



Sugar Alcohol based Materials for Seasonal Storage Applications

FP7 project - SAM.SSA

Sugar Alcohol based Materials for Seasonal Storage Applications

Workshop and Onsite Demonstration– CiCenergigune

Miñano, Alava, Spain



Session 1, Sub Session: Heat Transfer Enhancement



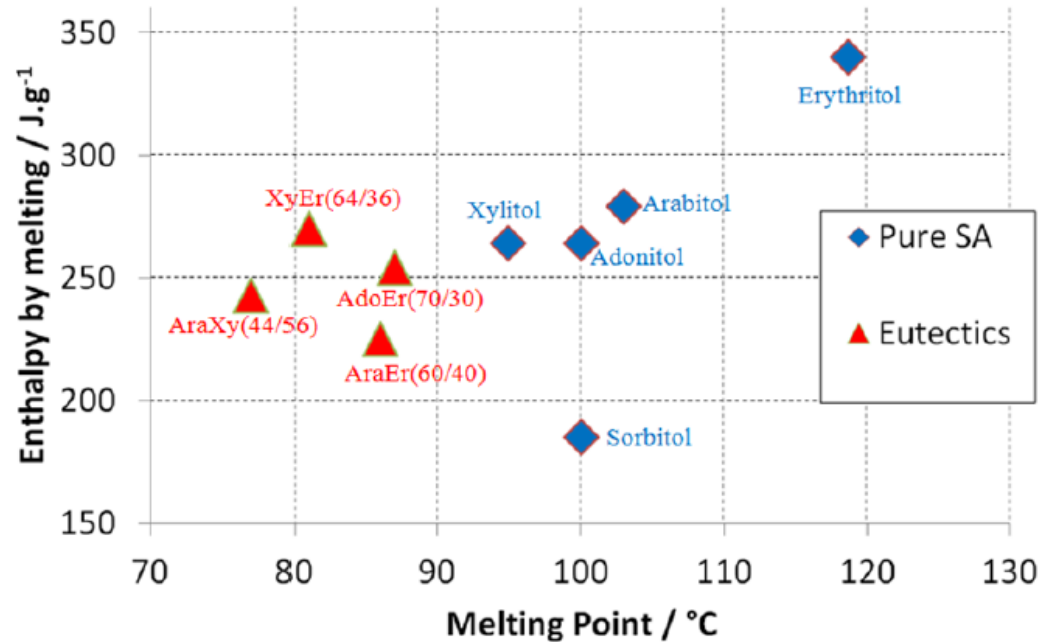
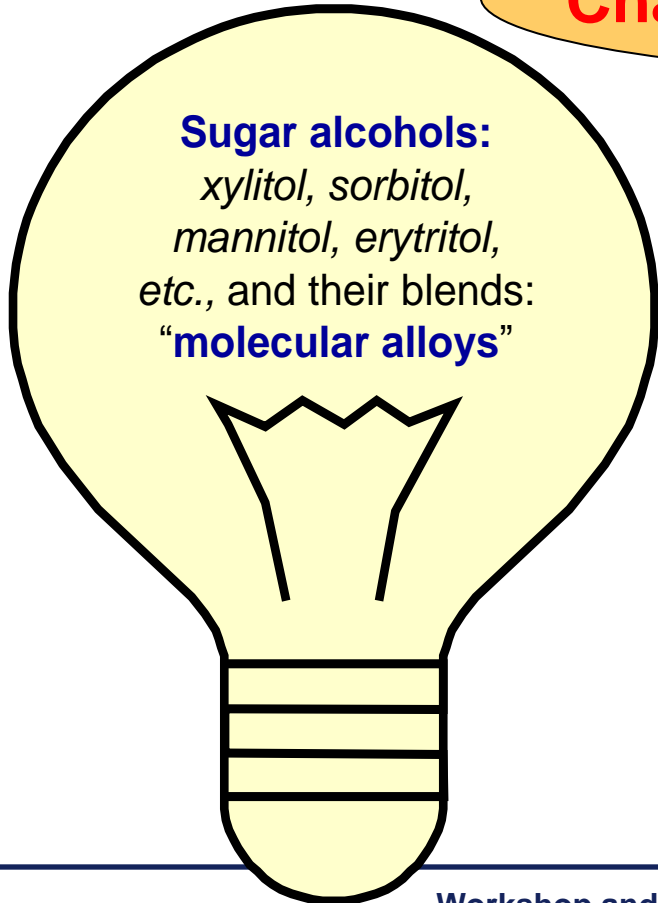
Institut Jean Lamour



Presented by: Alain CELZARD
Contributions by: Prasanta JANA
Vanessa FIERRO
Alain CELZARD

Phase-change materials are investigated for thermal energy storage from the 70's, but ...

Challenge = seasonal storage



Phase-change materials are investigated for thermal energy storage from the 70's, but ...

Challenge = seasonal storage

Sugar alcohols:
*xylitol, sorbitol,
mannitol, erytritol,
etc.*, and their blends:
“**molecular alloys**”



High energy density: compact storage systems



High undercooling : long-term storage



Possible crystallisation by thermal shock or other means: heat recovery at the desired moment



Poor thermal conductors

Thermal conductivity improvement

DEVELOPMENT OF HIGHLY POROUS CARBON MONOLITHS

- Open porosity higher than 80%
- Thermal conductivity within the range 3 – 10 W/m/K
- Cost less than 6 €/kg
- Wide pore size for easy and in-depth impregnation with SA

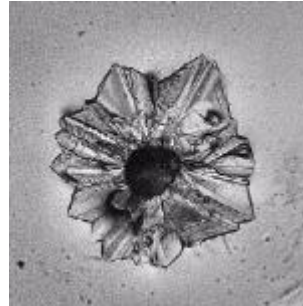
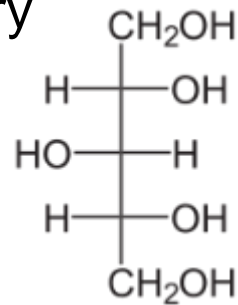
Average thermal conductivities wanted !

→ A very unusual request ...

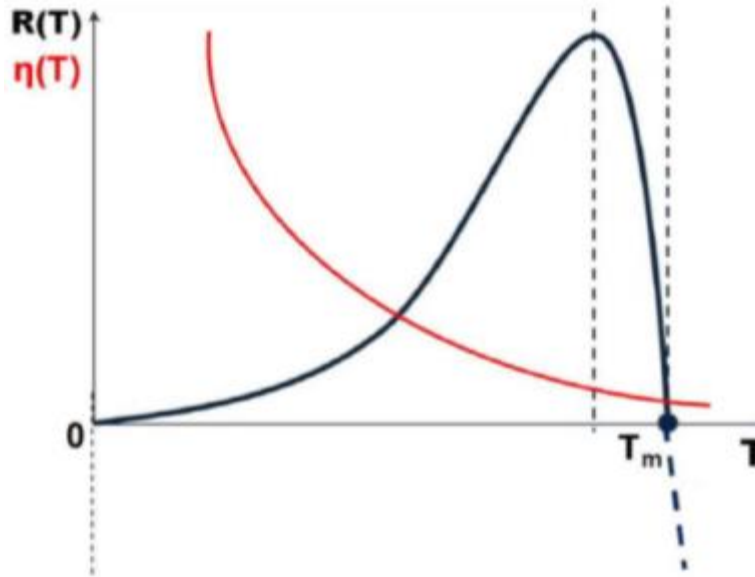
Why ?

Need of a medium conductivity related to the optimisation between:

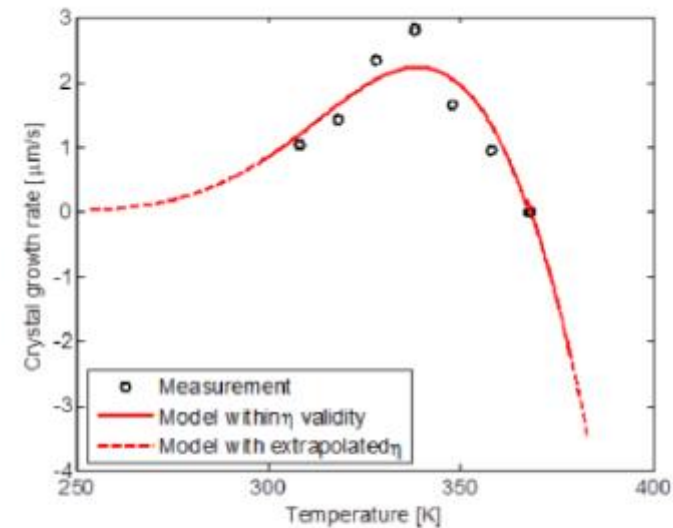
- Short time for heat delivery
- High power delivery



Crystallite
growth velocity
Viscosity



XYLITOL'S PROPERTIES



- Rozmanov Model¹

$$R(T) = C_1 e^{C_2/T} \sqrt{D(T)} [1 - C_3 e^{C_4/T}]$$

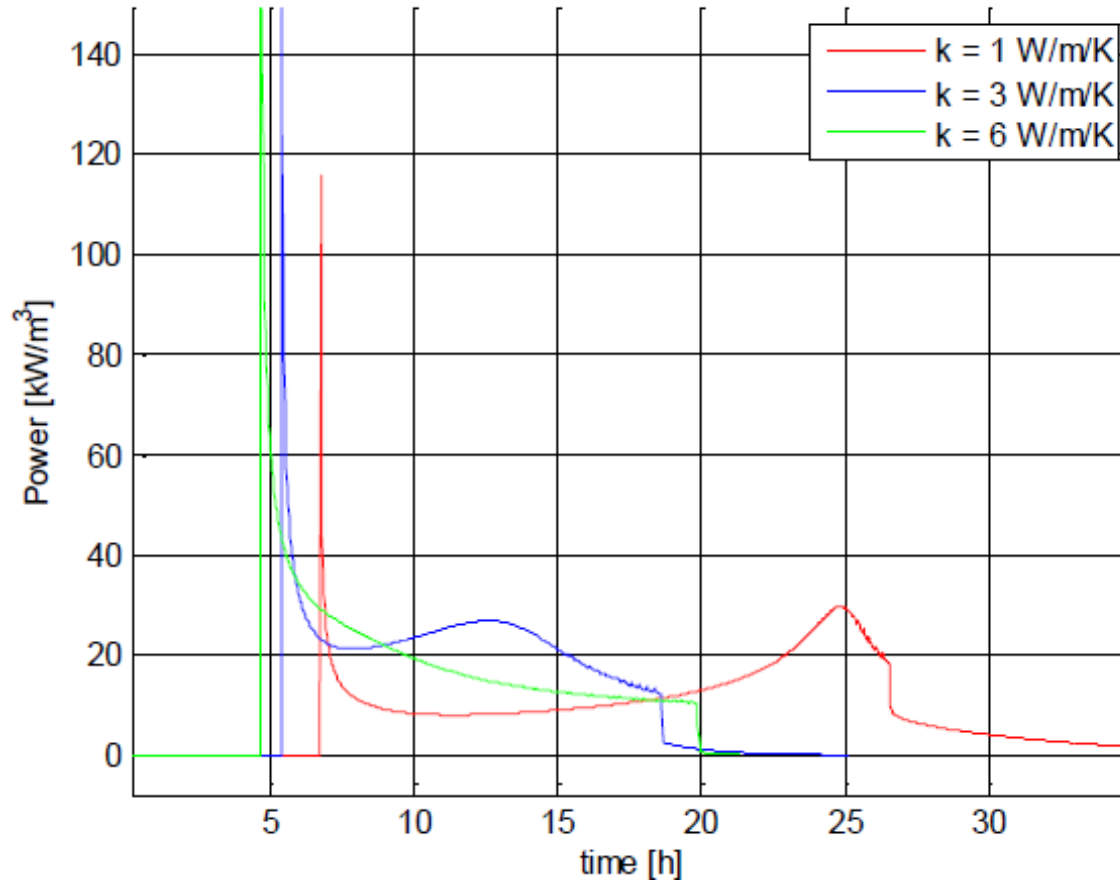
$$C_1 \equiv C_D C_A e^{\Delta S_{FA}/R}$$

$$C_2 \equiv -\Delta H_{FA} / R$$








$$C_3 \equiv e^{\Delta S_M/R}$$

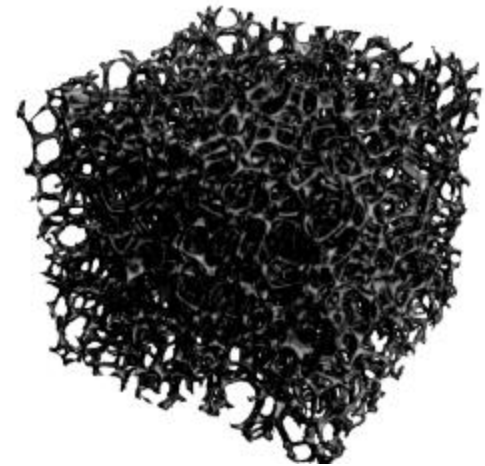
$$C_4 \equiv -\Delta H_M / R$$

Effect of the thermal conductivity of the porous host on delivered power:



Porous carbon matrices have many advantages :

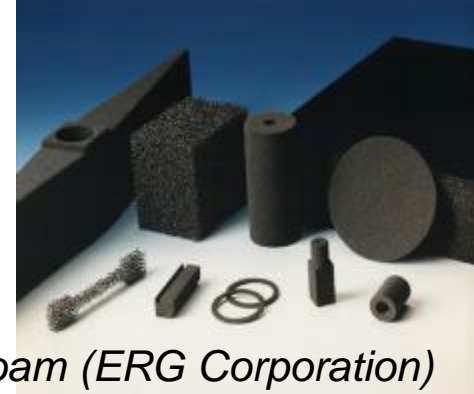
-  Cheaper than metal foams
-  Are much lighter than metal foams
-  Can have “green” precursors
-  Can be prepared with any porosity
-  Can have a broad range of physical properties
-  Can be functionalised and/or nanostructured
-  Require high-temperature treatment under inert atmosphere



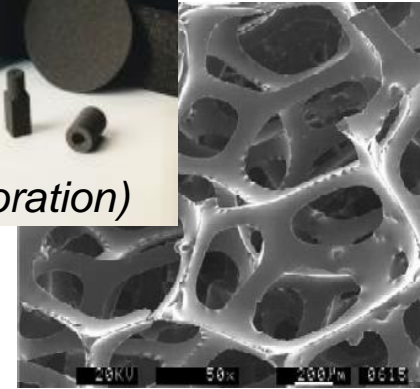
Most common carbon foams

Reticulated vitreous carbon (RVC) foams

(Derived from thermoset polymers)



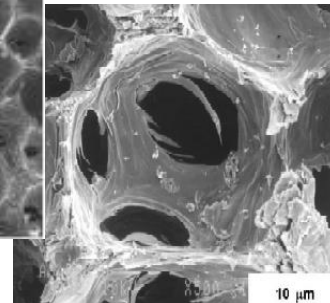
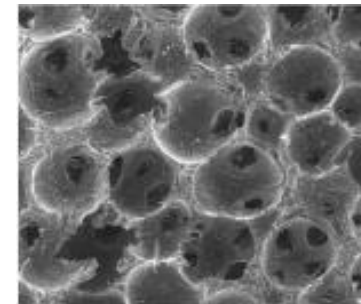
Duocel® RVC foam (ERG Corporation)



- ☹ Extremely low thermal conductivity
- ☹ Made from non-renewable resources
- ☹ Expensive

Cellular graphitic carbon (CGC) foams

(Derived from pitch or coal extracts)

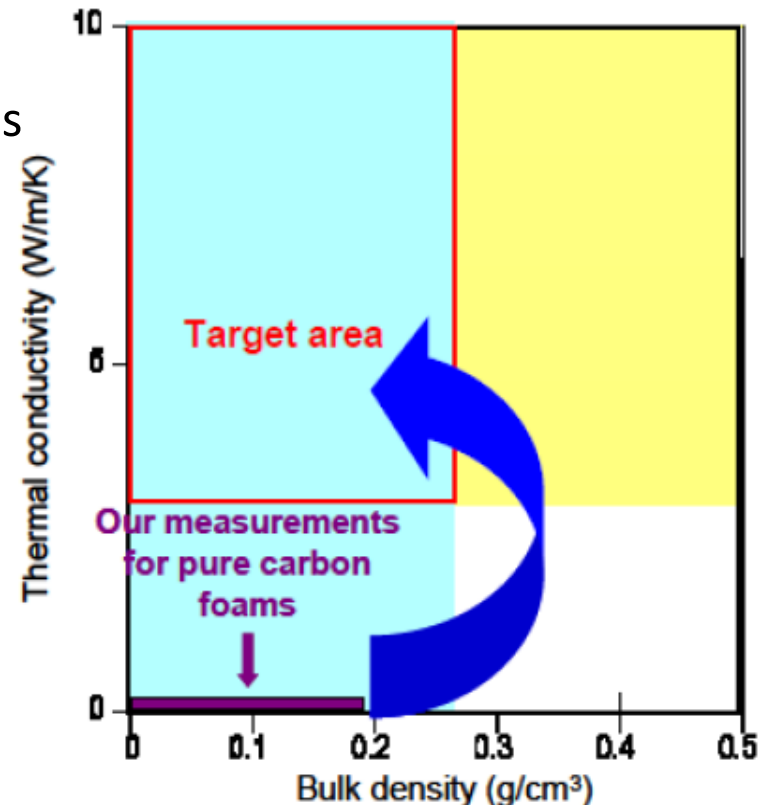
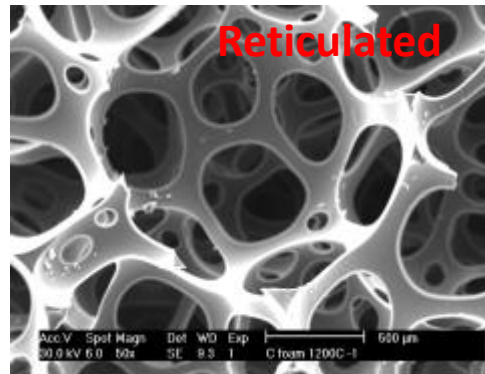
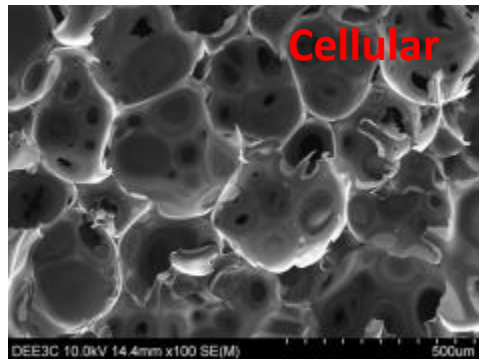


- ☹ Very high thermal conductivity
 - ☹ Made from non-renewable resources
 - ☹ Prohibitive cost
- POCOfoam® graphite foam (ORNL)*

What kind of porous matrices ?

CVC and RVC foams

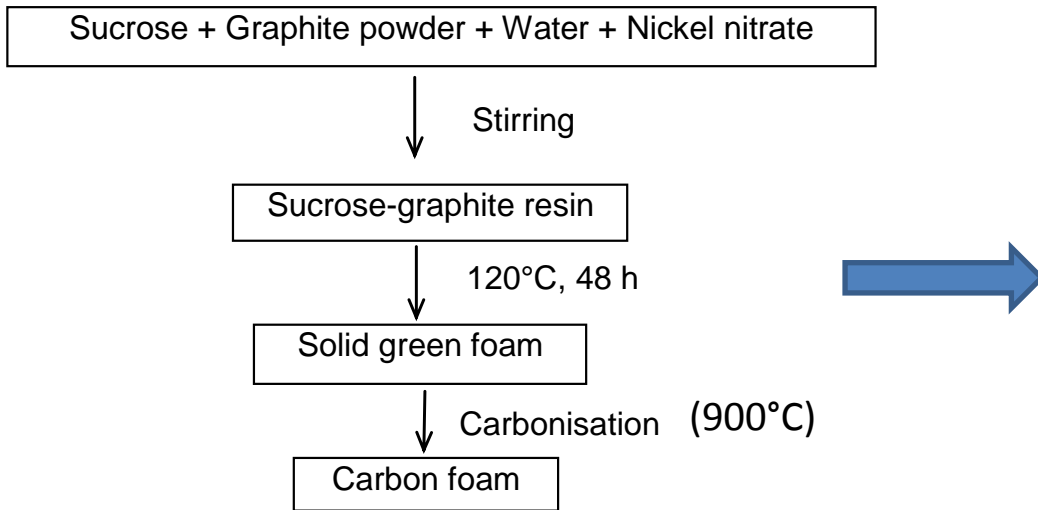
- 😊 Made from cheap (possibly renewable) resources
- 😊 Low cost
- 😞 Low thermal conductivity



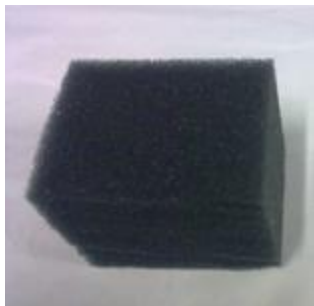
Strategy :

Preparing composite carbon foams containing a filler with a high thermal conductivity

Autogenous foaming of sucrose solutions



Template method based on PU foams



PU foam



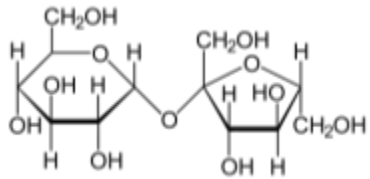
Polymeric foam cured at 150°C



Carbon foam pyrolysed at 1000°C

Thermally induced decomposition and resultant foaming

Decomposition of a nitrate whereas a sucrose solution is polymerized in acidic conditions, leading to a foamed carbon precursor obtained at 120°C.



Sucrose + Water + HNO₃ and/or metal nitrates + graphite

120°C in Teflon beaker, 48 h

Viscous resin, starting foaming

120°C, 48 h

Solid foam

900°C, 2 h

Composite carbon foam



Experimental design

Reasons:

- Need to maximise both porosity and thermal conductivity, whose changes are antagonistic
- Save time, cost and materials

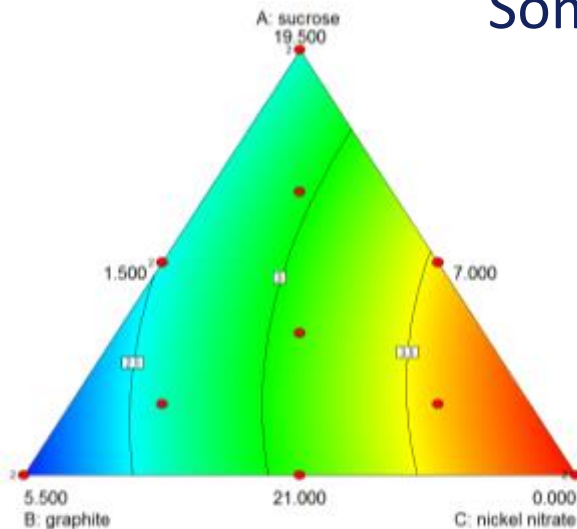
Principles :

- Choosing the most relevant parameters to be changed for preparing as few samples as possible
- From the experimental results and the corresponding modelling, being able to predict the properties of any other formulation

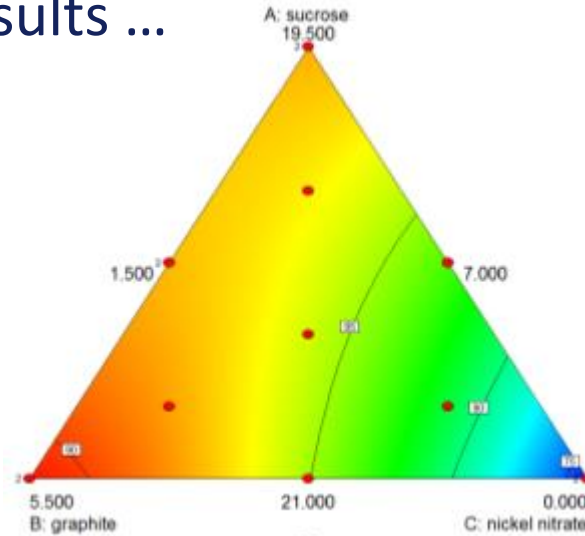
Implementation:

- Choice of a graphite and a catalyst leading to the best results: a natural graphite having the lowest available particle size on one hand, and nickel nitrate on the other hand
- Use of Design-Expert 8.0.7.1. software for optimising the amounts of all ingredients, using porosity and thermal conductivity as responses.

Some results ...



R1
Thermal conductivity



R2
Porosity

From the model:

$$R1 = -0.6536A - 4.61697B - 9.45242C + 0.34024AB + 0.56745AC + 0.16269BC$$

$$R2 = 8.13738A + 45.31808B - 125.15084C - 2.81767AB + 4.26041AC + 4.86517BC$$

If $A = 20$, $B = 6$, $C = 1$:

$R1 = 2.9277$ (model) versus 3.1 W/m/K (experiment)

$R2 = 85.784$ (model) versus 85.8% (experiment)



Carbon foams from sucrose

Same procedure applied to much bigger samples :

Slightly different ...

$$R1 = 0.016522 A + 0.049148 B + 1.17358 C + 0.00151433 AB - 0.012735 AC - 0.022849 BC$$

$$R2 = 0.92073 A + 1.40489 B - 3.7681 C - 0.016203 AB + 0.052576 AC + 0.08671 BC$$

... but more favourable results : less graphite and less nickel are required for getting the same results !

If $A = 80$, $B = 20$, $C = 2$:

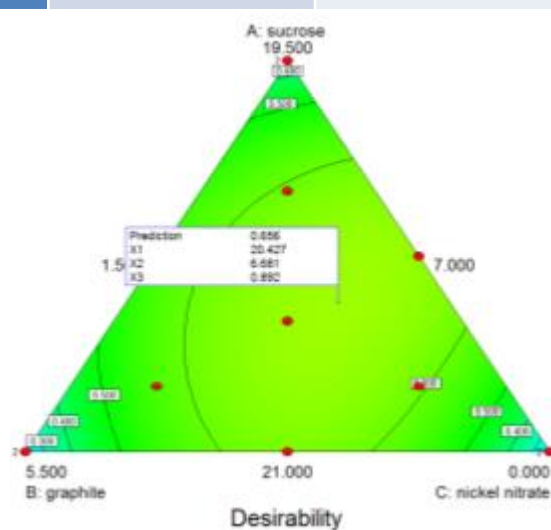
$R1 = 2.9144$ (model) versus 3.1 W/m/K (experiment)

$R2 = 85.664$ (model) versus 85.8% (experiment)

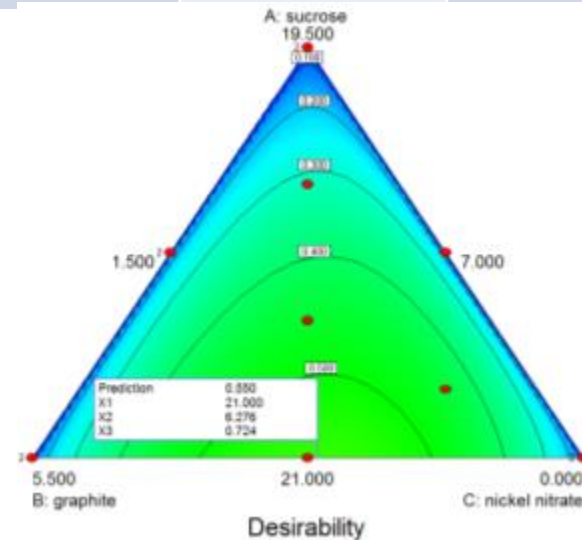
One step further : more constraints for maximising both conductivity and porosity

	Sucrose	Graphite	Ni nitrate	Conductivity	Porosity
Case #	A	B	C	R1	R2
1	Minimum	Minimum	Minimum	Maximum	Maximum
2	Maximum	Maximum	Maximum	Maximum	Maximum
3	In the range	In the range	In the range	Maximum	Maximum
4	In the range	Minimum	Minimum	Maximum	Maximum

Examples :

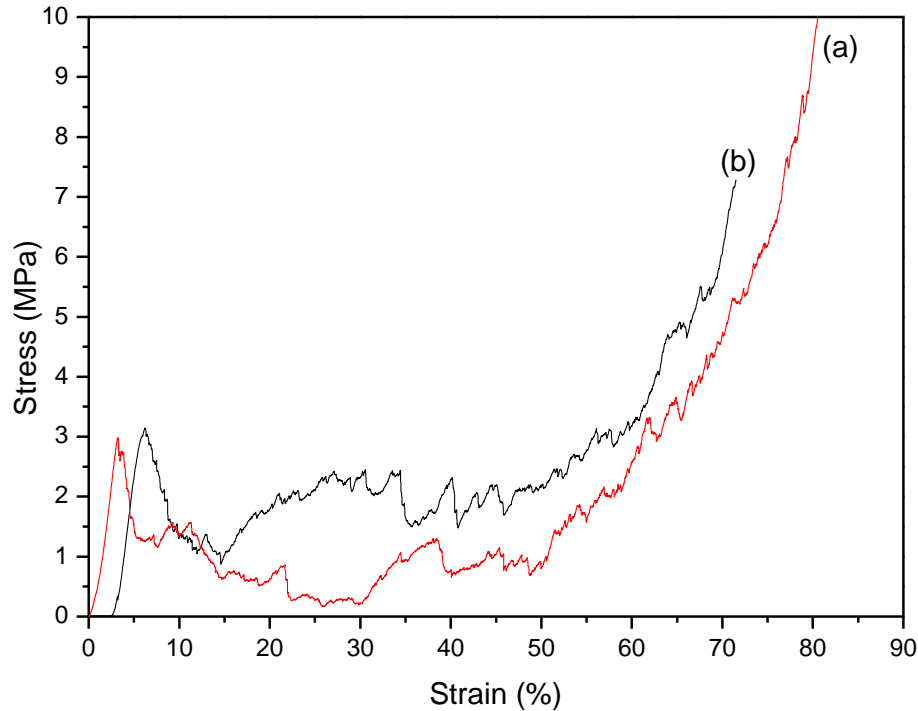


Cost is not important



Graphite and Ni need to be minimised

Mechanical properties of optimised foams :



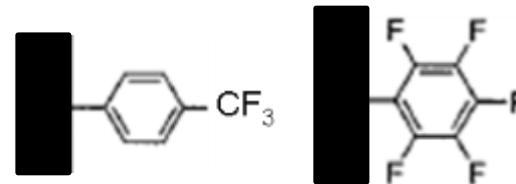
Composite foam	Compressive strength (MPa)	Elastic modulus (MPa)
Small sample	3.0	107.5
Big sample	3.1	107.9

Hydrophobisation of optimised foams :

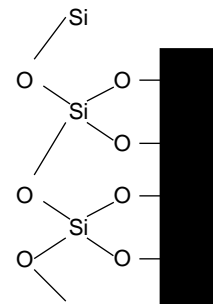
Different techniques used :

- *Direct chemical fluorination* → Foams of overall composition $CF_{0.04} - CF_{0.08}$

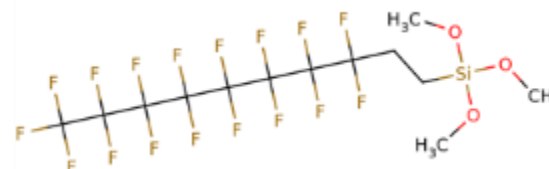
- *Electrochemical grafting of fluorinated groups*



- *Surface coating with silica by sol-gel method*

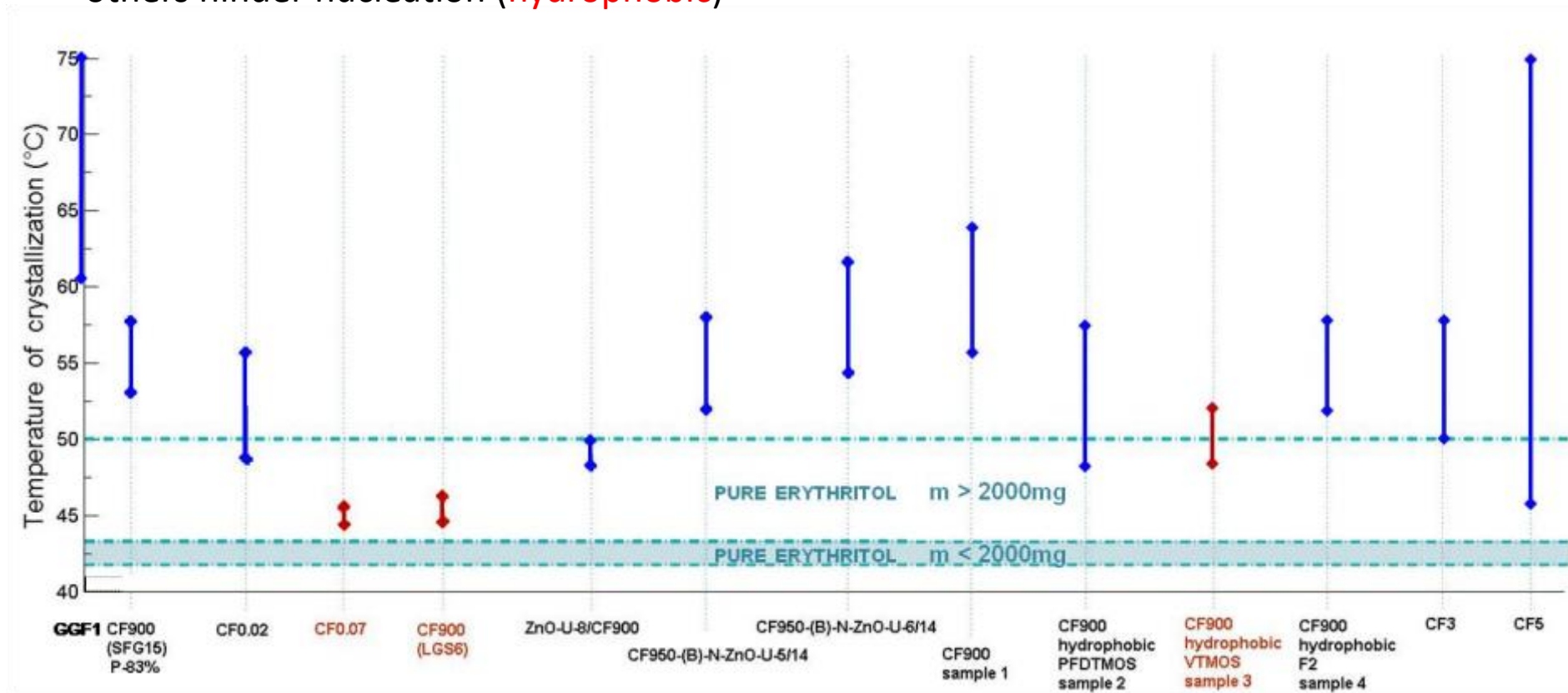


- *Chemical grafting of perfluoroalkyl chains*



Effect of hydrophobisation on subcooling :

Some foams promote nucleation (no hydrophobic effect),
others hinder nucleation (hydrophobic)



Conclusion :

Composite, graphitised, carbon foams made from sucrose and natural graphite are :

- cheap (~ 3 €/kg)
- highly porous (86%)
- easy to impregnate with sugar alcohols
- moderately conducting before ($\lambda \sim 3$ W/m/K) and after ($\lambda \sim 3.5$ W/m/K) impregnation with sugar alcohols
- resistant (3 MPa) and stiff (100 MPa) before impregnation
- even more after impregnation: 10 et 200 MPa, respectively
- promote or delay heterogeneous nucleation, depending on surface functionalisation





MASA Thermal Conductivity Improvement

WP 4 (MASA Thermal Conductivity Improvement)



Presented by: **Dr. Mani Karthik**
Work Package Leader: **Dr. Alain Celzard**
Participants: **Dr. Bruno D'Aguzzo** and
Dr. Abdessamad Faik



Graphite Composite Foam by Template Method

Tasks:

- ✓ Synthesis of graphite composite foam
- ✓ Structural characterization
- ✓ Impregnation of the matrix with PCMs (Erythritol)
- ✓ Thermophysical characterization
- ✓ Chemical stability of the PCMs with carbon matrix

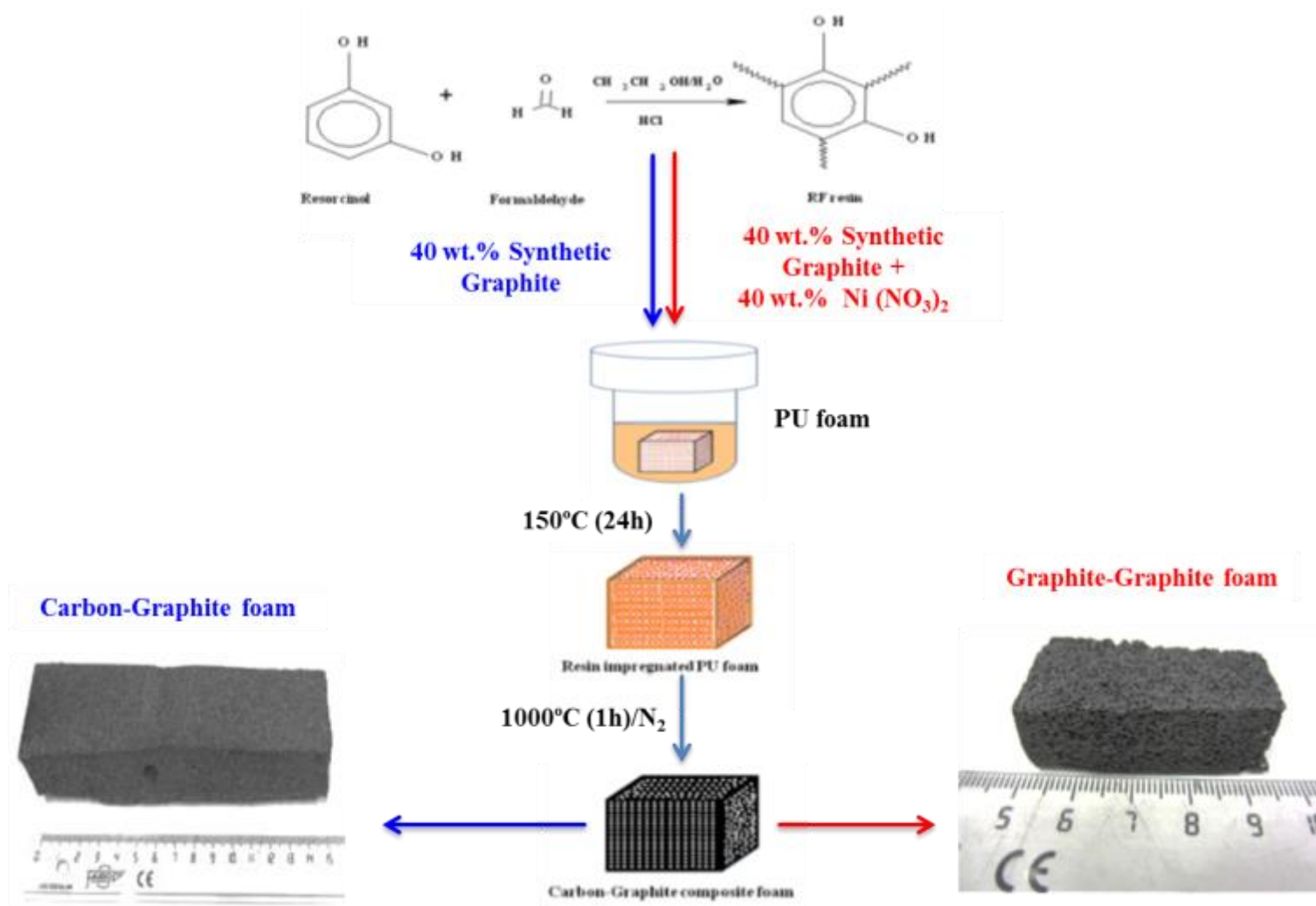
Target

- Porosity: 85 - 90 %
- Density: 0.25 - 0.35 g/cm³
- Thermal conductivity: 2 - 4 W.m⁻¹.K⁻¹
- Cost: 6 - 7 €/Kg
- Mechanical stability
- Hydrophobic

Results Achieved

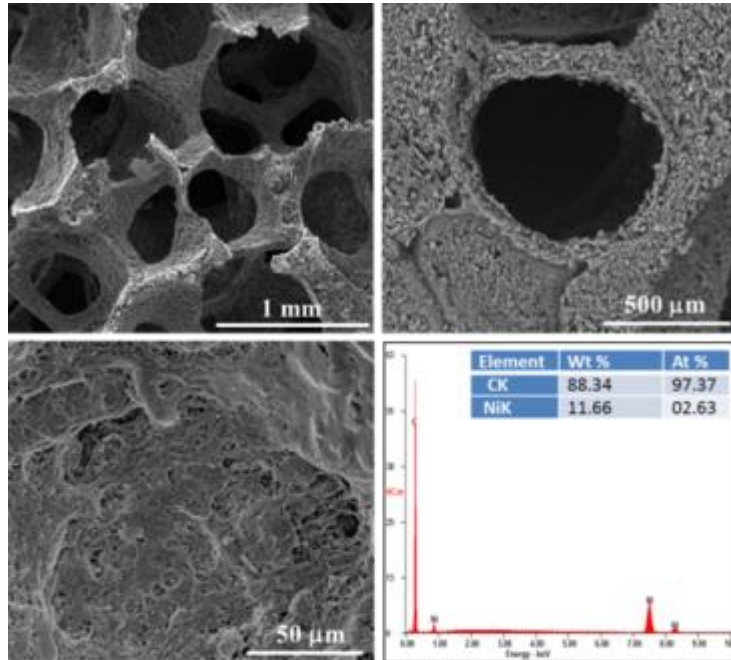
- ✓ Porosity: 70 - 88 %
- ✓ Density: 0.20 - 0.45 g/cm³
- ✓ Thermal conductivity: 2 - 4 W.m⁻¹.K⁻¹
- ✓ Cost: 3 - 7 €/Kg
- ✓ Mechanical stability : 0.4 - 1.3 MPa
- ✓ Hydrophobic: contact angle 120°

Preparation of Carbon-Graphite or Graphite-Graphite Composite Foams



Graphite Composite Foam

Surface Morphology - SEM



Properties of the Carbon Foams

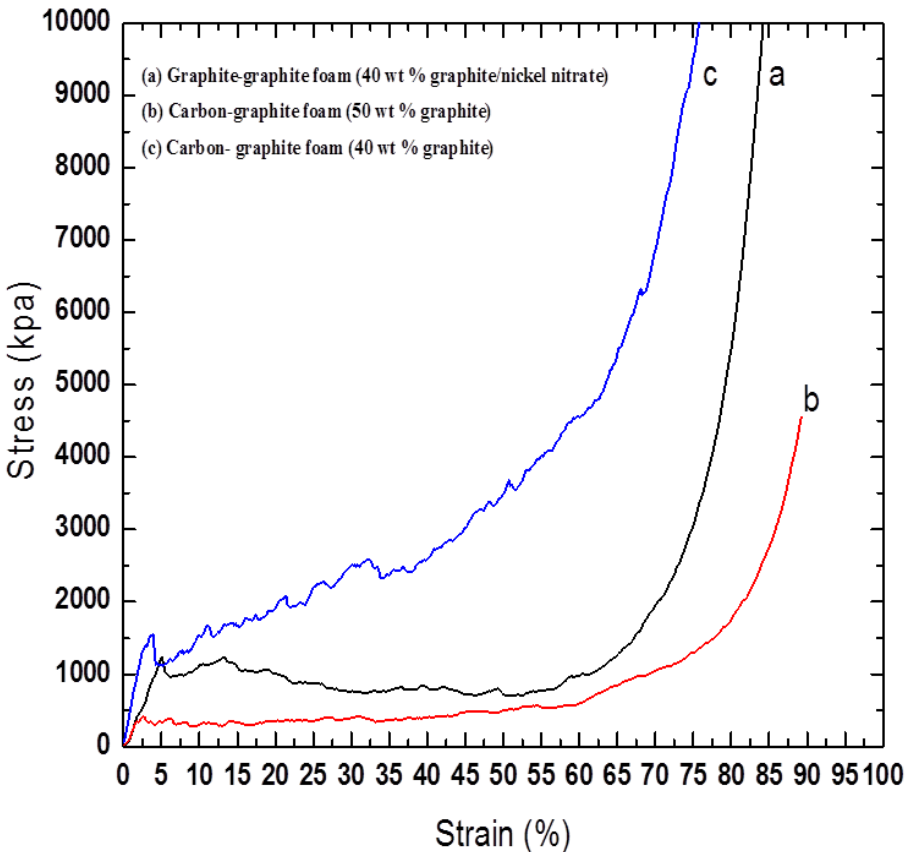
Samples	Composition Polymer/Graphite/Ni (wt. %)	Bulk Density (g/cm ³)	Total Porosity (%)
Carbon foam (CF1)	100/0/0	0.1500	93.3
Carbon-Graphite foam (CGF1)	60/40/0	0.2338	88.86
Carbon-Graphite foam (CGF2)	50/50/0	0.3768	82.06
Graphite-Graphite foam (GGF1)	60/40/40	0.4252	79.75

Target: Porosity: 85-90 %





Compressive stress-strain behavior of the carbon foams



Samples	Composition Polymer/Graphite/Ni (wt. %)	Compressive strength (MPa)	Elastic modulus (MPa)
Carbon-Graphite foam (CGF1)	60/40/0	1.30	54
Carbon-Graphite foam (CGF2)	50/50/0	0.40	24
Graphite-Graphite foam (GGF1)	60/40/40	0.42	23

Reticulated Vitreous Carbon (RVC)

Commercial “Ultramet” carbon foam

(0.16-0.76 MPa)

Commercial “ERG” carbon foam

(0.10-0.52 MPa)

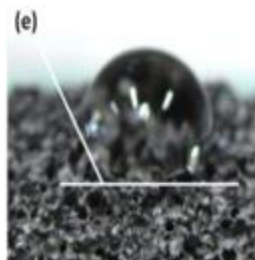
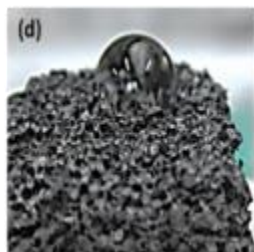
Compression Strength

(0.10-0.76 MPa)

Typical compressive stress-strain behavior of the composite carbon foams

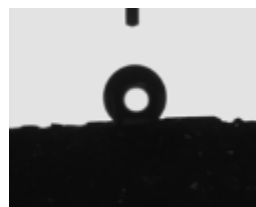
Surface Functionalization of Carbon Foams - Hydrophobic Carbon Foam

Water droplet on the surface of the carbon foam



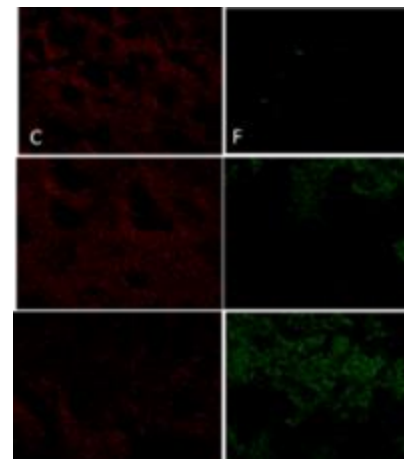
Graphite Foam

Contact Angle
Measurement

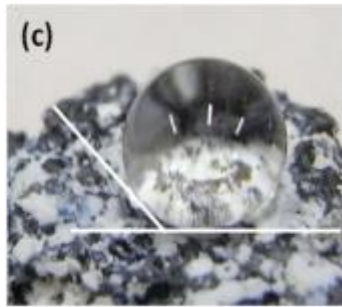
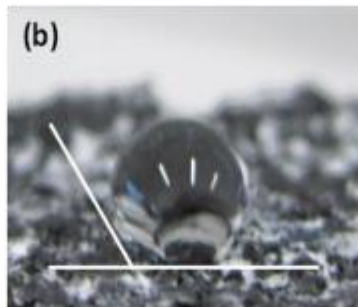
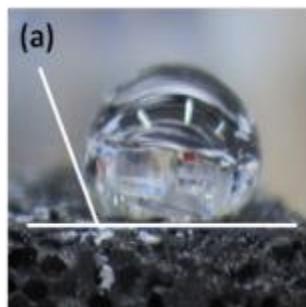


Contact Angle = 120°

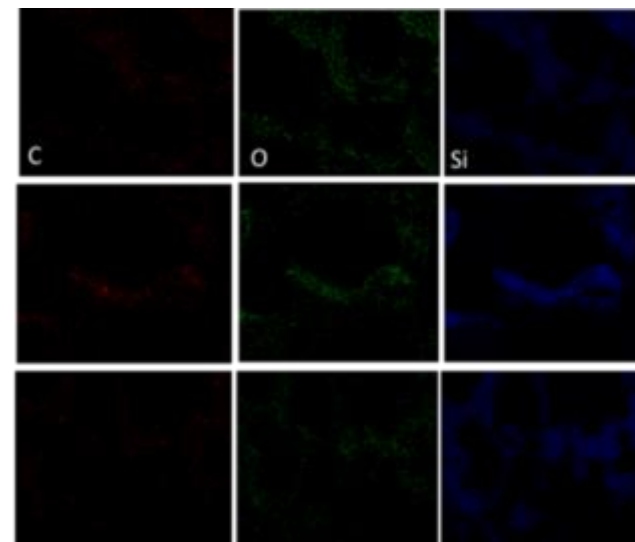
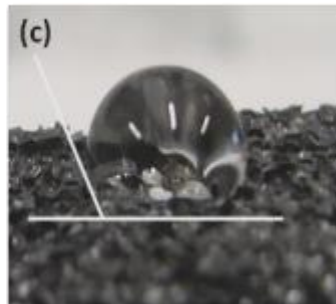
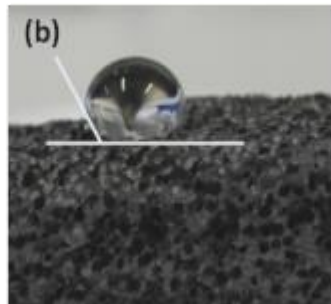
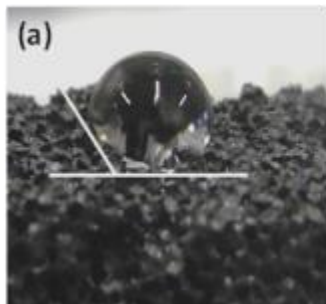
EDAX Mapping



Surface coating with polytetrafluoroethylene (PTFE)



Surface coating with tetraethyl orthosilicate (TEOS)





Preparation of Erythritol-Graphite Composite Foam

Sugar Alcohol Infiltration

- The erythritol infiltration was performed by placing a piece of carbon foam at the bottom of a pool of liquefied erythritol in a beaker/glass plate.
- After infiltration, the foam piece was removed from the beaker and allowed to cool down.
- The excess of erythritol in the outer surface of the carbon foam was removed by carefully scraping with a blade or knife.

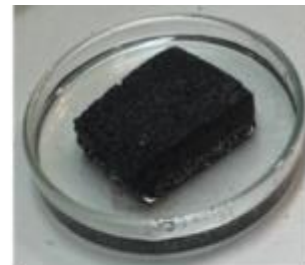
Impregnation of Sugar Alcohol



Sugar alcohol



Molten
Sugar alcohol



Molten
Sugar alcohol
+ Foam

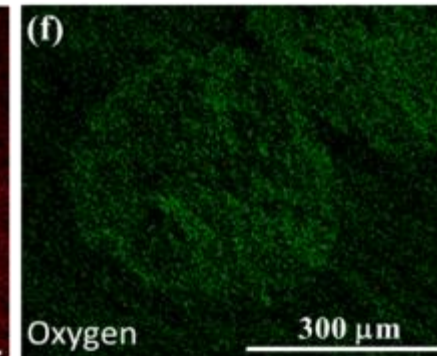
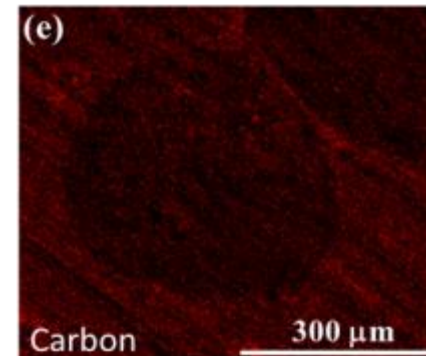
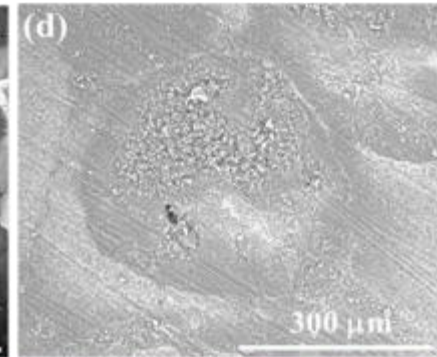
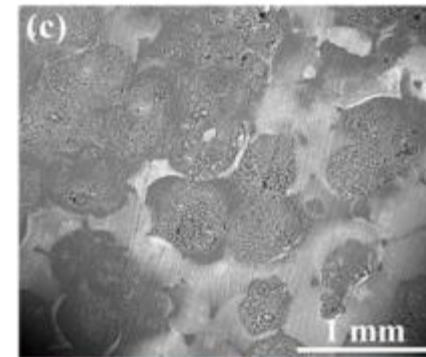
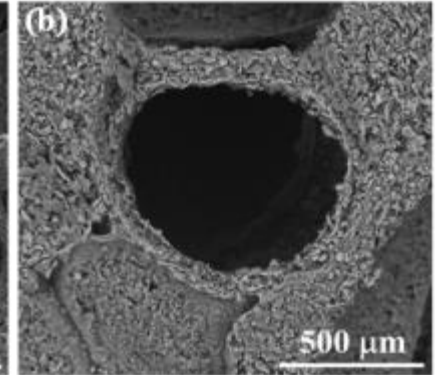
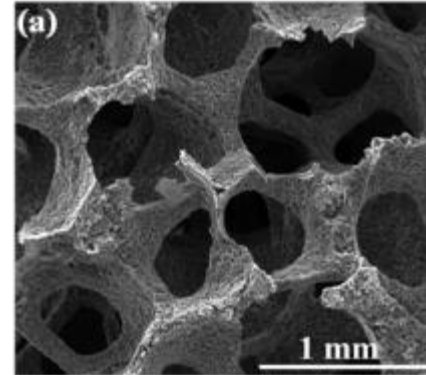
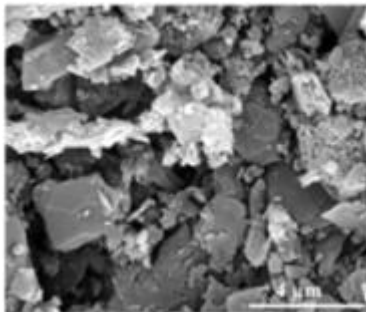
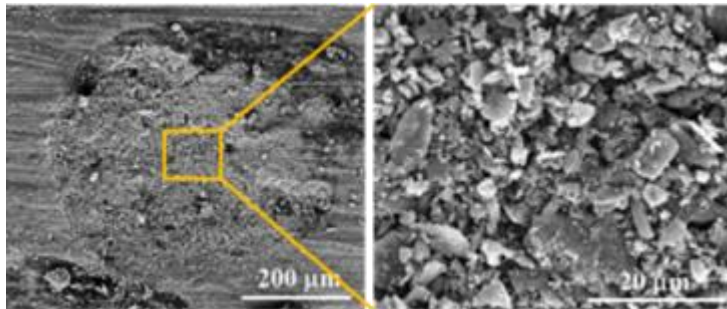
Infiltration of Sugar alcohol is ca. 70-80 wt % depends on the porosity of the carbon foam

Structure of Graphite Foam Before and After Erythritol Impregnation

Before impregnation

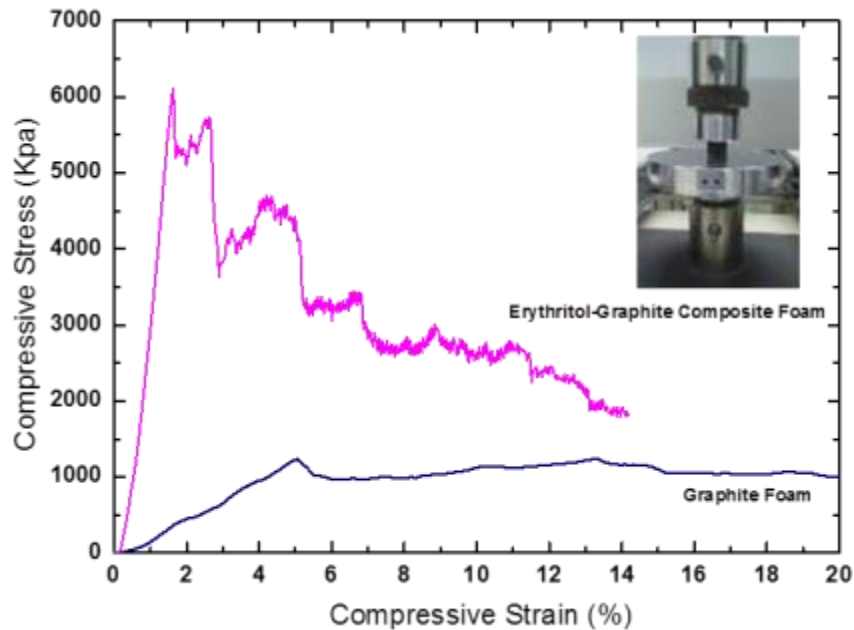


After impregnation

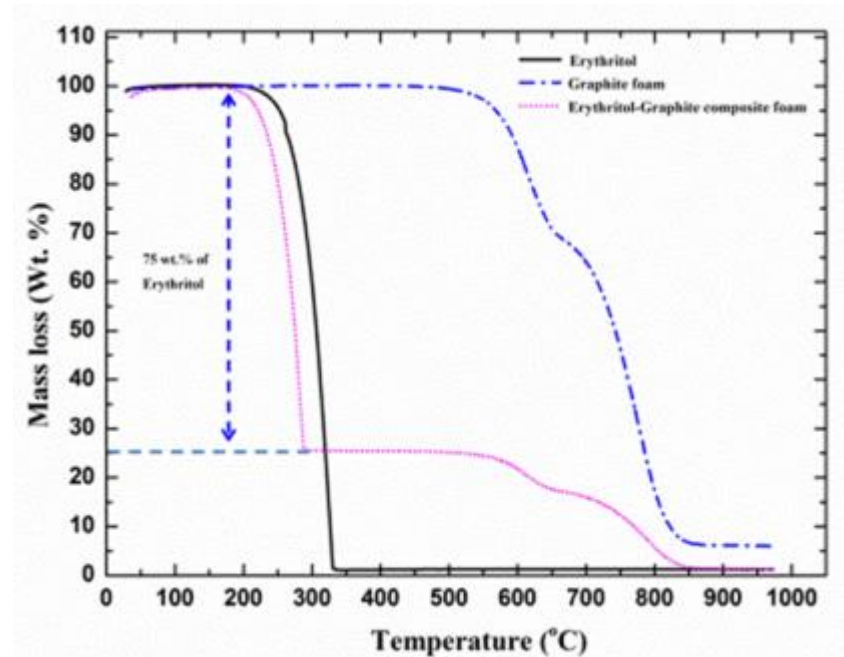


Characteristics of the Materials

Mechanical Stability



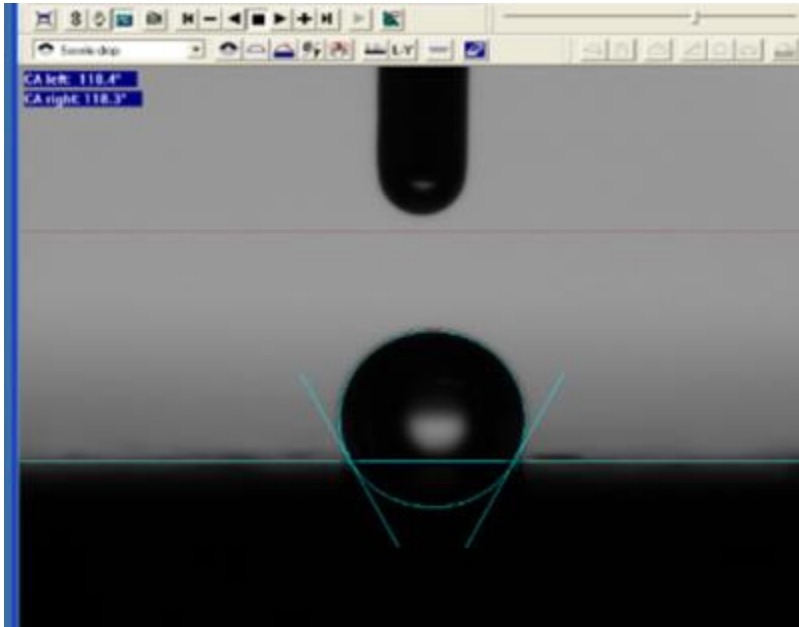
Thermal Stability



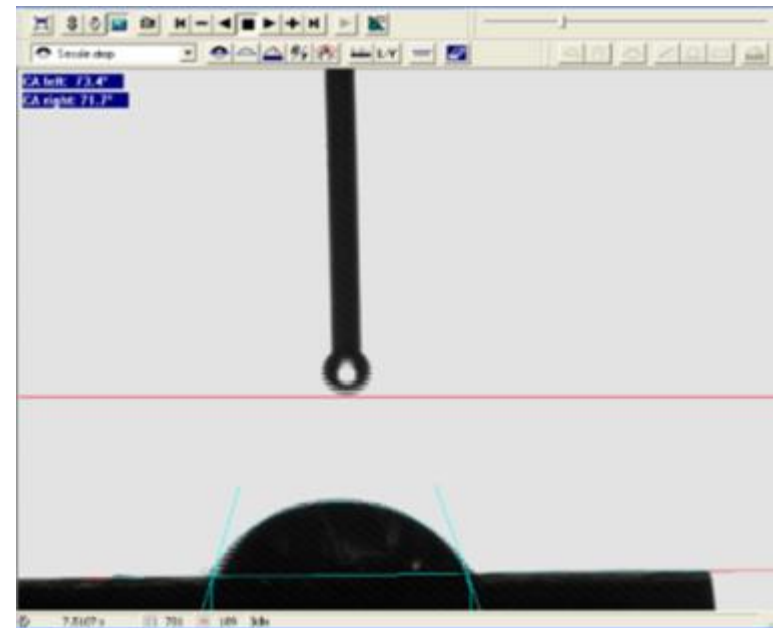
Samples	Bulk Density (g/cm ³)	Total Porosity (%)	Compressive Strength (MPa)	Elastic Modulus (MPa)	Infiltration of Erythritol (wt. %)
Graphite foam	0.35	80	1.2	24	-
Erythritol - Graphite composite foam	1.15	-	6.1	372	75



Contact Angle Measurement



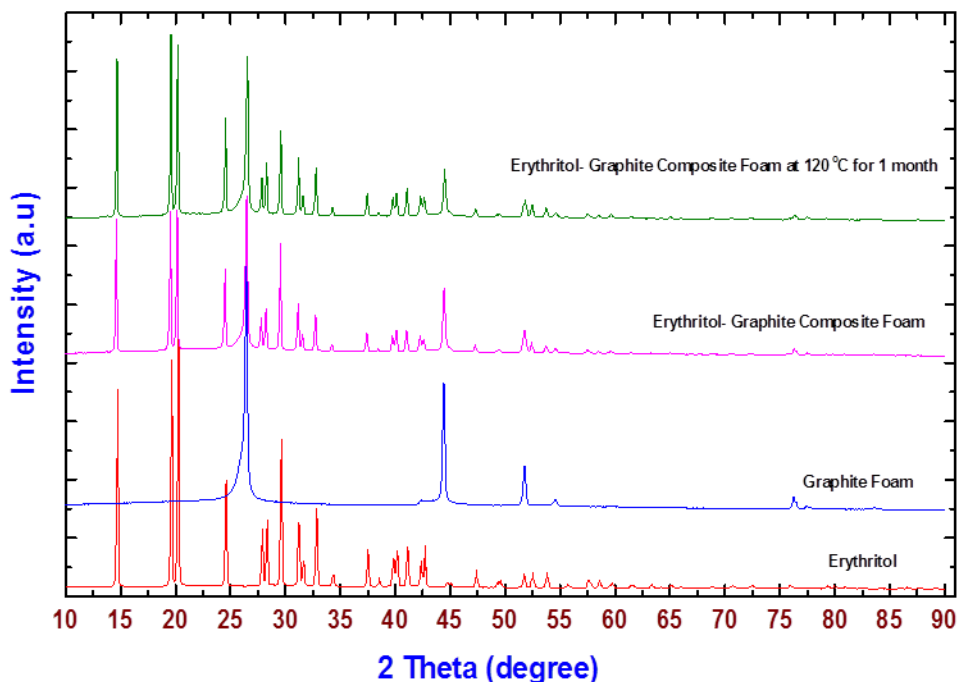
**Graphite composite foam
Hydrophobic**



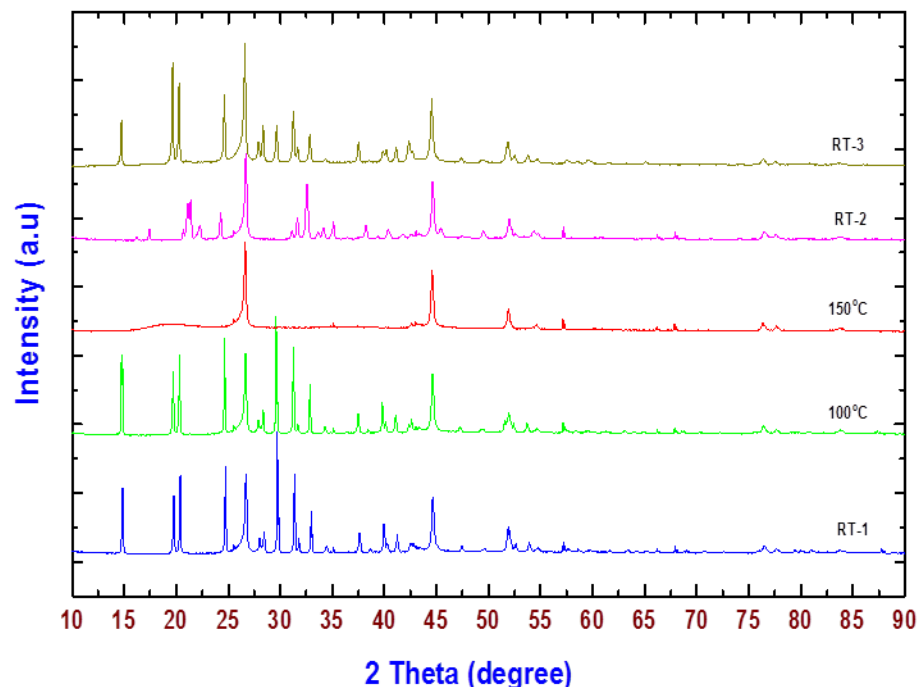
**Erythritol-Graphite Composite Foam
Hydrophilic**

Compatibility between Erythritol and Graphite Foam

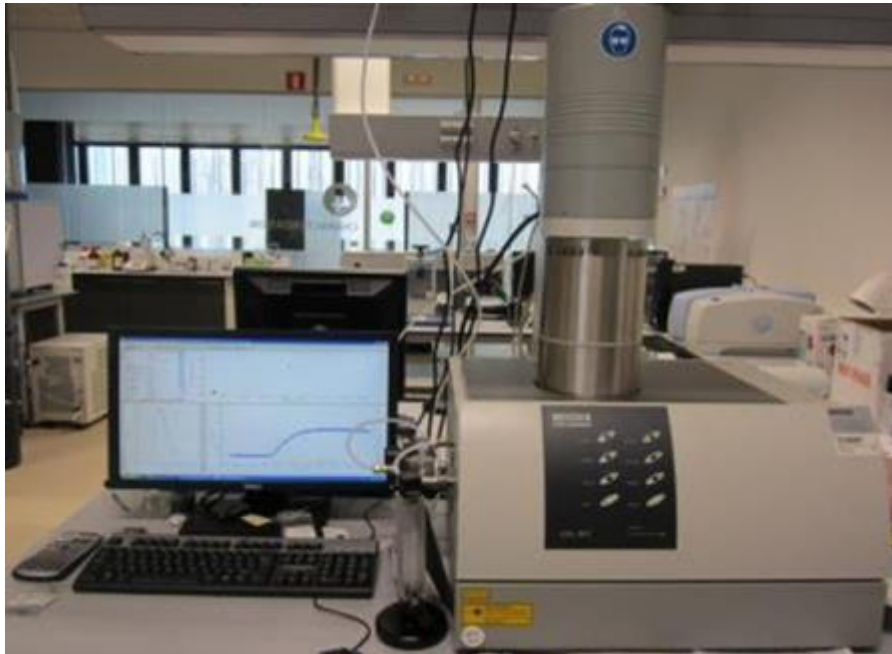
XRD Patterns



***In-situ* XRD Patterns (*In-situ* heating chamber)**



Thermal Conductivity Enhancement of PCM Composite



Laser Flash Apparatus (LFA 457, Netzsch)

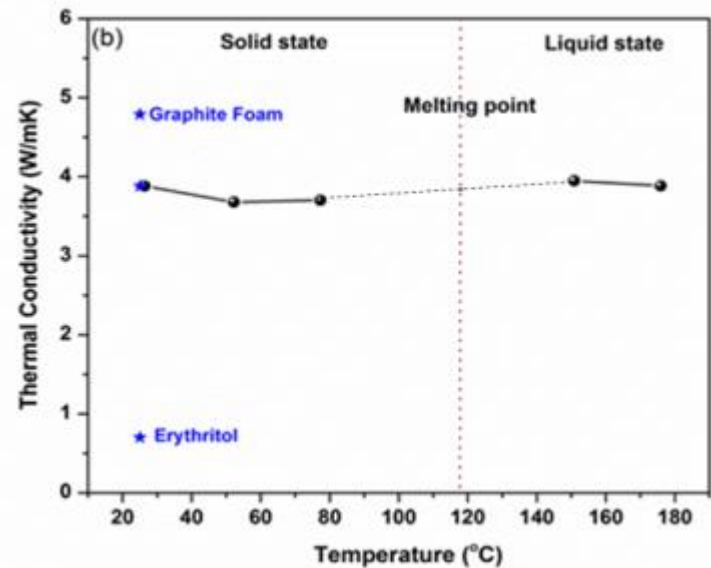
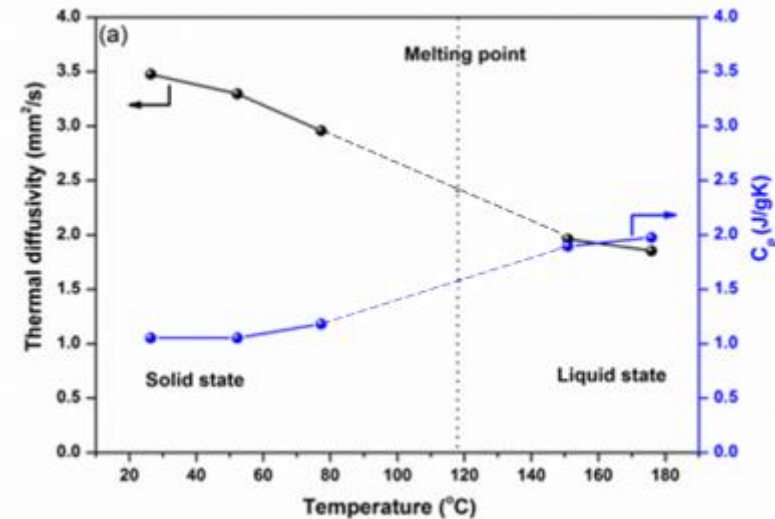
$$k = \alpha \cdot \rho \cdot C_p$$

where k is the thermal conductivity in W/mK

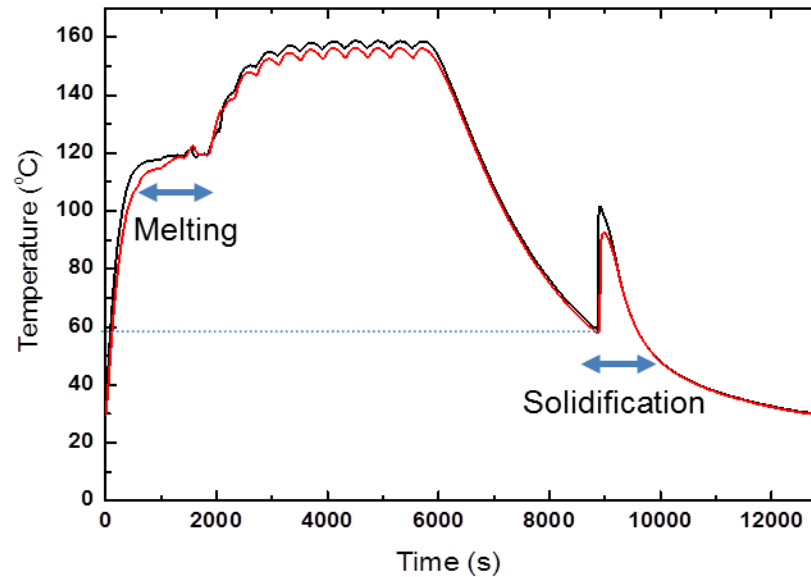
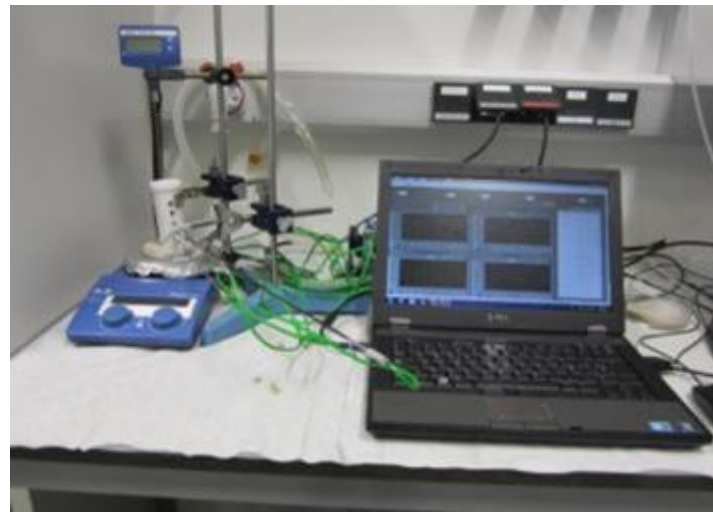
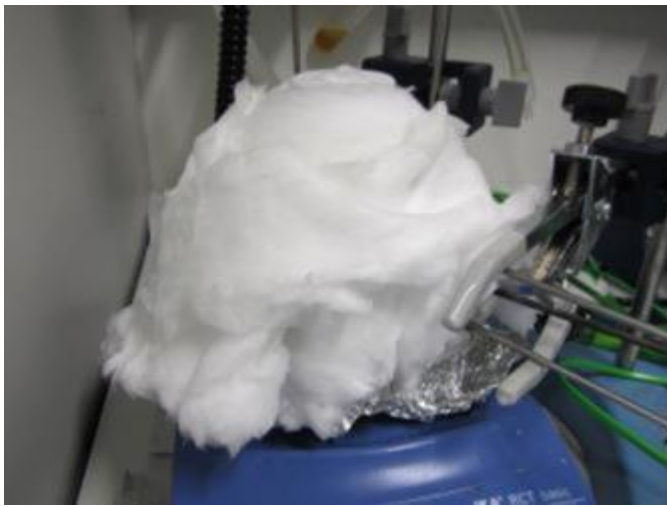
α is the thermal diffusivity in mm^2/s

ρ is the density in g/cm^3

C_p is the specific heat in $\text{J}/\text{g}\cdot\text{K}$



Small Experimental Device



Conclusions

- ✓ Carbon-graphite and graphite-graphite composite carbon foams were prepared by template method using commercially available polymeric foams (PU) as macroporous sacrificial template.
- ✓ Erythritol-graphite foam as a stable composite PCM was obtained by a simple incipient wetness impregnation method with high impregnation ratio.
- ✓ The in-situ XRD result clearly indicates that there is no chemical reaction between erythritol and graphite and thus the composite has not only good structural stability but also good compatibility between erythritol and graphite composite foam.
- ✓ It was found that the thermal conductivity of the erythritol-graphite composite foam (3.88 W/mK) was enhanced ca. 5 times higher as compared with that of pristine erythritol (i.e. 0.7 W/mK). This enhancement can significantly reduce the charging and discharging times of the PCM storage system.
- ✓ The PCM/foam composite has a melting point of 118 °C and latent heat of ca. 250 J/g which corresponds to the mass percentage (ca. 75 wt. %) of the erythritol within the composite foam.
- ✓ It can be concluded that the carbon matrix is not affecting the melting behaviour and enthalpy of the erythritol.