Polymères chargés bons conducteurs de chaleur: rêve ou réalité ?
- Conception, réalisation et analyse multi-échelle -

B. Garnier, F Danès

Laboratoire de Thermocinétique, UMR CNRS 6607
Polytech'Nantes

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- **Objectifs:**

amélioration de la conductivité des matériaux thermoplastiques
par l’ajout de charge conductrice de chaleur

- **Défi* :**

❑ conductivité thermique effective transversale λ : de 0.2 (polymère) à 2 W/ m K voir plus (4 à 6 W/m K ?)
❑ sans dégradation importante des propriétés mécaniques
❑ maintien d’un coût modéré

- **Applications :**

Echangeurs de chaleur, drains thermiques (automobile, électronique, électrotechnique…)

*:"High Thermal Conductivity Thermoplastic Compounds", Craft BRST - CT98-5302, Eur. Commis. DG12- HIAS, Nov. 1998/2001

Etat de l’art

- La difficulté de réaliser des polymères chargés bons conducteurs croit dans l’ordre suivant:

encres, colles, élastomères, thermodurcissables et ***thermoplastiques***

- Conductivité thermique de quelques thermoplastiques chargés :

	Matrice ($\lambda_{t,m}$/ W.m^{-1}K^{-1})	**Charge ($\lambda_{t,f}$/ W.m^{-1}K^{-1})**	**Forme**	**Taille µm**	**charge % vol.**	**$\lambda_{t,eff}$ W.m^{-1}K^{-1}**	**Ref.**
1	**PE (0.26)**	**graphite (210)**	**poudre**		**30**	**1.8**	**Agari 1986**
2	**PE (0.26)**	**Cu (390)**	**poudre**		**30**	**1.25**	**Agari 1986**
3	**PE (0.26)**	**Al_2O_3 (33)**	**poudre**		**33**	**0.75**	**Agari 1986**
4	**PP (0.26)**	**Al (220)**	**fibre**	**100/1250**	**15**	**0.72**	**Bigg 1986**
5	**PP (0.26)**	**Al (220)**	**fibre**	**100/1250**	**18.3**	**2.2**	**Bigg 1986**
6	**PE (0.47)**	**$CaC0_3$ (4,7)**	**poudre**		**47**	**1.25**	**Barta 1997**
7	**PC (0.19)**	**C(210)**	**fibre**	**8/ 3000**	**44**	**0.5**	**Srivastava 1997**
8	**PE (0.50)**	**Al (220)**	**poudre**	**40 80**	**33**	**3.6**	**Tavman 1996**

PC-polycarbonate, PE- polyéthylène, PP – polypropylène

GARNIER B., AGOUDJIL B., BOUDENNE A., Chap.18, pp.575-612, “Metallic particle filled polymer micro composites” in Polymer Composites: Volume 1, 1st ed, Ed.by Sabu Thomas,et al._ 2012 Wiley-VCH Verlag GmbH & Co. KGaA

1- Facteurs modifiés lors des essais et résultats *

2- Modélisation de la conductivité thermique effective

3- Résistance thermique de contact inclusion/matrice

*: "High Thermal Conductivity Thermoplastic Compounds", Craft BRST - CT98-5302,
Eur. Commis. DG12- HIAS, Nov. 1998/2001

1- Facteurs modifiés lors des essais et résultats

La conductivité thermique effective λ_t **dépend de:**

- la nature de la matrice,
- la nature, la taille, la forme et le taux volumique des inclusions,
- la nature et le taux volumique de tensioactif,
- des conditions de mise en œuvre (durée et intensité du mélangeage, température.) et
- des conditions de mise en forme (procédés de moulage, géométrie du moule, épaisseur de la pièce….)

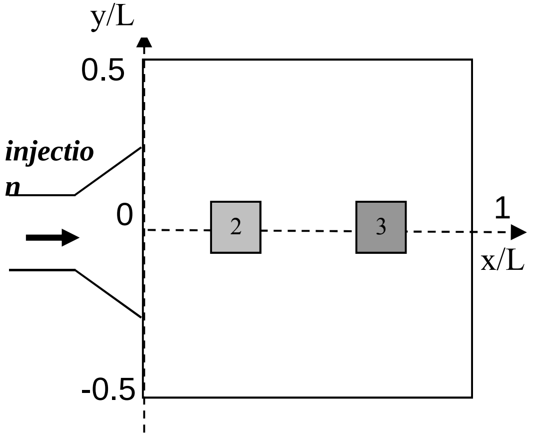
Effet de la nature et de la forme des inclusions

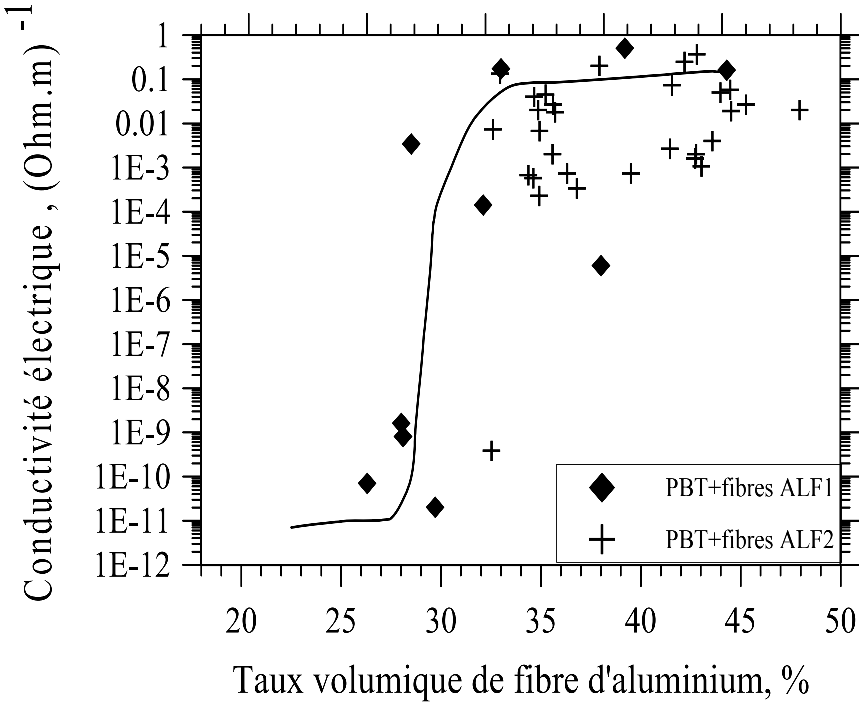
- **Matrice polymère:** polybutylene terephatalate PBT
- **Mise en œuvre et mise en forme :** procédés semi -industriels

Charge	Noir de fumée CB	Poudre d'aluminium*		Fibre d'aluminium ALF1*		Fibre d' aluminium ALF2*		Poudre d'aluminium + ALF1 + CB
ϕ, % en masse	12	27	41	27	41	37	61	16-15-2.7
$\lambda_{t,eff}$, W/ m K	0.37	0.48	0.79	0.49	0.92	0.61	1.42	0.5

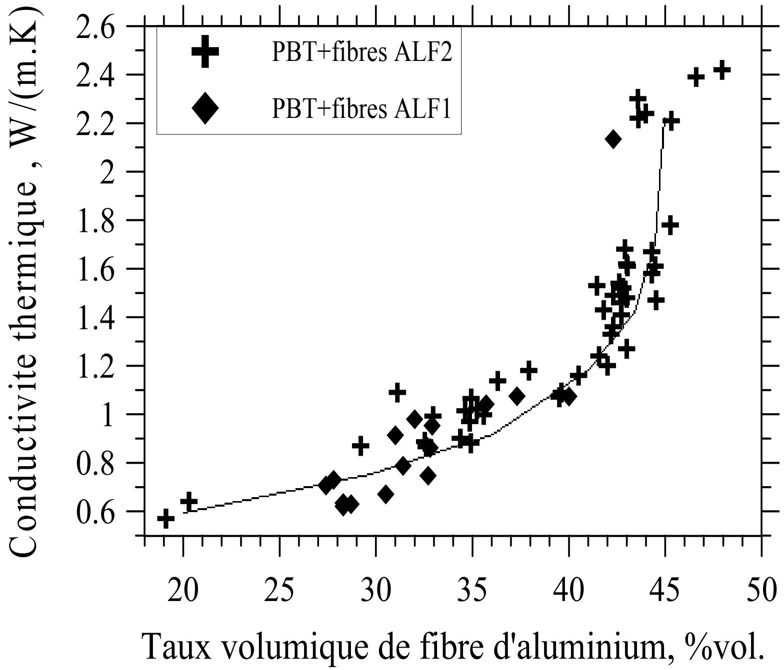
*: Al. powder (aver. diam.:300µm), ALF1 fiber (diam.:150µm, length: 1.1mm), ALF2 fiber (diam.: 90µm, length: 1.1mm)

Effet du taux de charge





conductivité électrique



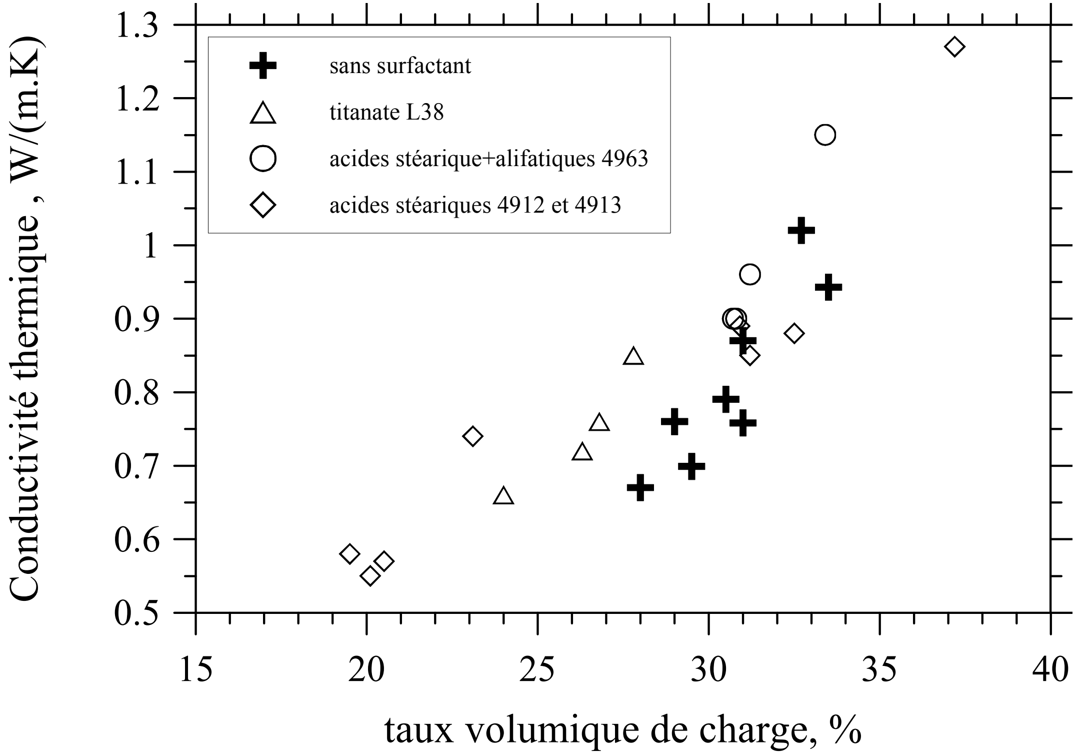
conductivité thermique

$$PBT+\ fibres\ d'aluminium\ \begin{cases} ALF1 : diam. 160\mu m \\ ALF2 : diam. 90\mu m \end{cases}$$

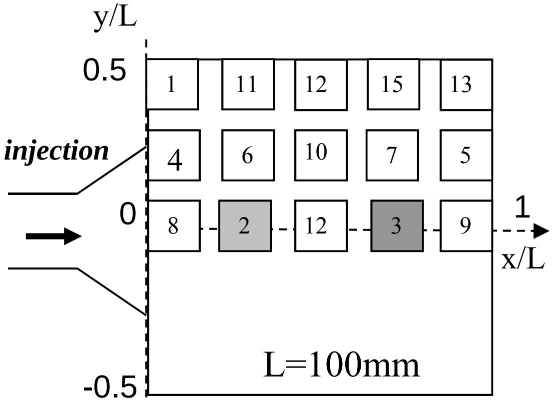
Garnier et al, Int J Thermophysics 2003

Effets des surfactants

Les surfactants (0.15% en masse) semblent augmenter la conductivité thermique



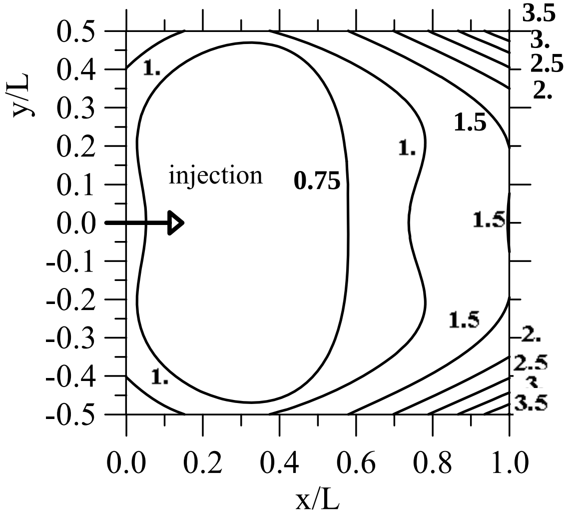
Uniformité de la distribution du taux de charge et des propriétés therm. et elect.



•Fibres AL diam.160µm; 32,7% vol. :

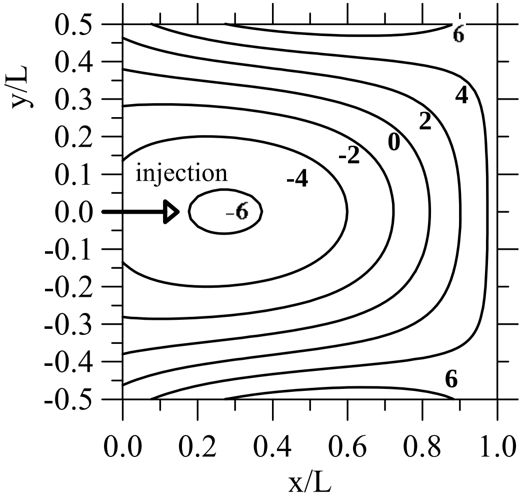
(a) **Cond. Thermique***

$$\lambda_{t,moy} = 0,90\,Wm^{-1}K^{-1}$$



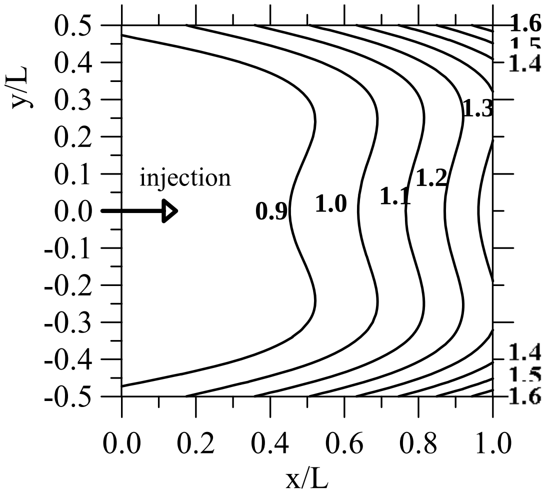
(b)**Log$_{10}$ de la cond. électrique***

$$\log_{10}(\lambda_{el}) = -5.22$$



(c) **Taux vol. de charge***

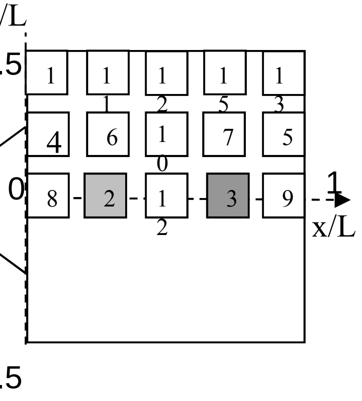
$$\phi_{moy} = 0,327$$



Danès et al., Comp. Sci. Techn. 2005

*: rapportée à la valeur moyenne dans la pièce

Uniformité de la distribution du taux de charge et des propriétés therm.



injection

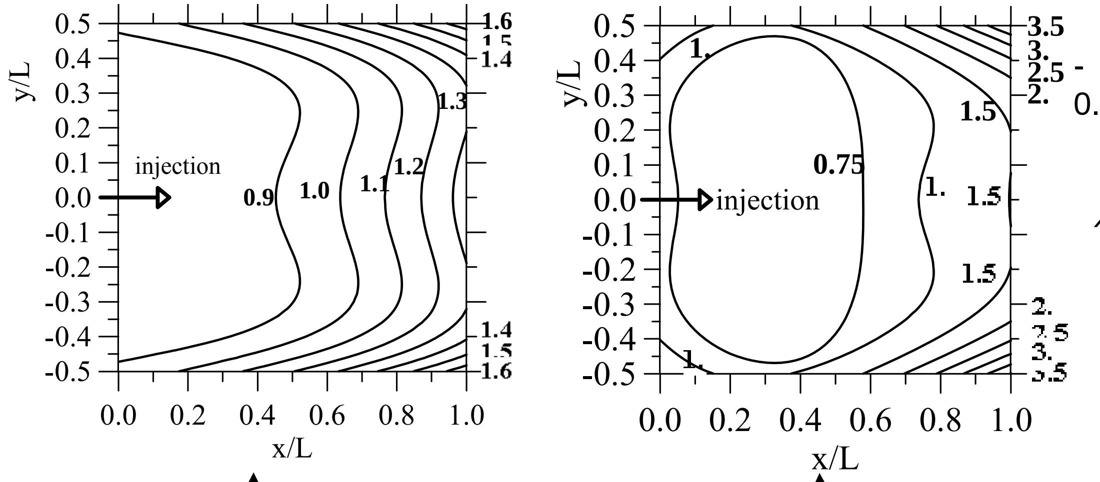
- **Fibres AL diam.160µm 32,7% vol. :**

$\phi_{moy} = 0,327$

s_ϕ =0,059

$\lambda_{t,moy} = 0,9\,Wm^{-1}K^{-1}$

$s_{\lambda t}$ =0,46



(a) **Taux vol. de charge***

(b) **Cond. Thermique***

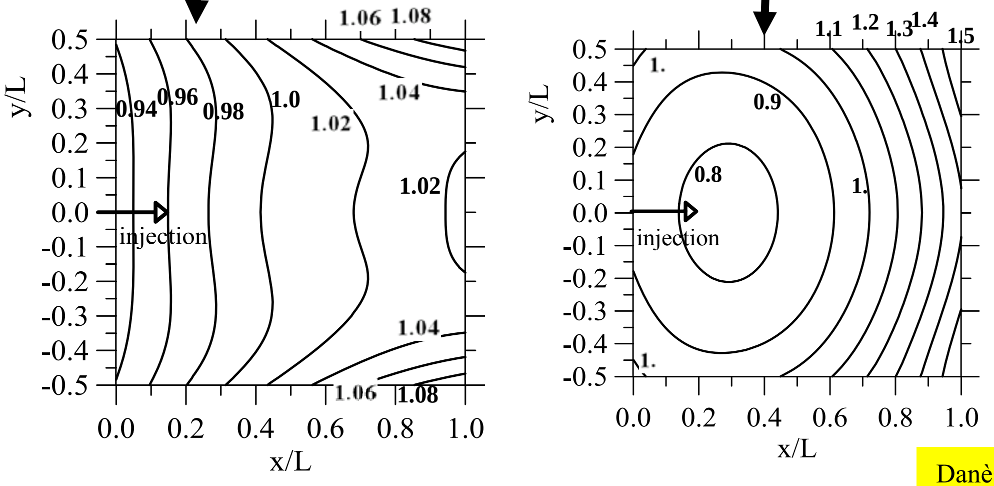
- **Fibres AL diam. 90µm 34,8% vol.:**

$\phi_{moy} = 0,348$

s_ϕ =0,013

$\lambda_{t,moy} = 1,1\,Wm^{-1}K^{-1}$

$s_{\lambda t}$ =0,23

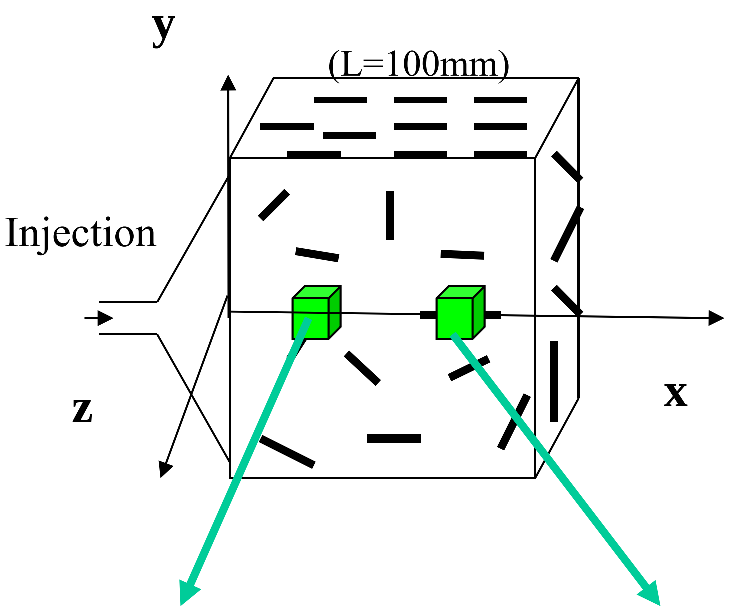


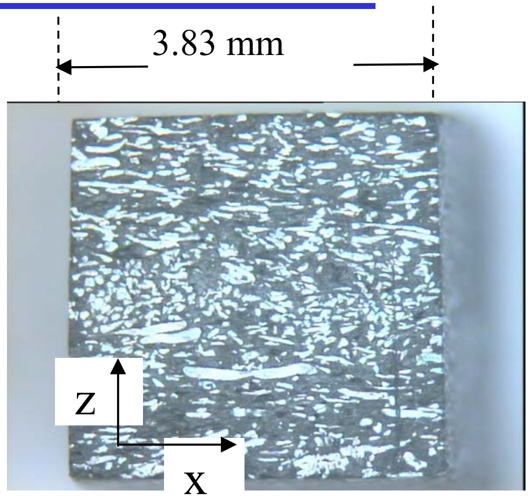
Danès et al., Comp. Sci. Techn. 2005

*: rapportée à la valeur moyenne dans la pièce

s: écart standard des mesures locales / moyenne de la pièce

Orientation des fibres et anisotropie des pièces



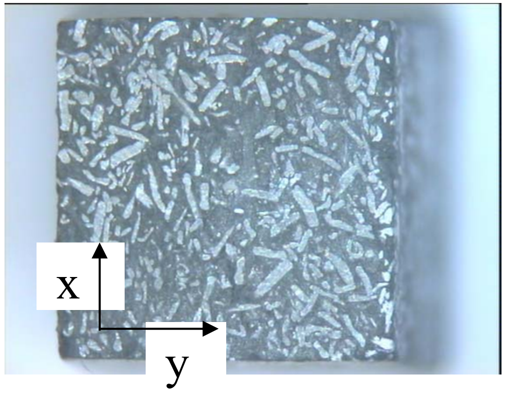


En x/L=0,175 et y/L=0:

λ_x= 7,0 W.m^{-1} K^{-1}
λ_y= 4,3 W.m^{-1} K^{-1}
λ_z= 1,6 W.m^{-1} K^{-1}

En x/L=0,825 et y/L=0:

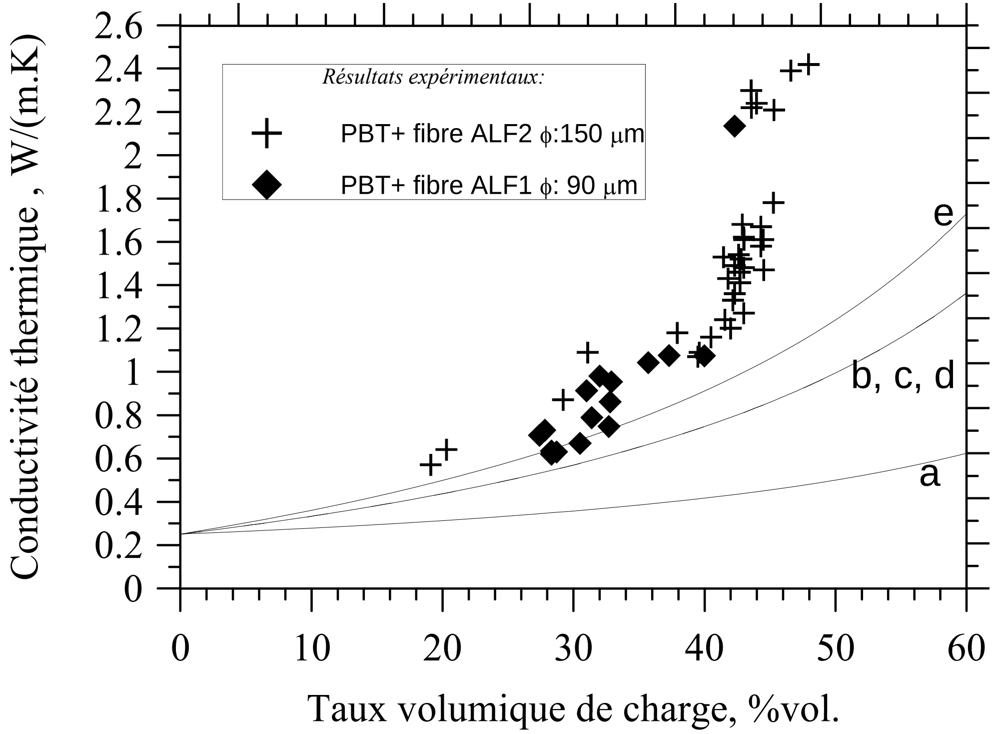
λ_x= 7,6 W.m^{-1} K^{-1}
λ_y= 5,0 W.m^{-1} K^{-1}
λ_z= 2,1 W.m^{-1} K^{-1}



$\boxed{\lambda_z << \lambda_y < \lambda_x}$

2- Modélisation de la conductivité thermique effective

•Les modèles physiques macroscopiques actuels (empiriques, semi empiriques) <u>sous estiment</u> λ_t pour $\lambda_t/\lambda_{matrice} > 3$



Modèles (bornes inférieures):

- a: Wiener 1912
- b: Hatta et Taya 1985
- c: Maxwell-Eucken 1932
- d: Nielsen 1974
- e: Hashin et Shtrikman 1962

Modélisation numérique (Eléments finis)

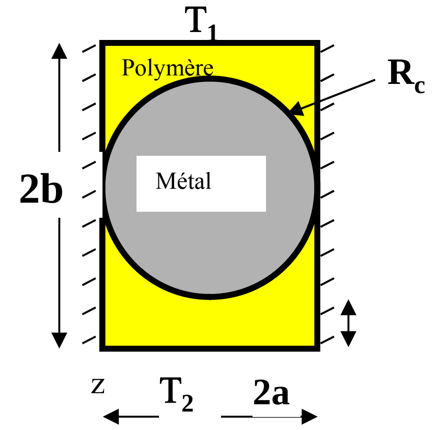
For the 3D finite element study of the effective thermal conductivity, we considered:

- the stationary heat conduction equation

-a tetragonal lattice of spherical inclusions of equal size

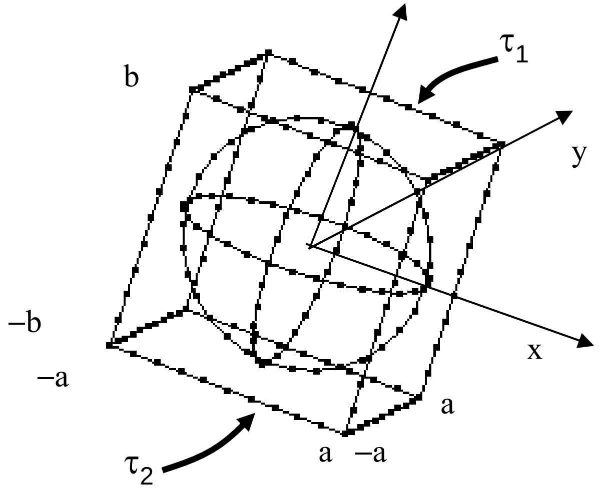
- a thermal contact resistance between inclusion and matrix

- adiabatic conditions for all faces except the top and bottom ones (i.e. for z=-b and z=b)



Elementary cell:

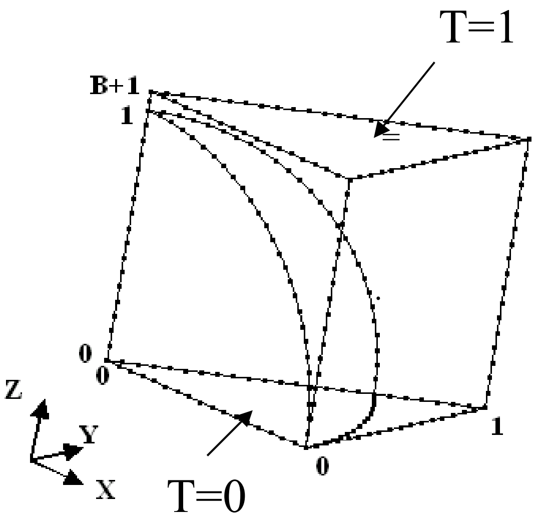
sphere of radius *a* centered in
a tetragonal cell of dimensions: 2*a* x2*a* x 2*b*



Filp C., Garnier B., Danes F. , J Heat Transfer 2007

Main features of the adopted model

- Using dimensionless physical quantities, this results in : $E=E(B,C,D)$



with: $E = \dfrac{\lambda_{eff}}{\lambda_m}$ and $\left\{ \begin{aligned} D &= \frac{\lambda_m}{\lambda_f} \\ C &= \frac{r_c\,\lambda_m}{a} \\ B &= \frac{b-a}{a} \end{aligned} \right.$

λ : thermal conductivity
r_c : thermal contact resistance
a: radius of the inclusion
b: half height of the tetragonal cell
m : matrix
f : filler
eff : effective (composite),

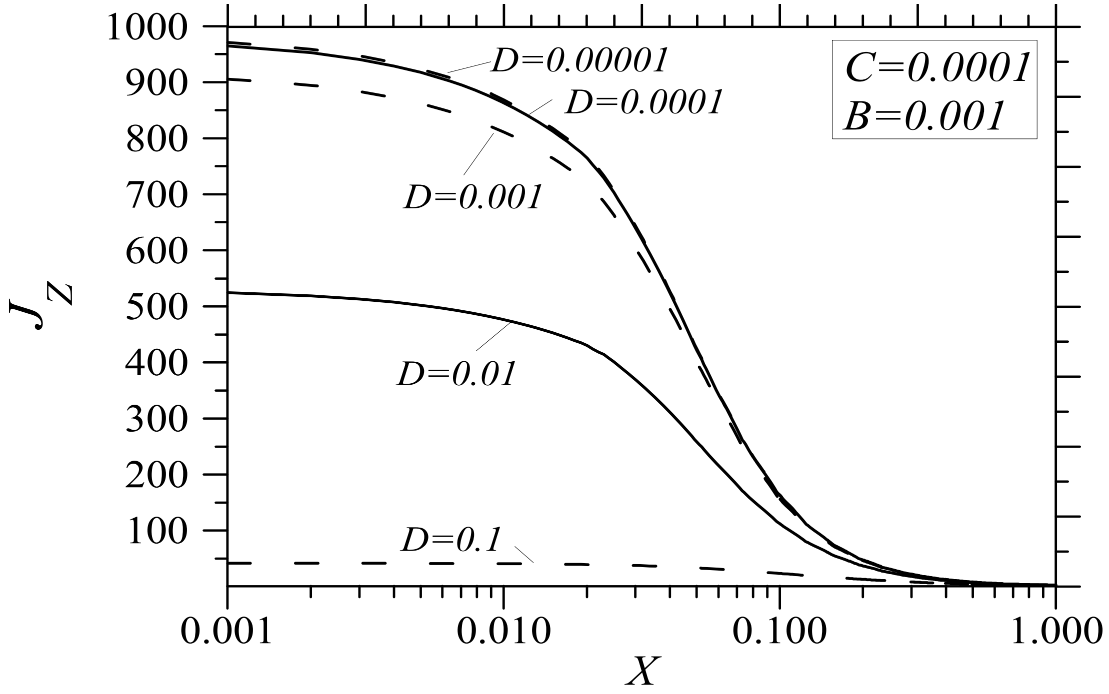
The filler amount φ is correlated *(tetragonal cell) to B* by: $\varphi = \dfrac{\textit{sphere volume}}{\textit{cell volume}} = \dfrac{\pi}{6(1+B)}$

Finite element (Comsol Multiphysics, 48000 to 58000 tetrahedra, Lagrange multipliers)

Distribution of longitudinal heat flux

The dimensionless heat flux J_Z crossing the elementary cell is calculated by:

$$J_Z = \left.\frac{\partial T}{\partial z}\right|_{z=0}$$



$$B = \frac{b-a}{a} \qquad C = \frac{r_c\ \lambda_m}{a} \qquad D = \frac{\lambda_m}{\lambda_f}$$

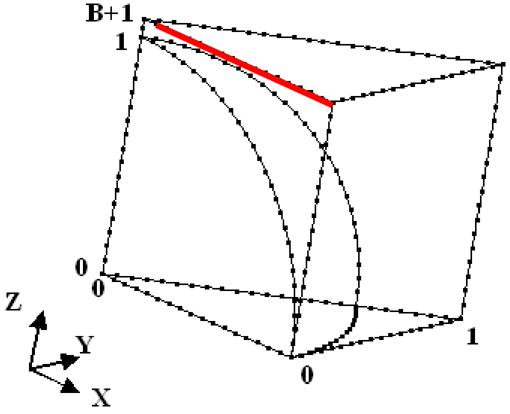


Fig. 2 : *Reduced heat flux* J_Z *vs D on the line (X=0, Y=0 ,Z=1.001) and (X=1,Y=0 Z=1.001)*

Validation of the numerical results

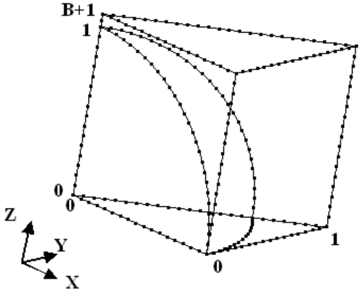
#	Parameters			Computed entity	Bibliographic source			This work	Discrepancy %
	B	*C*	*D*		author	Computing	value		
1	0	0	0	$\partial E/\partial \ln B$	[30]	analytic local	−1.571	−1.560	**.8**
2	0	0	.1	E	[27]	analytic global	3.47	3.473	**.1**
3	0	0	70000	E	[27]	analytic global	.344	.344	**0**
4	.7	0	0	E	[32]	finite elements	.48	.47	**2.1**
5	0	.5	.00001	E	[18]	analytic global	1.4478	1.44820	**.04**
6	0	.5	.1	E	[18]	analytic global	1.3135	1.31363	**.01**
7	0	2	.00001	E	[18]	analytic global	.7174	.71077	**.05**
8	0	3	.1	E	[18]	analytic global	.5910	.59183	**.13**

[18]: Cheng H.1997 ; [27]: Sangani A. 1982; [30]: Batchelor G.1977; [32]: Filip C. 2004

→ One can infer that the discrepancy is within 0.1% for E and within 1% for the slopes of E .vs. the logarithm of factors.

Effect of varied factors on E

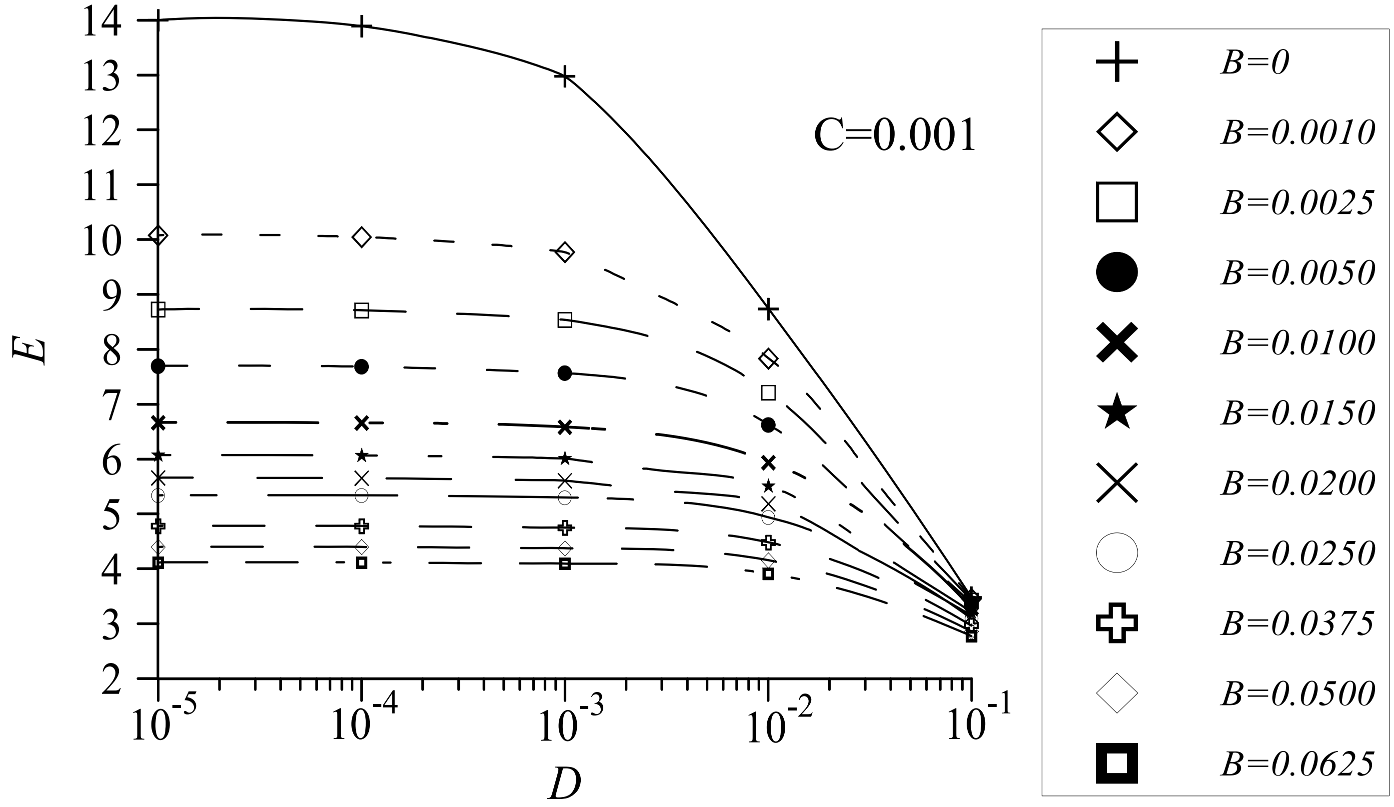
$$E = \frac{\lambda_{eff}}{\lambda_m}$$



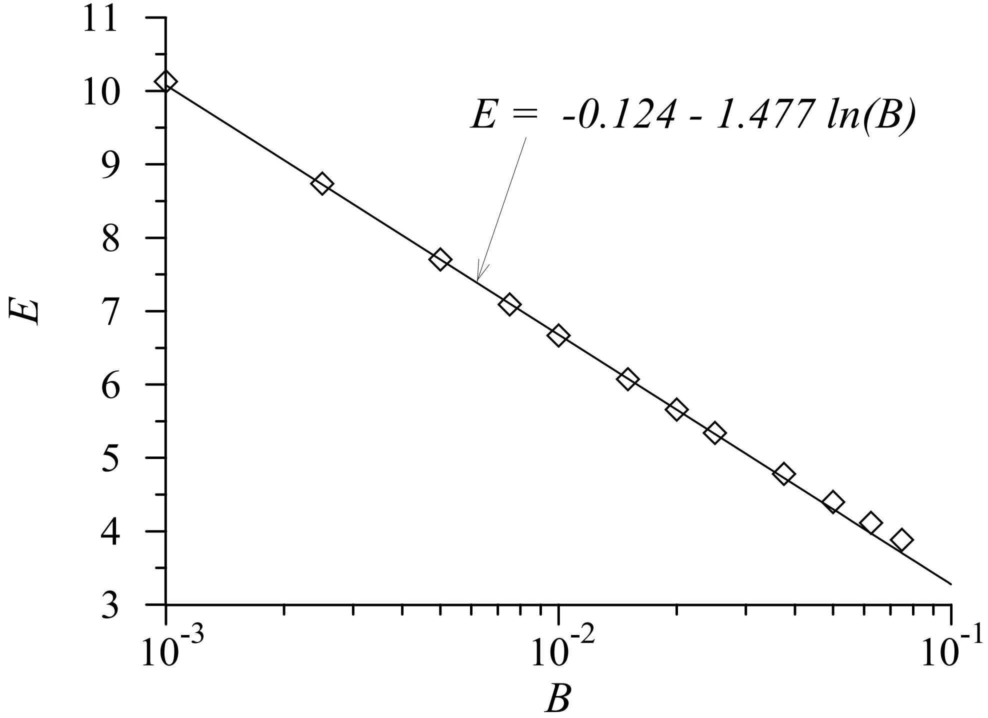
$$Q = \quad J_Z = \int_0^1 \left(\int_0^X \frac{\partial T}{\partial Z}\bigg|_{Z=0} dY \right) dX$$

$$E = 2\,Q(1+B)$$

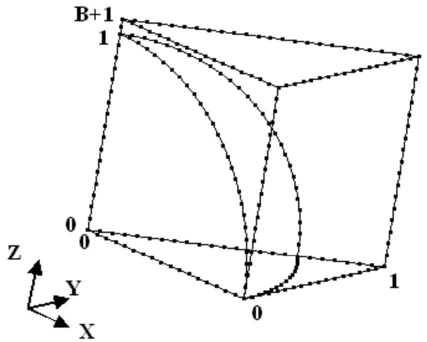
$$B = \frac{b-a}{a} \qquad C = \frac{r_c\,\lambda_m}{a} \qquad D = \frac{\lambda_m}{\lambda_f}$$



Magnitude effects



$E = -0.124 - 1.477\ln(B)$



$$B = \frac{b-a}{a} \qquad C = \frac{r_c\,\lambda_m}{a} \qquad D = \frac{\lambda_m}{\lambda_f}$$

Fig. 4: E*ffective conductivity E vs. B with* **B >> {C,D}**

Filp C., Garnier B., Danes F. , J Heat Transfer 2007

Effet de l’épaisseur de la paroi des billes creuses en aluminium (paramètre F)

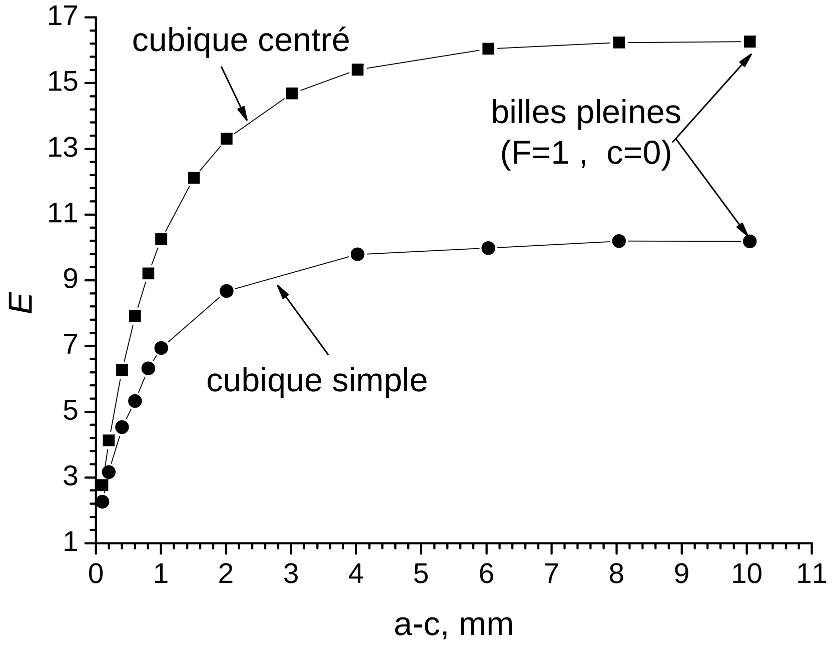
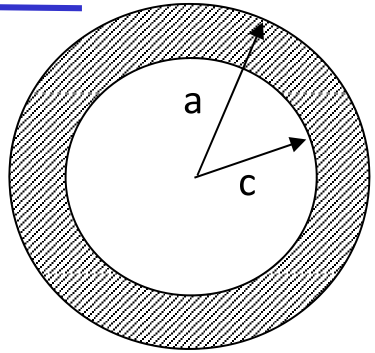


Fig. 7 : *Effet de l épaisseur de la paroi des billes creuses*



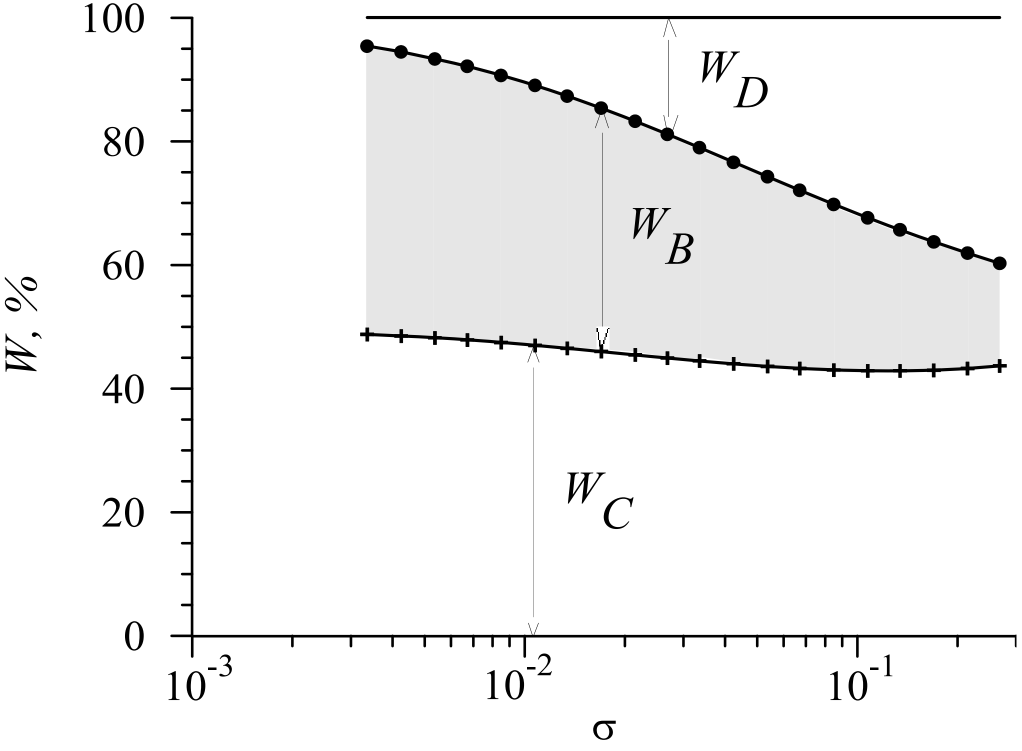
***a-c* =1.17mm** ***a*=10.05mm**

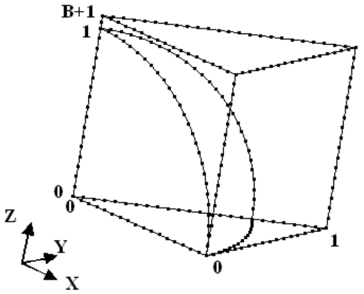
<u>Rq</u> : F=1 correspond au cas des <u>billes pleines</u>

Quantitative comparison of the effects of factors

21 factorial experiment plans 2^3

$$B = \frac{b-a}{a} \qquad C = \frac{r_c \lambda_m}{a} \qquad D = \frac{\lambda_m}{\lambda_f}$$





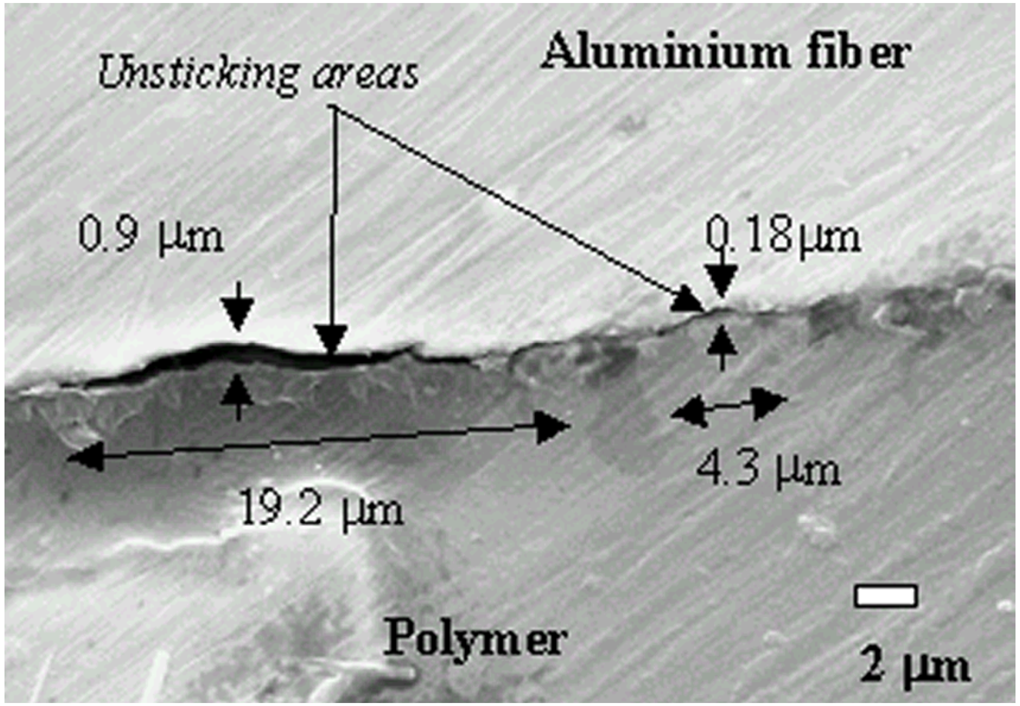
0.001<each factor <0.1

$\sigma = B+C+D$

Fig. 5: Weights of pure factors *B*, *C*, and *D* within the total variation of the effective longitudinal conductivity *E*, at nearby equal values of the three factors

Filp C., Garnier B., Danes F. , J Heat Transfer 2007

3- Résistance thermique de contact (RTC) inclusion/matrice



SEM analysis of the Aluminum/ PBT polymer interface

→ Comment mesurer localement la RTC particules d'aluminium / matrice polymère ?

Literature review on microscale methods for particle/ matrix thermal contact resistance measurement:

- methods with contact: the probe sample TCR does not appear to be much lower than the particle/matrix TCR under investigation

-modulated thermoreflectance: some order of magnitude for TCR at grain boundaries in aluminum nitride (Pelissonnier 1996)

→Not much TCR values between constituents were measured locally in polymer matrix composites

“Microphotomètre à pointe”

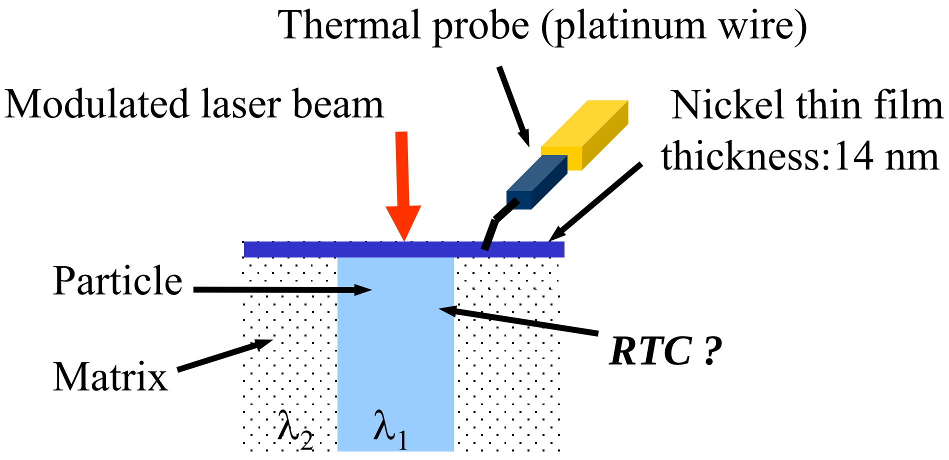
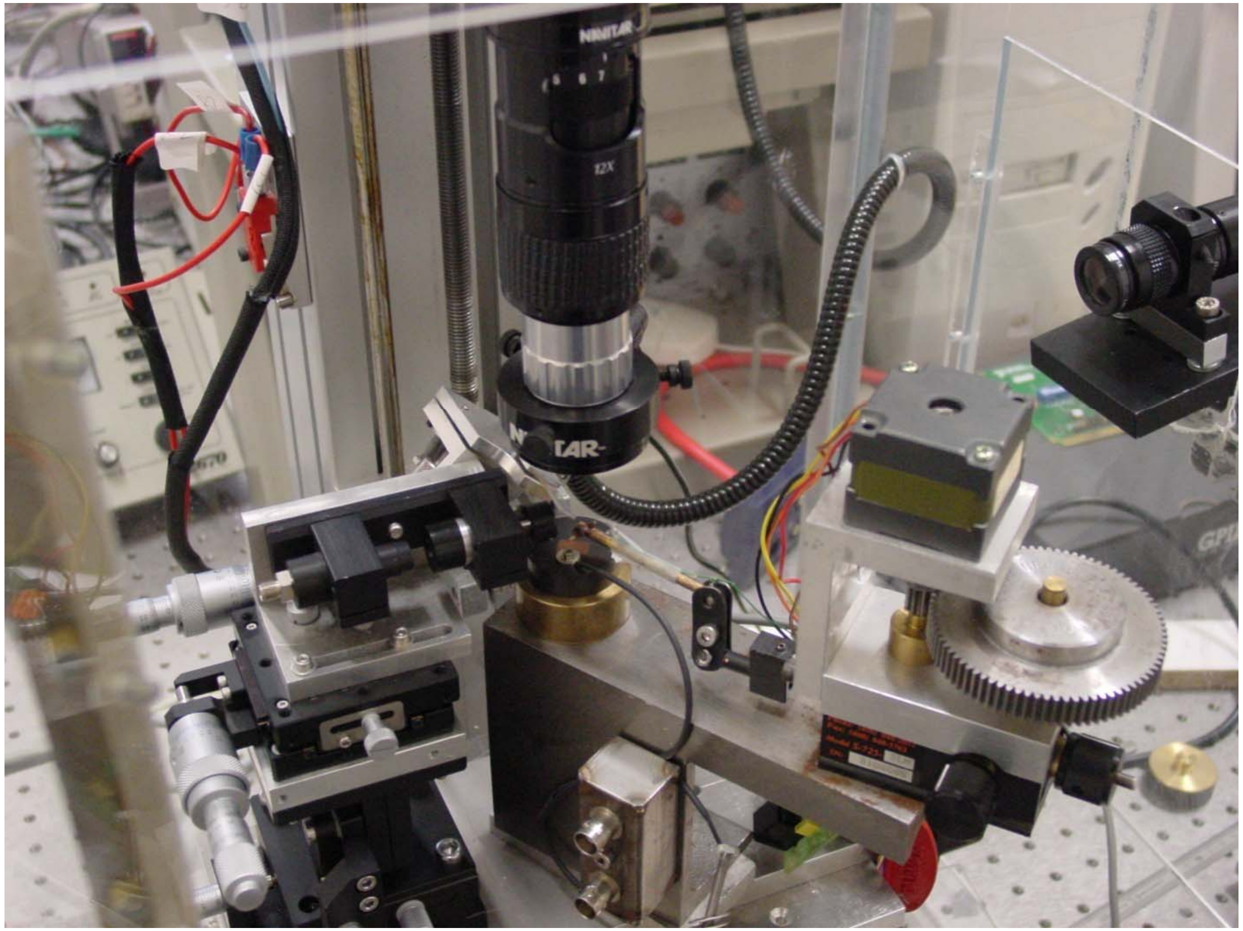


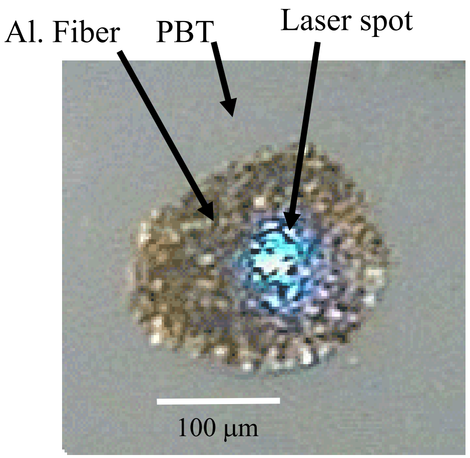
Fig. 1 : *TCR measurement procedure*

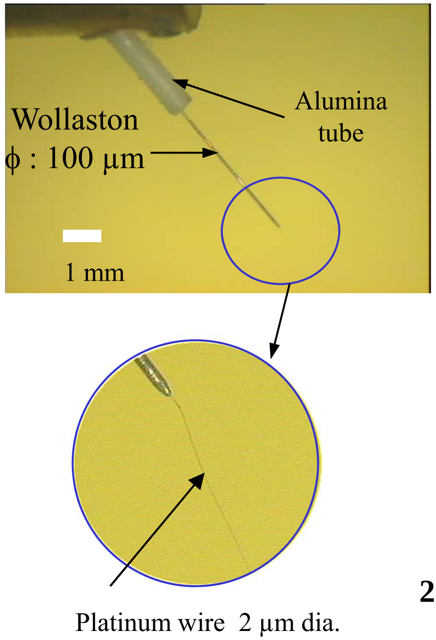
- **Heating:** modulated laser pump beam

- **Phase lag temperature measurement**: thermocouple with a nickel thin film (14nm thick) and a platinum wire (2 µm dia.)

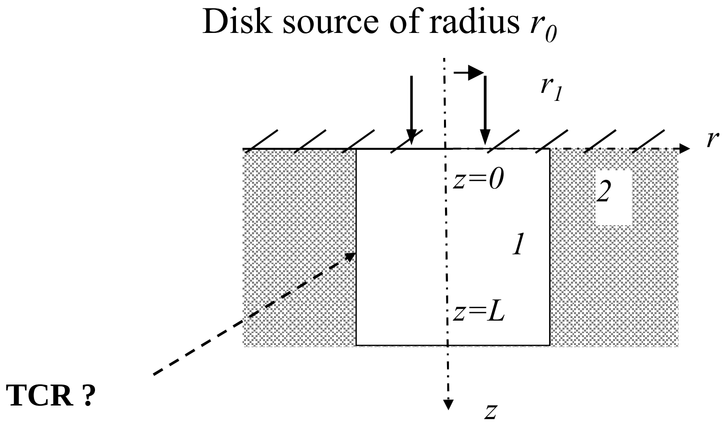
Experimental setup







Heat transfer model



2D cylindrical $\psi(r,z)$

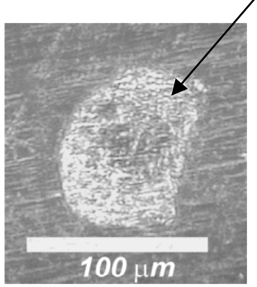
- $T(r,z,t) = real(\theta(r,z)\ \ e^{j2\pi f t})$
- Integral transform $\theta_i(r,0) = \sum_{k=1}^{\infty} L\left[A_{i,k} I_0(\sigma_{i,k} r) + B_{i,k} K_0(\sigma_{i,k} r)\right]$

  with $\delta_i = \sqrt{a_i / (\pi f)}$ and $\sigma_{i,k}^2 = (k\pi)^2 L^{-2} + 2j\delta_i^{-2}$
- $A_{i,k}$ and $B_{i,k}$ are solutions of :

$$\begin{bmatrix} 1 & -1 & -K_0(\sigma_{1,k}r_0)\ I_0^{-1}(\sigma_{1,k}r_0) & 0 \\ 1 & -1 & K_1(\sigma_{1,k}r_0)\ I_1^{-1}(\sigma_{1,k}r_0) & 0 \\ 0 & I_0(\sigma_{1,k}r_1) & K_0(\sigma_{1,k}r_1) & -\left[K_0(\sigma_{2,k}r_1)+R_c.\lambda_2.\sigma_{2,k}K_1(\sigma_{2,k}r_1)\right] \\ 0 & I_1(\sigma_{1,k}r_1) & -K_1(\sigma_{1,k}r_1) & \lambda_2.\sigma_{2,k}\lambda_1^{-1}.\sigma_{1,k}^{-1}.K_1(\sigma_{2,k}r_1) \end{bmatrix} \begin{Bmatrix} A_{0,k} \\ A_{1,k} \\ B_{1,k} \\ B_{2,k} \end{Bmatrix} = \begin{Bmatrix} -\lambda_1^{-1}.\sigma_{1,k}^{-2}.I_0^{-1}(\sigma_{1,k}r_0) \\ 0 \\ 0 \\ 0 \end{Bmatrix}$$

⟶ Temperature phase lag ψ : $\psi = arg(\theta)$.

Results



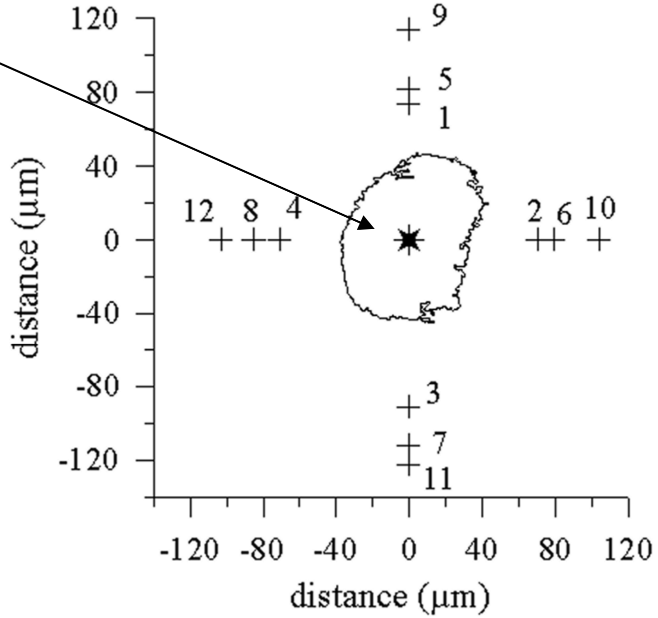


Figure 3. Aluminum fiber and locations of the temperature phase lag measurements

$$S(R) = \sum_{n=1}^{12} \left[\psi_{n,m} - \psi_{n,c}(R_c) \right]^2$$

TABLE I: ESTIMATED PARTICLE/MATRIX THERMAL CONTACT RESISTANCE

f, Hz	**0.1**	**0.2**	**0.5**	**1**	**2**
R_c, 10^{-5} m^{2}K/W	**3.6**	**3.0**	**3.3**	**5.2**	**5.4**

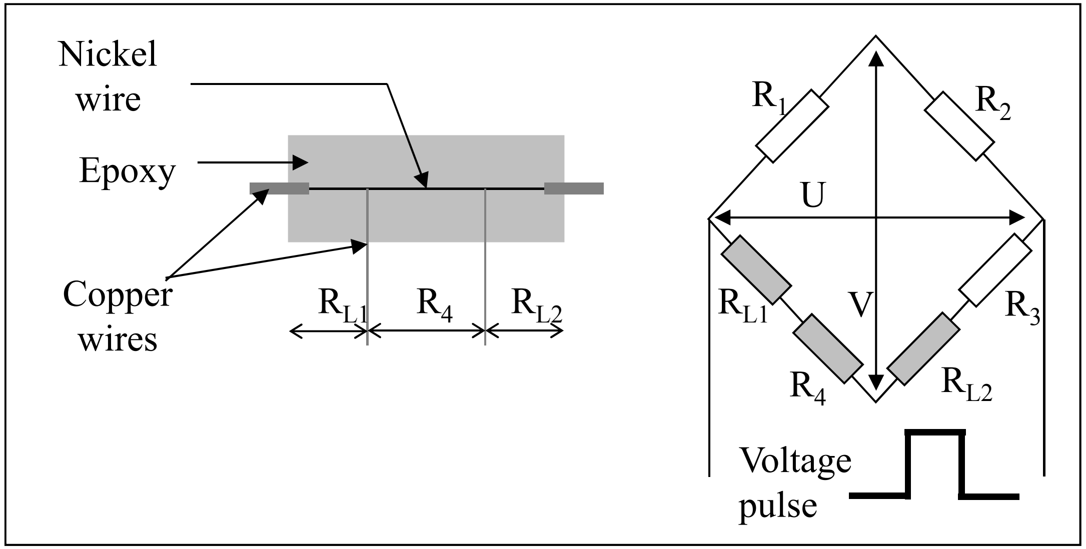
Average TCR value for PBT/alum. fiber: $\overline{R}_c = (3.81 \pm 0.59).10^{-5}$ m^2.K.W^{-1}

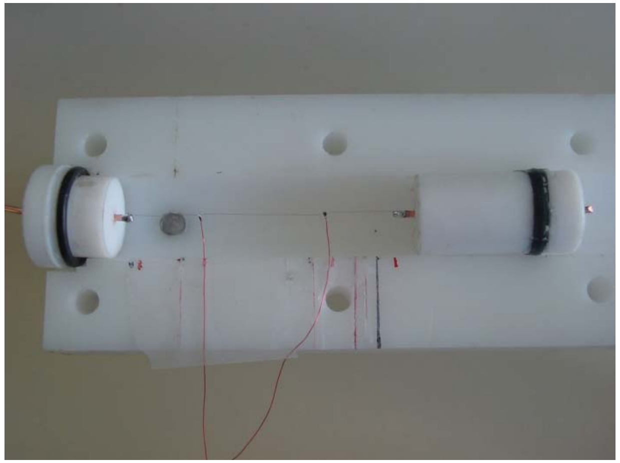
Garnier et al. IHTC12 2003

Macroscopic technique for TCR measurement between a wire and the surrounding matrix

EXPERIMENTAL SETUPS:

Three experimental setups with nickel wires of
ϕ = 25, 50 and 125 µm





Chapelle at al. IJTS 2009

Heat transfer model

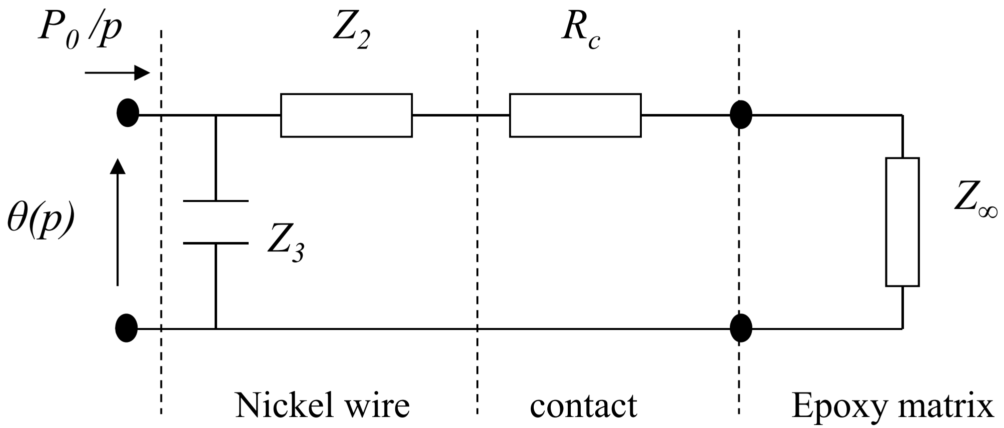


Figure 5. Equivalent impedance network

Laplace transform+ thermal quadrupoles (Maillet et al.2000):

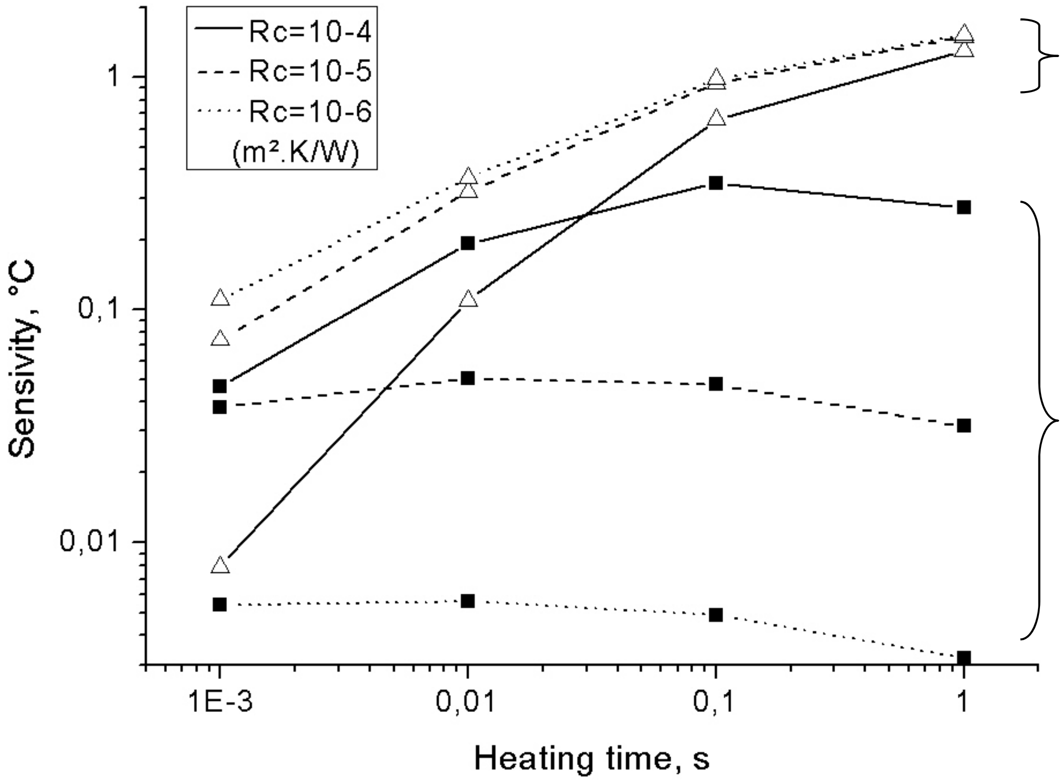
$$\theta(p,R_c)=\frac{P_0}{p}\cdot\frac{1}{\dfrac{1}{Z_3}+\dfrac{1}{Z_2+\dfrac{R_c}{2\pi Lr}+Z_\infty}}$$

$$Z_2=\frac{I_0(s)}{2.\pi.\lambda_{Ni}.L.s.I_1(s)}-\frac{1}{\rho_{Ni}.c_{Ni}.\pi.r^2.L.p}$$

$$Z_3=\frac{1}{\rho_{Ni}.c_{Ni}.\pi.r^2.L.p} \qquad s=r\sqrt{\frac{p}{a_{Ni}}}$$

$$Z_\infty=\frac{1}{2.\pi.\lambda_{ep}.L}\,\frac{K_0(s')}{s'.K_1(s')} \qquad s'=r\sqrt{\frac{p}{a_{ep}}}$$

Sensitivity analysis



$$\lambda_{ep} \frac{\partial T}{\partial \lambda_{ep}}$$

$$R_c \frac{\partial T}{\partial R_c}$$

→ For $R_c \cong 10^{-5} m^2 K / W$: the best heating time is 10ms

Results

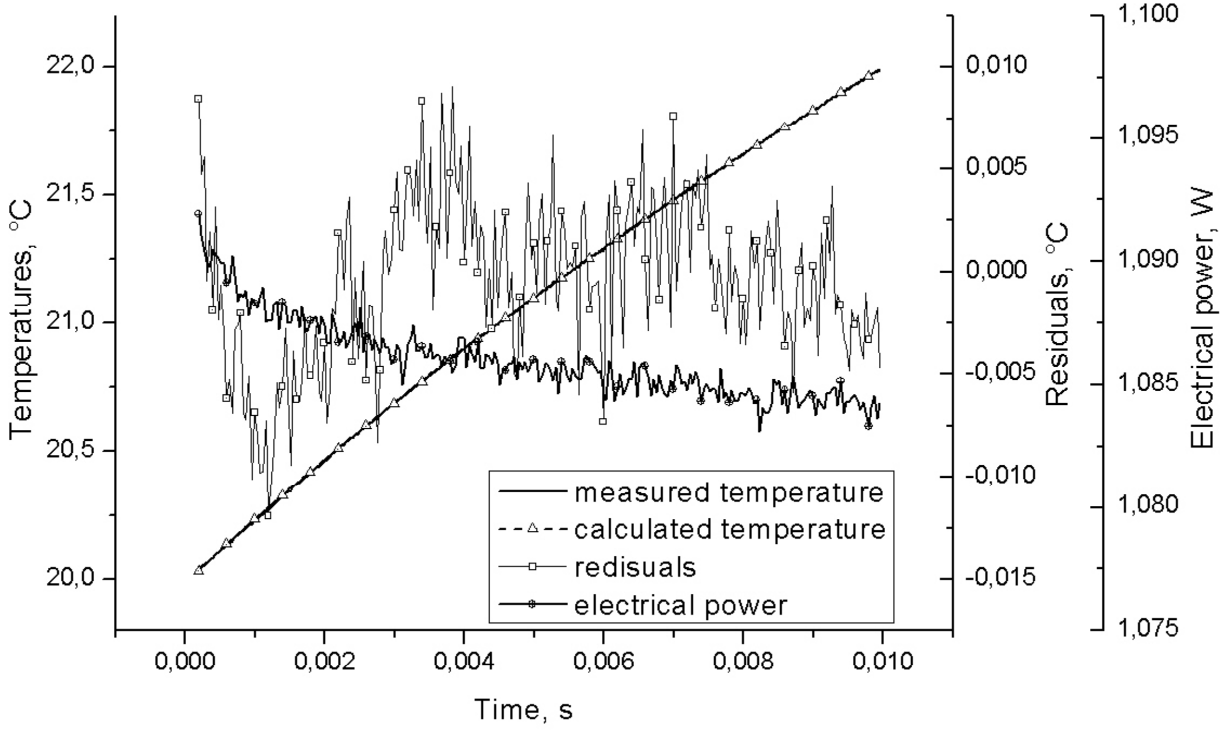
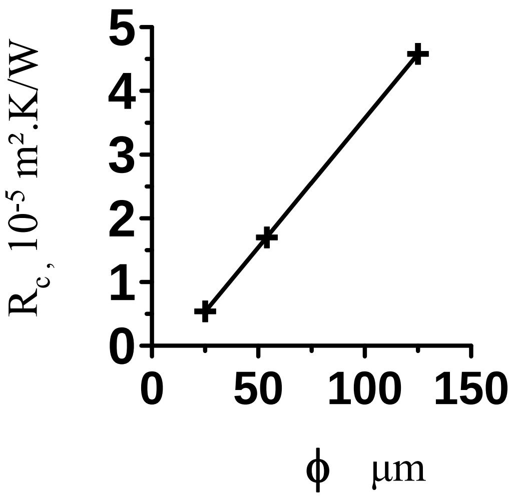


Figure 6. Measured and calculated temperatures, electrical power and residuals (wire with a 125µm diameter- test #1).

Results

TABLE II. MEASURED THERMAL CONTACT
RESISTANCES BETWEEN NICKEL WIRES AND EPOXY RESIN

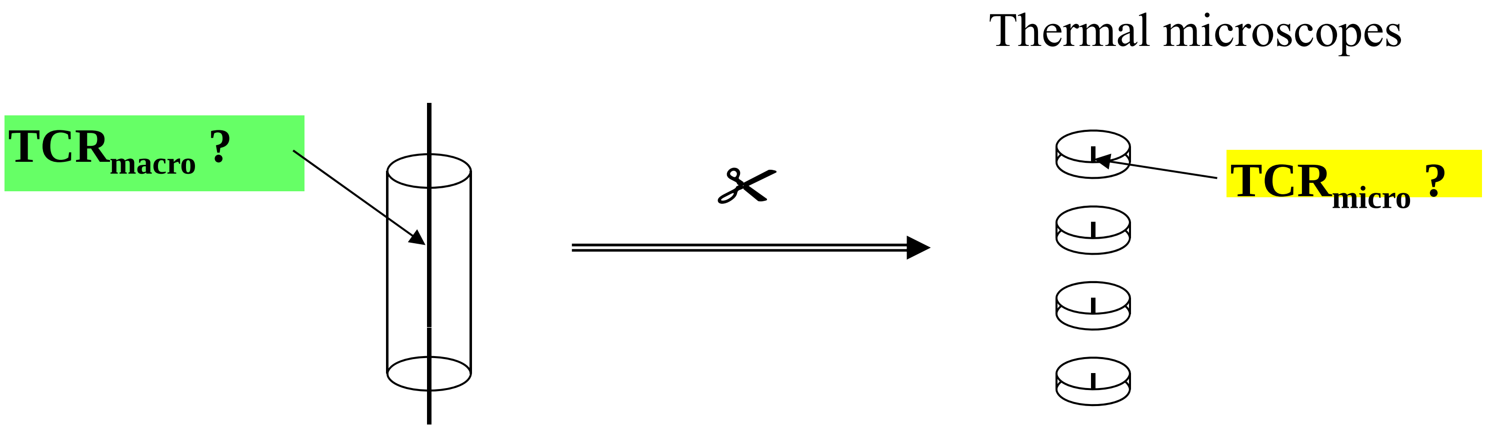
Test	1	2	3	4	5	Averaged R_c
R_{c}, 10^{-5} m².K/W(25µm wire dia.),	0.427	0.638	0.469	0.628	0.534	0.54
R_{c}, 10^{-5} m².K/W(50µm wire dia.),	1.28	1.66	1.63	1.83	2.08	1.70
R_c ,10^{-5} m².K/W (125µm wire dia.)	4.51	4.42	4.30	5.73	3.92	4.58



ϕ = 25, 50 and 125 µm

Future work :

1) $\mathrm{TCR}_{macro} \overset{?}{=} \mathrm{TCR}_{micro}$



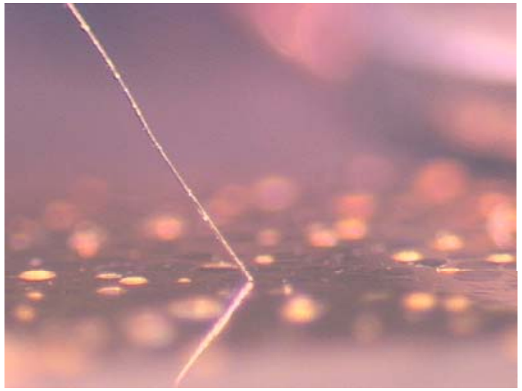
Thermal microscopes

TCR_{macro} ?

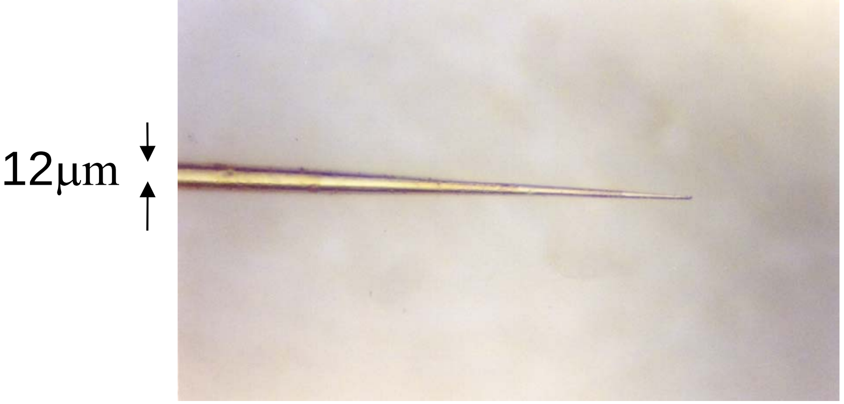
TCR_{micro} ?

Future work :

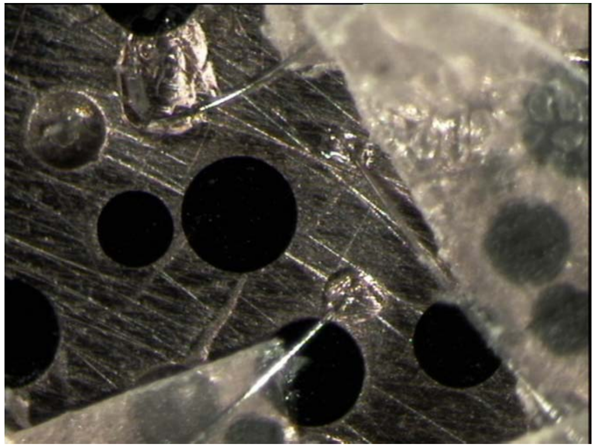
2) Thermal contact resistance between 300 µm carbon particle and copper matrix ?



Nickel wire diam 20µm



Chromel wire, diam. 12mm



Ultrasonic welding
(Nickel wire diam 20µm)

Conclusion

- The greatest transversal thermal conductivity obtained here is

2.2 W/ m K

(PBT + 43% vol. aluminum fiber – av. length 1.1 mm and av. diameter 0.09mm-)

- Further improvements (higher λ , better uniformity) could come from:

1. Polymer blend
2. Foam like metallic filler
3. Surfactant (?)
4. Further decrease of the filler size