

Study of Thermal Behaviour of Thermoset Polymer Matrix Filled with Micro and Nanoparticles

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Abstract: This paper addresses the study of thermal behaviour of thermoset polymer matrix filled with microparticles. A numerical model was developed with COMSOL Multiphysics to get a random spatial distribution of fillers in a representative volume element (RVE). This model was then compared to an analytical reference model (Hamilton model) and experimental results. This comparison highlights a good correlation between analytical and numerical models and a small divergence with experimental results.

Keywords: thermal conductivity, effective properties, random dispersion, macroparticles.

1. Introduction

Most of composites researches have been conducted on weight loss on structural equipments. However, other applications lead to researches focused on onboard equipments which are in contact with electrical components and need to be thermally conductive.

This work is a part of our on-going research in the frame of the THEOREM project. This project leaded by THALES Systèmes Aéroportés aims to develop a hybrid composite material made of a polymeric matrix filled with micro and nanoparticles and reinforced with long carbon fibres. This material should exhibit high thermal conductive properties.

The study of the improvement of thermal conductivity in a thermoset matrix was the first step of this collaborative project.

Various kinds of candidate fillers were examined on the basis of the thermal conductivity in order to determine the mass fraction to be introduced in the matrix to get the desired thermal conductivity.

2. Materials and Experiment

The thermoset matrix used for this preliminary study is the epoxy system LY556

(prepolymer), D230 (curing agent) manufactured by Hunstman. This thermoset matrix was filled with aluminium macroparticles (Z600) which were purchased at Toyal.

Filled prepolymer (LY556) masterbatches were obtained using a pale mixer with an initial filler mass fraction of 40%. Samples from masterbatches were diluted and mixed with a planetary mixer in order to get samples with filler mass fraction ranging between 0wt% and 70.5wt%. The curing agent was poured in the planetary mixer after the fillers/resin (i.e. prepolymer) mixing stage.

Small blocks (80x10x3 mm) of these filled epoxy matrices were cured in an oven for two hours at 80°C plus one hour at 120°C. Pellets were cut out from those blocks and submitted to a thermal diffusivity measurement performed on a NETZSCH Nanoflash LFA 447. The thermal conductivity is determined by the equation (1).

$$\lambda = a.C_p.\rho \quad (1)$$

where λ is the thermal conductivity of the sample, a is the thermal diffusivity of the sample, C_p is the specific heat capacity of the sample and ρ is the density of the sample.

Table 1 gathers experimental values of thermal diffusivity and thermal conductivity of samples (with standard deviation) filled with aluminium particles as a function of particles volume fraction.

Volume fraction v_p (%)	Thermal diffusivity (mm^2/s)	Thermal conductivity ($\text{W}/(\text{m.K})$)
0	0.140 (0.005)	0.207 (0.017)
5	0.178 (0.012)	0.270 (0.026)
15	0.270 (0.009)	0.380 (0.003)
30	0.415 (0.005)	0.597 (0.004)
50	0.788 (0.003)	1.270 (0.042)

Table 1. Gathering of experimental results – Coefficients of thermal diffusivity and conductivity as a function of particles volume fraction (Al particles)

3. Analytical models

The ultimate aim of this research program is to get a model enabling to understand the thermomechanical and the thermal behaviours of carbon fibres composites with macro or nanoparticles filled polymeric matrix.

The first step of this work consisted in modelling the behaviour of a representative volume element (RVE) of the filled epoxy matrix.

Analytical models defining thermal conductivity were investigated. Models considering a random dispersion of spherical particles were chosen. Those models were divided in two groups: those considering a perfect interface between the fillers and the polymeric matrix and those which are hypothesizing an imperfect interface. In this later case, this means that a thermal contact resistance between materials will be considered.

In the case of perfect interface, models considered were:

- Effective medium model [1]
- Hamilton-Crosser model [2]
- Lewis-Nielsen model [3, 4]
- Pal model [5]

In the case of imperfect interface, models considered were:

- Hasselman and Johnson model [6]

3.1. Effective medium model

$$\lambda_e = \lambda_m \left(I + \frac{3 v_p \left(\frac{\lambda_p}{\lambda_m} - I \right)}{\left(\frac{\lambda_p}{\lambda_m} + 2 \right) - v_p \left(\frac{\lambda_p}{\lambda_m} - I \right)} \right) \quad (2)$$

where λ_e is the effective thermal conductivity of composite, λ_m is the thermal conductivity of matrix, λ_p is the thermal conductivity of particles and v_p is the particles volume fraction.

This model defined by equation (2) is valid for small volume fraction ($v_p(\%)$) and only for spherical particles.

3.2. Hamilton-Crosser model

$$\lambda_c = \lambda_m \left[\frac{\lambda_p + (n-1)\lambda_m - (n-1)v_p(\lambda_m - \lambda_p)}{\lambda_p + (n-1)\lambda_m + v_p(\lambda_m - \lambda_p)} \right] \quad (3)$$

where λ_c , λ_m , λ_p are respectively the coefficients of thermal conductivities of composite, matrix and particles, v_p is the particles volume fraction and n is a shape factor. Factor n depends on the sphericity of the particle. For a spherical particle $n = 3$.

In this model, defined by equation (3), the geometric aspect of particles was taken into account with the factor n .

3.3. Lewis-Nielsen model

$$\lambda_c = \lambda_m \left(\frac{I + A B v_p}{I - B v_p \psi} \right) \quad (4)$$

with
$$B = \frac{\left(\frac{\lambda_p}{\lambda_m} \right) - I}{\frac{\lambda_p}{\lambda_m + A}} \quad (5)$$

and
$$\psi = 1 + \left(\frac{1 - \phi_m}{\phi_m^2} \right) \quad (6)$$

where λ_c , λ_m , λ_p are respectively the coefficients of thermal conductivities of composite, matrix and particles, v_p is the particles volume fraction and ϕ_m is the maximum packing fraction (in volume) of dispersed fillers. Coefficient A defined in equation (7) is dependent on Einstein generalized coefficient k_E which depends itself on shape and orientation of particles.

$$A = k_E - 1 \quad (7)$$

In the case of random packing of spherical particles $A = 1.5$ and $\phi_m = 63.7$ vol%.

In this model defined by equations above, the geometric aspect of particles and their distribution in the matrix was taken into account.

3.4. Pal model

The Pal model has the same definition as the Lewis-Nielsen model. It only differs in A value. In this case $A = 2$.

3.5. Hasselman and Johnson model

$$\lambda_e = \lambda_m \frac{2 \left(\frac{\lambda_m - \lambda_p}{\lambda_p} + \frac{\lambda_p}{a h_c} \right) v_p + \frac{\lambda_p}{\lambda_m} + \frac{2\lambda_p}{a h_c} + 2}{\left(1 - \frac{\lambda_p}{\lambda_m} + \frac{\lambda_p}{a h_c} \right) v_p + \frac{\lambda_p}{\lambda_m} + \frac{2\lambda_p}{a h_c} + 2} \quad (8)$$

where λ_c , λ_m , λ_p are respectively the coefficients of thermal conductivities of composite, matrix and particles, v_p is the particles volume fraction, a is the particle radius and h_c is the thermal boundary conductance which represents the interfacial thermal resistance.

This model, defined by equation (8), is valid for particles assumed well dispersed and in low concentration (i.e. no contact between particles).

3.6 Analytical results

To compare the changes in composite (i.e. polymeric matrix + fillers) thermal conductivity as a function of fillers volume fraction (v_p (%)), the epoxy matrix's coefficient of thermal conductivity was set at $\lambda_m = 0.207$ W/(m.K), while the coefficient of thermal conductivity of aluminium powder particles was set at $\lambda_p = 237$ W/(m.K). For aluminium particles their radius was considered constant: $a = 3$ μm . v_p value was varied from 0% to 95%. For Hasselman model the thermal boundary conductance h_c depends on matrix, particles and interface geometry. An exact value of this parameter was quite difficult to define. $h_c = 1.10^{-7}$ W/K was determined according to [1].

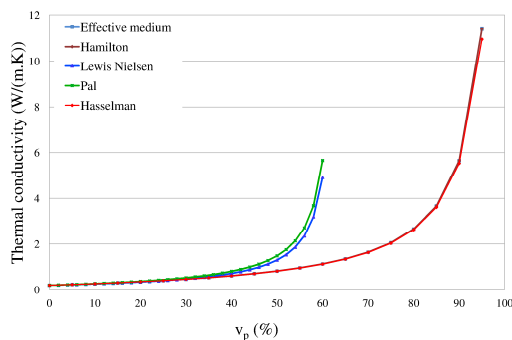


Figure 1. Comparison of the changes in composites coefficient of thermal conductivity as a function of particles volume fraction (v_p (%))

The results in Figure 1 clearly show that effective medium model and Hamilton-Crosser model have the same trends. Furthermore, Hamilton-Crosser model is close to Hasselman and Johnson model while particles volume fraction v_p remains lower than 60%. Lewis-Nielsen and Pal models are limited to a maximum value of packing fraction of particles which is 63.7 vol% in our case.

Despite curves plotted for v_p value up to 95%, it should be kept in mind that from physical point of view, given that i) aluminium particles are considered as spheres and ii) all particles are assumed to have the same radius (3 μm), the maximum particles volume fraction would be 63.7 vol% in the case of random dispersion (maximum packing factor).

4. Numerical models

Experimentally the fillers were dispersed by a mixer. This dispersion was considered as a random distribution. To model a representative volume element (RVE) of the filled epoxy matrix with COMSOL the main challenge was to get a spatial distribution of doping particles (Al) in the RVE. To this end, a random function (available under Java®) was used to generate points considered as the centres of particles. Particles were modelled as spheres and their volume was determined by the RVE and the fillers volume fraction. All the particles have the same radius but as it mentioned below changes in the radius were studied.

A non-penetration parameter was determined which allows only contacts between spheres. Heat equation was applied in the model in order to get the thermal conductivity of this isotropic doped matrix. The Fourier's equation (9) was used in COMSOL to define heat transfer:

$$\phi_S = -\lambda_h \overrightarrow{\text{grad}T} \quad (9)$$

where Φ_S is the surface heat flux, λ_h is the homogenized thermal conductivity of doped matrix and T is the temperature.

4.1. Algorithm definition

The definition of the algorithm used to generate the geometry on COMSOL was explained on Figure 2. This algorithm was

developed on Java® and compiled to obtain a COMSOL file.

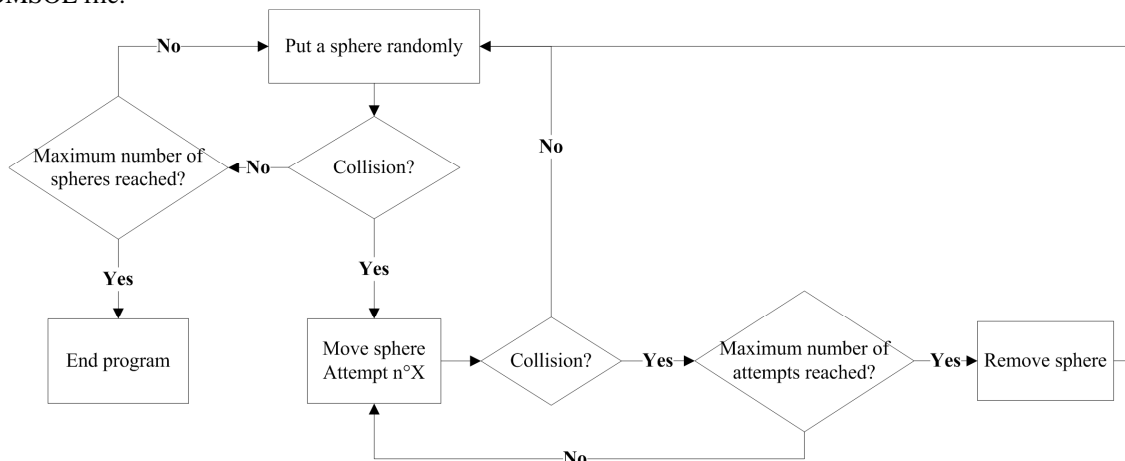


Figure 2. Algorithm definition

4.2. Sensitivity study

This program was tested to verify its limits and a sensitivity study was developed to optimize the model boundaries.

To choose the best sizes of RVE and mesh different parameters were varied: the RVE size (i.e. cube edge length), the particles radius, the particles volume fraction and the mesh size. To validate the model, the thermal conductivity has to remain the same independently to those parameters.

The thermal conductivity values were compared as function of:

- Particles volume fraction v_p : 1%, 3%, 5%, and 10%.
- Particles radius R : 1 μm and 3 μm .
- RVE size (i.e. cube edge length) L : 25 μm , 50 μm , 90 μm and 100 μm .
- Mesh size: mesh size was varied from coarse to extra fine, this mean the total number of tetrahedral elements was varied and the total volume (spheres + cube) was measured thus an average volume per element was defined. That means higher is the average volume per element coarser is the mesh size.

As shown in Figure 3, in the case of the sensitivity study, an initial temperature $T_0 = 0$ K and a surface heat flux $\Phi_S = 1\text{W}/\text{m}^2$ were defined as input parameters and boundary conditions according to equation (9). The thermal

conductivity of the model was then gathered from this same equation.

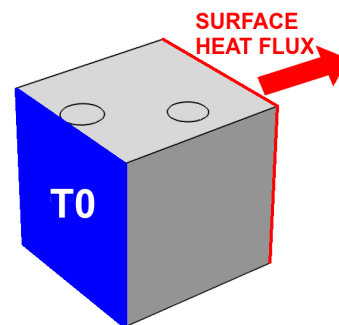


Figure 3. Boundary conditions

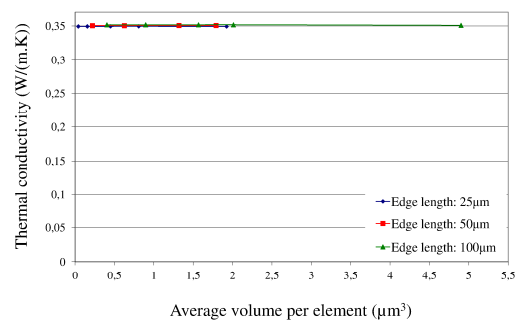


Figure 4. Evolution of thermal conductivity as a function of mesh size and RVE size – $R = 3$ μm and $v_p = 3\%$

As shown in Figure 4 it can be noticed that the coefficient of thermal conductivity is not

strongly impacted by changes in RVE size and mesh size (i.e. average volume per element). Further to this comment the cube edge length (i.e. RVE size) was fixed to $L = 25 \mu\text{m}$ for decrease the numbers of element, thus the computing time.

In Figure 5 it was observed the influence of the particles radius on the thermal conductivity and it can be highlighted that this coefficient was not impacted by the variation on the radius value.

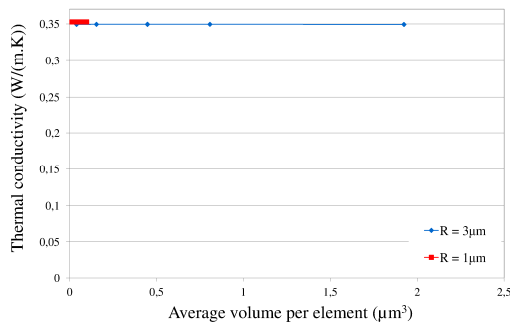


Figure 5. Evolution of thermal conductivity as a function of mesh size and particles radius $R - v_p = 3\%$ and $L = 25 \mu\text{m}$

As shown in Figure 6 and as expected, increasing the particles volume fraction results in an increase in the coefficient of thermal conductivity.

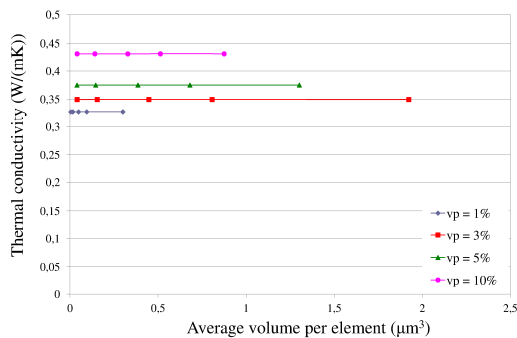


Figure 6. Evolution of thermal conductivity as a function of mesh size and particles volume fraction $v_p - R = 3 \mu\text{m}$ and $L = 25 \mu\text{m}$

Concerning the method, i.e. the finite element modelling, it was observed that this modelling becomes quickly limited when increasing the particles volume fraction v_p (%). Indeed, for particles volume fraction higher than 15% meshing becomes very complex or even impossible due to space between particles which

becomes too small. To conclude, parameters were fixed by this study:

- A cube edge length of $25 \mu\text{m}$
- A coarse mesh size

The number of element was decreased by those parameters values, therefore this involve a faster computing time and no effect on the value of the thermal conductivity coefficient.

4.3. Numerical results

In order to perform a comparison between numerical, analytical and experimental results, the following input parameters were chosen for finite element modelling:

- RVE: cube edge length $L = 25 \mu\text{m}$
- Initial temperature: $T_0 = 293.15 \text{ K}$
- Surface heat flux: $\Phi_s = 2.106 \text{ W/m}^2$
- Thermal conductivity of matrix: $\lambda_m = 0.207 \text{ W/(m.K)}$
- Thermal conductivity of particles: $\lambda_p = 237 \text{ W/(m.K)}$
- Radius fillers: $R = 3 \mu\text{m}$
- Particles volume fraction: $v_p = 3\%, 5\%, 10\%$

As shown in Figure 7, the gradient temperature induced by the surface heat flux is given by this simulation (here in the case of $v_p = 5\%$ and $R = 3 \mu\text{m}$). The homogenized thermal conductivity was deduced according to equation (9).

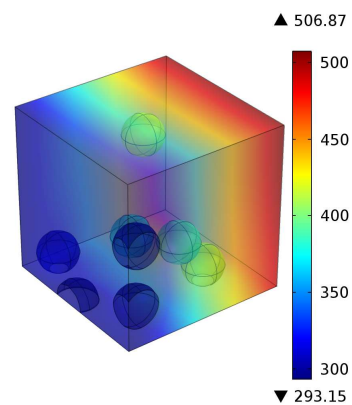


Figure 7. Temperature distribution (K) for $v_p = 5\%$ and $R = 3 \mu\text{m}$

As shown in Figure 8, it can be noticed the influence of particles on the isothermal contours.

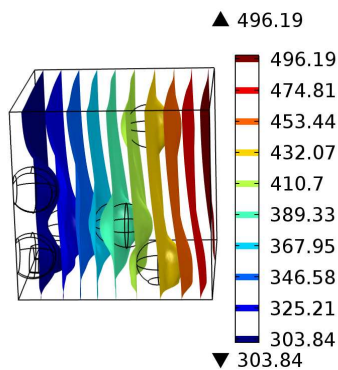


Figure 8. Isothermal contours (K) $v_p = 5\%$ and $R = 3 \mu\text{m}$

As shown in Figures 9 and 10 the numerical model is near analytical models.

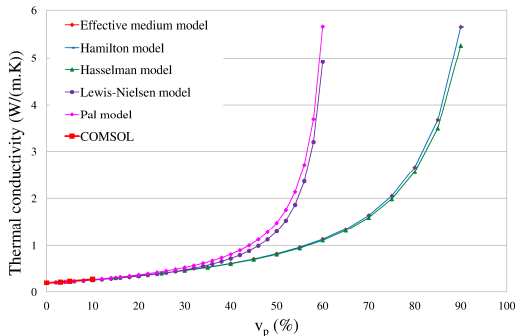


Figure 9. Comparison of thermal conductivity values as a function of v_p (%) between numerical and analytical models

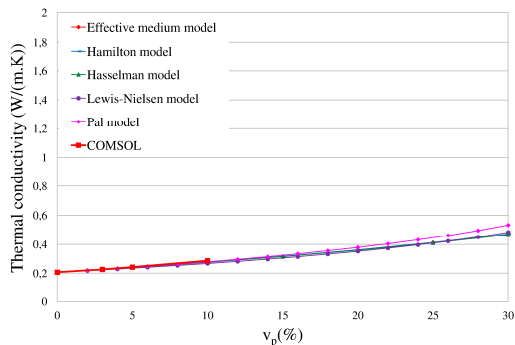


Figure 10. Detail of the previous comparison

As defined in Section 3.6., Hamilton and effective medium models have the same trends. Hasselman model was really closed to the two previous models and its definition is the most complex due to the thermal boundary conductance value (i.e. h_c) which is complicated

to define. According to those data, Hamilton model was considered as the analytical reference model.

5. Discussion

In Figure 11 and Table 2, it was compared the thermal conductivity values of Hamilton model, COMSOL simulations and experimental results. As plotted in Figure 11 it can be noticed that experimental thermal conductivity values diverge from Hamilton model and COMSOL simulations values.

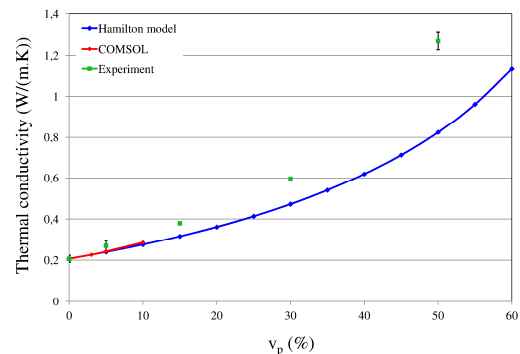


Figure 11. Comparison of thermal conductivity values as a function of v_p (%) – Hamilton model, COMSOL simulations and experimental results

v_p (%)	Hamilton model (W/(m.K))	Experiment (W/(m.K))	COMSOL (W/(m.K))
0	0.207	0.207 (0.017)	0.207
3	N.D	N.D	0.226
5	0.240	0.270 (0.026)	0.242
10	0.276	N.D.	0.286
15	0.316	0.380 (0.004)	N.D

Table 2. Thermal conductivity values for Hamilton model, experiment (standard deviation) and COMSOL simulation (N.D.: No Data)

This difference could be explain by the fact that experimental thermal conductivity is calculated, thus depends on specific heat capacity C_p and density ρ as defined in equation (1).

Those parameters were determined by approximate methods:

- For C_p by the Nanoflash device (ratio method)
- For ρ by a ratio between the mass of the sample and the shape of the sample which was considered as a perfect

cylinder, thus an approximate volume was obtained.

6. Conclusions

A program to get a random spatial dispersion of spherical microparticles in a representative volume element has been developed. This three-dimensional modelling enables the thermal properties of a polymeric matrix filled with particles (it can be either micro or nanoparticles) to be predicted. It should be mentioned that the capabilities of a conventional PC (i.e. 16 Go RAM) act has a hindrance for finite element computation. Effectively increasing the particles volume fraction in the RVE results in an exponential increase in the number of elements and quickly limit the use of finite element method (i.e. maximum particles volume fraction $v_{pMAXI}(\%)$ 15%).

However, from a physical point of view, this is not a problem. The ultimate application is to use a filled matrix to produce composites reinforced with long fibres. This means that the viscosity of this filled matrix has to be maintained as low as possible even if it is aimed to increase the thermal conductivity matrix, the particles volume fraction remains limited. The results of 3D finite element modelling exhibit a good correlation with Hamilton analytical model. The small divergence between experimental and theoretical results is attributed to errors in physical properties measurements. To verify this assumption new measurements of C_p by DSC (Differential Scanning Calorimetry) are required.

To improve thermal behaviour of the matrix, more experiments, with other types of fillers (including nanofillers), are in progress. In consequence another program will be developed, for other particles shape like in Figure 12, based on the present one.

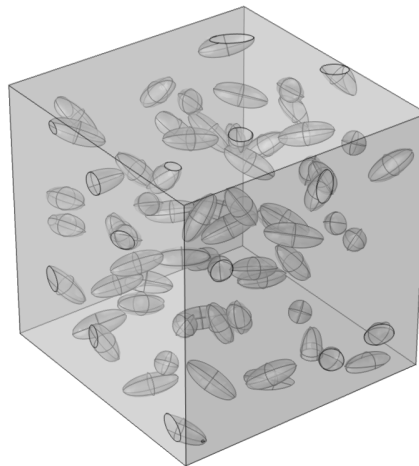


Figure 12. Random dispersion of ellipsoidal particles

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