios and 2 and 6% volumetric percentages

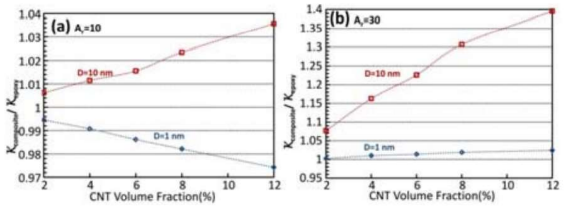

Figure 6: Effect of volumetric percentages of CNT on the optimal thermal conductivity for two diameters of 1 nm and 10 nm on the 10 and 30 aspect ratio.

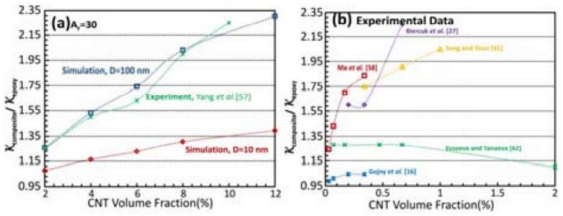

Figure 7: Comparison of laboratory results with multi-scale simulation results

Our findings have been compared with a study on CNT epoxy nanocomposites carried out by Yang et al. in a famous laboratory [73]. As it turns out, the simulation results for CNTs with an aspect ratio of 30 and a diameter of 100 nm are consistent with high accuracy with laboratory results. On the other hand, CNTs with a diameter of 10 nm have lower estimates than the experimental results. Also, figure 8 (b) compared experimental results related to the thermal conductivity of CNT epoxy nanocomposites. Some laboratory results are based on weight percentage and not volume percentage. Therefore, the density of CNT and epoxy is considered 1.8 [24] and 1.21 [25] gr/cm3, respectively, to convert weight percentage to volume percentage. As can be seen, the variations and differences in the measured laboratory values of the thermal conductivity related to the CNT epoxy nanocomposites are significant [29-19, 23, 26]. Based on multi-scale modeling, the difference between the experimental results can be simply due to the difference in diameter and length of CNT nanofillers inside epoxy in different laboratory samples. Therefore, the strength of interatomic interactions in the contact area between the CNT and the epoxy matrix, which is related to the chemistry of the nanocomposite, can be effective in interfacial thermal conductivity and thus in reducing or increasing the thermal conductivity of the whole nanocomposite. In summary, the results of multi-scale modeling suggest that CNTs with larger diameters and lengths and stronger interfacial contact (resulting in lower thermal resistance) can

increase the thermal conductivity of polymeric materials.

Conclusion

In this research, with the development of reactive molecular dynamics simulation and finite element modeling, the coefficient of CNT-thermal epoxy nanocomposite was investigated. For this purpose, an atomic model of cured epoxy with a hardener with a single layer CNT was designed. This simulated the heat transfer process in interfacial contact between matrix and CNT, and the coefficient of interference thermal conductivity in the interfacial contact was obtained. In the final stage, several continuous models of representative volume element (RVE) were constructed by finite element to evaluate the thermal conductivity of epoxy nanocomposites on a macro scale. In finite element analysis, the interfacial thermal conductivity obtained from the atomic model is used as the amount of thermal conductivity of the contact elements between the filler and the matrix. Advanced multidimensional modeling can draw essential findings related to heat transfer in CNT polymer nanocomposites. The results show that the interfacial heat conductivity in the contact phase between the epoxy and the nanofiller is crucial in the heat transfer of the nanocomposites when the CNT diameter is in the nanometer range. It has been shown that with increasing the diameter of CNTs, the thermal conductivity of the nanocomposite increases as a result of suppressing the thermal resistance in the contact phase. The results of multi-scale modeling show that the addition of CNT fillers with larger diameters has a high potential for heat transfer in polymer composites. It was also concluded that increasing the diameter at high aspect ratios significantly increased the optimal thermal conductivity. As the CNT aspect ratio increases, the optimal thermal conductivity also increases. In this regard, it is observed that the aspect ratio is more effective in increasing the effective thermal conductivity of the nanocomposite at higher CNT diameters. Finally, the effect of the volume percentage of CNT carbon nanotubes on the increase of optimal thermal conductivity was investigated. A significant effect of larger diameters was observed in this increase. This multidimensional research provides valuable insights into heat transfer in polymer nanocomposites to help design polymeric materials with high thermal conductivity properties.

References

[1] S. Plimpton, Fast parallel algorithms for short-range molecular dynamics, J. Comput. Phys. (1995). doi:10.1006/jcph.1995.1039.

[2] L. Lindsay, D.A. Broido, Optimized Tersoff and Brenner empirical potential parameters for lattice dynamics and phonon thermal transport in carbon nanotubes and graphene, Phys. Rev. B - Condens. Matter Mater. Phys. (2010). doi:10.1103/PhysRevB.81.205441.

[3] H. Sun, The COMPASS force field: Parameterization and validation for phosphazenes, Comput. Theor. Polym. Sci. (1998). doi:10.1016/S1089-3156(98)00042-7.

[4] H. Sun, COMPASS: An ab Initio Force-Field Optimized for Condensed-Phase ApplicationsOverview with Details on Alkane and Benzene Compounds, J. Phys. Chem. B. (1998). doi:10.1021/jp980939v.

[5] B. Mortazavi, O. Benzerara, H. Meyer, J. Bardon, S. Ahzi, Combined molecular dynamics-finite element multiscale modeling of thermal conduction in graphene epoxy nanocomposites, Carbon N. Y. 60 (2013) 356– 365. doi:https://doi.org/10.1016/j.carbon.2013.04.048.

[6] R. Ganji, A. Pakniat, M.R. Armat, M. Tabatabaeichehr, H. Mortazavi, The effect of self-management educational program on pain intensity in elderly patients with knee osteoarthritis: A randomized clinical trial, Open Access Maced. J. Med. Sci. (2018). doi:10.3889/oamjms.2018.225.

[7] H. Mortazavi, Could art therapy reduce the death anxiety of patients with advanced cancer? An interesting question that deserves to be investigated, Indian J. Palliat. Care. (2018). doi:10.4103/IJPC.IJPC_7_18.

[8] C. Li, A. Strachan, Molecular simulations of crosslinking process of thermosetting polymers, Polymer (Guildf). (2010). doi:10.1016/j.polymer.2010.10.033.

[9] G. Levita, S. De Petris, A. Marchetti, A. Lazzeri, Crosslink density and fracture toughness of epoxy resins, J. Mater. Sci. (1991). doi:10.1007/BF01130180.

[10]M. Ogata, N. Kinjo, T. Kawata, Effects of crosslinking on physical properties of phenol–formaldehyde novolac cured epoxy resins, J. Appl. Polym. Sci. (1993). doi:10.1002/app.1993.070480403.

[11] I. Yarovsky, E. Evans, Computer simulation of structure and properties of crosslinked polymers: Application to epoxy resins, Polymer (Guildf). (2001). doi:10.1016/S0032-3861(01)00634-6.

[12] C. Li, A. Strachan, Molecular dynamics predictions of thermal and mechanical properties of thermoset polymer EPON862/DETDA, Polymer (Guildf). (2011). doi:10.1016/j.polymer.2011.04.041.

[13] F.G. Garcia, B.G. Soares, V.J.R.R. Pita, R. Sánchez, J. Rieumont, Mechanical properties of epoxy networks based on DGEBA and aliphatic amines, J. Appl. Polym. Sci. (2007). doi:10.1002/app.24895.

[14] B. Mortazavi, H. Yang, F. Mohebbi, G. Cuniberti, T. Rabczuk, Graphene or h-BN paraffin composite structures for the thermal management of Li-ion batteries: A multiscale

investigation, Appl. Energy. (2017). doi:10.1016/j.apenergy.2017.05.175.

[15] C.F. Carlborg, J. Shiomi, S. Maruyama, Thermal boundary resistance between single-walled carbon nanotubes and surrounding matrices, Phys. Rev. B - Condens. Matter Mater. Phys. (2008). doi:10.1103/PhysRevB.78.205406.

[16] S.T. Huxtable, D.G. Cahill, S. Shenogin, L. Xue, R. Ozisik, P. Barone, M. Usrey, M.S. Strano, G. Siddons, M. Shim, P. Keblinski, Interfacial heat flow in carbon nanotube suspensions, Nat. Mater. (2003). doi:10.1038/nmat996.

[17] Z.Y. Ong, E. Pop, Molecular dynamics simulation of thermal boundary conductance between carbon nanotubes and SiO2, Phys. Rev. B - Condens. Matter Mater. Phys. (2010). doi:10.1103/PhysRevB.81.155408.

[18] W. Yan, X. Gao, W. Xu, C. Ding, Z. Luo, Z. Zhang, Heat transfer performance of epoxy resin Flows in a horizontal twisted tube, Appl. Therm. Eng. (2017). doi:10.1016/j.applthermaleng.2017.08.013.

[19] F.H. Gojny, M.H.G. Wichmann, B. Fiedler, I.A. Kinloch, W. Bauhofer, A.H. Windle, K. Schulte, Evaluation and identification of electrical and thermal conduction mechanisms in carbon nanotube/epoxy composites, Polymer (Guildf). 47 (2006) 2036–2045. doi:https://doi.org/10.1016/j.polymer.2006.01.029.

[20] A.A. Balandin, Thermal properties of graphene and nanostructured carbon materials, Nat. Mater. (2011). doi:10.1038/nmat3064.

[21] C.W. Chang, A.M. Fennimore, A. Afanasiev, D. Okawa, T. Ikuno, H. Garcia, D. Li, A. Majumdar, A. Zettl, Isotope Effect on the Thermal Conductivity of Boron Nitride Nanotubes, Phys. Rev. Lett. 97 (2006) 85901. doi:10.1103/PhysRevLett.97.085901.

[22] B. Mortazavi, J. Bardon, S. Ahzi, Interphase effect on the elastic and thermal conductivity response of polymer nanocomposite materials: 3D finite element study, Comput. Mater. Sci. (2013). doi:10.1016/ j.commatsci.2012.11.035.

[23] K. Yang, M. Gu, Y. Guo, X. Pan, G. Mu, Effects of carbon nanotube functionalization on the mechanical and thermal properties of epoxy composites, Carbon N. Y. 47 (2009) 1723–1737. doi:https://doi.org/10.1016/ j. carbon.2009.02.029.

[24]P.C. Ma, J.-K. Kim, B.Z. Tang, Effects of silane functionalization on the properties of carbon nanotube/epoxy nanocomposites, Compos. Sci. Technol. 67 (2007) 2965–2972. doi:https://doi.org/10.1016/ j.compscitech.2007.05.006.

[25]K.W. Garrett, H.M. Rosenberg, The thermal conductivity of epoxy-resin / powder composite materials, J. Phys. D. Appl. Phys. (1974). doi:10.1088/0022-3727/7/9/311.

[26]M.J. Biercuk, M.C. Llaguno, M. Radosavljevic, J.K. Hyun, A.T. Johnson, J.E. Fischer, Carbon nanotube composites for thermal management, Appl. Phys. Lett. (2002). doi:10.1063/1.1469696.

[27]L.E. Evseeva, S.A. Tanaeva, Thermal conductivity of micro-and nanostructural epoxy composites at low temperatures, Mech. Compos. Mater. (2008). doi:10.1007/s11029-008-0010-1.

[28]Y.S. Song, J.R. Youn, Influence of dispersion states of carbon nanotubes on physical properties of epoxy nanocomposites, Carbon N. Y. 43 (2005) 1378–1385. doi:https://doi.org/10.1016/j.carbon.2005.01.007.

[29] P.C. Ma, B.Z. Tang, J.K. Kim, Effect of CNT decoration with silver nanoparticles on electrical conductivity of CNT-polymer composites, Carbon N. Y. (2008). doi:10.1016/j.carbon.2008.06.048.