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Identification of Thermal Properties and Thermodynamic Model for a Cement Mortar Containing PCM by Using Inverse Method

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Abstract

The support of this study is a cement mortar containing a micro-encapsulated phase change material (PCM). The aim of this article is to identify by an inverse method the thermophysical properties of this composite material and all the parameters that are needed to build a physical model able to simulate the thermal behavior of a material containing PCM with accuracy. This approach consist in estimating different parameters that take place in the analytical relation of the enthalpy as a function of the temperature (h(T)) by comparing the response of the model with experimental results (here, heat flux measurement). A simplex algorithm allowed to minimize the quadratic criterion associated. The results obtained by inverse method are then analyzed and compared by experimental results obtained by direct method.

Keywords: Phase Change Material, Identification, Enthalpy method

1. Introduction

The thermal behavior models of phase change materials are not always reliable [1,2] and can lead to significant errors in the evaluation of surface temperatures and on the amount of heat exchanged [3]. It can also lead to errors of conception by making the choice of a PCM unsuited to the application considered [4]. This is mainly due to a wrong interpretation of calorimetric measures made by DSC and to an abusive use of a numerical model based on the "Cp equivalent" method [3,5]. The model used here is based on the enthalpy method, assuming that PCM has the same

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behavior than a binary solution. Thermophysical properties have to be determined precisely and that is what we propose to do in this work.

2. Material studied

The sample studied is a cement mortar with embedded micro-capsules of PCM produced by BASF (Micronal PCM® DS 5001 X). In its commercial catalog, BASF precises that this powder PCM is constituted of paraffin micro-capsules in a very strong acrylic binder in order to make it tight and formaldehyde free. The heat storage capacity of the material given by the manufacturer is 110 kJ/kg and the melting temperature around 26°C. A DSC was carried during the "ANR-MICMCP" project on the PCM implemented. The latent heat found was 99 kJ/kg.

The composite material manufactured contains about $12\%_w$ PCM. The sample dimensions are 250 x 250 x 40 mm^3, and it is dried in the laboratory during more than two months before the experiences. The sample mass was controlled before and after the testing period. No significant change was observed. This shows that the water content was constant during the tests. The sample mass is 3.53 kg and its density (ρ) is 1412 $kg.m^{-3}$.

Nomenclature

Symbols:

c	heat capacity, $J.kg^{-1}.K^{-1}$
F	heat flux density, $W.m^{-2}$
h	heat transfer coefficient, $W.m^{-2}.K^{-1}$
h()	enthalpy, $J.Kg^{-1}$
L	Latent Heat, $J.kg^{-1}$
SumF	Sum of heat fluxes entering the sample, $W.m^{-2}$
T	temperature, K
X	sensitivity

Greek Letters:

Δ	Variation of a parameter
λ	Thermal conductivity, $W.m^{-1}.K^{-1}$
ψ	PCM mass fraction, %
ρ	density, kg m^{-3}

Subscript / Superscript:

A	pure substance
l	left side
L	liquid
m	mean value
M	end of fusion (liquidus)
p	parameter
P	set of parameters
pl	plate
r	right side
s	solid
sim	simulated

3. Experimental set up

The experimental set up used in this study was presented previously [6,7]. It is composed of two heat exchanger plates to impose the surface temperature on the larger surfaces of the sample. The heat flux density and the surfaces temperatures are simultaneously measured. An insulated ring is placed around the sample in order to ensure that the heat transfer is mono-dimensional in the thickness of the material and fluxmeters. Thus, the boundary conditions imposed are a succession of ramp and constant heating/cooling so as to make PCM changing successively from liquid to solid state. The heat flux measured by this way will be used in the identification process. Before that, using a direct method with adapted experimental protocol, apparent thermo-physical properties of the composite material (λ_s, λ_L, c_s, c_L, L_A, T_M) can be evaluated. These protocols were detailed for a mortar of the same nature but with a higher percentage of PCM in [6]. For the current composite material, thermal conductivity is 0.55±0.02 $W.m^{-1}.K^{-1}$, solid and liquid heat capacities are 1119±56 $J.kg^{-1}.K^{-1}$, and 1080±54 $J.kg^{-1}.K^{-1}$, latent heat is 11590±1160 $J.Kg^{-1}$.

Fig. 1 presents an example of measures realized for 4 hours long heating and cooling ramps. Similar tests were carried for 3h, 4h, 5h and 6h. We chose by convention that the heat flux was positive from the left to the right. During the heating process, the left side of the material absorbs energy: the sign of the heat flux (F_l) is thus positive. On the right, the material stocks also energy but because of our convention, the heat flux (F_r) is negative. To evaluate the quantity of energy charged (or discharged during cooling) by the material, it is therefore necessary to subtract left and right heat fluxes. This is in fact the heat flux integrant that we note *SumF*. On Fig.1, we can notice that right and left heat fluxes are not exactly identical although the thermal solicitation is. This difference can be explained by heterogeneity of the material linked to its implementation or to different contact resistances between fluxmeters and sample on the two sides. That is why we decided to study the impact on the identification of thermal properties to take into account the sum of heat fluxes or distinct lateral heat fluxes in independent way.

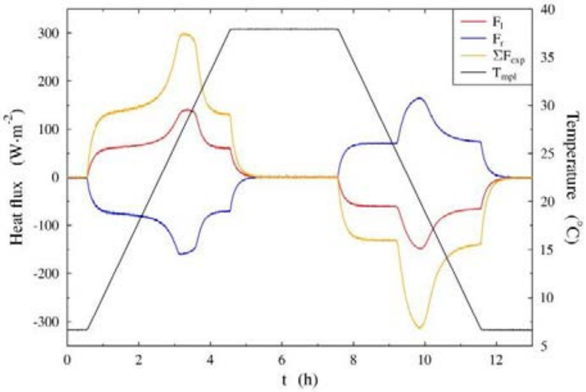

Fig. 1. 4 hours ramps imposed to the material between 7 and 38°C

4. Thermodynamical model

The model used to simulate the mortar behavior was detailed in [7]. It is based on the hypothesis that the material has a thermodynamic behavior similar to the one of a binary solution. 1D conduction model considered with Robin boundary conditions using h_l and h_r heat transfer coefficients between the fluxmeters and the sample, in order to take into account contact resistance due to glue, are used. Finite volume method is used to simulate conduction inside the material considering an enthalpy that varies as a function of the temperature. The corresponding equation of state is:

$$h(T) = \begin{cases} if\ T < T_M : c_S(T - T_M) + c_L(T_M - T_A) + \ \psi\, L_A\left(1 - \frac{T_A - T_M}{T_A - T}\right) + (c_S - c_L)(T_A - T_M)\, l\, n\left(\frac{T_A - T}{T_A - T_M}\right) \\ if\ T \geq T_M : c_L(T - T_M) \end{cases} \quad (1)$$

With $c_i = (1 - \psi)c_{\mathrm{S,mortar}} + \ \psi\, c_{i,mcp}$ (i being either S or L)

The validity and the high potential of this model compared to Cp equivalent methods was presented and demonstrated in [5].

5. Inversion method

An identification method by inversion is used to determine every thermophysical characteristics of the mortar (conductivity, solid and liquid heat capacity, latent heat, characteristic temperatures of phase change) and of the experimental set up (heat transfer coefficients between fluxmeters and sample). The classical way is to minimize an "objective function" that indicates the difference between experimental and numerical results by testing a set of parameters that have to be identified. In our case, this function is built with quadratic sum of deviation between measured and simulated heat flux signals.

6. Study of sensitivity coefficients

In this study, nine parameters have to be determined in the case where identification is carried on right and left heat fluxes. The objective of this sensitivity analysis is to verify that the parameters that have to be identified have a significant effect on the heat fluxes and that it will be therefore possible to estimate them. This study is based on the calculation of sensitivity functions. A variation Δp of one unknown parameter is introduced in the model in order to calculate the relative variation of the heat fluxes sum ($\mathrm{SumF}=F_l$-F_r). The sensitivity function X_p [8] of the heat fluxes sum corresponding to p parameter is then defined by:

$$X_p(p) = \frac{\Delta SomF(p)}{\frac{\Delta p}{p}} \quad (4)$$

In our study, the nine parameters that have to be identified are thermal conductivities (λ_s, λ_L), heat capacities (c_s, c_L), latent heat (L_A), melting temperature of the melting (T_M), melting temperature of the main component (T_A) and heat exchange coefficients between the fluxmeters and the sample (h_g, h_d). For each parameter, a relative variation of 1% is applied. Fig. 2a represents sensitivity functions of these parameters on a test with 4 hours ramps.

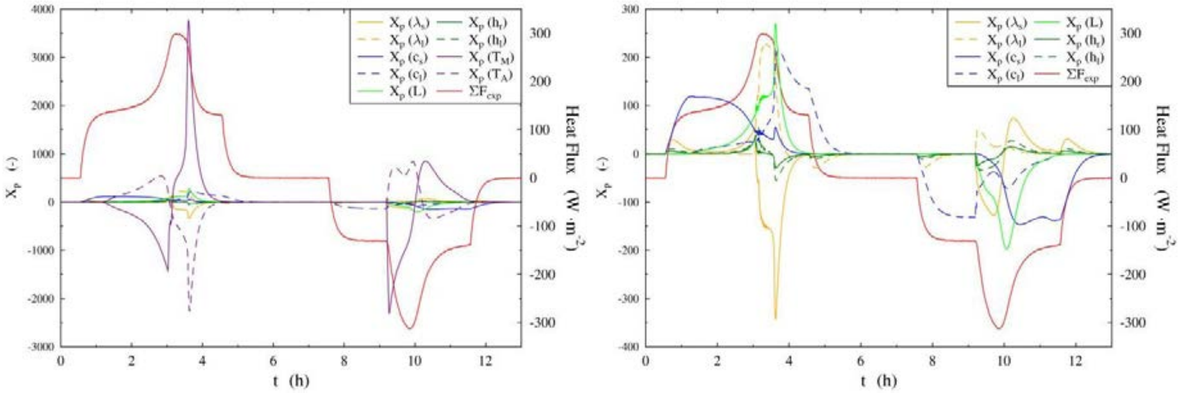

Fig. 2a. Sensitivity coefficient for (a) 9 parameters (b) 7 parameters

On Fig. 2a it appears that sensitivity to parameters T_M and T_A have the higher values when phase change occurs. These high values hide the other sensitivities, that is why it was deleted in Fig. 2b. It indicates that along the test, sensitivity functions are not nil and that it reaches minima and maxima uncorrelated. These observations comfort us that the simultaneous identification of the parameters is possible with this kind of test.

7. Results and discussion

First, identification was realized on heat fluxes sum considering the same contact resistance for the two sides of the sample. It allows to reduce the number of parameters to eight. However, as it was precised in the paragraph "experimental set up", F_l and F_r are not exactly identical (Fig. 1). This is certainly due to the heterogeneity of the material, imperfections of the surface finish or a different implementation of the sensor. Then, a second approach was used considering separately right and left heat fluxes (F_r and F_l) and heat transfer coefficients (h_r and h_l). The identification that uses heat fluxes sum (SumF) is designated "1R_c" because only one contact resistance equal on the both sides is considered and the identification that uses separately left and right heat fluxes is designated "2R_c".

Table 1. Identification (a) "1R_c" with SumF (b) "2R_c" with F_r and F_l

(a)	Min relative error	**Mean value**	Max relative error		(b)	Min relative error	**Mean value**	Max relative error
h	-5.3%	**138**	5.2%		**h_d**	-5.7%	**176**	4.8%
T_M	0.0%	**25.47**	0.0%		**h_g**	-1.9%	**85**	4.2%
T_A	0.0%	**26.67**	0.1%		**T_M**	-0.2%	**25.48**	0.2%
L_A	-0.7%	**11540**	0.5%		**T_A**	-0.8%	**26.68**	0.7%
c_s	-0.1%	**1102**	0.1%		**L_A**	-3.0%	**11487**	2.0%
c_L	-0.1%	**1064**	0.0%		**c_s**	-0.9%	**1104**	1.4%
λ_s	-0.7%	**0.575**	0.9%		**c_L**	-0.3%	**1064**	0.3%
λ_L	-0.4%	**0.574**	0.5%		**λ_s**	-0.6%	**0.636**	0.9%
					λ_L	-0.5%	**0.625**	0.6%

Parameter identification was carried for ramps of 6h, 5h, 4h and 3h in both cases. Table 1 presents the mean values for each parameter and the maximum and minimum relative variations associated. The variations between these different values are very low (less than 1%) concerning parameters c_s, $c_{L,}$ T_M, T_A and L_A. For h values, a large difference between h_r and h_g can be noticed (factor 2). Let's precise that the mean value calculated with h_r and h_g is equal to 130 W.m^{-2}.K^{-1} which is very close to the value of 138 W.m^{-2}.K^{-1} and gives a contact resistance very low (7.7 10^{-3} m².K/W). Identifications of thermal conductivities give values that are very close together for the two methods for λ_s and λ_L. It means that PCM state has no influence on the apparent conductivity of the composite material. However, for these conductivities, we can see a notable difference (around 10%) between both methods.

Fig. 3 represents h(T) function drawn using results presented in Table 1. Identification (a) "1R$_c$" with SumF (b) "2R$_c$" with F_r and F_lTable 1. It appears that both enthalpy curves are almost identical. Whatever the heating or cooling rate these curves are equivalent. It is logical considering the results of identification. The only values that differ are heat exchange coefficients and conductivities nonetheless these parameters are not considered in the enthalpy function. However, these parameters take place in the heat flux calculation in transient state.

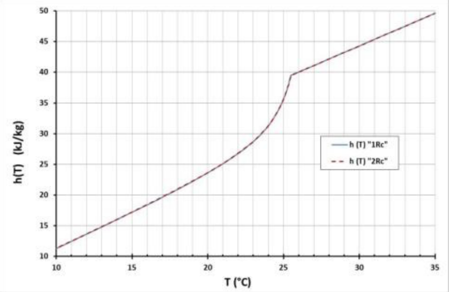

Fig.3. Enthalpy h(T)

Fig. 4 shows the heat fluxes calculated with the model thanks to two sets of parameters from the two methods. Fig. 4a shows a small variation between these three curves. It indicates that both methods allow to represent the thermal behavior of the material during melting and solidification phases although they are not identical. To be more precise, if we compare energy exchanged during heating / cooling cycles, the variation between the experimental data and the calculated one thanks to parameter set "1R$_c$" is 0.5% and 0.3% for "2R$_c$".

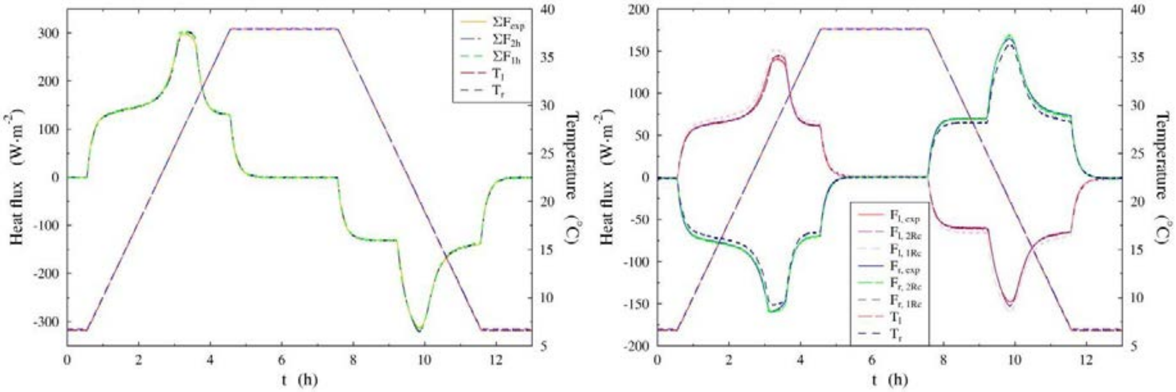

Fig. 4. Comparison between measured and calculated values (a) for SumF (b) for F_r and F_l

Fig. 4b represents heat fluxes on left and right sides for measures and calculations. It appears in this case, that the 1R$_c$ and 2R$_c$ calculated heat fluxes are a little bit different. The experimental curves F_r and F_l are almost superimposed with heat fluxes calculated with method 2R$_c$. The identification method that considers independently heat exchange coefficients on both sides of the sample seems to be more efficient. Now, let's compare thermophysical properties given in paragraph 3, obtained by direct a method [6], to the current ones (see Table 2).

Table 2. Comparison between identification methods

	Experimental	"1R_c"	"2R_c"
T_M	25/26°C	25.47	25.48
L_A	11590 ±1160	0.4%	0.9%
c_s	1119 ± 56	1.5%	1.3%
c_L	1080 ± 54	1.5%	1.5%
λ_s	0.507 ± 0.02	-13.4%	-25.3%
λ_L	0.512 ± 0.02	-12.2%	-22.2%

This table shows a very low variation between the values estimated by a direct method that uses fluxmetric experimental set up and the one identified by inverse method excepted for thermal conductivity. It can be explained by the fact that thermal conductivity is estimated without considering contact resistances that are not "measurable". If we consider the contact resistances estimated by inverse method in the calculation made for experimental method, the value of conductivity found (0.65 $W.m^{-1}.K^{-1}$) is very close to the one estimated with method "2R_c".

8. Conclusion

This study demonstrates that it is possible to determine thermophysical properties of a composite material with PCM by using a fluxmetric experimental disposal and inverse methods. As it is possible with the thermogram of DSC, inverse methods allows to establish enthalpy curve as a function of the temperature (h(T)) that is characteristic of the thermodynamic behavior of the material. The application of thermal ramps allows to solicit the composite material in transient state and to cause a phase change. A sensitivity analysis shows that nine parameters influencing thermal transfers could be identified by this kind of solicitation. It has shown moreover that although it introduces an additional parameter, it was preferable to consider separately both heat fluxes measured than to consider heat fluxes sum that supposes perfectly symmetric exchanges in the sample. Using direct methods with experimental measures, calorific capacities and latent heat can be estimated. It is less easy for the estimation of the thermal conductivity because contact resistances between the sensor and the sample cannot be neglected and that they can be different. This work shows that fluxmetric experimental measures allow identification of the parameters that are essential for reliable numerical simulations of the thermal behavior of this kind of material.

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