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Thermal analysis by DSC of Phase Change Materials, study of the damage effect

Sarra Drissi [a,b,c], Anissa Eddhahak [d,*], Sabine Caré [b], Jamel Neji [c]

[a] Université Paris-Est—Institut de recherche en constructibilité, ESTP, 28 Avenue du Président Wilson, 94234 Cachan cedex, France
[b] Université Paris-Est, Laboratoire Navier (UMR 8205), CNRS, ENPC, IFSTTAR, 6—8 Av. Blaise Pascal, 77455 Marne La Vallée, France
[c] Université Tunis El Manar—Laboratoire de Matériaux, d'Optimisation et d'Energie pour la Durabilité, LAMOED Ecole Nationale d'Ingénieurs de Tunis, BP 37, Le belvédère 1002, Tunis
[d] Laboratory PIMM, CNRS UMR 8006, Arts et Métiers ParisTech, 151 bd de l'Hôpital, 75013 Paris, France.

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ABSTRACT

This paper deals with an experimental study of Phase Change Materials (PCMs) by DSC and focuses particularly on the influence of PCMs damage on their thermodynamic properties. First, different series of tests were performed on non-damaged PCMs (reference) using different masses and heating rates in order to optimize the choice of the experimental parameters used in DSC test. Accordingly, the specific heats at solid, liquid phases and the latent heats of PCMs were obtained. In addition, a fast approximate approach was suggested for the determination of the heat capacity of PCMs from a direct exploitation of the heat flux curves obtained by scanning PCMs at different heating rates. Finally, damaged PCMs were investigated and their thermal properties (specific heat and phase change enthalpy) were compared to the reference PCMs. It was shown from the obtained results that low heating rates are more suitable for PCMs scanning during DSC measurements in order to ensure a thermodynamic equilibrium within the sample. Furthermore, the results highlighted that damage of PCMs can lead to the loss of their specific heat capacity of about 28% compared to the non-damaged PCMs.

1. Introduction

During recent years, the total world energy consumption and the associated CO_2 emissions in commercial and residential buildings are rising dramatically [1]. To cope-up with this hazardous situation, the solar Thermal-Energy Storage (TES) in building structures has shown to be a promising solution aiming to the reduction of the energy consumption and the improvement of the indoor thermal conditions [2]. One of the options for the achievement of the TES technology is the use of Phase Change Materials (PCMs) which have the ability to store and release a high amount of energy by latent heat [3]. Typically classified into three families: organic, inorganic and eutectic [4,5], PCMs have shown good stability and compatibility with the cement-based construction materials [6], thereby offering a rational and intelligent management of the energy use in buildings. From apart the environmental and economical benefits of PCMs technology, the thermal comfort of the occupants can be significantly improved [7,8] in both domestic and commercial buildings by the decreasing of the indoor temperature on the one hand, and the smoothing of the thermal fluctuations on the other one [9].

PCMs can be microencapsulated in a polymer shell in order to prevent the leakage of the core material during their melting. The microencapsulation technique is also advantageous because it provides an exchange surface between PCMs and the surrounding material contributing therefore to the improvement of the thermal transfer conditions. The morphology of microcapsules depends mainly on the core material and the deposition process of the shell. There are three basic morphologies of microcapsules: Mononuclear, Polynuclear and matrix-encapsulation. In addition to these morphologies, microcapsules can also be monocuclear with multiple shells, or they may form clusters of microcapsules. For further information regarding PCMs encapsulation technique, the readers could consult the detailed review papers of [10,11] where some investigations on microencapsulated PCMs for thermal energy storage in building applications are described.

So far, many researchers have focused on the use of PCMs in building sector and their association with the construction materials (concrete, gypsum…) in order to enhance the overall thermal inertia of the structure. A particular interest has been paid to organic PCMs, for instance, which present several attractive properties making them good candidates for incorporation in the building materials. Some of their advantages can be their

* Corresponding author. Tel.: +33 6 99 24 76 66.
E-mail addresses: sdrissi@adm.estp.fr (S. Drissi), anissa.EDDHAHAK@ensam.eu (A. Eddhahak), sabine.care@ifsttar.fr (S. Caré), jamel.neji@enit.rnu.tn (J. Neji).

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Nomenclature

Latin letters

Cp	Specific heat capacity (J/kg K)
k	Calibration coefficient
m	Mass (kg)
R_f	Thermal resistance of furnace (K/W)
T	Temperature (K)
t	Time (s)

Greek letters

β	Heating/cooling rate (K/min)
Φ	Heat fluxes (W)
ΔH	Latent heat (J/kg)

Superscripts

r	reference
s	sample

Subscripts

m	melting
s	solid
l	liquid

availability in a large temperature range, their chemical stability, the little super-cooling phenomenon and phase segregation, etc. Meshgin et al. [12] focused on the study of the thermal and mechanical properties of concrete modified with PCMs. Later on, Hunger et al., [13] used microencapsulated PCMs in self-compacting concrete and studied their effect on the concrete behavior. Recently, Eddhahak et al. [14] worked on the effect of PCMs when incorporated in cement Portland concrete and used a multi-scale approach to evaluate the thermal properties of the PCM-concrete. The main conclusions drawn from these works can be summarized in the improvement of the heat storage capacity of the PCM-concrete on the one hand, and the loss of its mechanical strength with the addition of PCMs on the other one. More recently, it was highlighted in a previous work [15] some reasons which could explain the decrease of the mechanical strength of concrete with PCMs by the investigation of the cement hydration reaction track. Although the numerous studies and the extensive literature focused on PCMs, many queries are still raised regarding this technology and its sustainability from an energy efficiency point of view especially when integrated in the construction material. In our sense, this confusion can be associated to the fact that the PCMs characteristics themselves are not sufficiently well controlled because of the lack of specific standards and methods for the tabulation and exploitation of results derived from experiments [16,17]. For instance, the determination of the thermodynamic properties of PCMs is not straightforward as it can be imagined, since typical heating and cooling rates used in DSC measurements (5–10 K/min) are in anyway compatible for PCMs case and much attention has to be paid to the test parametric control in order to avoid wrong estimations of their thermal characteristics [18]. More precisely, the influence of the heating rate taking into account the investigated volume has been studied in very few papers but more research is needed [19]. Thus, in order to control the performance of the PCM-based material, the inherent properties of PCMs themselves shall be well known with sufficient accuracy. In this context, many researches focused on the investigation of the thermal properties of PCMs. Jin et al. [20], for instance, suggested a new experimental method by DSC called the partially-melted DSC method, for the determination of the melting temperature range of PCMs. However, the estimation of the starting melting temperature was not accurately determined by the authors. Barreneche et al. [21] focused on the comparison of dynamic and step DSC modes for the investigation of organic and inorganic PCMs. They concluded that both methods can be suitable for paraffin materials and recommended a slower scanning rate for their study. Nevertheless, no quantitative information on the optimal sample mass was given in their study.

All of these works focused on the study of PCMs properties in their natural state but to our knowledge, no research has been undertaken to study the PCMs in their modified or damaged state in relation with the messy aspects of processing. Namely, it shall be emphasized that PCMs can be subjected to damage when incorporated in the cementitious mixture. Furthermore, it was revealed by SEM observations of PCM-concrete in a previous research [13] that the concrete manufacture can lead to the capsules deterioration especially when PCMs are introduced at the first stage of the mixing process. It shall be emphasized that PCMs damage can exhibit several drawbacks since their deterioration may result in the breakage of the polymer shell capsules and therefore the leakage of the paraffin active material in the surrounding matrix. Accordingly, both energy efficiency and stability of damaged PCMs and their effective contribution to the improvement of the thermal characteristics of the construction material are questioned. In order to determine the effect of PCM damage on their thermodynamic properties, it is first necessary to assess reliable and accurate experimental methods for their investigation. This means that the experimental parameters related to the experimental configuration have to be properly controlled.

In this context, the aim of the present research is twofold

(i) To perform first a thermal analysis of PCMs by DSC in order to identify and optimize the set of experimental parameters to be used for PCMs testing by DSC; and
(ii) to draw conclusions from the results DSC parameters optimization in order to provide qualitative and quantitative information as regards the influence of PCMs damage on their thermodynamic properties.

2. Materials and methods

2.1. PCMs description

Organic paraffinic PCMs called Micronal® DS 5038X in powder form (from BASF) are considered in this study. They are composed of a mixture of paraffin waxes with a melting point of 25 °C and a phase change enthalpy of 100 kJ/kg according to the manufacturer. The paraffin is microencapsulated in a plastic layer of polymethyl methacrylate (PMMA). The microencapsulation technique is used to facilitate the incorporation of the phase change material into the construction material and to prevent the paraffin leakage during the PCMs melting.

2.2. Damaged PCMs

In order to study the effect of PCMs deterioration on their thermodynamic properties, some capsules were intentionally