STUDY OF THERMAL BEHAVIOUR OF THERMOSET POLYMER MATRIX FILLED WITH MICRO AND NANOPARTICLES

B. Reine[1*], J. Di Tomaso[2], G. Dusserre[1], P. A. Olivier[1]

[1]*Université de Toulouse; UPS, INSA, Mines Albi, ISAE; ICA (Institut Clément Ader) IUT, Dept. GMP, 133C avenue du Rangueil, BP 67701, 31077 Toulouse Cedex 4, France*
[2]*RESCOLL Société de Recherche, 8, Allée Geoffroy Saint-Hilaire, CS 30021, F-33615, PESSAC Cedex, France*
**benedicte.reine@iut-tlse3.fr*

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Abstract
This paper proposes a study of thermal behaviour of thermoset polymer matrix filled with microparticles. A numerical model (finite elements) was developed to get a random spatial distribution of fillers in a representative volume element (RVE). This model was compared to analytical models (Effective medium, Hamilton-Crosser, Lewis-Nielsen, Pal and Hasselman-Johnson models) and experimental results. Compared to experimental results the most convincing analytical model was Hamilton-Crosser model.

1 Introduction

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 first step of this multipartners (RESCOLL, CANOE, LCPO, LATELEC, and MIPNET) project focused on the improvement of a thermoset matrix thermal conductivity. Various kind of candidate fillers were examined on the basis of the thermal conductivity: Al, NiAl, NiB, graphite in order to determine the mass fraction to introduce 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 Hunstmann. This thermoset matrix is filled with Aluminium macroparticules (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 D230 curing agent was poured in the planetary mixer after the fillers/resin (i.e. prepolymer) mixing stage.

Small blocs (80 x 10 x 3 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 blocs and submitted to a thermal conductivity measurement performed on a NETZSCH Nanoflash LFA 447.
This equipment measures the thermal diffusivity of pellets. The thermal conductivity is determined by equation below.

$$\lambda = aC_p\rho \tag{1}$$

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

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

Mass fraction (%)	Volume fraction (%)	Thermal diffusivity (mm^2/s)	Thermal conductivity (W/(m.K))
0	0	0.140	0.207
11.2	5	0.178	0.270
29.7	15	0.270	0.380
50.6	30	0.415	0.597
70.5	50	0.788	1.270

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

3 Modelling

3.1 Analytical models

Thermal conductivity analytical models can be 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 we focused on:

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

In the case of imperfect interface we focused on:

- Hasselman and Johnson model [6]

3.1.1 Effective medium model

$$\lambda_e = \lambda_m\left(1+\frac{3v_p\left(\frac{\lambda_p}{\lambda_m}-1\right)}{\left(\frac{\lambda_p}{\lambda_m}+2\right)-v_p\left(\frac{\lambda_p}{\lambda_m}-1\right)}\right) \tag{2}$$

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 is valid for small volume fraction (v_p%) and only for spherical particles.

3.1.2 Hamilton Crosser model

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

where λ_c, λ_m, λ_p are respectively the coefficients of thermal conductivity 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 $n = 3$.

This model takes into account the geometric aspect of particles with factor n.

3.1.3 Lewis Nielsen model

$$\lambda_c = \lambda_m \left(\frac{1 + ABv_p}{1 - Bv_p\psi} \right) \tag{4}$$

with

$$B = \frac{\frac{\lambda_p}{\lambda_m} - 1}{\frac{\lambda_p}{\lambda_m} + A} \tag{5}$$

and

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

where λ_c, λ_m, λ_p are respectively the coefficients of thermal conductivity of composite, matrix and particles, v_p is the particles volume fraction, $\emptyset_m$ is the maximum packing fraction 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.

$$A = k_E - 1 \tag{7}$$

In the case of a random packing of spherical particles $A = 1.5$ and $\emptyset_m = 0.637$. This model takes into account the geometric aspect of particles and their distribution in the matrix.

3.1.4 Pal model

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

3.1.5 Hasselman and Johnson model

$$\lambda_e = \lambda_m \frac{2\left(\frac{\lambda_m}{\lambda_p} - \frac{\lambda_p}{ah_c} - 1 \right) v_p + \frac{\lambda_p}{\lambda_m} + \frac{2\lambda_p}{ah_c} + 2}{\left(1 - \frac{\lambda_p}{\lambda_m} + \frac{\lambda_p}{ah_c} \right) v_p + \frac{\lambda_p}{\lambda_m} + \frac{2\lambda_p}{ah_c} + 2} \tag{8}$$

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

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

3.1.6 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 λ_m = 0.207 W/(m.K), while the coefficient of thermal conductivity of aluminium powder particles was set at λ_p = 237 W/(m.K). For aluminium particles their radius was considered constant: a = 3 µm. We varied v_p from 0% to 100%.
For Hasselman model the thermal boundary conductance h_c depends on matrix, particles, and interface geometry. It is quite difficult to define an exact value. We determined $h_c = 1.10^{-7}$ W/K according to [1].

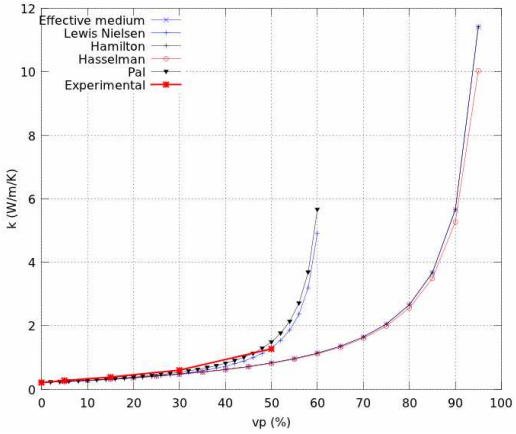

Figure 1. Comparison of the changes in composite coefficient of thermal conductivity k (W/m.K) as a function of particles volume fraction v_p(%)

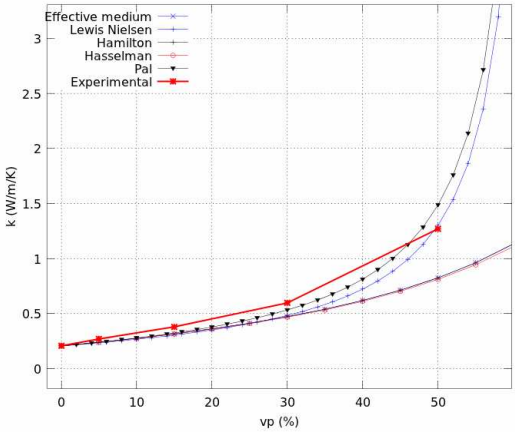

Figure 2. Detail of the previous comparison

Figure 1 results clearly show that effective medium model and Hamilton model have the same trends. Furthermore, Hamilton model is close to Hasselman model while particles volume fraction v_p remains lower than 60%. Lewis-Nielsen model and Pal model are limited to a maximum value of packing fraction of particles which is 0.637 (or 63.7%) in our case.
Despite curves plotted for v_p values up to 95%, it should be kept in mind that from a 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 74% (maximum packing factor).
Figure 2 highlights that experimental results are close to Hamilton, Hasselman and effective medium models. As we saw previously Hamilton model and effective medium model have the same trends and Hasselman model is the most complicate model, thus we chose Hamilton model as analytical reference model.
The difference between analytical models and experimental results could be explained by the fact that experimental thermal conductivity is calculated, thus depends on heat capacity C_p. Furthermore we pointed out C_p measured by Nanoflash was different from that one determine by DSC (Differential Scanning Calorimetry) and that involves a difference on thermal

conductivity about ± 20%. We could explain that difference by the fact that the determination of C_p used by Nanoflash is an approximate method.

3.2 Numerical models

The software used for this study was COMSOL Multiphysics. As already said 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 a macro or nanoparticles-filled polymeric matrix. The very first step of this work consisted in modelling the behaviour of a representative volume element (RVE) of the filled epoxy matrix. 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 particles have the same radius but as it mentioned below changes in this radius were studied.
We determined a non-penetration parameter which allows only contacts between spheres.
Heat equation was applied in the model in order to get the conductivity of this isotropic doped matrix.
To choose the best size of RVE and mesh we varied different parameters: the RVE size, the particles radius, the volume fraction of particles, the mesh size and we verified thermal conductivity remained the same independently to those parameters. As shown in Figure 3 we defined as input parameters and boundary conditions an initial temperature T_0 = 0 K and a surface heat flux $\varnothing_S$ = 1 W/m^2. Thermal conductivity was determined by Fourier equation (9).

$$\phi_S = -\lambda_h \overrightarrow{gradT} \tag{9}$$

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

The epoxy matrix's coefficient of thermal conductivity was set at λ_m = 0.321 W/(m.K) while the coefficient of thermal conductivity of particles was set at λ_p = 237 W/(m.K).

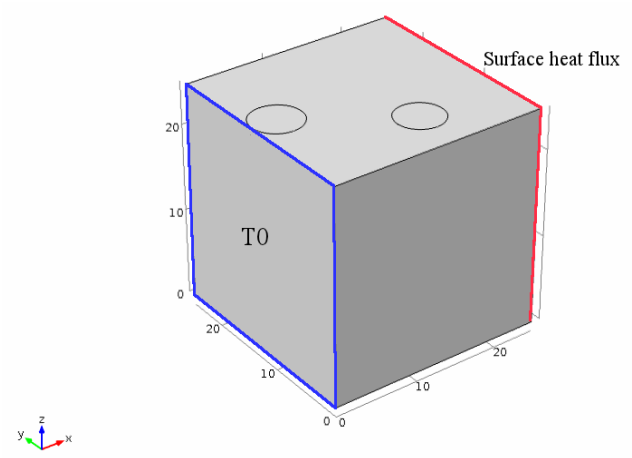

Figure 3. Boundary conditions

We compared the thermal conductivity values as functions of:

- Particles volume fraction v_p: 1%, 3%, 5% and 10%
- Particles radius: 1µm, 3µm.
- RVE size: 25µm, 50µm, 90µm or 100µm (length of a cube edge)

- Mesh: we varied mesh size from coarse to extra fine, this mean we varied the total number of tetrahedral elements and we measured the total volume (spheres + cube), thus we defined an average volume per element. That means higher is the average volume per element coarser is the mesh size.

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 and this whatever the radius particles or the particles volume fraction were.

Effectively as shown by results obtained with v_p = 5% and Al spheres radius R = 3 µm (i.e. curves plotted in blue in Figure 4) changing the RVE size from 25 µm cube edge length up to 90 µm do not induce any modification in the coefficient of thermal conductivity (0.375 W/(m.K)). Moreover changing the mesh size from coarse to extra fine (i.e. from high to low values of average volume per element) do not induce any modification too.

As expected increasing the particles volume fraction results in an increase in coefficient of thermal conductivity. These changes in the coefficient of thermal conductivity as a function of v_p (%) will be compared to those predicted by Hamilton analytical model and experimental results.

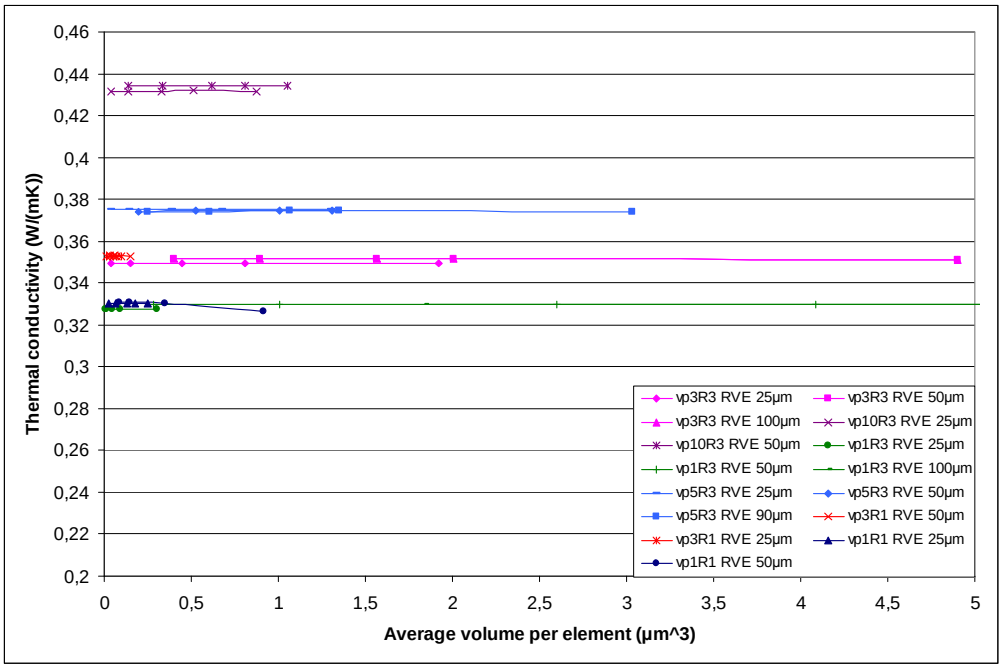

Figure 4. Thermal conductivity progress as a function of v_p, particles radius R and RVE size

Concerning the method, i.e. finite elements modelling, it was observed that this modelling becomes quickly limited when increasing v_p(%). Effectively, 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 on the RVE size, we choose:

- A cube edge length of 25 µm because it is smaller, therefore there is less elements.
- A coarse mesh size because there is less elements too.

Those two parameters permit faster calculus and whatever the cube edge length there is no effect on the thermal conductivity.

The epoxy matrix's coefficient of thermal conductivity was set at λ_m = 0.207 W/(m.K) following new measurement of this coefficient. We did not redo the sensitivity study because we considered this coefficient has no influence on the conclusion of this study.

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

- RVE: cube edge length: 25 µm
- Initial temperature: T_0 = 293.15 K
- Surface heat flux: $\varnothing_S = 2.10^6$ W/m^2
- Thermal conductivity of matrix: λ_m = 0.207 W/(m.K)
- Thermal conductivity of fillers: λ_p = 237 W/(m.K)
- Radius fillers : R = 3 µm
- Volume fraction of particles: v_p = 3%, 5%, 10%

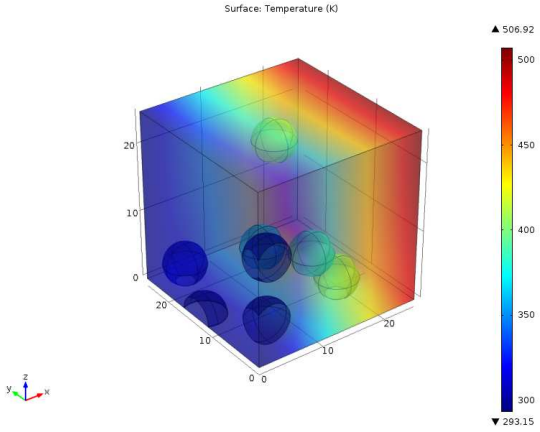

Figure 5. Temperature (K) distribution for v_p = 5%, R = 3µm

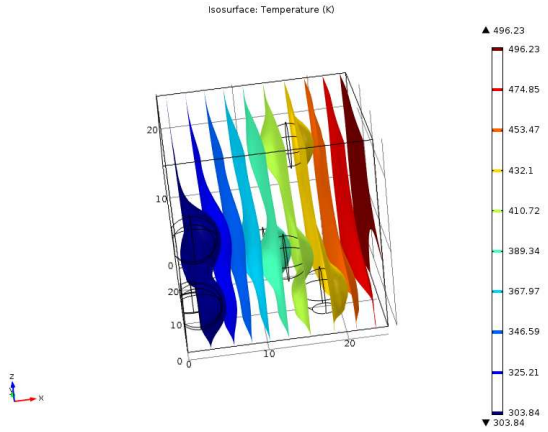

Figure 6. Isothermal contours (K) for v_p = 5%, R = 3 µm

Figure 5 shows temperature distribution for v_p = 5% and a particle radius R = 3 µm. This simulation gives us the gradient temperature induced by the surface heat flux. We could deduce the homogenized thermal conductivity according to equation (9).
As shown in Figure 6 it can be noticed the impact of particles on the isothermal contours.

4 Results

Table 2 gathers values of coefficient of thermal conductivity experimentally measured, and computed owing Hamilton analytical model and owing finite elements method. Figure 7 plotted a comparison of these results.

v_p (%)	Hamilton model	Experiment	COMSOL simulations
0	0.207	0.207	0.207
3	-	-	0.226
5	0.240	0.270	0.242
10	0.276	-	0.286
15	0.316	0.380	-

Table 2. Thermal conductivity values for Hamilton model, experiment and COMSOL simulations (W/(m.K)).

As plotted in Figure 7 it can be noticed that experimental thermal conductivity values are not the same as Hamilton model and COMSOL simulations. As we explained in section 3.1.6, we plotted Hamilton model with ± 20% on thermal conductivity value of matrix to see if experimental results correlate better with those new values.

As we could see experimental values diverge from Hamilton model, even if we consider an initial value of thermal conductivity of matrix increased by 20%. This divergence could be due to an error on C_p value as we supposed in section 3.1.6.
Furthermore Hamilton model, with initial value of thermal conductivity of matrix and COMSOL simulations have the same trends.

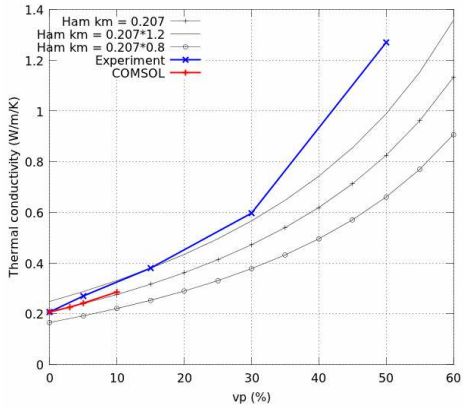

Figure 7. Comparison between Hamilton model, experiment and COMSOL simulations

5 Conclusion

A program to get a random dispersion of spherical micro-particles in a representative element volume 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 MO RAM) act has a hindrance for finite elements 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 FEM (i.e. $V_{pMAXI} \cong 20\%$). Nevertheless, from a physical point of view this is not a problem. In fact the ultimate application is to use a filled matrix to produce composites reinforced with long fibres. This means that this filled matrix has to kept a as low as possible viscosity. Consequently, even if it is aimed to increase the matrix thermal conductivity the particles volume fraction remains limited.
The results of 3D finite elements 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. In fact experimental C_p value given by Nanoflash does not seem to be correct. This means that and new measurements of C_p by DSC are required.
To improve thermal behaviour of matrix, more experiments, with other types of fillers (including nanofillers), are in progress. In consequence we will develop another program, based on the one present in this article, for other shape particles.

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