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Article

Thermal Conductivity of Polymer Composites Filled with Nanofillers

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Abstract: Polymer nanocomposites are composed of polymer materials reinforced with nano fillers.In the present study the effective thermal conductivity of the composites filled with nanofillers has been investigated using commercially available finite element software ABAQUS 6.11. The nanofillers used were alumina particles and multi-walled carbon nanotubes (MWNTs) and the matrix was considered to be made of epoxy. For the analysis 2D and 3D Representative Volume Elements (RVEs) were generated using Random Sequential Adsorption (RSA) algorithm using MATLAB and Python scripts. Thermal conductivity was found out for 2D and 3D RVEs for different area and weight fractions respectively. Two different shapes of the alumina nanoparticles were considered: spherical (circular) and ellipsoidal (elliptical) for 3D (2D) analysis. It was found that the thermal conductivity was increased with the addition of nanofillers. The increase in thermal conductivity was approximately same for both types of inclusions at corresponding area or weight fractions in 2D or 3D analysis. The results showed that addition of MWNTs to the composites lead to a significant increase in thermal conductivity than spherical or ellipsoidal inclusions.

Keywords: polymer nanocomposites; thermal conductivity; finite element analysis; ABAQUS

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1. Introduction

Polymer nanocomposites are the materials which have nanoparticles dispersed in a polymer matrix. These nanoparticles can be of any shape but there is a restriction on their dimension that is atleast one of the dimensions must be in between 10-100 nm. These nanoparticles are dispersed so as to improve the properties of the polymer materials. Polymeric nanocomposites have polymeric materials such as thermoplastics, thermosets or elastomers and a nano reinforcing material. As the scale changes from micro to nano, physical and chemical properties change drastically. Nanocomposites have reinforcing particles of nano dimension so they have high surface to volume ratio and due to high surface area the interaction between reinforced particles increases and thus the properties like strength, stiffness etc. get increased.

Addition of nanofillers to the composite materials improve thermal conductivity thus nanocomposites have the potential to replace the metallic parts in electrical appliances. Increasing the thermal conductivity of the polymer composites has been a major concern and finds application in aerospace and electronics packaging industry where the heat dissipation becomes important [1,2]. These composites with nanofillers can be used as heat sinks in electrical systems if they have thermal conductivity around 1 to 30 W/mK [3]. For fuel cell applications, these nanocomposites must have thermal conductivity around 10 W/mK [4]. Higher thermal conductivity in nanocomposites can be achieved by addition of high weight fractions of suitable nanofillers. However, it is the functional properties of nanocomposites that are the main driving force in nanocomposite development. Functional properties such as barrier [5–7], flammability resistance [8] and ablation performance [9] are all greatly improved by the addition of small volume fractions of nanofillers.

It is known that the properties of composite materials are a function of the volume (weight) fractions, properties and orientations of the constituent phases. So to increase the thermal conductivity of the polymers fillers having high thermal conductivity must be used. It has been found that carbon nanotubes have exceptionally high thermal conductivity. Single walled CNTs have

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thermal conductivity of 6000 W/mK while that of multi walled carbon nano tubes is around 3000 W/mK.

The effect of shape, size, orientation and type of nano filler on thermal conductivity has been extensively studied by different research groups. Tekce et al.[10] investigated the effect of shapes of nanofillers of copper powders such as plates, fibers and spheres on thermal conductivity of polymer composites. Gojny et al. [11] reported the influence of the type of carbon nanotube (single-walled carbon nanotubes, double-walled carbon nanotubes and multi-walled carbon nanotubes) on the thermal conductivity of polymer composites.

Different research groups have developed different finite element models to investigate the effect of shape, size, orientation and type of filler on the thermal conductivity of polymer composites. Kumlutas and Tavman [12] investigated the effect of volume fraction of fillers on thermal conductivity of composites.

The main objective behind carrying out this study is to find out the effect of type, shape and area or weight fraction of fillers on the thermal conductivity of the composite material using finite element method. Two different shaped fillers are considered for the analysis and thermal conductivity has been compared for same area or weight fractions.

2. Numerical Approach

To carry out the finite element analysis the geometric model of the component is needed. To perform analysis of the polymer nanocomposites geometric models of the composites are required so RVEs are generated which is discussed in later sections.

2.1. Representative Volume Element

It is stated in Nemat-Nasser and Hori, that RVE for a material point of a continuum is a material volume which is statistically representative for the infinitesimal material neighborhood of that material point[13]. It is the smallest volume over which if any material property is calculated it will be same as that of whole composite. In other words, it represents the composite as a whole. RVE has the same volume or area fraction as that of whole composite and gives the properties of the composite if proper boundary conditions are imposed upon it. The rationale behind using RVE as the starting point instead of whole composite for analysis is that it requires less computational time and resources to perform analysis on RVEs.

One of the major challenges in the selection of RVE is its size because of two major constraints mentioned as below:

1. It should be large enough to capture all the inhomogeneities and represent them as a whole.
2. It should be as small as possible so as to reduce the computational resources.

Drugan and Willis state that the minimum size of the RVE is the smallest volume element of the composite that is “statistically representative of the composite" [14]. They proved in their research that the minimum size of any RVE should be atleast equal to the twice of the diameter of the inclusion particles and found the results to be in good agreement with the experimental values and reported maximum error of only 5%.

At macroscopic level, in a composite generally an array is defined and then RVE is defined. Figures 1(a) and 1(b) show the two macroscopic arrays and the corresponding RVEs.

2.2. Generation of RVEs using RSA Algorithm

In the present work, RVE with randomly oriented spherical particles have been generated to represent the composite. The RVEs have been generated using Random Sequential Adsorption Algorithm (RSA Algorithm). The radius of the spherical (circular) nanoparticles was taken as 17.5 nanometers. Major radius of ellipsoidal (elliptical) nanoparticles was also 17.5 nm while minor radii were kept 10 nm.

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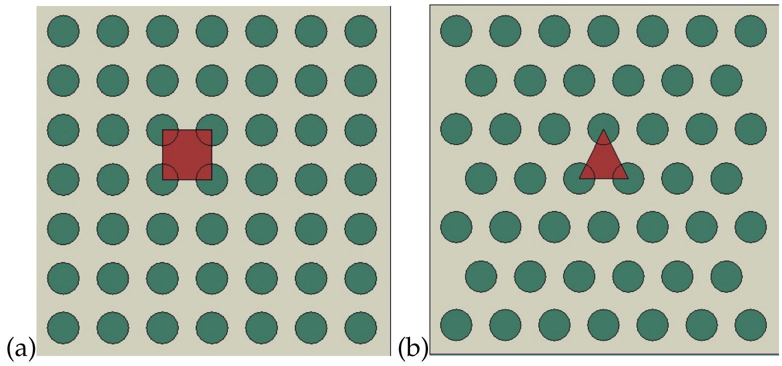

Figure 1. (a) Square array with square RVE **(b)** Hexagonal array with triangular array

Following steps are involved in generation of RVEs using RSA algorithm:

1. First of all the dimensions of the RVE and inclusions are chosen.
2. Then a random particle of the desired shape is generated.
3. It is checked if the particle is inside the RVE or not. If the particle is completely outside the RVE then it should be rejected and if it is completely inside then it is retained. Another case is encountered when the particle intersects with the boundaries of the RVE in that case it can either be discarded or the part inside the RVE is retained and the part lying outside the RVE is replicated as it is on the opposite boundary or face but lying inside.
4. Similarly another particle is generated but then it is checked if it is intersecting with another already pre-existing particle inside the RVE. If it is intersecting with any of the pre-existing particles then they it is discarded.
5. Following steps 3 and steps 4 the particles are generated till the desired volume/weight fraction is achieved.

The RVE was generated using RSA algorithm to provide for user specified minimum distance between neighbour fillers. The centre distance between the neighbour fillers was kept equal to 2r+c, where r is the radius of the circular (spherical) inclusions and major radius of the elliptical (ellipsoidal) inclusions and 'c' is any arbitrary number chosen appropriately. Here value of 'c' was taken as 3nm.

From MATLAB code (presented in Appendix) the centres of the spheres and ellipsoids were extracted and using PYTHON scripts the RVEs with different weight fractions were generated in ABAQUS. Different RVEs were generated with the same area or weight fractions taken for different shaped inclusions but the number of inclusions were different in each case. The motivation behind keeping the area or weight fractions same is to check the effect of shape of the inclusions on effective thermal conductivity of the nanocomposites.

2.3. Finite Element Model

Once the Python scripts were generated, RVEs in ABAQUS were generated suitable material properties and boundary conditions were applied which are discussed further. The particles are assumed to be perfectly bonded to the matrix. In the present study matrix of epoxy has been taken while alumina and MWNTs as nanofillers have been taken into consideration for the analysis. 2D RVEs with circular and elliptical inclusions are shown in Figures 2(a) and 2(b).

In case of MWNTs, they have been modeled as isotropic solid cylinders having diameter of 25 nm and length of 30 nm as shown in Figure 3.

3D RVEs with spherical and ellipsoidal fillers are as shown in Figures 4(a) and 4(b).

Material properties are shown below in Table 1.

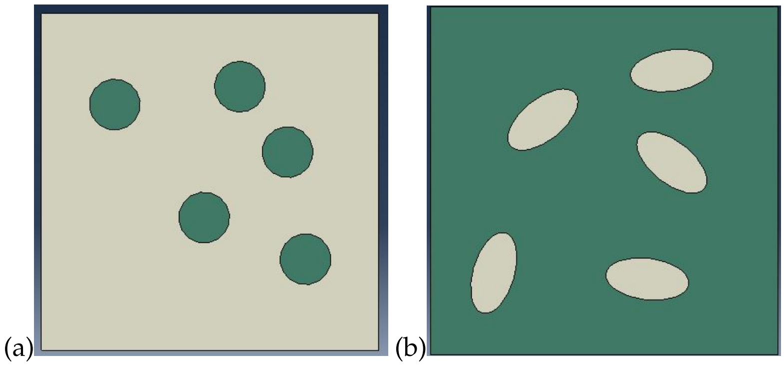

Figure 2. 2D RVEs with **(a)** circular inclusions **(b)** elliptical inclusions

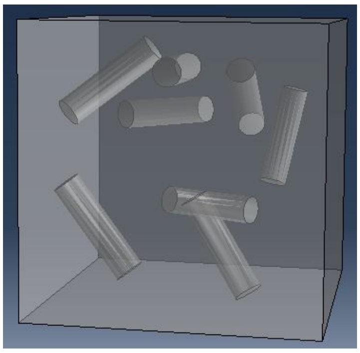

Figure 3. 3D RVE with cylindrical inclusions generated in ABAQUS

Table 1. Material Properties of Matrix and Fillers

Property	Matrix	Fillers
Thermal Conductivity	0.208 W/mK	36 W/mK for alumina 3000 W/mK for MWNT
Density	1.17 g/cm^3	4 g/cm^3 for alumina 1.75 g/cm^3 for MWNT

Since RVE is used in place of composite to determine the effective material properties so choice of appropriate boundary conditions become important. Using such boundary conditions through which RVE can simulate the response of the whole composite is known as numerical homogenisation. So, to simulate the response of the polymer nanocomposites as a whole periodic boundary conditions have been imposed.

Figures 5(a) and 5(b) show the boundary conditions imposed on 3D and 2D RVEs. Heat flux boundary conditions are imposed on faces (edges) orthogonal to the conduction axis. The four (two) lateral faces (edges) to the conduction axis are insulated to realize periodic boundary conditions. The effective thermal conductivity λ_i along the conduction axis x_i is defined by Fourier's steady-state heat conduction equation given as:

$$Q_i = -\lambda_i \frac{dT_i}{dx_i}$$

where i denotes three (two) principal directions for 3D (2D) RVE, Q_i is the heat flux and $\frac{dT_i}{dx_i}$ is the temperature gradient. For cubic RVE of length L effective thermal conductivity λ_i is computed as below:

$$\lambda_i = \frac{Q_i L}{\Delta T_i}$$

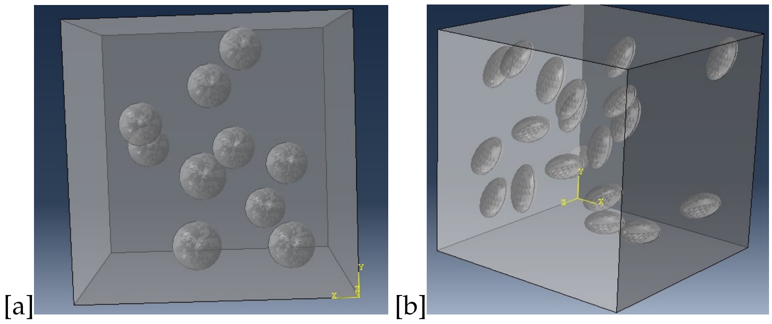

Figure 4. 3D RVEs with **(a)** spherical inclusions **(b)** ellipsoidal inclusions

where ΔT_i is the temperature drop across the length of the RVE. Effective thermal conductivity was calculated along the principal directions and average effective thermal conductivity is given as:

$$\lambda = \frac{\sum_{i=1}^{n} \lambda_i}{n}$$

where n is the number of principal directions for RVE. For 3D case, it is 3 while for 2D case its value is 2. So, for 2D analysis for each case 2 RVEs were simulated and for 3D analysis 3 RVEs were simulated to get the average value of effective thermal conductivity.

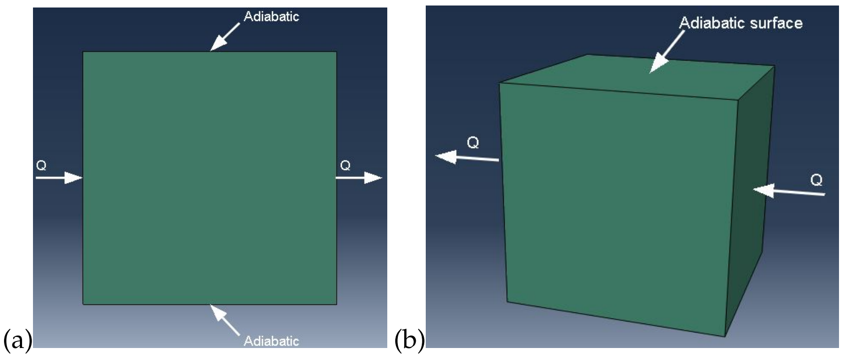

Figure 5. Periodic boundary conditions for **(a)** 2D RVE **(b)** 3D RVE

3. Results and Discussion

In order to capture the effect of weight or area fraction of nanofillers on the thermal conductivity different RVEs with varying weight or area fraction were simulated it was found that the as the fraction of the nanofillers increases the effective thermal conductivity also increases. The reason behind this increase is that at higher fractions the particles show good inter connectivity among themselves and form conductive chains thus greatly contribute towards the thermal conductivity of the polymer nanocomposites. Two different shaped inclusions were also considered to find out the the effect of shape of the filler and it was found that at the same weight (area) fractions the value of effective thermal conductivity was almost same for spherical (circular) and ellipsoidal (elliptical) inclusions as shown in Figures 6(a) and 6(b).

Further the analysis was carried out with MWNT as filler and it was found that MWNTs had a significant effect on thermal conductivity as compared to the alumina nanoparticles. It was found that for the same weight fractions the increase in thermal conductivity due to addition of MWNTs is much higher than that of alumina nanoparticles. The reasons behind such significant increase are that MWNTs easily form conductive chains as than alumina nanoparticles and their thermal conductivity is much higher. It can be observed from Figure 7 that the as the weight fraction increases thermal conductivity increases drastically and it becomes arounnd five times than that of neat epoxy.

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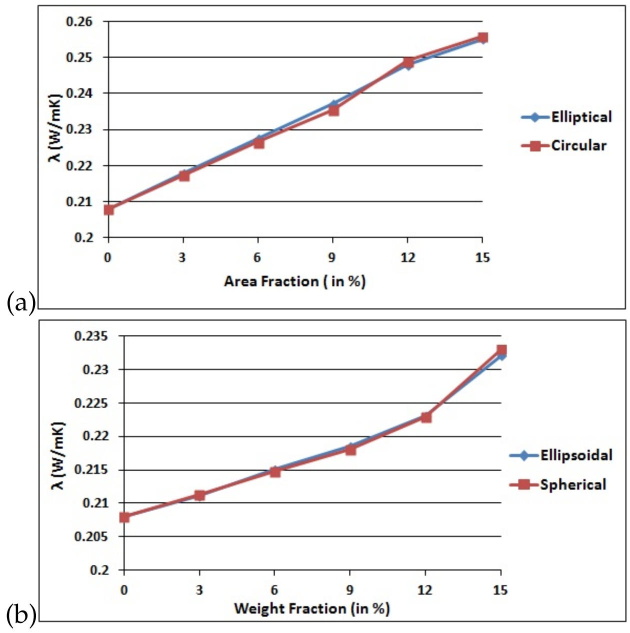

Figure 6. Comparison of effective thermal conductivity at different fractions for **(a)** 2D RVE and **[b]** 3D RVE

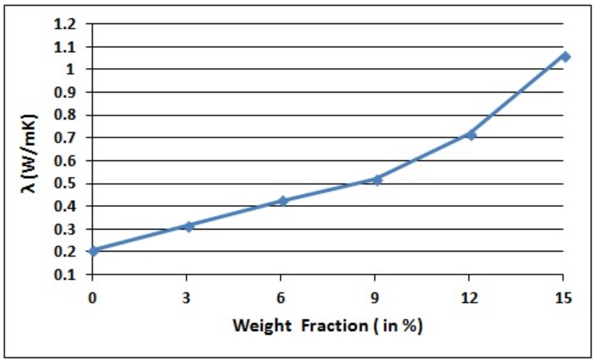

Figure 7. Variation of effective thermal conductivity with weight fraction MWNT as inclusion

Appendix. MATLAB code for generation of cubic RVE with spherical inclusions

Here the MATLAB code has been presented which was used to determine the centres of the spheres. Similar code was written for the generation of elliptical and cylindrical inclusions with minor changes like parametric equations and dimensions. This code uses the steps described in section 2.2. Some of the key points related to the MATLAB code are mentioned as below:

1. ***rand*** function was used for generating matrix of N x 3 random numbers which were used as centers of the spheres. It was ensured that all the spheres with those centers were lying completely inside the RVE.
2. The first set of the matrix was used as center of the first sphere.
3. For any n^{th} sphere distances were checked with (n-1) spheres, so in all (n*(n-1))/2 distances were checked. If all the distances were greater than or equal to 2*r+c then only spheres were generated using that coordinate.
4. All the centers which passed the constraint mentioned in step 3 were saved in Excel file which were further used in PYTHON script.

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```
clc
clear all
hold on
grid on
filename='rve3dCC.xlsx'   %generation of files to write the co-ordinates of centre
filename='rve3dDD.xlsx'
filename='rve3dEE.xlsx'
a=292;   %side of rve
x=[0;a;a;0;0;a;a;0;0;0;0;0;a;a;a;a];
y=[0;0;a;a;a;a;0;0;0;a;a;0;0;0;a;a];
z=[0;0;0;0;a;a;a;a;0;0;a;a;a;0;0;a];
plot3(x,y,z)
b=1;
r=17.5  %radius of sphere
n=25   % assumed number which will be sufficient
random=r+(a-2*r)*rand(n,3) % a+(b-a)*rand(n,2)a is the lower limit and b is the upper limit
for i=1:1:n

    c(i)=random(i,1);  %extracting the x,y and z co-ordinates
    d(i)=random(i,2);
    e(i)=random(i,3);
end
j=0;
for u=0:pi/18:pi
    i=0
    j=j+1
    for w=0:pi/9:2*pi
        i=i+1
        x(i,j)=[c(1)+r*sin(u)*cos(w)];   %parametric equation for sphere
        y(i,j)=[d(1)+r*sin(u)*sin(w)];
        z(i,j)=[e(1)+r*cos(u)];
    end

end
surf(x,y,z)


       for i=2:1:n
           f=0
           for k=1:1:i-1

               aa(k)=sqrt((c(i)-c(k))*(c(i)-c(k))+(d(i)-d(k))*(d(i)-d(k))+(e(i)-e(k))*(e(i)-e(k)));
               if(aa(k)>(2*r+3)) %checking if distance is greater than specified value
                   f=f+1;

                   if (f==i-1)
                       j=0;
for u=0:pi/18:pi
    p=0
    j=j+1
```

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```
    for w=0:pi/9:2*pi
        p=p+1;

        x(p,j)=[c(i)+r*sin(u)*cos(w)];
        y(p,j)=[d(i)+r*sin(u)*sin(w)];
        z(p,j)=[e(i)+r*cos(u)];


        end

        end
        C(b)=[c(i)]
        D(b)=[d(i)]'
        E(b)=[e(i)]'
        b=b+1;

surf(x,y,z)
 beta = 0.01;
brighten(beta)
                   end
               end
           end

       end
       CC=C'
       DD=D'
       EE=E'

xlswrite('rve3dCC.xlsx',CC)  % writing the centres to the corresponding files
xlswrite('rve3dDD.xlsx',DD)
xlswrite('rve3dEE.xlsx',EE)
```

References

1. J. Schuster, D. Heider, K. Sharp and M. Glowania, *Compos. Sci. Technol.*, **2008**, *68*, 2085–2091.
2. J. Zeng, R. Fu, S. Agathopoulos, S. Zhang, X. Song and H. He,*J. Electron. Packag.*, **2009**, *131*, 1–7.
3. King JA, Tucker KW, Vogt BD, Weber EH, Quan C. Electrically and thermally conductive nylon 6,6. *Polym Compos*, **1999**; *20(5)* :643–54.
4. Cunningham BD, Huang J, Baid DG. Review of materials and processing methods used in the production of bipolar plates for fuel cells. *Int Mater Rev*, **2007**; *52(1)* :1–13.
5. Yano K, Usuki A, Okada A, Kurauchi T, Kamigaito O. *Journal of Polymer Science Part A: Polymer Chemistry*, **1993**; *31*:2493.
6. Messersmith PB, Giannelis EP. *Chemistry of Materials*, **1994**; *6* :1719.
7. Messersmith PB, Giannelis EP. *Journal of Polymer Science Part A: Polymer Chemistry*, **1995** ; *33* :1047.
8. Gilman JW. *Applied Clay Science*, **1999** ;*15* :31.
9. Vaia RA, Price G, Ruth PN, Nguyen HT, Lichtenhan *J. Applied Clay Science*, **1999** ;*15* :67.
10. Tekce HS, Kumlutas D, Tavman IH. Effect of particle shape on thermal conductivity of copper reinforced polymer composites. *J Reinf Plast Comp*, **2007** ;*26(10)* :113–21.
11. Gojny FH, Wichmann MHG, Fiedler B, Kinloch IA, Bauhofer W, Windle AH, et al. Evaluation and identification of electrical and thermal conduction mechanisms in carbon nanotube/epoxy composites.*Polymer*, **2006** ;*47* :2036–45.

12. Kumlutas D, Tavman IH. A numerical and experimental study on thermal conductivity of particle filled polymer composites. *J Thermoplast Compos*, **2006** ;*19* :441–55.
13. J.M. Tyrus, M. Gosz, E. DeSantiago A local finite element implementation for imposing periodic boundary conditions on composite micromechanical models, *International Journal of Solids and Structures*, **2007**; *44*, 2972–2989.
14. Drugan, W., Willis, J., A micromechanics-based nonlocal constitutive equation and estimates of representative volume element size for elastic composites. *Journal of the Mechanics and Physics of Solids*, **1996**; *44*, 497–524