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En Sciences Pour l'Ingénieur

Caractérisation thermophysique de nanocomposites, effets de la taille et de la forme des particules

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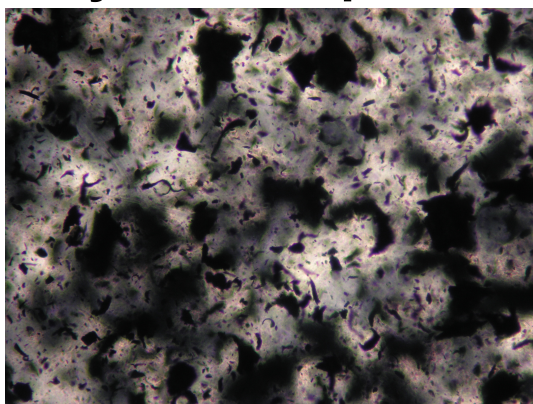


Plan



1. Quels matériaux ?
2. Quelles propriétés ?
3. Comment ?
4. Effets de la taille et de la forme des particules
5. Synthèse
6. Travaux actuels
7. Conclusions

Polymer composites

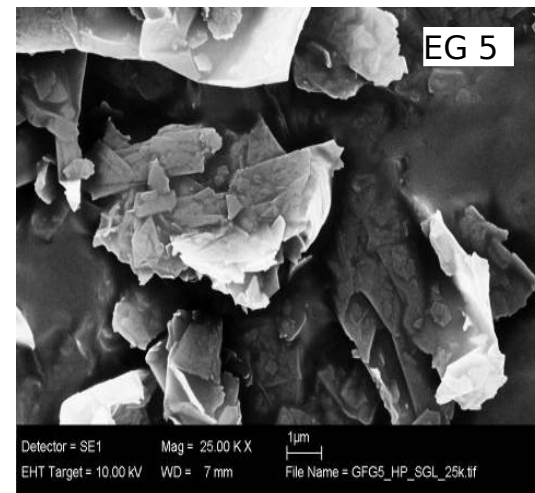
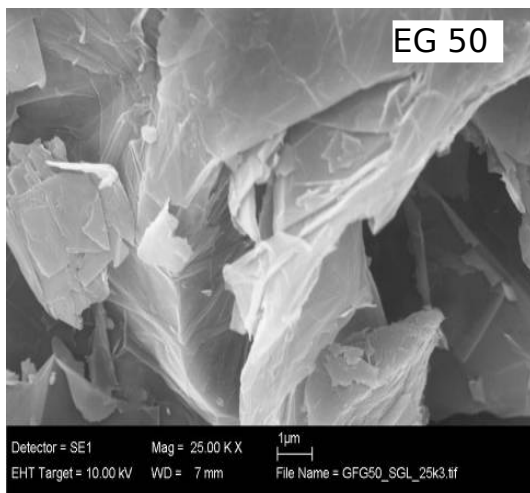


Poly Ethylene

- HDPE : $k = 0.39 \text{ Wm}^{-1}\text{K}^{-1}$
- LDPE : $k = 0.34 \text{ Wm}^{-1}\text{K}^{-1}$

Expanded Graphite

- Flaky shape, lateral size:
5, 50, 200 and 500 μm
- Thickness $\approx 50 \text{ nm}$
- $k = 300 \text{ Wm}^{-1}\text{K}^{-1}$ (In-plane)

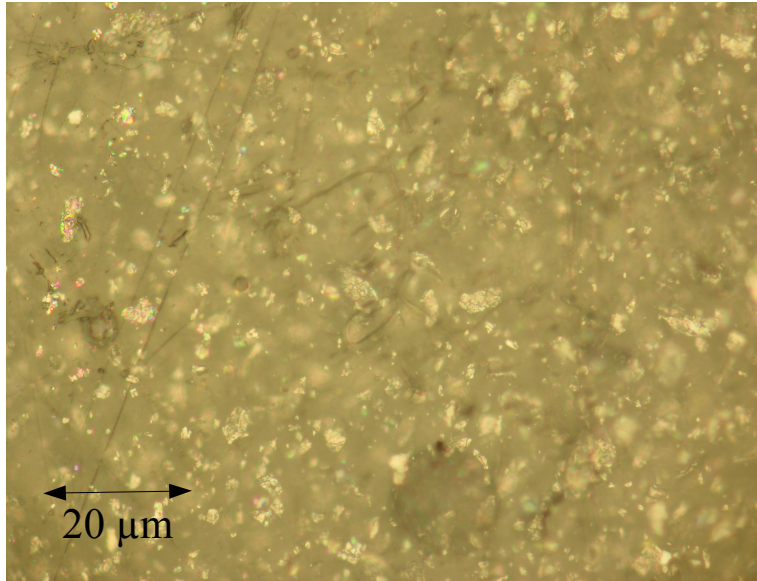


SEM micrographs of expanded graphite particles

<i>Lateral size:</i>	<i>Aspect ratio:</i>	<i>Thickness:</i>
EG500: $\leq 500 \mu\text{m}$	$\rho = 10000$	$\approx 50 \text{ nm}$
EG200: $\leq 200 \mu\text{m}$	$\rho = 4000$	$\approx 50 \text{ nm}$
EG50: $\leq 50 \mu\text{m}$	$\rho = 1000$	$\approx 50 \text{ nm}$
EG5: $5 \mu\text{m}$	$\rho = 100$	$\approx 50 \text{ nm}$

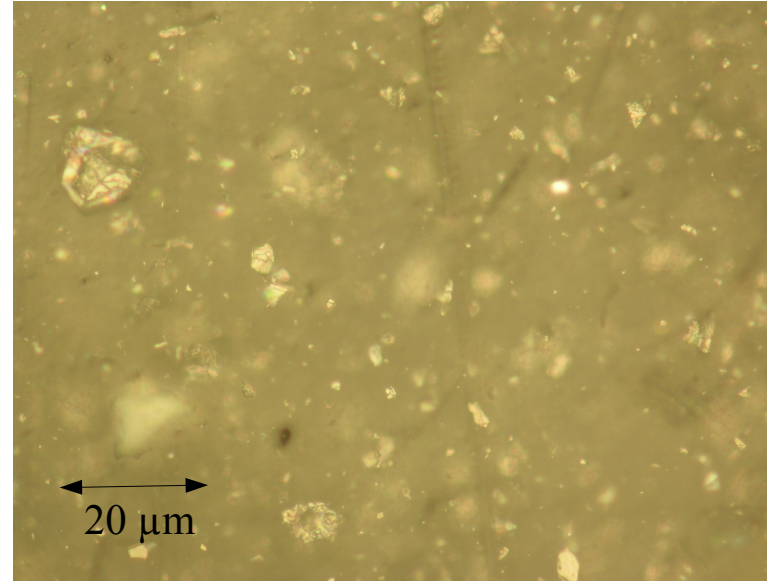
Graphite fraction : 0 to 40 % in weigh, 0 to 23% in volume

Samples description



EG5

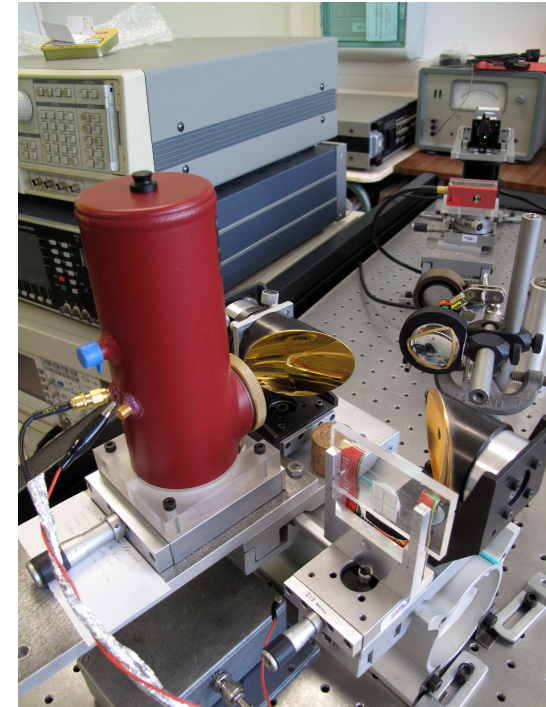
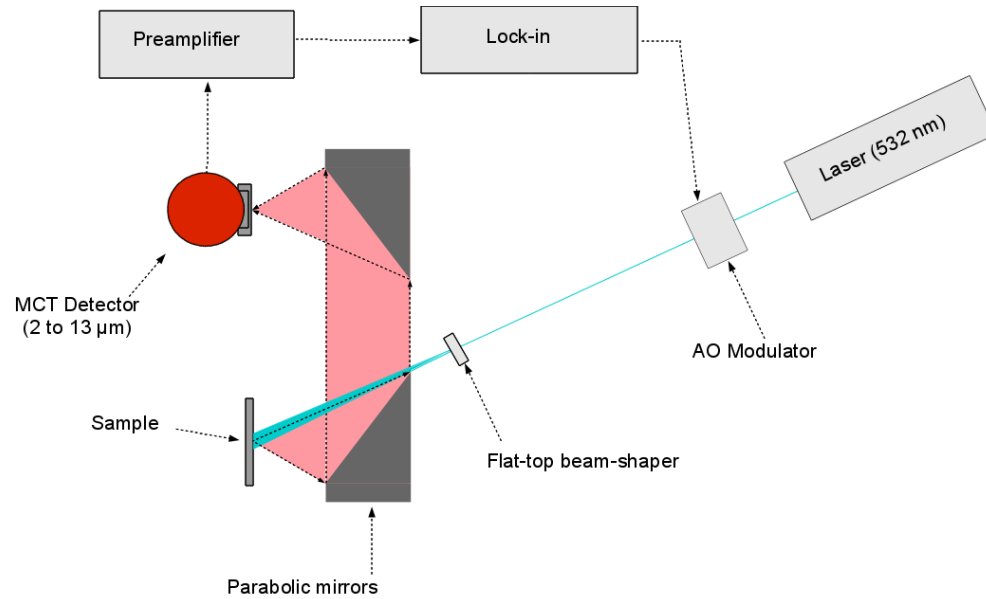
Aspect ratio ≈ 100



EG50

Theoretical aspect ratio ≈ 1000

Real aspect ratio ≈ 300



Frequency range: 0.1 Hz to 1 MHz

- 1 kHz to 1 MHz for thin films characterisation
- 0.1 Hz to 100 Hz for polymer composites

Experimental results

- amplitude A (mV) $\propto T_{AC}$
- phase ($^{\circ}$)

- increase of sample temperature $\approx 1^{\circ}\text{C}$
- experimental data depend on thermo-optical parameters of the sample

1D model - Surface thermal impedance:

$$Z_{FD} = \frac{(1-i)t}{2\sqrt{2\pi f} e} \frac{(t-1) + (t+1)M^{-2} - 2te^{-\beta d} M^{-1}}{(t^2-1)(1-M^{-2})}$$

Thermo-optical parameters:

$$M = e^{(1+i)d/\mu}$$

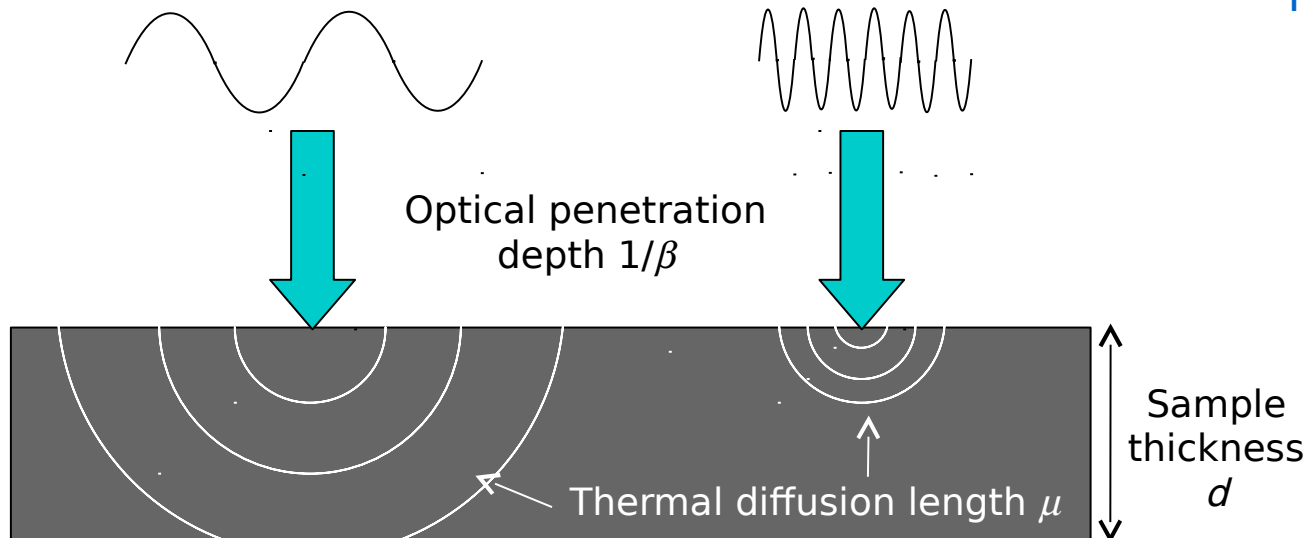
$$t = \frac{1-i}{2} \beta \mu$$

Low f :

Sample thermally thin: $\mu > d$

High f :

Sample thermally thick: $\mu < d$



Thermal diffusion length

$$\mu = \sqrt{\frac{a}{\pi f}}$$

Cut-off frequency
 $f_c (\mu = d) = 1-10$ Hz
thermal diffusivity



Sensitivity to thermo-optical parameters



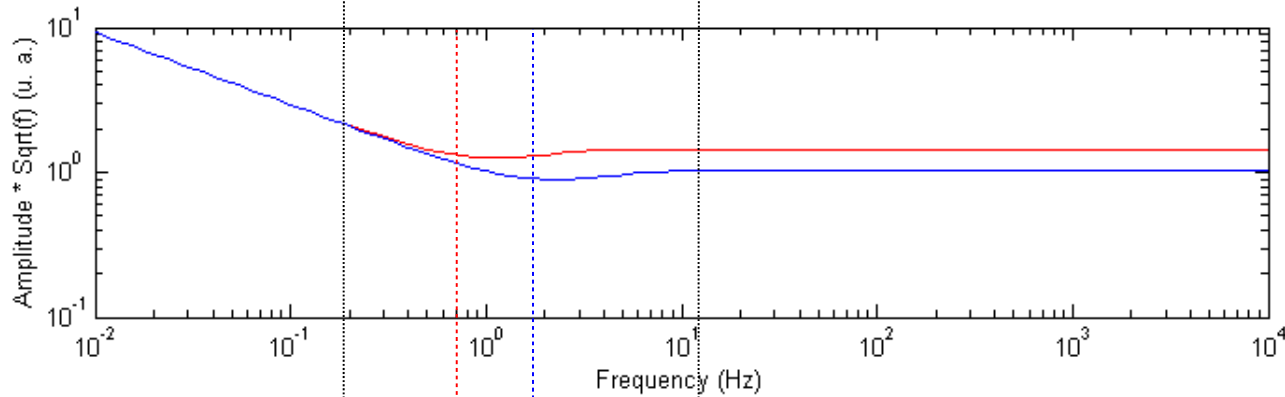
Thermally thin compartment:

Volumetric heat capacity $C = \rho c_p$

Thermal diffusivity
 $a = k/C$

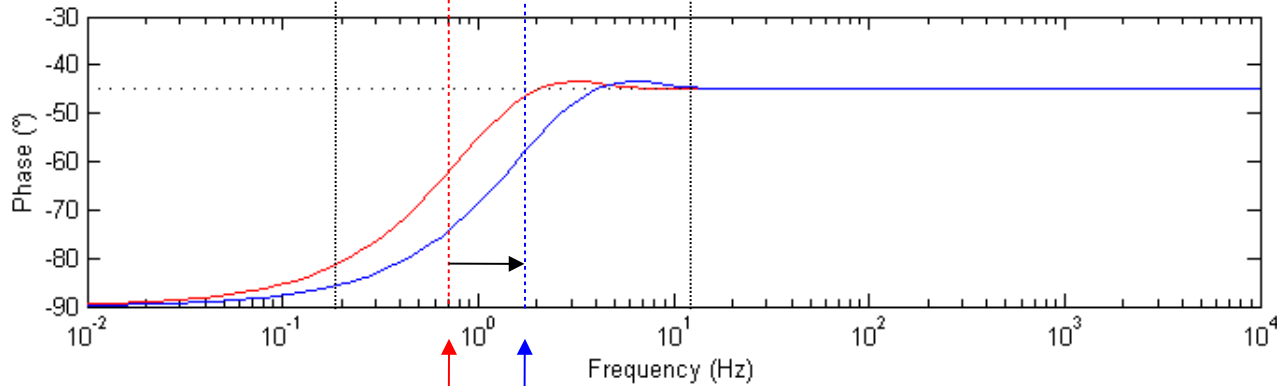
Thermally thick compartment:

Thermal effusivity: $e = (kC)^{1/2}$



$k = 0.4 \text{ Wm}^{-1}\text{K}^{-1}$
 $\beta = \infty$

$k = 0.8 \text{ Wm}^{-1}\text{K}^{-1}$
 $\beta = \infty$



$\mu = d$ $\mu = d$



Sensitivity to thermo-optical parameters



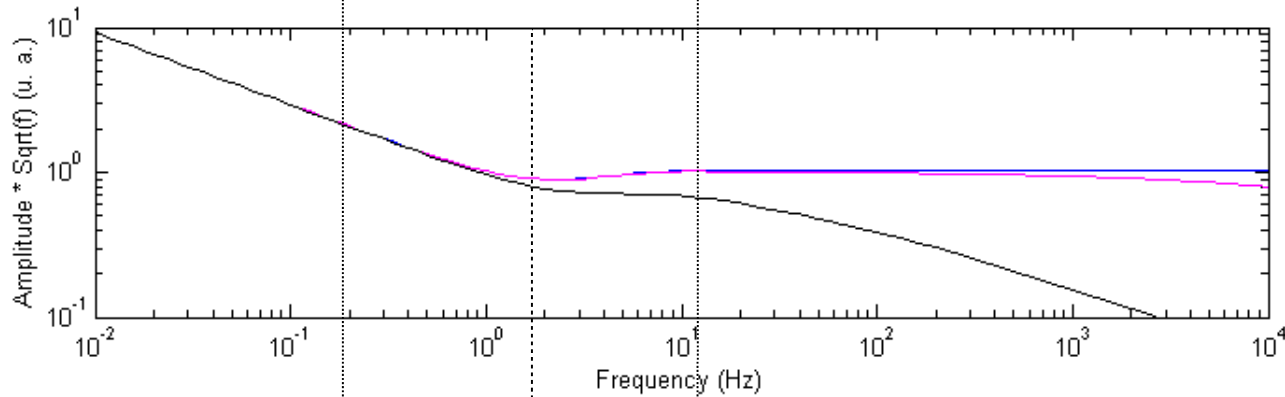
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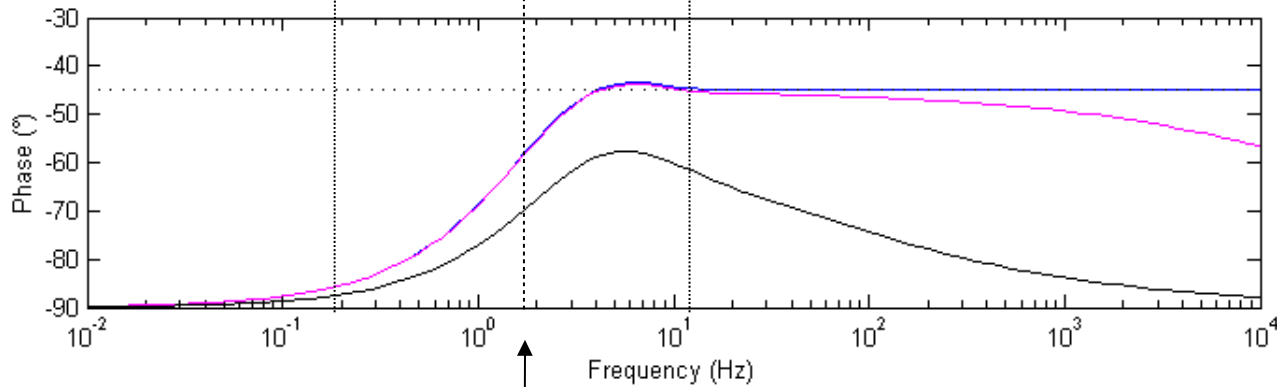
Thermally thick compartment:

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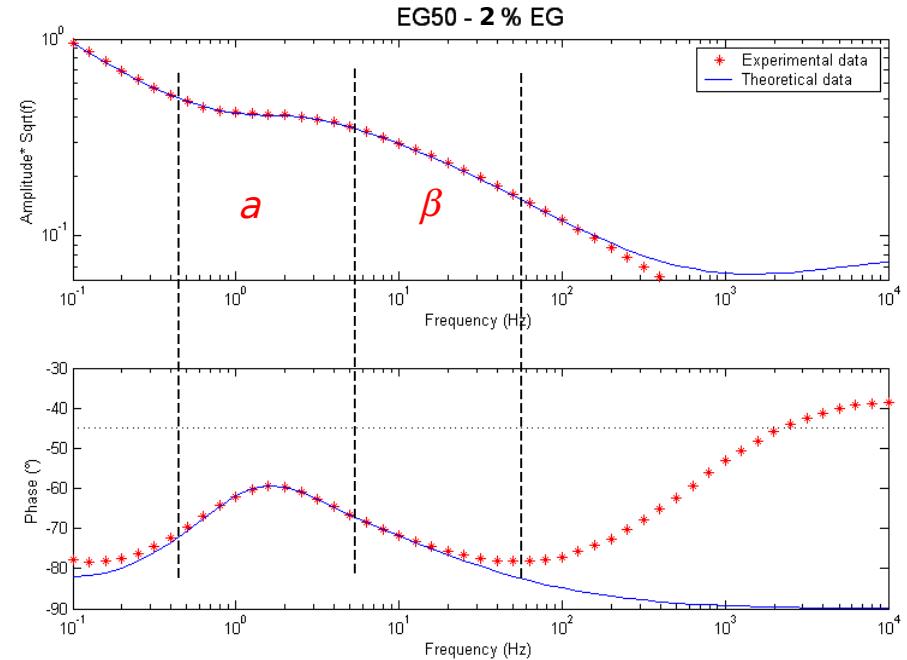
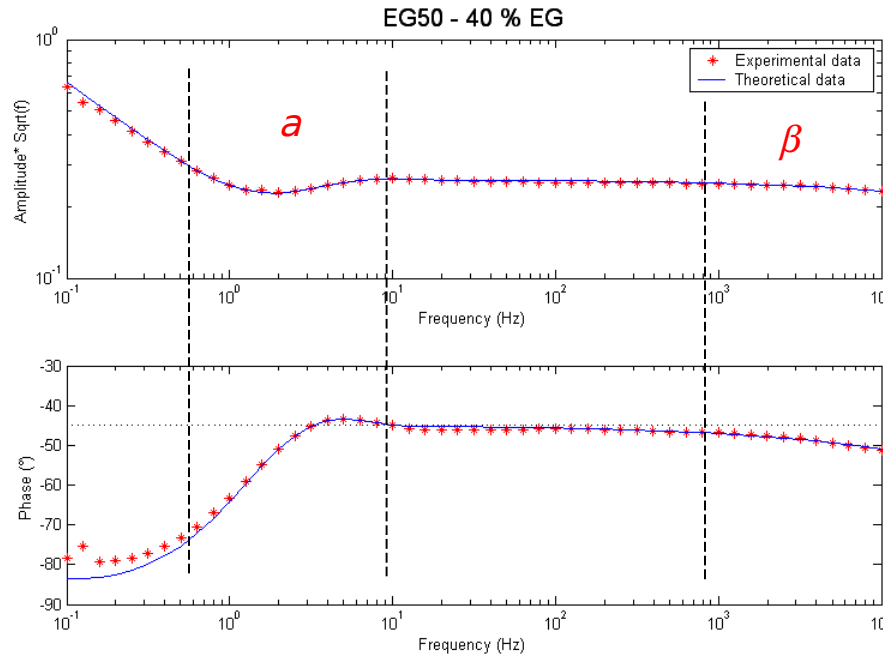
$k = 0.8 \text{ Wm}^{-1}\text{K}^{-1}$
 $\beta = \infty$

$k = 0.8 \text{ Wm}^{-1}\text{K}^{-1}$
 $\beta = 10^6 \text{ m}^{-1}$
EG 40 %



$k = 0.8 \text{ Wm}^{-1}\text{K}^{-1}$
 $\beta = 2 \cdot 10^4 \text{ m}^{-1}$
EG 2 %

$\mu = d$



Fit parameters: a and β

$$a = 12.3 \cdot 10^{-7} \text{ m}^2\text{s}^{-1}$$

$$\beta = 2.5 \cdot 10^6 \text{ m}^{-1}$$

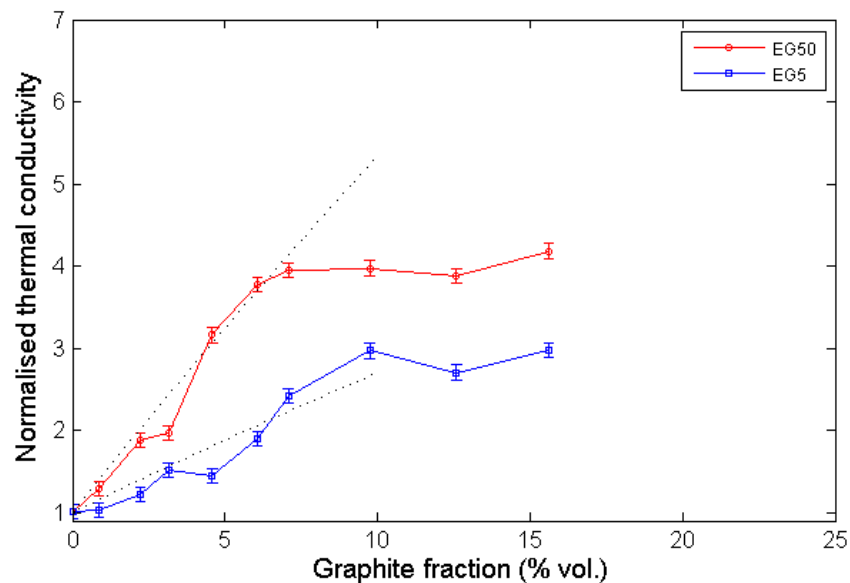
$$d = 0.33 \text{ mm}$$

$$a = 2.9 \cdot 10^{-7} \text{ m}^2\text{s}^{-1}$$

$$\beta = 0.02 \cdot 10^6 \text{ m}^{-1}$$

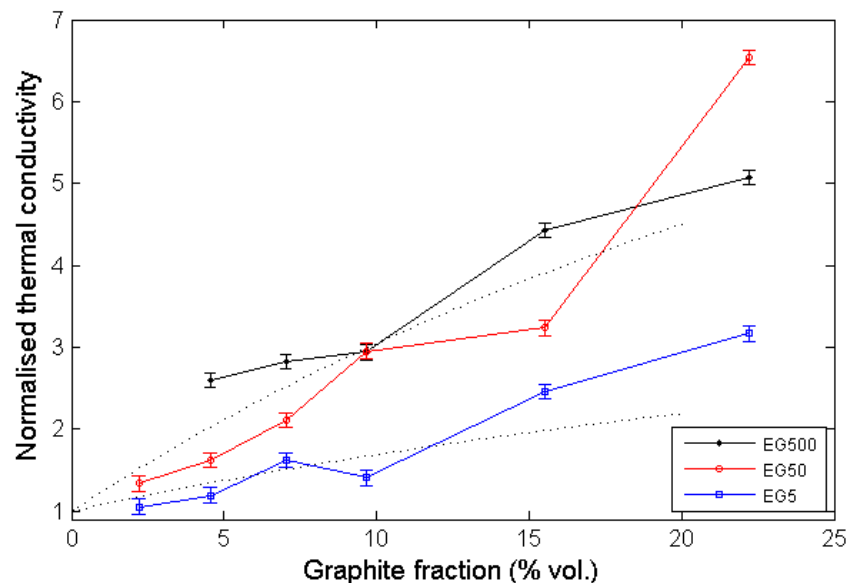
$$d = 0.32 \text{ mm}$$

HDPE

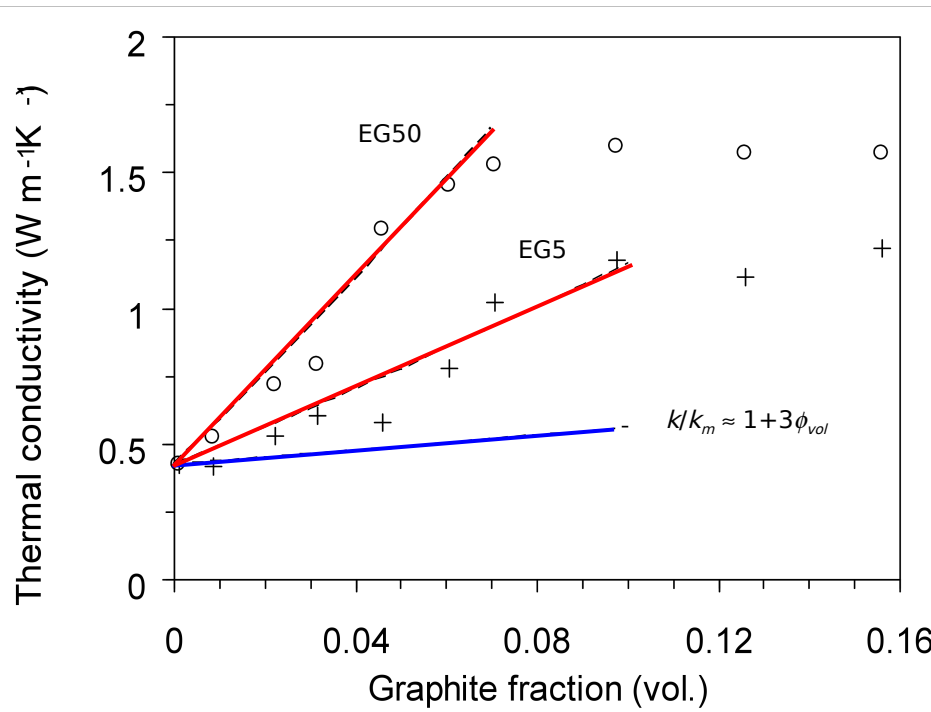


- Increase up to 4 times for 7 % of graphite
- Higher conductivity for higher particles
- Saturation for high concentration

LDPE



- Increase up to 4 times for ~15 % of graphite
- Higher conductivity for higher particles
- No saturation
- Problem for EG500:
Size of particle ~ thickness of sample



Fit with effective medium models:

— Nan et al. [J. Appl. Phys. 81, 6692 (1997)]:

$a_k = R_{th} k_m$ - Kapitza radius

a_1, a_3 - particle radii

$$k \text{ enhancement: } \frac{\Delta k_{eff}}{k_m} = \frac{8\phi a_1}{3\pi a_k}$$

From fit: $R_{th} = 2.1 \cdot 10^{-7} \text{ m}^2 \text{K/W}$

— Maxwell model, $R_{th} = 0$, spherical particles

Conclusions: - k enhancement > 3 for $\phi \leq 0.1$
 - R_{th} and particle size have opposite effects

- M. Chirtoc, N. Horny, I. Tavman, A. Turgut, I. Kökey and M. Osmatova, *Int. Journal of Thermal Sciences* **62**, 50-55 (2012).
- M. Chirtoc · N. Horny · J.-F. Henry · A. Turgut · I. Kökey · I. Tavman · M. Omastová, *Int J Thermophys* **33**, 2110–2117 (2012).

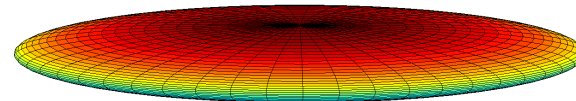
- Maxwell and Lord Rayleigh ==> Classical approach, spherical, non-interacting particles,
- *Hamilton-Crosser; Fricke*: shape effect,
- Hasselman and Johnson ==> Thermal boundary resistance effect,
- *Nan, Birringer, Clarke, Gleiter* [J. Appl. Phys. 81, 6692 (1997)] ==> Effective medium approximation formulation for the effective thermal conductivity of arbitrary particulate composites with interfacial thermal resistance based on multiscattering theory (no interaction between particles).

Expanded graphite :

- thickness = 50 nm

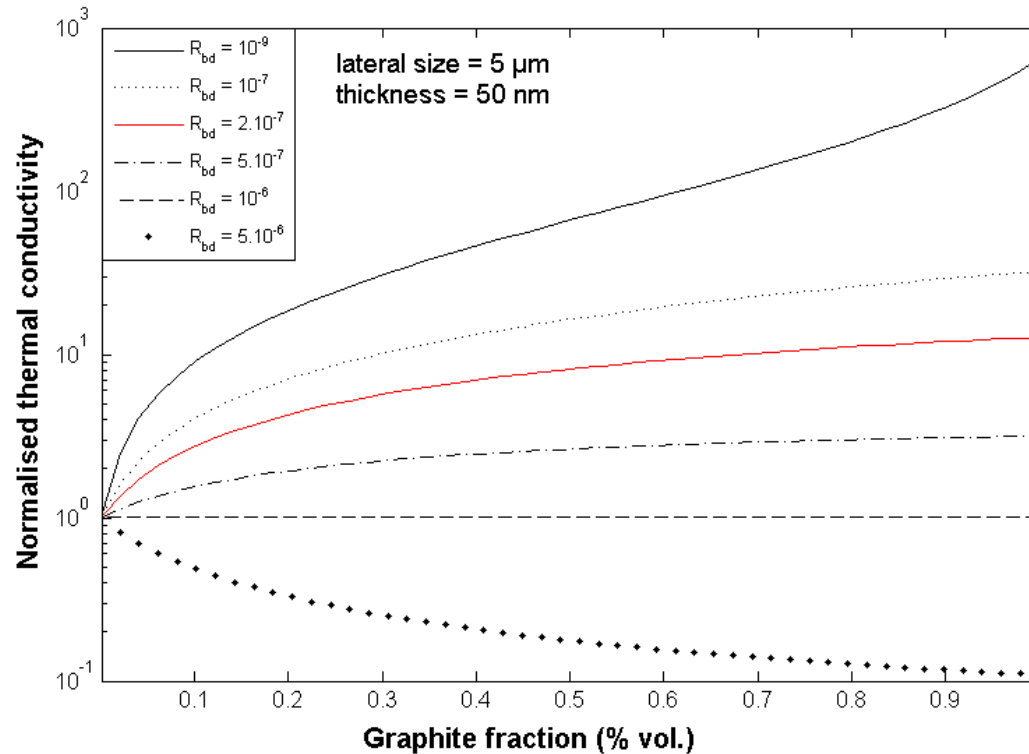
- size : 5, 50, 200 and 500 μm

Oblate form



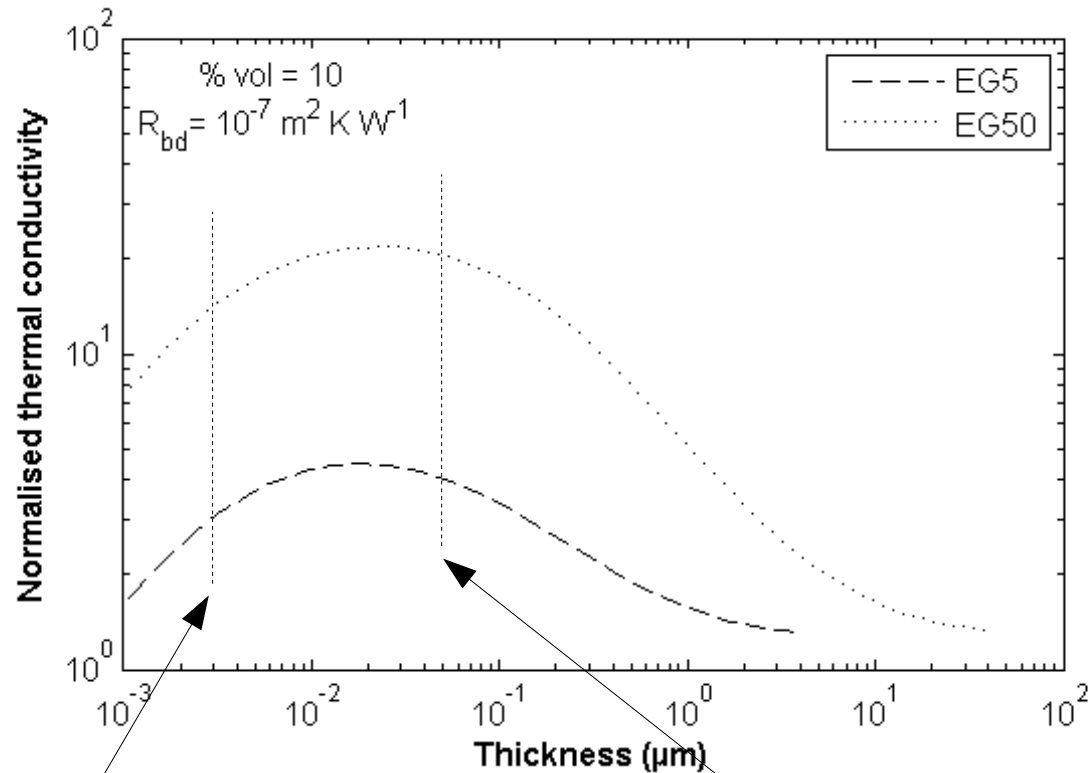
$$k_{eff} = \frac{k}{k_m} = 1 + \frac{\phi_{vol} (2\beta_{11} + \beta_{33})}{3 - \phi_{vol} (2\beta_{11} L_{11} + \beta_{33} L_{33})}$$

Interfacial thermal resistance



Necessity of good interface :
→ fonctionnalization

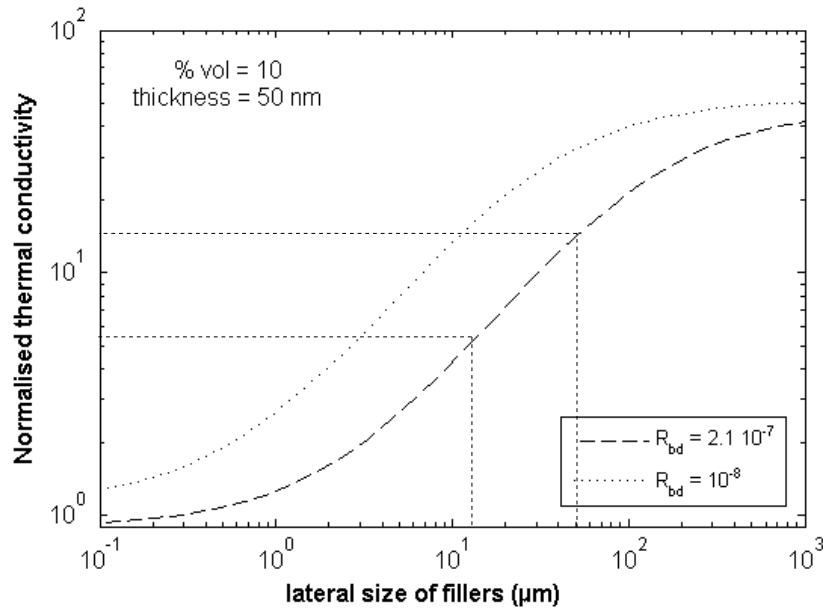
Thickness of filler



Graphene (10 layers = 3.35 nm)

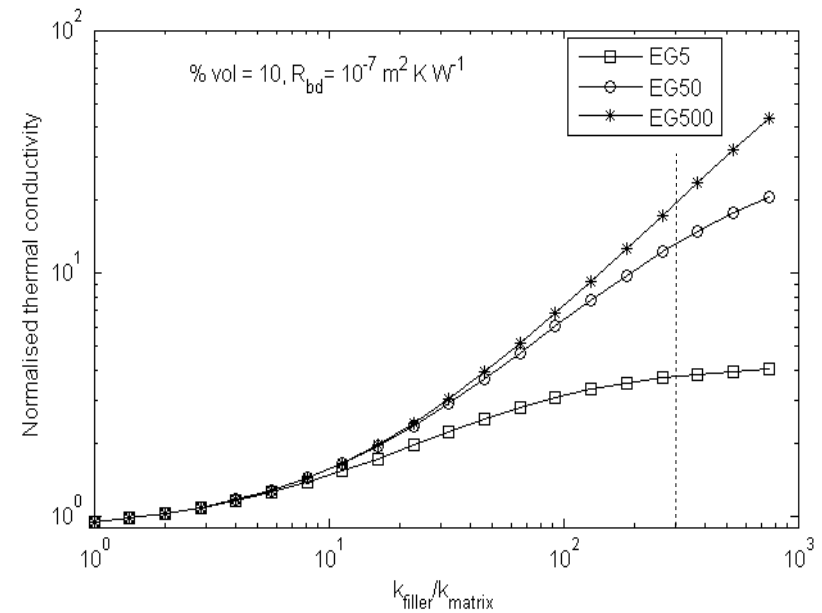
Expanded graphite (50 nm)

Effect of the lateral size of the filler

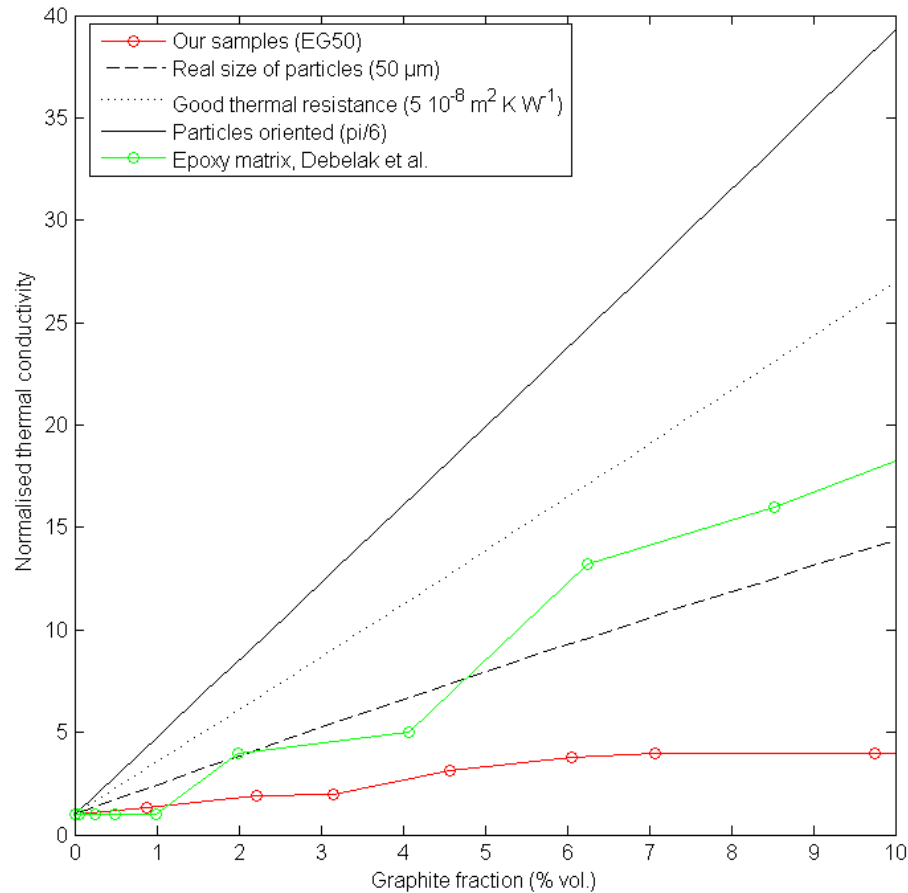


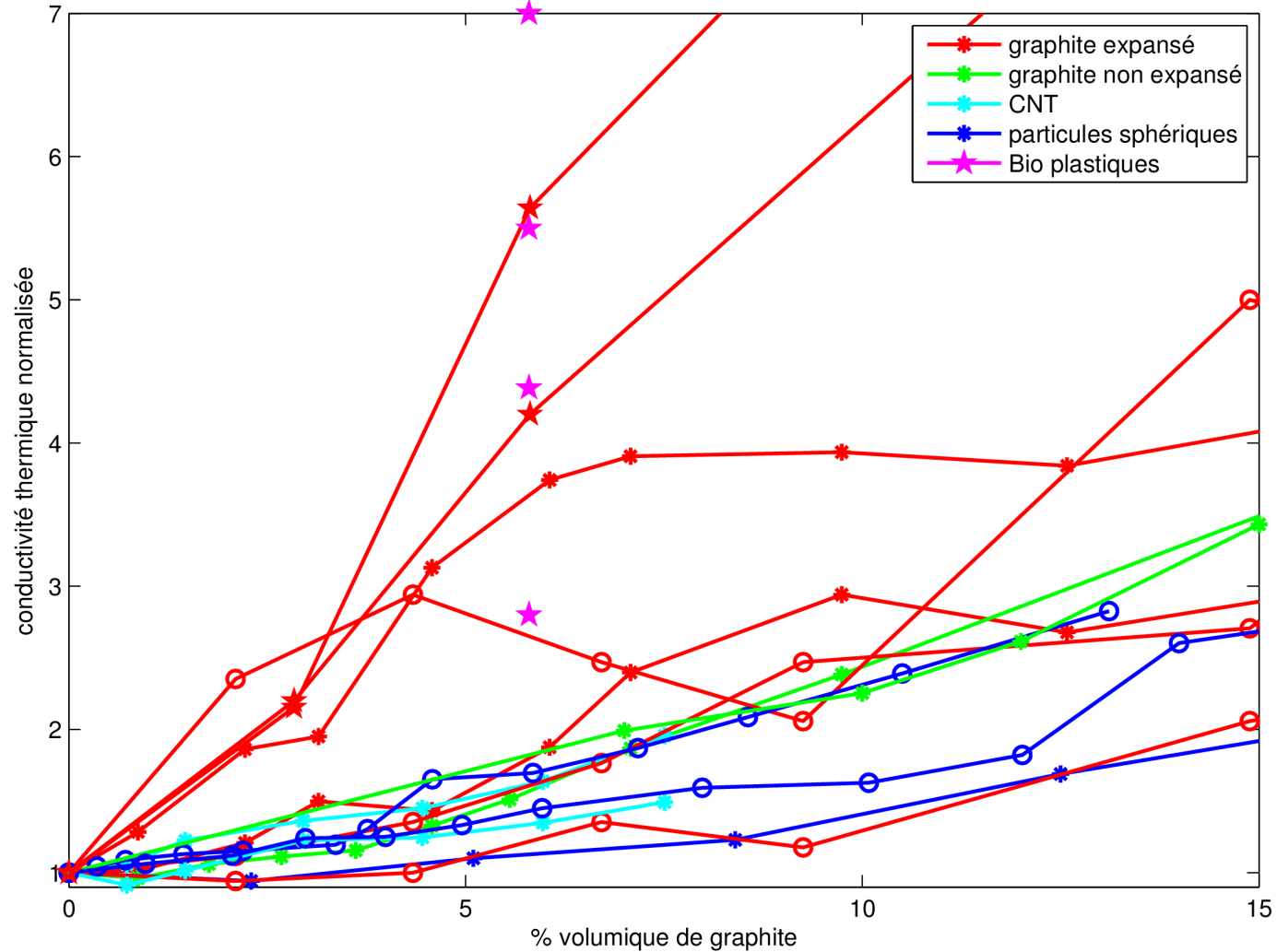
Factor 2 with real size of particles

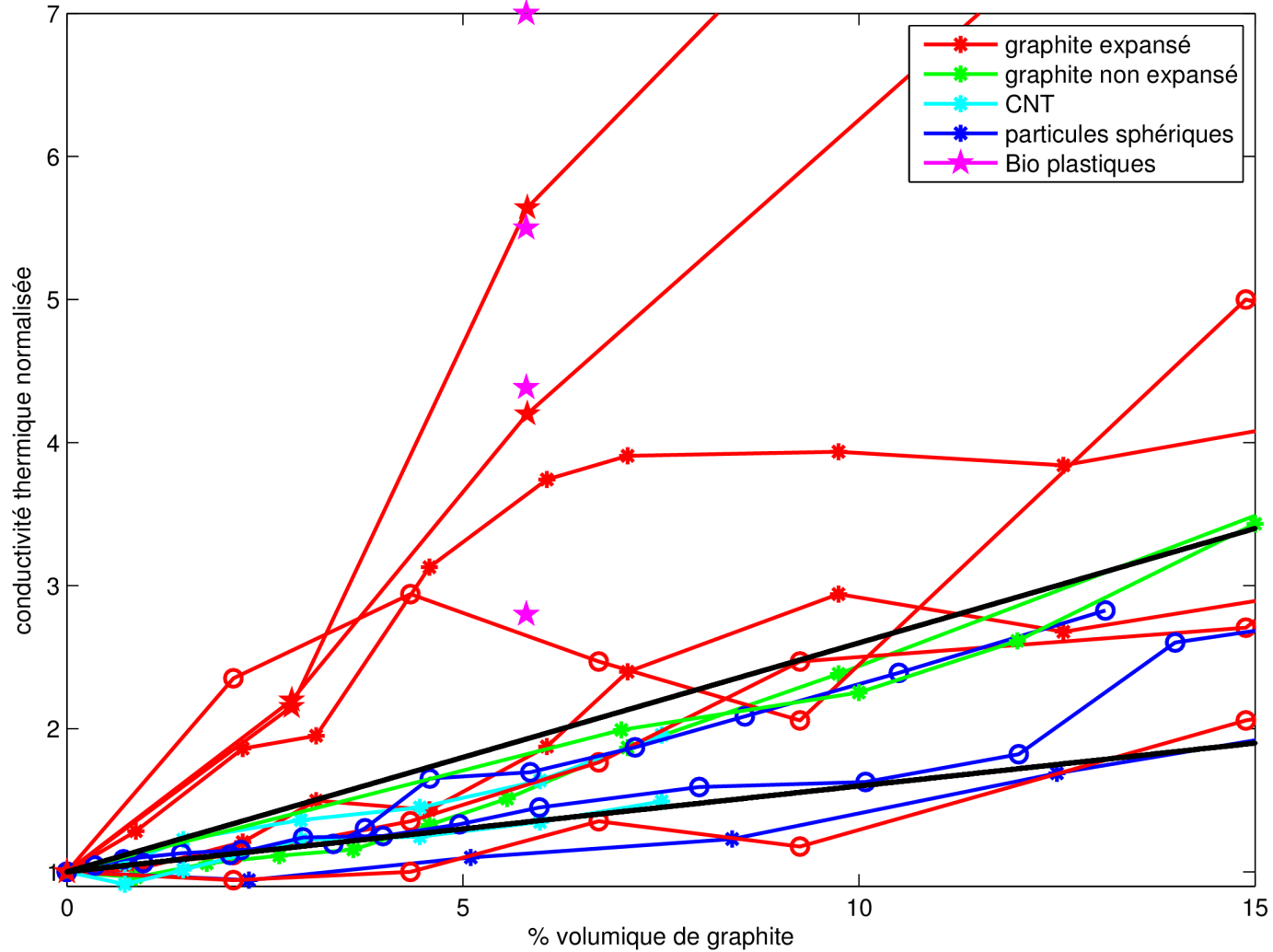
Ratio of thermal conductivity filler/matrix

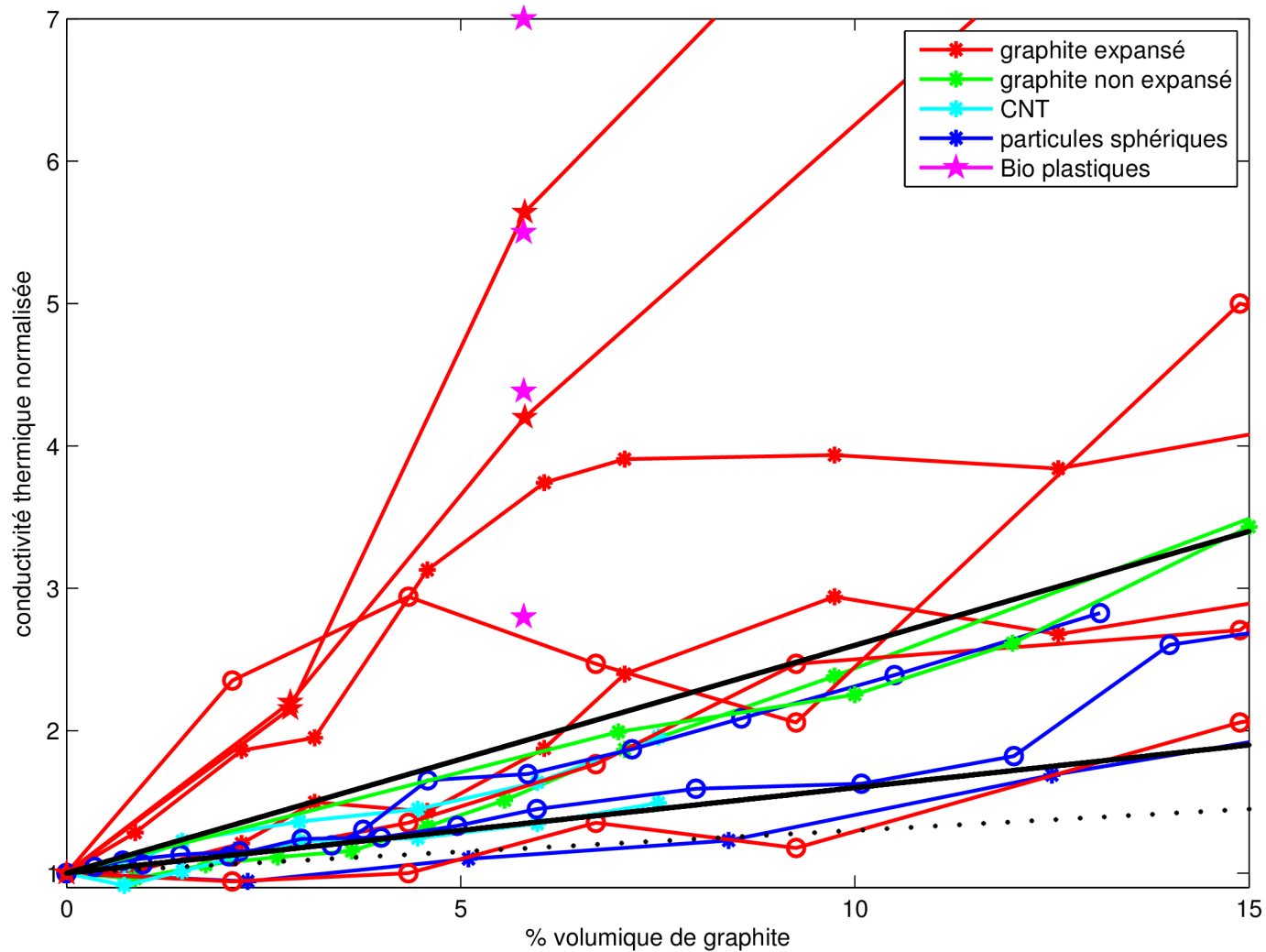


Saturation for small particles
==> No necessity to use diamond
with polymer matrix...









Influence des charges sur les propriétés mécaniques, de transfert thermique et sur la structure morphologique de nanocomposites à base de bioplastique

Y. Kanake

- Nanocomposites étudiés

Matrices

- Acide Polylactique (PLA)
PLA plastifié avec 15% de Triéthyl citrate
- Poly butylène succinate (PBS)

Charges : graphite expansé et montmorillonite

- Modes d'élaboration
 - Voie fondue
 - Voie solvant

EG 200

	PBS 10% EG200 Bivis	PBS 10% EG200 Mélangeur	PLA15 10 % EG 200 bivis	PLA15 10 % EG200 Mélangeur	particule pure EG 200
moyenne de taille (150-200 μm) %	30,98	34,95	23,90	27,97	38,87
inf moy (%)	58,15	44,17	67,73	62,94	41,84
sup moy (%)	10,87	20,87	8,37	9,09	19,29

EG 50

	PBS 10 % EG50 Bivis	PBS 10 % EG50 Mélangeur	PLA15 10 % EG50 Bivis	PLA15 10 % EG 50 Mélangeur	Particules pure EG50
moyenne de taille (45- 55 μ m) %	1,85	1,74	1,99	5,35	2,59
inf moy (%)	92,85	89,17	88,77	68,35	91,78
sup moy (%)	5,31	9,09	9,24	26,30	5,63

- Radiométrie photothermique infrarouge comme moyen de caractérisation des composites:
 - Avantages: grande précision, sans contact, échantillons minces, échantillons semi-transparents,
 - Inconvénients: échantillons minces, échantillons transparents,
- Nanocomposites : augmentation faible des propriétés thermiques,
- Le graphite expansé semble cependant être le meilleur candidat en raison de ses bonnes propriétés thermiques et de son grand facteur de forme.
- Paramètres clés : * résistance thermique d'interface,
 - * taille réelle des particules,
 - * Orientation des particules.
- Matrice bio-sourcée: bonnes interfaces sans fonctionnaliser



Merci pour votre attention