Composite Structures 137 (2016) 9–17

Contents lists available at ScienceDirect

Composite Structures

journal homepage: www.elsevier.com/locate/compstruct

Computational homogenization in RVE models with material periodic conditions for CNT polymer composites

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ARTICLE INFO

Article history:
Available online 10 November 2015

Keyword:
Homogenization
RVE models
Composites
Material periodic conditions
Modeling
Percolation analysis

ABSTRACT

RVE models with material periodic conditions are developed in generating a 3D network of fillers within the RVE. Computational homogenization in 3D RVE models is achieved using two approaches. In the first approach, statistical analysis with number of realizations is performed with increasing RVE size of randomly generated CNT within polymer. In statistical analysis, the filler that exceeds the RVE are translated until they find new spatial location within RVE. Simulations with increasing RVE size are performed until the standard deviation of computed apparent property for each RVE size is minimum to predict the critical RVE size. In the second approach, RVE models with material periodic boundary conditions are developed, which involve placing fillers that exceed the RVE into their respective position on the opposite face of RVE as if the RVE is part of a larger network of RVEs. Percolation threshold analysis of CNT filled polymer composites is presented using both computational homogenization approaches. It is demonstrated that computational homogenized models with material periodic conditions are independent of RVE size and provide homogenized results and are computationally efficient compared to statistical models.

1. Introduction

Carbon nanotube (CNT) reinforced polymer composites are finding increased interest due to their conductive properties in addition to their excellent mechanical properties. Many review articles [1] and research papers have been published in the last decade on CNT based polymer composites. Polymer/CNT composite films and fibers are also attractive in many potential applications such as sensors and electronics [2–4]. While significant insights have been achieved on various processing techniques in the manufacturing of CNT polymer composites, there are still many unresolved issues that need to be addressed theoretically and experimentally to harness the maximum benefit from these random heterogeneous materials.

Homogenization techniques allow heterogeneous materials such as composites, to be treated by continuum models, thus simplifying the computational analysis of these materials. Homogenization methods have extensively been used to estimate effective properties of random heterogeneous materials from the knowledge of the constitutive laws and spatial distribution of the constituents [5]. In homogenization methods the proposed estimations are given for random composite media with an infinite extension, and can therefore be denoted as asymptotic estimates [6]. Computational homogenization methods use numerical techniques and simulations on samples of the microstructure. In these models the notion of representative volume element (RVE) is of paramount importance [7]. There are many definitions for RVE in literature [8]. The RVE is the smallest volume over which a measurement can be made that yields a property value representative of the whole [5]. In continuum mechanics for a heterogeneous material, RVE can be considered as a volume that represents a composite statistically, which is small enough to be considered for macroscopic property representation and sufficiently large to ensure the independence of boundary conditions [9]. The overall properties of a sufficiently large domain in a random medium are deterministic and is independent of the type of boundary conditions, which requires a rather large size of RVE [10]. This rigorously justifies the fact that one can numerically compute the homogenized properties by simulating a single realization of a large heterogeneous medium. For volumes smaller than the RVE, a representative property cannot be defined and the continuum description of the material involves statistical volume element (SVE) and random fields.

Limited quantitative knowledge is available about critical RVE sizes of various engineering materials relating the size of RVE of the heterogeneous material to the characteristics length of inclusions [8]. For example in the case of reinforced elastic composites,

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http://dx.doi.org/10.1016/j.compstruct.2015.11.013
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the minimum proposed 2D RVE size is equal to twice the reinforcement diameter [11]. Numerical techniques can be used to compute the homogenized properties by the simulation of one single realization of the large medium and also in determining a critical size of RVE. For example Monte-Carlo simulations [12] were used to predict RVE size of disordered distributions of spheres in a matrix.

Statistical RVE models with spatially distributed 3D network of filler material represent an idealization of the actual structure of CNT polymer composite. In our previous work, statistical RVE based 3D models [13] with quick what-if analysis were presented to quantify the effects of various process parameters on the desired properties of CNT polymer composites. In these models the choice of statistical RVE is usually not unique, but it should be large enough to represent the filler morphology and spatial distribution and as small as possible to reduce the computation cost. Determining a critical size of such statistical RVE [13], which can predict a homogenized property of interest, is computationally very expensive. Computational homogenization [14,15] with material periodic boundary conditions is one alternative to reduce the computational complexity. In computational homogenization approaches, material periodic boundary conditions are applied to the RVE, which involve placing fillers that exceed the RVE into their respective position as if the RVE is part of a larger network of RVEs. The property of interest may include mechanical properties such as elastic moduli, percolation threshold, electrical and thermal properties, and other averaged quantities that are used to describe physical systems.

In this work, RVE models with a 3D network of fillers within the RVE are developed with algorithms for various boundary wall conditions. Computational homogenization in 3D RVE models is achieved using two approaches. In the first approach, statistical analysis with number of realizations is performed with increasing RVE size of randomly generated CNT within polymer. In statistical analysis, the filler that exceeds the RVE are translated until they find new spatial location within RVE. Simulations with increasing RVE size are performed until the standard deviation of computed property is minimum to predict the critical RVE size. In the second approach, RVE models with material periodic boundary conditions are developed, which involve placing fillers that exceed the RVE into their respective position on the opposite face of RVE as if the RVE is part of a larger network of RVEs. The following sections describe the development of RVE models with various boundary wall conditions and material periodicity. A computational methodology with seamless integration of analytical and CAD tools [13] is adopted to develop statistical analysis models of varying RVE size with translate boundary conditions. An efficient percolation threshold algorithm is developed to monitor filler-to-filler shortest distance in predicting the percolated network within RVE. Percolation threshold analysis of CNT filled polymer composites is presented using both computational homogenization approaches.

2. Algorithms for material periodicity and statistical analysis

2.1. Boundary wall conditions

RVE-based 3D models [13] are extended with boundary wall conditions in generating a 3D network of fillers within the RVE. Filler morphology and spatial distribution are determined either using random variables or probability distribution functions from image analysis [16] of experimental composite. If added filler is not within the boundaries of the RVE, instead of discarding the entire filler, various boundary wall condition algorithms are applied to the filler.

To develop a robust algorithm for wall boundary conditions many cases of CNT crossing the RVE boundaries are considered. Fig. 1 shows schematic of the cases considered, which include translate (Fig. 1(a)), cut-off (Fig. 1(b)) and 2D and 3D boundary crossings of material periodic conditions (Fig. 1(c)). The translate boundary wall condition involves moving the fillers that exceed the RVE until they find a new spatial location based on filler-to-filler distance algorithm. The cut-off boundary condition involves locally trimming the exceeded fillers around the limits of the RVE. The material periodic boundary condition involves placing the fillers that exceed the RVE into their respective position on the opposite face of RVE as if the RVE were part of a larger set of RVEs.

2.2. RVE models with material periodicity

RVE models with straight and wavy CNT fillers are considered. Fig. 2 illustrates the steps involved in the algorithm application of material periodic boundary conditions for wavy CNTs. The CNTs are generated within the RVE using a spline function defined by number of segments. The first point of the spline is located randomly within RVE and subsequent segment points are generated by the maximum angle defining the waviness of CNT [17]. If the original CNT spline is defined by five segments, as shown in Fig. 2, each portion of CNT crossing and within the RVE boundary are redefined using five segment points when periodic boundary conditions are applied. At the end of boundary conditions process, each portion crossing the RVE boundaries is shifted to opposite faces of RVE as shown in Fig. 2 and each portion of CNT crossing and within the RVE boundary retains the filler morphology with periodicity.

For RVE of 2000 nm cube with 0.2% volume fraction of filler, various material periodic conditions are shown in Figs. 3–5 for various applications. In the 3D analysis for mechanical or electrical property characterization any combination of these conditions can be used as appropriate. For example, if the 3D RVE models are used for predicting the effective mechanical properties of polymer composite [18,19], the 2D faces in the loading direction (X) are subjected to translate boundary conditions and the filler are relocated inside the RVE in the X direction and periodic boundary conditions are applied in other to faces, Y and Z. This condition is denoted as 1-3-3 as shown in Fig. 3. If the 3D RVE models are used for predicting percolation analysis as discussed in the later part of this paper and for predicting the effective electrical conductivity of CNT composite, the 2D faces in X direction, where the voltage is applied are subjected cut-off boundary conditions and periodic boundary conditions are applied in other to faces Y and Z. This condition is denoted as 2-3-3 as shown in Fig. 4. If the RVE models are used for quantifying the electrical conductivity of composite system using resistor–capacitor (R–C) approach [20] periodic boundary conditions are applied on all three faces of RVE. This condition is denoted as 3-3-3 as shown in Fig. 5. Fig. 6 illustrates material periodic boundary conditions, which involves placing the fillers that exceed the RVE into their respective position on the opposite face of RVE as if the RVE with 3-3-3 boundary conditions were part of a larger set of RVEs.

2.3. RVE models for statistical analysis

RVE models with random distribution of CNT within polymer are developed for statistical analysis. In all statistical analysis models, translate boundary wall conditions are used by moving the fillers that exceed the RVE until they find a new spatial locations within RVE as shown in Fig. 7. To predict the critical RVE size, models with increased RVE sizes are developed as shown in Fig. 8. Fig. 9 shows models with increased volume fraction for each RVE size.

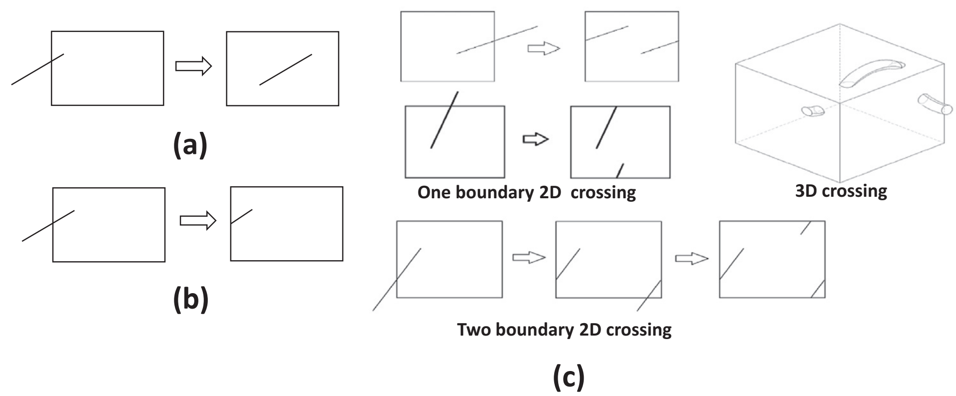

Fig. 1. Schematic of boundary wall condition cases (a) translate (b) cut-off and (c) material Periodicity.

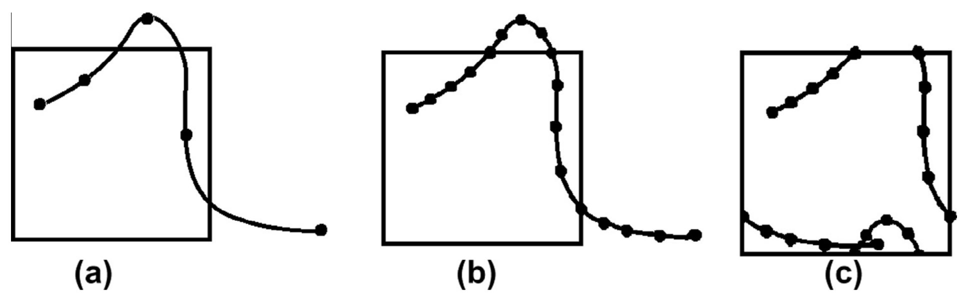

Fig. 2. Steps in applying periodic boundary conditions (a) CNT defined by five segments with two sections within boundary and two sections outside boundary (b) redefine each section with five segments (c) CNT after boundary conditions.

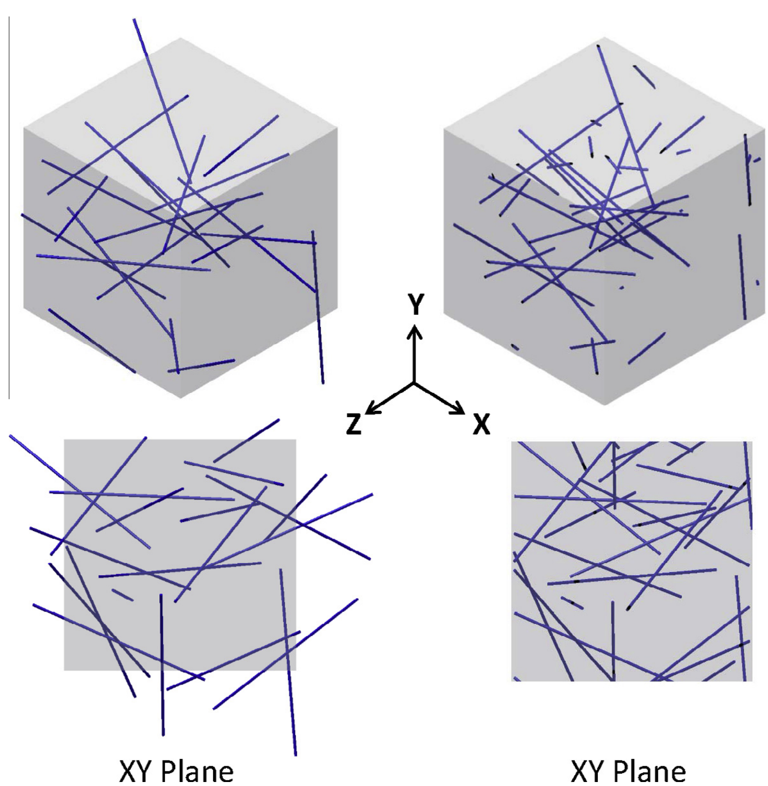

Fig. 3. 1-3-3 Boundary condition – translate in X, periodic in Y and Z, RVE: $2000 \times 2000 \times 2000$ nm, volume fraction: 0.2%.

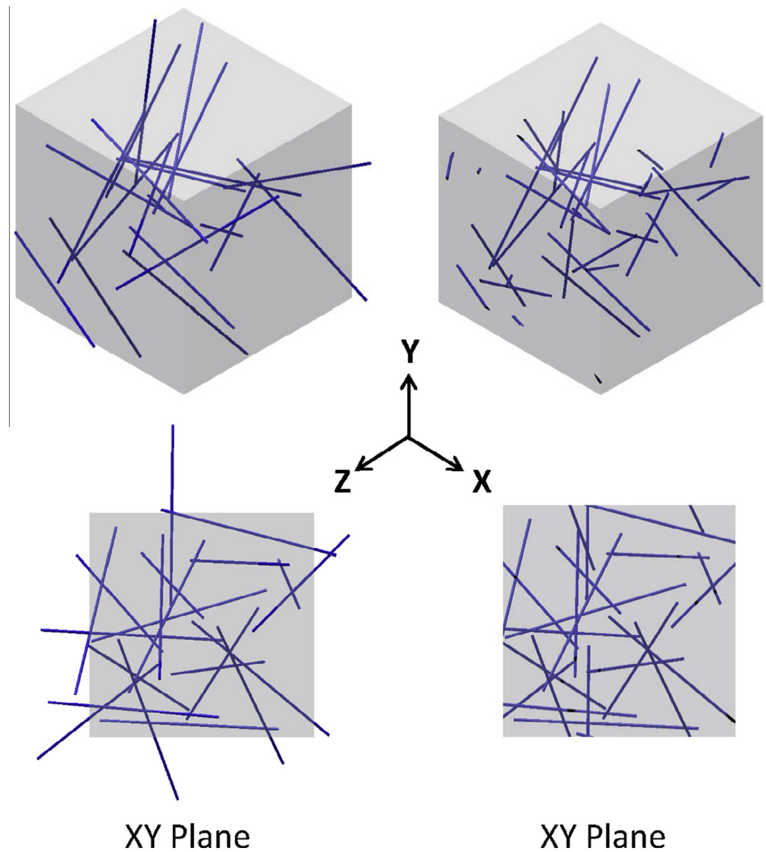

Fig. 4. 2-3-3 Boundary condition: cut-off in *X*, periodic in *Y* and *Z*, RVE: 2000 × 2000 × 2000 nm, volume fraction: 0.2%.

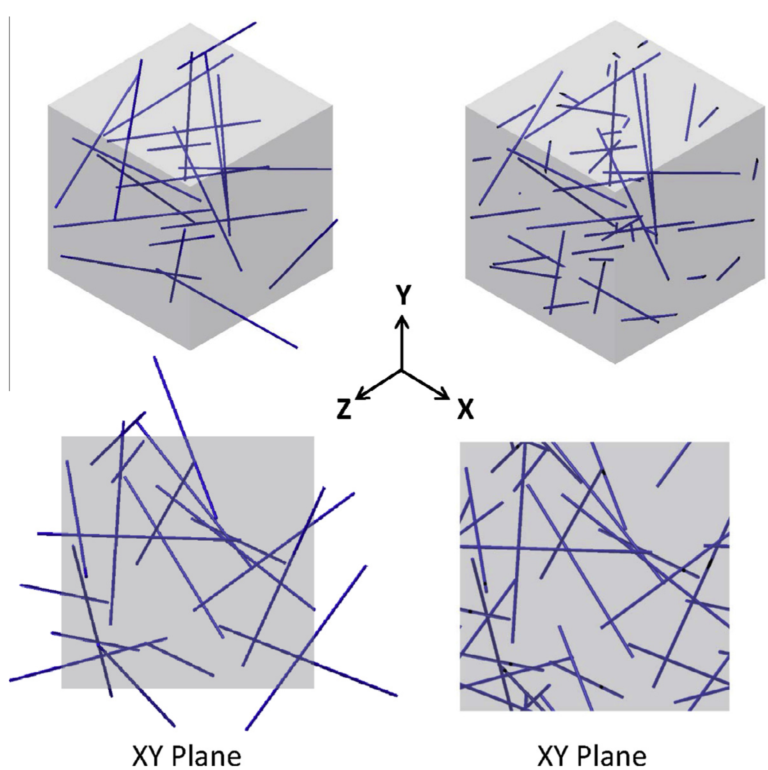

Fig. 5. 3-3-3 Boundary conditions: periodic in *X*, *Y* and *Z*, RVE: 2000 × 2000 × 2000 nm, volume fraction: 0.2%.

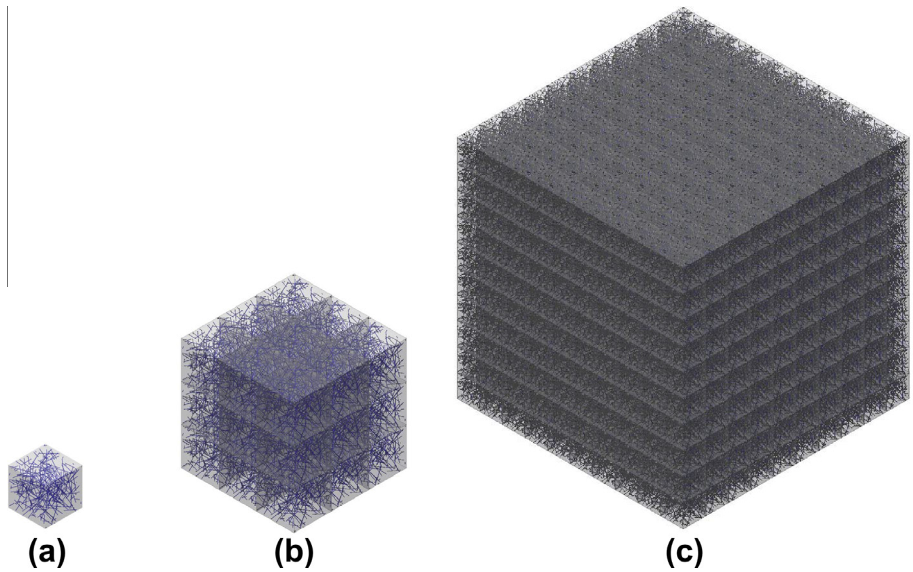

Fig. 6. Illustration of large RVE sample with periodically repeated RVEs. (a) RVE: 3000 × 3000 × 3000 nm (b) 9000 × 9000 × 9000 nm (c) 30 × 30 × 30 μ.

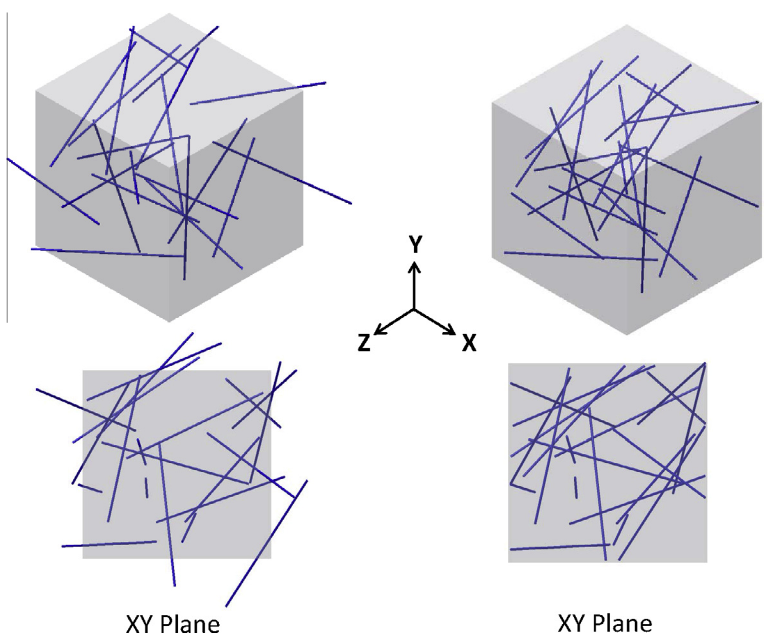

Fig. 7. 1-1-1 Boundary condition – translate in *X*, *Y* and *Z*, RVE 2000 × 2000 × 2000 nm, volume fraction: 0.2%.

3. Results and discussion

3.1. Percolation analysis in CNT polymer composites

Experimental findings in CNT reinforced polymeric matrix materials have shown that conductivity follows a percolation like behavior [21]. The electrical conductivity of a composite is generally characterized by its dependence on the filler volume fraction. At low filler loadings, the conductivity of the composite is still very close to that of the pure polymer matrix. At some critical loading, called the percolation threshold, the conductivity increases several orders of magnitude with very little increase in the filler amount. Many theoretical [22] and simulation models [23] based on filler volume fraction are proposed in the literature to predict the percolation threshold and conductivity behavior of composites. Percolation analysis of CNT/polymer composites is considered in this paper to demonstrate the developed computational homogenization models. Both statistical analysis models with translate boundary conditions (1-1-1) and homogenization models with material periodic boundary conditions (2-3-3) are used to predict the percolation threshold. A percolation threshold algorithm (see Fig. 10) with boundary wall conditions is developed to monitor the shortest distance between added fillers in predicting the volume fraction at which a 3D network of percolated network is formed within RVE.

3.2. Statistical analysis and critical RVE size

Simulations for percolation analysis are conducted for various RVE sizes. As mentioned earlier, the RVE size is usually not unique, but it should be large enough to represent the filler morphology and spatial distribution to predict a homogenized apparent prop-

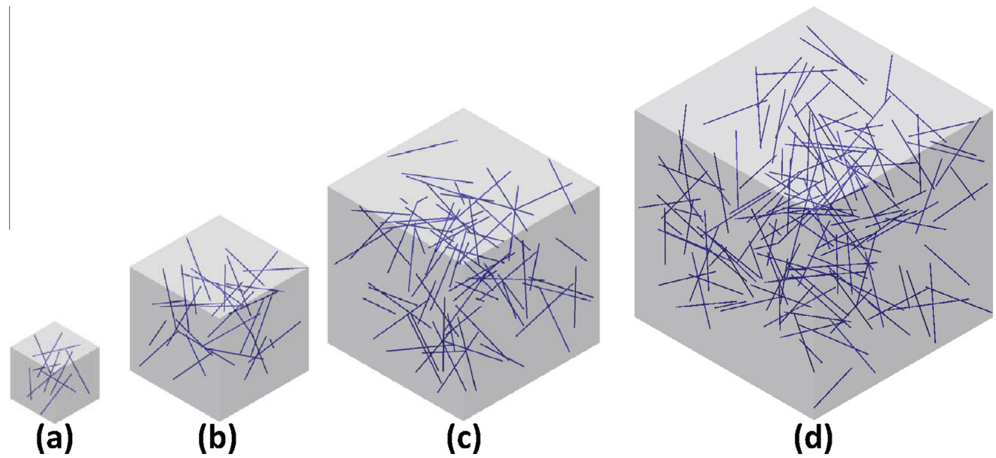

Fig. 8. RVE models for statistical analysis – (a) RVE: 2000 × 2000 × 2000 nm (b) 3000 × 3000 × 3000 nm (c) 4000 × 4000 × 4000 nm (d) 5000 × 5000 × 5000 nm, volume fraction: 0.1%.

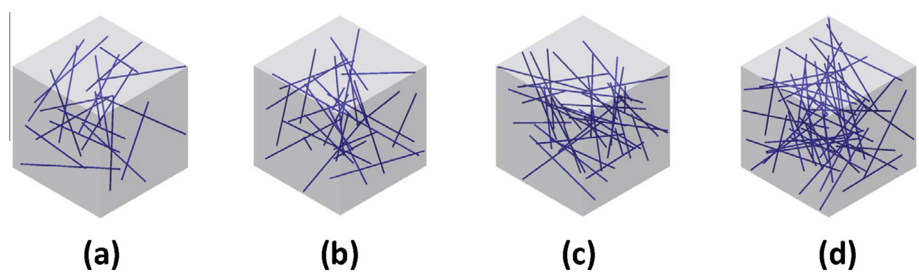

Fig. 9. RVE models for statistical analysis – (a) volume fraction: 0.2% (b) volume fraction: 0.3% (c) volume fraction: 0.4% (d) volume fraction: 0.5%, RVE: 2000 × 2000 × 2000 nm.

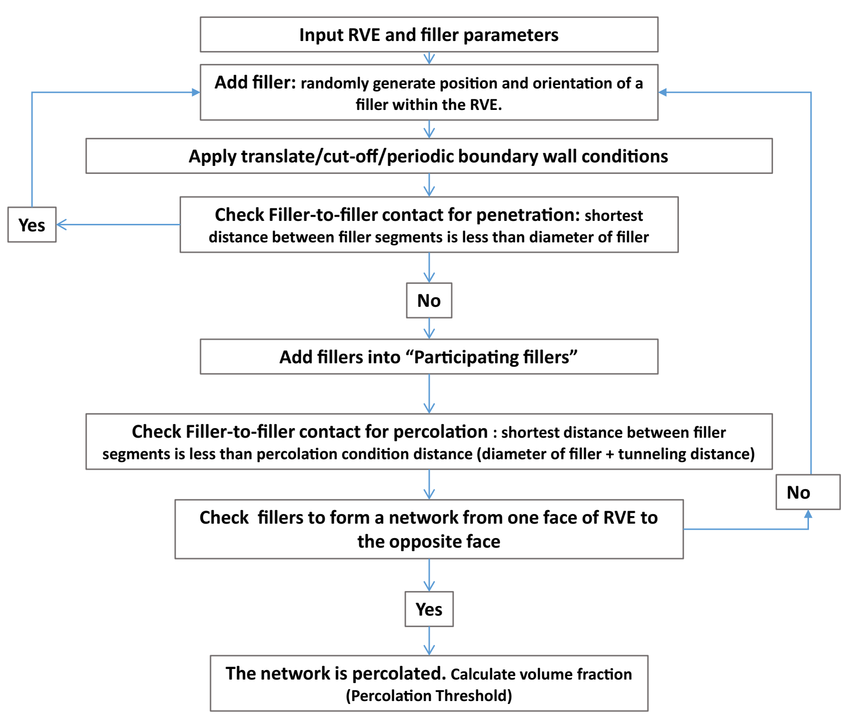

Fig. 10. Percolation threshold algorithm with boundary conditions.

erty of interest. For each RVE size CNTs are randomly added to polymer block. Translate boundary conditions (1-1-1, see Fig. 7) are used by moving the CNTs that exceed the RVE until they find a new spatial location within RVE. A percolation threshold algorithm (see Fig. 10) is used to track the CNTs, whose center-to-center distance is equal to the diameter of the CNT. Fig. 11 shows the 3D network evolution during a typical statistical analysis for a specific RVE size. Percolation in X direction is defined

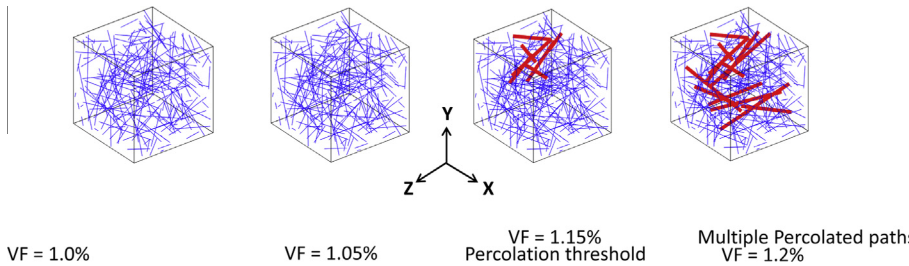

Fig. 11. Statistical analysis illustration of 3D network evolution for percolation and multiple percolated paths.

when a conductivity path is achieved with connecting CNTs in the *XY* plane as shown in Fig. 11 with bold CNTs. The volume fraction at which percolation happens is defined as percolation threshold. Because of the repeated random sampling of fillers within RVE used in the percolation analysis, the percolation threshold obtained varies when the analysis is repeated for the same RVE size as shown in Fig. 12. Percolation analysis for each RVE size is conducted for ten realizations and the percolation threshold values are plotted for each RVE size as shown in Fig. 12 represented by unfilled circles. When the cubic RVE size is increased the statistical variation in the predicted percolation threshold values (unfilled circles) reduced as shown in the Fig. 12. For a critical cubic RVE size of 4250 nm the standard deviation of percolation threshold values for ten realizations is less than 0.1, which is considered as a homogenized result.

Fig. 13 shows comparison of percolation threshold values for various CNT aspect ratios. Predicted critical RVE size of 4250 nm with varying aspect ratio of CNT is used for this purpose. The percolation threshold values averaged over ten simulations match very well with the values reported in the literature [24].

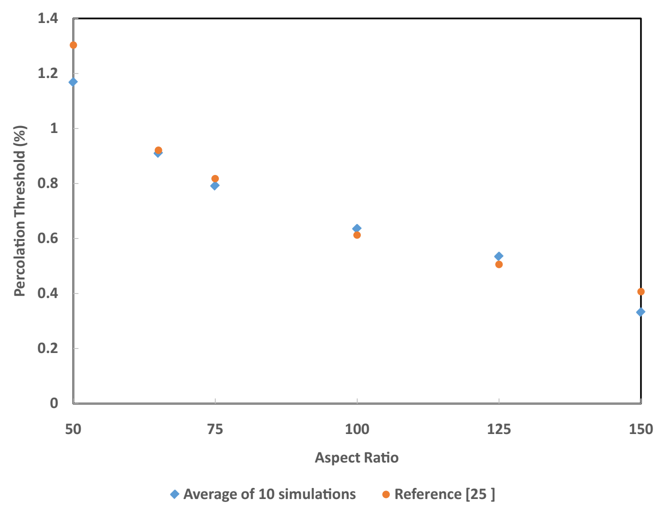

Fig. 13. Validation of percolation analysis: effect of aspect ratio.

3.3. Computational homogenization models with material periodicity

The percolation analysis using statistical models with translation boundary conditions (1-1-1) presented in the previous section indicates that the predicted percolation threshold values are dependent on RVE size. The percolation threshold values predicted exhibit statistical variation and are more scattered when the analysis is repeated for the same RVE size. For larger RVE sizes the scatter in the predicted percolation threshold gradually reduced leading to more homogenized results as shown in Fig. 12. It is also important to note that percolation analysis with statistical models requires large RVE size to arrive at more homogenized results and are thus computationally expensive. Percolation analysis is also performed using computational homogenization models with material periodic boundary conditions to study the effect of boundary conditions and RVE size. 2-3-3 material periodic boundary conditions (see Fig. 4) are used and the analysis is repeated for each RVE studied. Fig. 12 shows percolation threshold values pre-

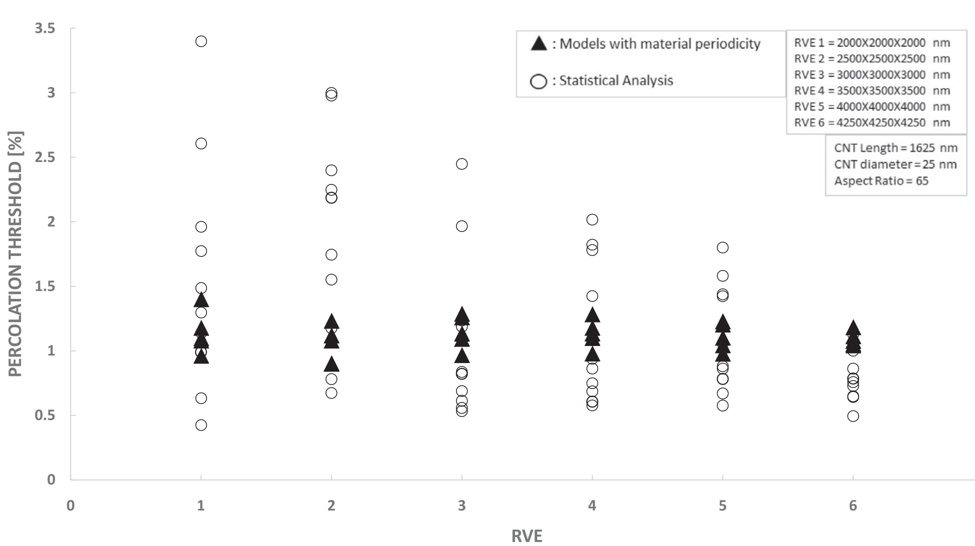

Fig. 12. Percolation threshold results comparison and critical RVE size for statistical analysis.

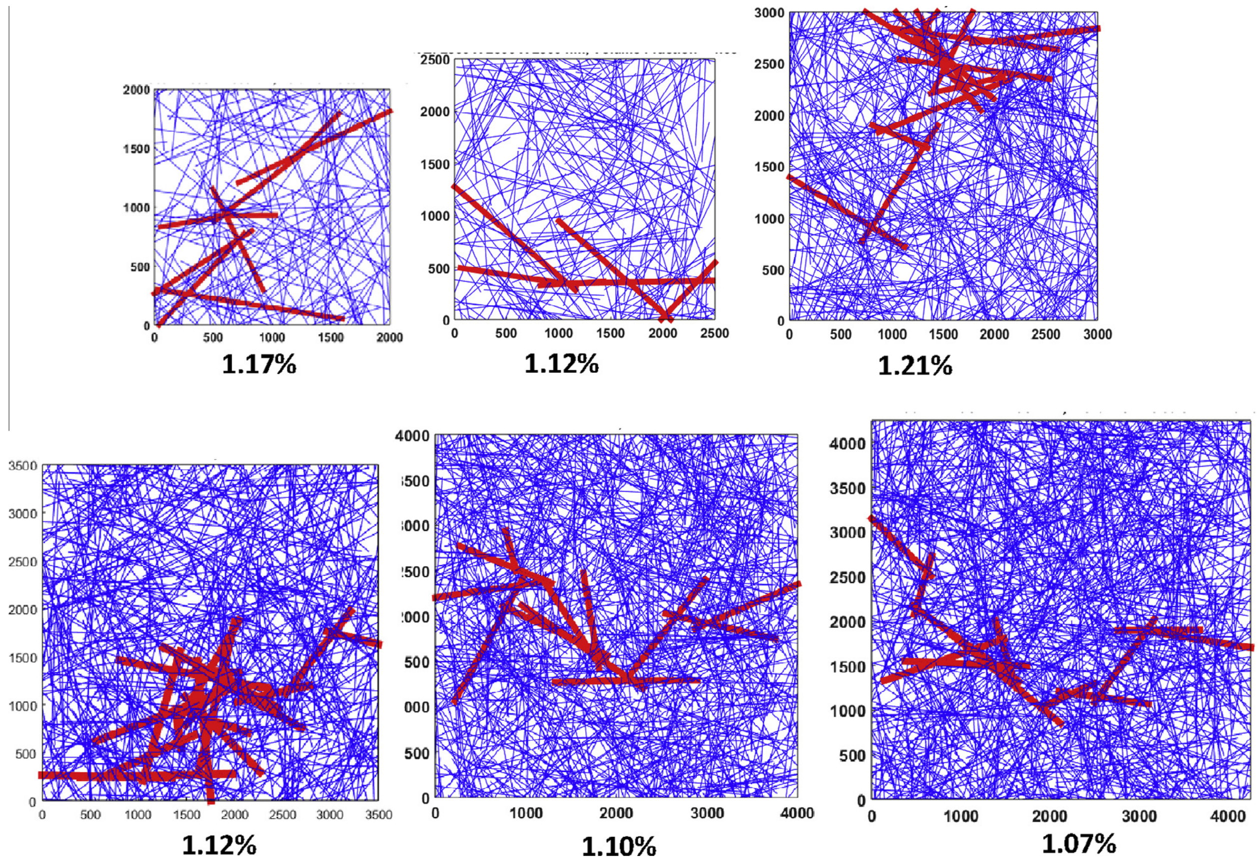

Fig. 14. Percolation threshold values for models with material periodicity.

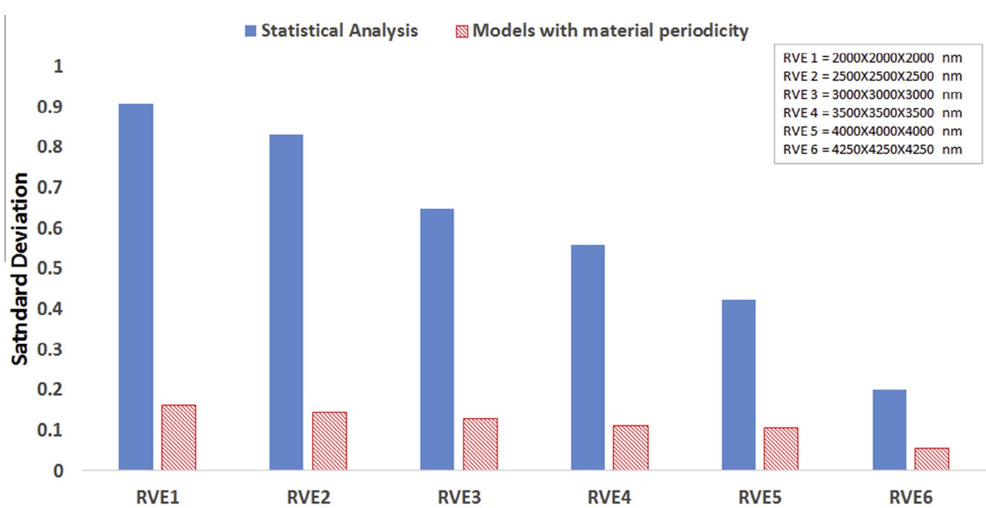

Fig. 15. Standard deviation of percolation threshold values for various realizations.

dicted with material periodic conditions (filled triangles) for each RVE size. As shown in Fig. 12, the statistical variation and scatter in percolation threshold values is low for models with material periodicity compared to statistical analysis models. Therefore only five simulations are performed for each RVE size. It is also noted from Fig. 12 that the percolation threshold values predicted by models with material periodic conditions (filled triangles) are essentially independent of RVE size indicating that the results are homogeneous and can be obtained with less computational effort and smaller RVE size.

Fig. 14 shows percolation threshold values for models with material periodicity for various RVE sizes. As can be seen from Fig. 14, a homogenized value of percolation threshold is achieved independent of RVE size. Fig. 15 shows standard deviation of percolation threshold values for various realizations using models with material periodicity which are consistently low for all RVE sizes studied. The standard deviation of percolation threshold values with statistical analysis on the other hand is very high for smaller RVE size and gradually reduces towards a homogenized solution for a large critical RVE size.

4. Conclusions

3D RVE models with various boundary conditions for analysis of composites with nanofillers are presented. Statistical analysis with number of realizations is performed with increasing RVE size of randomly generated CNT within polymer block. In statistical analysis, the filler that exceed the RVE are translated until they find new spatial location within RVE. Simulations with increasing RVE size are performed until the standard deviation of computed apparent property for each RVE size is minimum (<0.1) to predict the critical RVE size. The percolation analysis using statistical models with translation boundary conditions indicates that the predicted percolation threshold values are dependent on RVE size. The percolation threshold values predicted exhibit statistical variation and are more scattered when the analysis is repeated for the same RVE size. For larger RVE sizes, the scatter in the predicted percolation threshold gradually reduces leading to more homogenized results. Statistical analysis models with translate boundary conditions are computationally expensive requiring many realizations of large random media to predict homogenized results. RVE models with material periodic boundary conditions are developed, which involve placing fillers that exceed the RVE into their respective position on the opposite face of RVE as if the RVE is part of a larger network of RVEs. It is demonstrated that computational homogenized models with material periodic conditions are independent of RVE size and provide homogenized results and are computationally efficient compared to statistical models. The standard deviation of percolation threshold values for various realizations using models with material periodic conditions is consistently low for all RVE sizes studied. The standard deviation of percolation threshold values with statistical analysis on the other hand is very high for smaller RVE size and gradually reduces towards a homogenized solution for a large critical RVE size. The 3D RVE models with material periodicity presented in this work are attractive for homogeneous mechanical and electrical property estimation of CNT–polymer composite structures.

Acknowledgements

Support to Song through President's Undergraduate Research Award (PURA), Georgia Tech, and Support to Krishnaswamy through Multidisciplinary Materials Information Network Seed Grant from Institute of Materials, Georgia Tech is acknowledged.

References

[1] Hussain F, Hojjati M, Okamoto M, Gorga RE. Review article: polymer-matrix nanocomposites, processing, manufacturing, and application: an overview. J Compos Mater 2006;40:1511–75.
[2] Baughman RH, Zakhidov AA, de Heer WA. Carbon nanotubes – the route toward applications. Science 2002;297:787–92.
[3] Chae HG, Minus ML, Kumar S. Oriented and exfoliated single wall carbon nanotubes in polyacrylonitrile. Polymer 2006;47:3494–504.
[4] Alibeigloo A. Three-dimensional thermoelasticity solution of functionally graded carbon nanotube reinforced composite plate embedded in piezoelectric sensor and actuator layers. Compos Struct 2014;118:482–95.
[5] Hill R. Elastic properties of reinforced solids: some theoretical principles. J Mech Phys Solids 1963;11:357–72.
[6] Nezamabadi S, Potier-Ferry M, Zahrouni H, Yvonnet J. Compressive failure of composites: a computational homogenization approach. Compos Struct 2015;127:60–8.
[7] Kanit T, Forest S, Galliet I, Mounoury V, Jeulin D. Determination of the size of the representative volume element for random composites: statistical and numerical approach. Int J Solids Struct 2003;40:3647–79.
[8] Gitman IM, Askes H, Sluys LJ. Representative volume: existence and size determination. Eng Fract Mech 2007;74:2518–34.
[9] Ostoja-Starzewski M. Material spatial randomness: From statistical to representative volume element. Probab Eng Mech 2006;21:112–32.
[10] Sab K. On the homogenization and the simulation of random materials. Eur J Mech Solids 1992;11:585–607.
[11] Drugan WJ, Willis JR. A micromechanics-based nonlocal constitutive equation and estimates of representative volume element size for elastic composites. J Mech Phys Solids 1996;44:497–524.
[12] Gusev AA. Representative volume element size for elastic composites: a numerical study. J Mech Phys Solids 1997;45:1449–59.
[13] Pucha RV, Worthy J. Representative volume element-based design and analysis tools for composite materials with nanofillers. J Compos Mater 2014;48:2117–29.
[14] Otero F, Oller S, Martinez X, Salomón O. Numerical homogenization for composite materials analysis. Comparison with other micro mechanical formulations. Compos Struct 2015;122:405–16.
[15] Geers MGD, Kouznetsova VG, Brekelmans WAM. Multi-scale computational homogenization: trends and challenges. J Comput Appl Math 2010;234:2175–82.
[16] Bhuiyan MA, Pucha RV, Worthy J, Karevan M, Kalaitzidou K. Understanding the effect of CNT characteristics on the tensile modulus of CNT reinforced polypropylene using finite element analysis. Comput Mater Sci 2013;79:368–76.
[17] Dalmas F, Dendievel R, Chazeau L, Cavaillé J-Y, Gauthier C. Carbon nanotube-filled polymer composites. Numerical simulation of electrical conductivity in three-dimensional entangled fibrous networks. Acta Mater 2006;54:2923–31.
[18] Bhuiyan MA, Pucha RV, Worthy J, Karevan M, Kalaitzidou K. Defining the lower and upper limit of the effective modulus of CNT/polypropylene composites through integration of modeling and experiments. Compos Struct 2013;95:80–7.
[19] Qi L, Tian W, Zhou J. Numerical evaluation of effective elastic properties of composites reinforced by spatially randomly distributed short fibers with certain aspect ratio. Compos Struct 2015;131:843–51.
[20] Flandin L, Verdier M, Boutherin B, Brechet Y, Cavaillé JY. A 3-D numerical simulation of AC electrical properties of short fiber composites. J Polym Sci B Polym Phys 1999;37:805–14.
[21] Bauhofer W, Kovacs JZ. A review and analysis of electrical percolation in carbon nanotube polymer composites. Compos Sci Technol 2009;69:1486–98.
[22] Chen Y, Pan F, Wang S, Liu B, Zhang J. Theoretical estimation on the percolation threshold for polymer matrix composites with hybrid fillers. Compos Struct 2015;124:292–9.
[23] Berhan L, Sastry AM. Modeling percolation in high-aspect-ratio fiber systems. I. Soft-core versus hard-core models. Phys Rev E 2007;75:041120.
[24] Hu N, Masuda Z, Yan C, Yamamoto G, Fukunaga H, Hashida T. The electrical properties of polymer nanocomposites with carbon nanotube fillers. Nanotechnology 2008;19:215701.