THERMAL AND MECHANICAL BEHAVIOUR OF PAN AND PITCH-BASED CARBON FIBER WOVEN FABRIC REINFORCED PARTICLE FILLED EPOXY COMPOSITES

T.L. Nguyen[a], P. A. Olivier[a*]

[a]*Institut Clément Ader, Département GMP, I.U.T Paul Sabatier, 133C avenue de Rangueil - 31077 TOULOUSE CEDEX 4 – France*
**philippe.olivier@iut-tlse3.fr*

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Abstract
This work consists of developing composite materials with enhanced thermal properties, especially over the transverse (through thickness) direction. New carbon fiber reinforced polymer (CFRP) is then developed by using two methods: The first one consists of doping the polymer matrix with conductive micro particles and the second one consists of using PITCH-based carbon fiber woven fabrics. The results will be discussed on the mechanical and thermal behavior of these materials. The use of PITCH-based woven fabric enables to improve the conductivity, particularly when the 3D effect of geometry is much stronger. Finite element simulations of thermal conductivity of such structures are also carried out.

1. Introduction

In this work, composite materials with enhanced thermal properties are developed. The final composite materials must not only be lightweight but also exhibit a high thermal conductivity, especially over the transverse (through thickness) direction. However, composite materials, particularly unidirectional or 2D laminar composites, exhibit very bad transverse thermal conductivity. This limit is mainly due to the thermal isolation of the matrix and the low radial thermal conductivity of the carbon fibers. In the literature, many methods have been proposed in order to improve the thermal conductivity of composite materials. These methods can be divided in two groups: the first one consists of creating a conductive resin such as the doping of matrix with metal particles [3] or array of carbon nanotubes. Concerning the second group, one can cite the choice of high thermal conductivity fiber and fabric reinforcement (2D, 3D structure) to enhance thermal conductivity over the transverse direction [4].

Two methods to improve the thermal conductivity of CFRP composites have been proposed in this work. The first one consists of doping the polymer matrix (thermoset epoxy resin) with conductive micro particles. The second one consists of using woven fabrics of PITCH-based carbon fibers. The idea is to create a highly conductive path across the thickness direction of composites material thanks to the very high longitudinal thermal conductivity of PICTH-based fibers. However, PITCH-based carbon fibers often exhibit a very high modulus which leads to the difficulty on weaving the fabric, especially for 3D structure [4]. In our work, we propose the use of Interlock fabric which is easier to weave and offer also a 3D effect. In what follows, the material and forming process of our samples: a unidirectional composite and an Interlock composite will be introduced. Thermal and mechanical characterization of theses samples will be presented. Simulations to predict the thermal conductivity of these materials using analytical and numerical models will be also carried out.

2. The materials and forming process

In our study, the PITCH-based carbon fiber CN-90-60S (XN-90-60S) of Granoc was chosen. This fiber exhibits a very high thermal conductivity in the fiber axis direction (~500 W/m.°K). Table 1 shows the properties of this fiber.

Filament	Young modulus (GPa)	Tensile strength (MPa)	Ultimate elongation (%)	Density (g/cm^3)	Yield (g/1000m)	Longitudinal thermal conductivity (W/m.°K)
6000	860	3430	0.4	2.19	880	500

Table 1. Properties of fiber CN-90-60S (XN-90-60S) of GRANOC (Nippon Graphite Fibre Corp.)

However, no data on the transverse thermal conductivity could be found on the literature. In fact, the carbon fibers are transversely isotropic, that means they exhibit different thermal conductivity in radial and longitudinal direction. Like other PITCH-based fibers, the Young modulus of this fiber is very high with a very small ultimate elongation. Concerning the forming process, an epoxy resin with low viscosity has been used. The curing cycle consists of 5 hours at 50°C and then 1 hour at 100°C with 1 hour at 100°C of post-curing. The temperature of glass transition is then 104.2 (°C). As we discussed, Interlock fabric made of CN-90-60S carbon fiber is used. Figure 1 shows the structure of this fabric 2.5D layer to layer Interlock. We can see that it is composed of 4 layers with a contexture of 4x14 yarns/cm. Samples for mechanical and thermal characterization are obtained by RTM process. For comparison, unidirectional samples obtained by winding filament are also characterized.

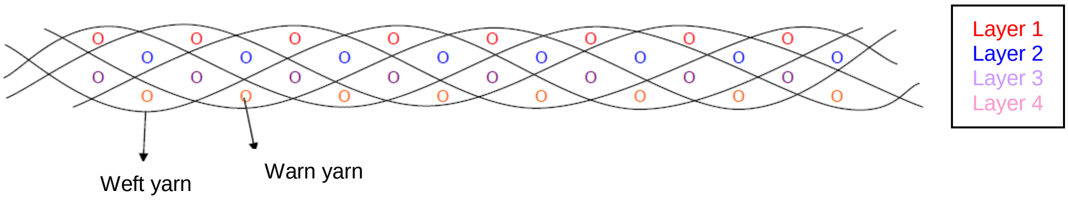

Figure 1. Architecture of Interlock 2.5D layer to layer fabric

3. Mechanical and thermal characterization

The mechanical characterization consists of measurement of mass density, fiber volume fraction and tensile strength. Mass density ρ was obtained by the Archimedes water-immersion method at room temperature. The values are respectively 1301 and 1460 (kg/m^3) for Unidirectional and Interlock Composite. The fiber volume fraction is obtained using acid dissolution for Interlock composites. Due to its limited dimension, the fiber volume fraction is obtained using SEM (scanning electron microscope) images treatment. The values are respectively 48.27 ± 6.68 and 40.64 ± 2.83 (%) for Unidirectional and Interlock Composite. It is noticed that the unidirectional composite elaborated by filament winding exhibits a higher fiber volume fraction. Tensile strength of Interlock Composites is 409 (MPa). We can see that, due to its very high Young modulus and their undulated structure, PITCH-based carbon fiber woven fabrics do not improve very significantly the mechanical behaviour of the final composite. Thermal diffusivity D is obtained by using Flash laser technique thanks to LFA 457 MicroFlash Apparatus. Table 2 shows the results of thermal characterization over the thickness (transverse) direction at room temperature. The specific heat capacity C_p is measured by using the DSC (Differential scanning calorimetry). The thermal conductivity is then computed by using the following equation:

$$\lambda = \rho C_p D \quad (1)$$

	Thermal diffusivity (m^2/s)	Specific heat (J/kg.°K)	Thermal conductivity (W/(m.°K))
Unidirectionnal	0.326×10^{-6}	962	0.408 ± 0.034
Interlock	0.850×10^{-6}	1094	1.359 ± 0.069

Table 2. Thermal characterization over the transverse (through thickness) direction

Let us note that the isotropic thermal conductivity of resin is 0.1455 (W/m.°K). As we can see, Interlock composite exhibits a higher transverse thermal conductivity than unidirectional one (about 3 times higher). Moreover, the fiber volume fraction of Interlock is smaller. So it is proved that the Interlock structure has improved the thermal management of the composite material. As discussed, this improvement is obtained thank to the 3D effect of Interlock structure. These results also confirm that the longitudinal conductivity of CN-90-60S fibers is much higher than the radial one. Figure 2 shows an observation by optical microscope of Interlock composite along warn and weft yarns direction. We can see that the fiber in weft direction cross the thickness of composite. In order to take into account the undulation of fibers in numerical model, the ratio between amplitude and length of undulation is measured. This value is 32.9 for warn yarns and 7.2 for weft yarns.

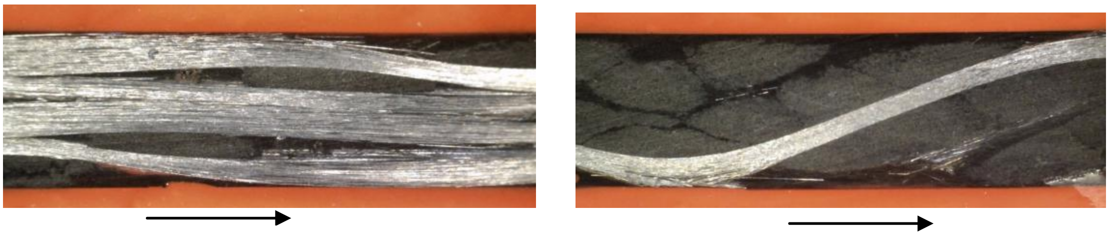

Figure 2. Observation using optical microscope of Interlock Composite

In fact, each yarn is composed of a certain number of fiber (filament). This number can vary from hundred to thousand depending on the size of filament and size of yarns. Here, the value given by the producer is 6000 filament/yarn. The cross section of the fiber is circular, and the cross section of the thread is elliptic. Hence, the thermal conductivity of yarn is different from fiber because of the presence of air at initial state, and resin/micro-porosities in final composite. Figure 3 (left) shows an SEM image of yarns with the presence of fiber and resin/micro-porosities. One can measure directly the thermal conductivity of yarns as presented in the work of Yamashita et al. [6]. However, this kind of measure is difficult due to the small dimension of yarns and other parameters such as thermal resistance. Therefore, as we will see in the next part, many models have been proposed to predict the thermal conductivity of yarns. In order to determine or predict this value (and then the thermal conductivity of composites), it is important to determine the fiber volume fraction in yarns. For example, in [2], this value is defined as 60%. In our work, this value is determined by

SEM image treatment thanks to the ImageJ software (we supposed that there exists no micro-porosities). Figure 3 (right) shows an example of the treated image of corresponding SEM observation.

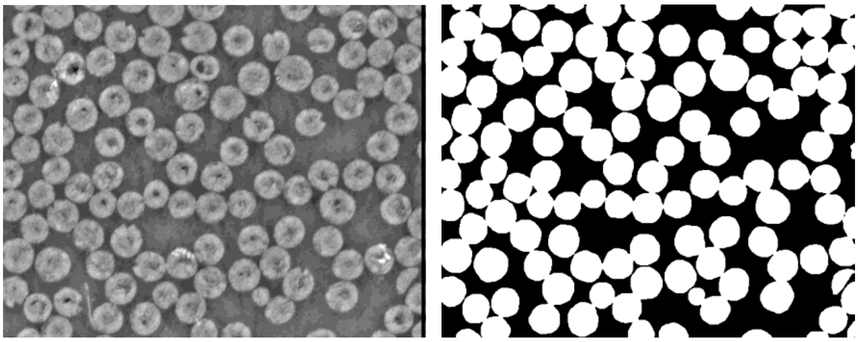

Figure 3. SEM observations of yarns of Interlock composite (Magnification 1000) (left) and Image treatment by ImageJ (right)

4. Simulation

In this part, firstly, we are going to present the analytical models to predict the thermal conductivity over the transverse direction of unidirectional composite. Inverse computations are then used to define thermal conductivity of fiber. Lastly, this value is used to predict thermal conductivity of Interlock composite. In most of works, to characterize the effective transverse thermal conductivity λ_{ft} of a sample, a classical method is used which consists of using the one-dimensional Fourier's conduction equation:

$$Q = -\lambda_{te} \times A \times gradT \tag{2}$$

where Q the rate of effective heat flow (W), A cross-sectional area through which the heat flows (m^2). The gradient of temperature $gradT$ is known by applying different and constant temperature $(T_1 - T_2)$ at the two faces of the sample and so we obtain $gradT = (T_1 - T_2)/L$ where L is the thickness of the sample.

4.1. Unidirectional Composite

Many analytical models exist to predict the transverse thermal conductivity of unidirectional composites. In fact, for the longitudinal thermal conductivity, the Rule of Mixtures (ROM) relation is widely used based on the parallel circuit analogy:

$$\lambda_{cl} = \lambda_{fl} v_f + \lambda_m (1 - v_f) \tag{3}$$

where λ_{cl} is the effective longitudinal conductivity of composites, λ_{fl} the longitudinal conductivity of fiber, λ_m the thermal conductivity of matrix and v_f the volume fraction of fiber. In the contrary, for the transverse (through thickness) direction, which is perpendicular to the axe of fibers, the parallel ROM did not work and many models have been proposed in order to predict and satisfy the experimental data. We are going to present here the most widely used models [5] in order to, with the result of our experimental data on unidirectional composites, determine the value of radial thermal conductivity of fiber. Table 3 shows the formulae of investigated models to predict the effective transverse thermal conductivity λ_{te}. λ_{ft} is the radial (transverse) thermal conductivity of fiber.

Rule of Mixture : Series $\lambda_{te} = \dfrac{\lambda_{ft}\lambda_m}{\lambda_{ft}(1-v_f)+\lambda_m v_f}$	(4)
Springer-Tsai $\lambda_{te} = \lambda_m\left[1-2\sqrt{\dfrac{v_f}{\pi}}+\dfrac{1}{B}\left(\pi-\dfrac{4}{\sqrt{1-\left(B^2 v_f/\pi\right)}}\tan^{-1}\left(\dfrac{\sqrt{1-B^2 v_f/\pi}}{1+\sqrt{B^2 v_f/\pi}}\right)\right)\right]$ with $B = 2\left(\dfrac{\lambda_m}{\lambda_{ft}}-1\right)$ with square arrangement of circular cross section	(5)
Halpin-Tsai $\lambda_{te} = \lambda_m\left[\dfrac{1+\zeta\eta v_f}{1-\eta v_f}\right]$; $\eta = \dfrac{(\lambda_{ft}/\lambda_m)-1}{(\lambda_{ft}/\lambda_m)+\zeta}$ with $\zeta = 1$ for a circular cross section	(6)
Lewis-Nielsen $\lambda_{te} = \lambda_m\left[\dfrac{1+ABv_f}{1-Bv_f\psi}\right]$; $B = \dfrac{(\lambda_{ft}/\lambda_m)-1}{(\lambda_{ft}/\lambda_m)+A}$; $\psi = 1+\left(\dfrac{1-\varphi_m}{\varphi_m{}^2}\right)v_f$ with $A = 0.5$ and $\varphi_m = 0.785$ the maximal volume fraction for cubic distribution of fiber	(7)
Hasselman and Johnson $\lambda_{te} = \lambda_m \dfrac{\left(\lambda_{ft}/\lambda_m - 1 - \lambda_{ft}/(ah_c)\right)v_f + 1 + \lambda_{ft}/(ah_c) + \lambda_{ft}/\lambda_m}{\left(-\lambda_{ft}/\lambda_m + 1 + \lambda_{ft}/(ah_c)\right)v_f + 1 + \lambda_{ft}/(ah_c) + \lambda_{ft}/\lambda_m}$ with the thermal conductance $h_c = 10^7$ and the fiber radius $a = 5.10^{-6}(m)$	(8)

Table 3. Analytical models to predict transverse thermal conductivity of unidirectional composites

Figure 4 shows the value of λ_{te} as a function of λ_{ft} obtained by presented analytical models and experimental results of the unidirectional composite (volume fraction of 48.27 %). With $\lambda_{fl} = 500$ and $\lambda_m = 0.1455$ (W/m.°K), the value of λ_{ft} is chosen varying from 1 (W/m.°K) to 50 (W/m.°K). We can see that the values obtained from series ROM are the lowest values and do not fit the experimental results. It is due to the fact that it does not take into account the shape, the size or the distribution of fiber in the matrix. In this test case, the Halpin-Tsai, Lewis and Nielsen, Hasselman and Johnson provide the best results for the prediction of λ_{te} and these models show the nearly the same tendency. It is important to note that all these models show an asymptotic behavior. That means from a certain value of λ_{ft}, the effective thermal conductivity of the composite is only a function of filler content. It is then very difficult to determine λ_{ft} by inverse computation. Moreover, as there is an uncertainty on the measure, if we take into account the measured lower/upper bound of the volume fraction in the models, the results will vary considerably. As discussed in [8], this problem lies in that fact that the conductivity of the fiber exceeds greatly the conductivity of the matrix. It leads to a great sensibility of the results to the value of λ_{ft} and the used model.

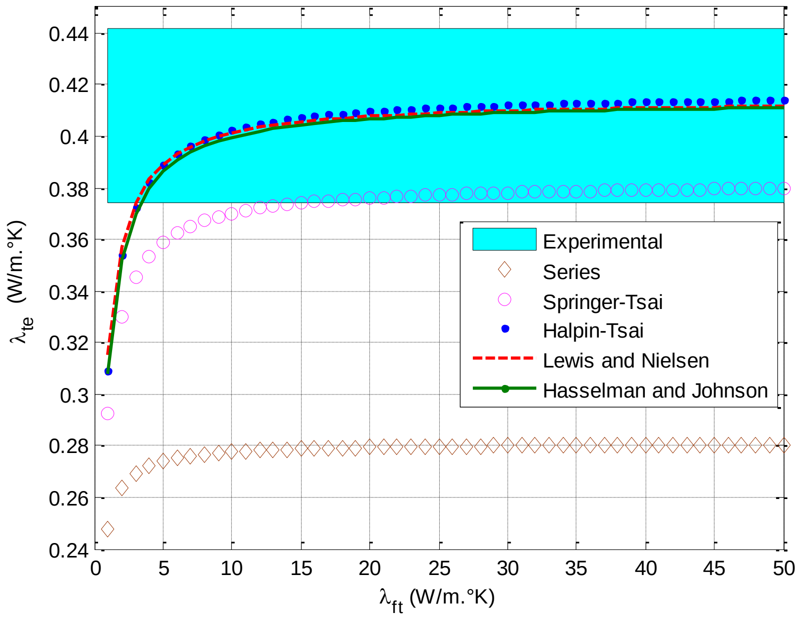

Figure 4. Transverse thermal conductivity of composites in function of radial thermal conductivity of fiber

4.2. Interlock Composite

In this part, we are going to propose a numerical model to predict the thermal conductivity of Composites made of Interlock fabric. In the literature, some works have been proposed for the modelling of thermal conductivity of textile fabric, including 2D and 3D fabric. For 2D fabric, in [7], the authors used analytical models presented in the previous part by considering in these models the doped resin and the textile fabric. But the structure of fiber is not taken into account. The analogy between heat conduction and electrical circuits has been also used in many works to predict thermal conductivity of textile fabric composites. But none of these works have treated the case of Interlock fabric. In this part, we propose the use FEM (Abaqus © software) to predict the thermal conductivity of our Interlock composite. The experimental result in the previous part is used to demonstrate the robustness of our model. As discussed the input for this model is : $\lambda_m = 0.1455$ (W/m.°K), $\lambda_{fl} = 500$ (W/m.°K). The radial thermal conductivity of fiber is chosen as $\lambda_{ft} = 11$ (W/m.°K).

4.2.1. Thermal conductivity of yarns

The SEM image treatment by ImageJ allows us to determine the fiber volume fraction in yarns is 72.4% +- 3.89 %. We propose here to use the analytical models presented in the previous part to predict the thermal conductivity of yarns as it is composed of straight continuous fibers and resin like unidirectional composites. Therefore, the parallel ROM is used to compute the longitudinal conductivity of yarns $\lambda_{yl} = 362$ (W/m.°K). For the transverse direction, the Lewis and Nielsen model which provide good assumption of mixture (straight fiber and resin) is used. Moreover, this model is valid until a volume fraction of 78.5%. We obtain then the value of radial thermal conductivity of yarns $\lambda_{yt} = 1.76$ (W/m.°K).

4.2.2. Model to prediction the thermal conductivity of Interlock fabric composite

Table 4 shows the geometrical properties of our model. For the sake of simplicity, the warp yarn is supposed to be straight.

warp yarns		**weft yarns**		**Distance between yarns (mm)**	
Width (mm)	Thickness (mm)	Width (mm)	Thickness (mm)	warp yarns	weft yarns
20	10	40	3	1	2

Table 4. Geometrical properties of the model

The warp yarns are interlaced. These geometrical properties lead to a ratio between the amplitude and the length of weft yarns is 6.46 which is coherent with experimental value 7.2 (see Figure 2). Let us note that local axes are used according to the orientation of yarns. In reality, the cross section of yarns is elliptical. As proposed by El Hage [1], in order to obtain a small shape factor and to simplify the meshing process, the cross section of yarns is composed of 2 demi circles of the thickness diameter and 1 rectangle. Thus, Figure 5 shows the VER of our Interlock 2.5D fabric composite with a contexture of 4x14 yarns/cm.

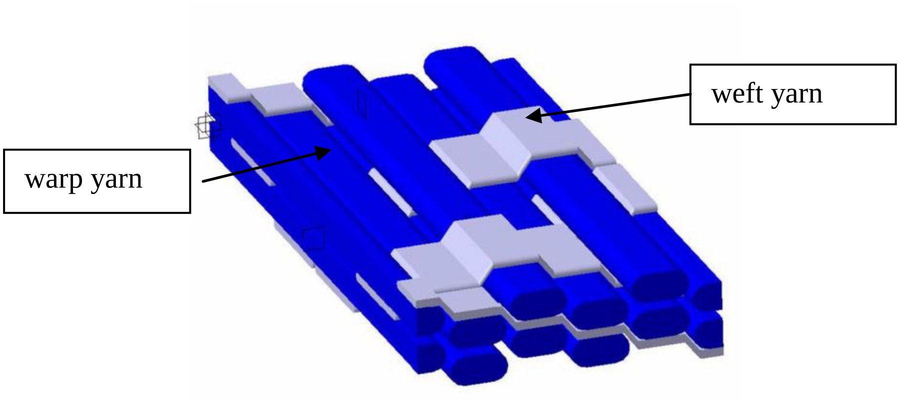

Figure 5. VER of Interlock 2.5D fabric composite

We apply a constant temperature T_1, T_2 at the two faces of the VER. The average heat flux is then computed on the surfaces. The effective thermal conductivity is computed using Fourier‘s law. In order to homogenize the flux, a very thin layer is proposed in both the up/bottom surfaces of VER. Table 5 shows the results obtained with difference resin layer thickness (with respect to yarn thickness). Let us remind that the experimental thermal conductivity is 1.35 (W/m.°K) and the fiber volume fraction is 40.64 ± 2.83 (%).

Resin layer thickness/yarn thickness	2%	**1%**	0.5%
Volume fraction of fiber (%)	40.50	**40.73**	40.84
λ_{ct} Composites (W/m.°K)	0.98	**1.26**	1.54

Table 5. Effective thermal conductivity of Interlock Composite as a function of resin layer thickness

We can see that as the resin layer thickness increases, the value of λ_{ct} decreases because of the high thermal isolation of resin. The volume fraction does not vary significantly. With the assumption of 1% resin layer thickness, we obtain a $\lambda_{ct} = 1.26\,(\text{W/m.°K})$ which is coherent with experimental data.

4.2.3. Interlock Composite with doped resin

Let us study now the thermal conductivity of Interlock Composite with doped resin. Copper particles are used as filler. By using Flash laser technique, the experimental thermal conductivity of doped resin with different volume fraction of Copper particles is shown in Table 6. We can see that doping the resin enhances greatly its conductivity. By using the previous analytical and numerical model, transverse thermal conductivity of Interlock composite with Copper doped resin (λ_{ct} Composites) is obtained. As discussed, the thickness of resin layer is chosen as 1% (w.r.t yarn thickness). It is noted that Composite with doped resin exhibits better transverse conductivity, this value is nearly tripled with 15% volume fraction of Cu. Experimental tests are being prepared.

λ (W/(m.°K))	**Pure resin**	**Doped resin Cu 5%**	**Doped resin Cu 10%**	**Doped resin Cu 15%**
Resin (experimental)	0.1455	0.3117	0.4806	0.7038
Yarns (longitudinal)	362	362	362	362
Yarns (transverse)	1.76	3.20	4.25	5.26
λ_{ct} Composites	1.26	2.09	2.73	3.40

Table 6. Simulation of thermal conductivity of Interlock fabric composite with Copper doped resin

5. Conclusion

In this paper, Interlock PITCH-based woven fabric composites have been studied. These composite materials show its enhanced thermal conductivity over the through thickness direction with respect to unidirectional composites. Analytical models have been used to predict the thermal conductivity of unidirectional composite which then used to compute the radial thermal conductivity of fiber. The result is very sensible as the conductivity of fiber exceeds greatly the conductivity of the matrix. Numerical models have been proposed to predict the thermal conductivity of Interlock composites which showed a good agreement with respect to experimental results.

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