

SUPPORTING INFORMATION

Enhanced thermal buffering of phase change materials by intra-microcapsule sub per mille CNT dopant

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i. Formal definition of the Observed Effusivity in this paper

The process of heat transfer, in the case of PCM present within the matrix material, is modelled by the reaction-heat equation

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} - S(t) \quad (\text{S1})$$

where $\alpha = k/(\rho c_p)$ denotes the thermal diffusivity of the medium and $S(t)$ is the volumetric heat sink associated with the integrated effect of the PCM.

In 2000, Kulish and Lage proposed an elegant method, which allows one to obtain analytical (closed-form) solutions to various energy transport problems.¹ The method is based on employing generalised differentiation, which in many cases leads to the use of fractional order derivatives (fractional calculus). The solutions thus obtained are in the form of the Volterra-type integral equations, which relate the local values of an intensive property (e.g., temperature, mass concentration, velocity) and the corresponding energy flux (e.g., heat flux, mass flux, shear stress). Those solutions are valid everywhere within the domain of interest and, which is of extreme importance, remain valid on the domain boundaries. Therefore, the method does not require one to solve for the entire domain and, hence, is a non-field analytical method. This method was shown to be extremely effective when applied to solving transient diffusion problems² and then, it was generalised by Frankel for finite domains.³ In papers^{4,5} it was extended to solve analytically ultra-fast heat transfer problems described by the hyperbolic heat conduction equation without source term as well as the dual-phase-lag model proposed by Tzou.⁶ The same method was then extended to problems of ultra-fast heat transfer in domains with moving boundaries.⁷ The case of solutions containing the heat source term was considered in.⁸ A generalisation of the method was proposed in.⁹

In the case, when the heat transfer process is modelled by Equation S1, the integral relation between the local values of temperature, T , and the corresponding heat flux, q'' , is given by

$$T(x,t) = T_0 + \frac{1}{\sqrt{\pi k \rho c_p}} \int_0^t \frac{q''(x,\zeta) d\zeta}{\sqrt{1-\zeta}} - \beta(t) \quad (\text{S2}),$$

where $\beta(t)$ is a contribution from the volumetric heat sink (see ² for details).

As can be seen from the first term in the right side of Equation S2, the effusivity of the matrix material given by

$$e = \sqrt{k \rho c_p} \quad (\text{S3})$$

is the main control parameter of the heat transfer process in question.

As was pointed out in^{10,11}, an analytical description of the effect, produced by randomly distributed sources/sinks, is an extremely challenging task, because such a description requires defining surface integrals over the entire boundary, which separates the matrix material from the PCM. To overcome this difficulty, instead of dealing with Equation S2, one can consider the following equation:

$$T(x,t) = T_0 + \frac{1}{\sqrt{\pi e_{obs}(t)}} \int_0^t \frac{q''(x,\zeta) d\zeta}{\sqrt{1-\zeta}} \quad (S4)$$

In the latter equations, the effect from the heat sinks is incorporated into the so-called effective (observed) effusivity. From comparing Equation S2 and S4, it becomes obvious that $e_{obs} \geq \sqrt{k\rho C_p}$.

The surface temperature (at $x=0$) is given by

$$T(0,t) = T_0 + \frac{1}{\sqrt{\pi e_{obs}(0,t)}} \int_0^t \frac{q''(0,\zeta) d\zeta}{\sqrt{1-\zeta}} \quad (S5).$$

Physically, this means that when phase transition does not take place, the presence of the PCM will have no effect on the overall thermal performance of the bulk material. Note also that the observed value of the effusivity does not remain constant, but must vary with temperature. Now, although no exact mathematical expression for the sink term is available, it is still possible to make some assumptions about the heat sink behavior from the physics of the problem. For instance, it is obvious that the effect of PCM becomes fully pronounced only when the value of temperature reaches the phase-change temperature. The effect disappears, if the temperature continues to increase afterwards. Hence, it is reasonable to assume that the transient behaviour of the heat sink, associated with the presence of PCM, can be modelled as a narrow pulse, which mathematically is equivalent to the Gaussian (bell-shaped curve or normal distribution), that is

$$S(t) \sim \exp\left[-\left(\frac{t - t_{phc}}{\sigma}\right)^2\right] \quad (\text{S6}),$$

where t_{phc} is the moment of time, at which the phase change occurs and the variance σ equals the average duration of the phase change process.

The C-therm thermal analyzer determine the effusivity of a sample matrix by the so called transient plane source method (TPSM). The principle of the method is based on local generation of heat at the interface between two phases that can be approximated to semi-infinite with unidimensional heat flow and no surface resistance. The change of temperature of the surface, $T_{(0,t)}$ following a step change in the supply of heat at the interface starting at time 0 depends on the effusivities of sensor (e_1) and sample phases(e_2):

$$T_{(0,t)} = T_0 + \frac{K\sqrt{t}}{e_1 + e_2} \quad (\text{S7})$$

Where K is a constant (which depends on the heat rate). Thus, if $T_{(0,t)}$ can measured accurately as a function of time, and K and e_1 are known based on pre-calibration, then the dependence of the surface temperature on time allows calculation of the effusivity of the sample matrix, e_2 .

Note that since Eqs. 2, 4 and 5 exhibit the same dependence on the effusivity and on the observed effusivity, then e_{obs} can be determined by the same way that the effusivity, e_2 is determined.

Observe from Figure 2, 3, 4, and 7, that the changes in the heat flow and physical properties follow a nearly Gaussian pattern with the maximal changes occurring at the phase-change (melting) temperature.

ii. Supplementary experimental details

GC-MS analysis of microcapsule extracts

GC-MS experiments were performed on 6890N gas chromatograph coupled to 5973 mass spectrometry detector (Agilent Technologies, USA). Chromatographic separation was achieved on DB-5MS capillary column (Agilent Technologies, USA; 25 m x 0.25 mm, 0.25 μm thickness) at He flow of 1 $\text{ml}\cdot\text{min}^{-1}$. Sample in dichloromethane (1 μl) was injected in splitless mode (inlet temperature 280 $^{\circ}\text{C}$); oven initial temperature was set up to 35 $^{\circ}\text{C}$ (hold time 4 min), then the constant gradient of 20 $^{\circ}\cdot\text{min}^{-1}$ was applied till 280 $^{\circ}\text{C}$ (hold time 8 min). Data acquisition and analysis was performed using Mass Hunter software (Agilent Technologies, USA). Reference materials mix, containing 10 $\text{mg}\cdot\text{L}^{-1}$ of toluene and 2 $\text{mg}\cdot\text{L}^{-1}$ of n-octadecane (both used in the CNT-PCM synthesis), was prepared by dissolution in dichloromethane.

Total ion chromatogram (TIC) of the reference materials is demonstrated in frame (a) of Figure S1, and the extracted ion chromatograms (EIC) for m/z 91 (a toluene fragment) and m/z 85 (octadecane fragment) are presented in frames (d) and (g) correspondingly.

In order to check whether there is residual toluene entrapped in the microcapsules during the synthetic steps, the CNT-PCMs samples containing 0.006 and 0.05 wt% CNT (5 mg each) were soaked in 1 ml of dichloromethane for 3 h and then filtered through 0.22 μm PTFE filter. The filtrate was injected to GC-MS using the same method as for reference substances solution. The TIC and EIC chromatograms (for m/z 91 and 85) for the extract of CNT-PCMs with 0.006 wt% and 0.05 wt% are shown correspondingly in frames (d-f) and (g-i) of Figure S1.

iii. Supporting tables and figures

Table S1. Effect of sub per mille CNT introduction on the effusivity and thermal conductivity.

	Inter microcapsule introduction of CNTs	Intra microcapsule introduction of CNTs
Far from phase transition e.g. at 12 and 40 °C	DECREASE Figure 4 and 7c	NO EFFECT Figure 2a
During phase transition	DECREASE Figure 4 and 7c	INCREASE Figure 2b and 7a

Table S2. Thermophysical properties of CNT-PCM powders with different CNT loadings.

CNT loading	Heat of fusion	Thermal conductivity at 12 °C	Thermal conductivity at 40 °C	Observed thermal conductivity at 28 °C	Observed effusivity	Thermal efficiency
wt %	$J \cdot g^{-1}$	$W \cdot m^{-1} \cdot K^{-1}$	$W \cdot m^{-1} \cdot K^{-1}$	$W \cdot m^{-1} \cdot K^{-1}$	$W \cdot s^{0.5} \cdot K^{-1} \cdot m^{-2}$	%
0	216	0.125	0.1	1.9	2687	90.6
0.001	223	0.118	0.097	3.0	3048	93.5
0.002	212	0.117	0.105	6.4	3470	88.9
0.006	218	0.12	0.1	11.9	3657	91.4
0.05	217	0.122	0.103	170.9	3690	91.0

0.05	208	0.11	0.098	>200.0	4164	87.2
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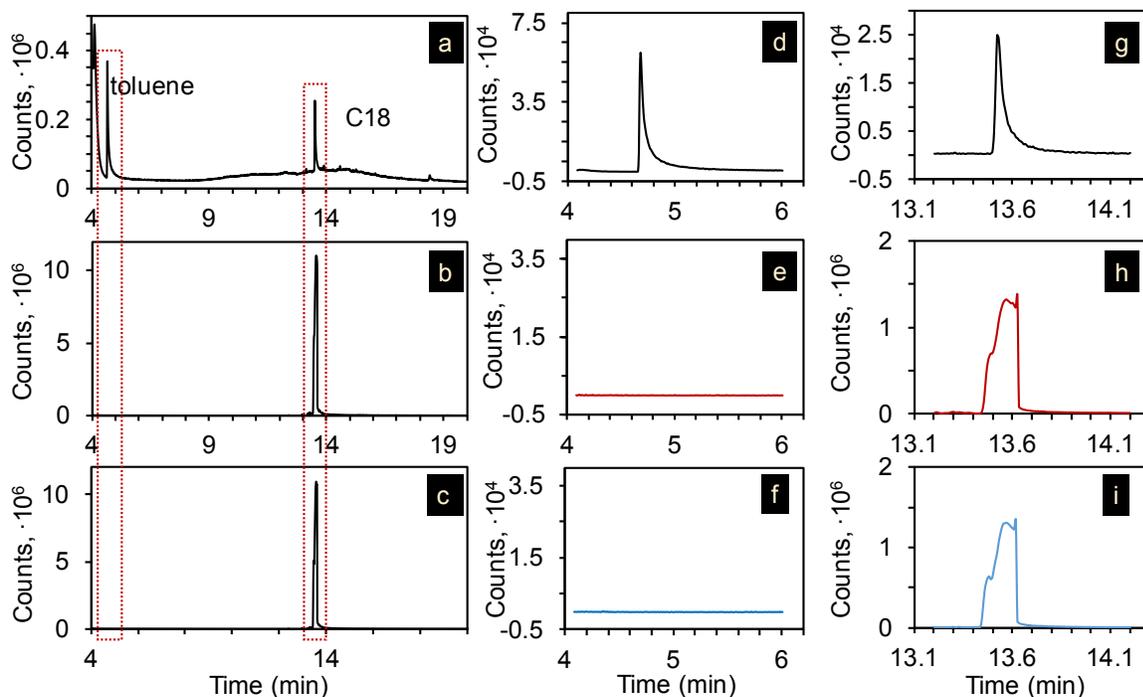


Figure S1. GC-MS analysis of CNT-PCM extracts. Frames (a-c) represent the total ion current (TIC) chromatograms, frames (d-f) represent the extracted ion chromatograms (EIC) for m/z 91 (characteristic fragment of toluene), frames (g-h) represent extracted ion chromatograms (EIC) for m/z 85 (characteristic fragment of octadecane). Upper row: reference materials in dichloromethane; middle row: dichloromethane extract of CNT-PCMs containing 0.006 wt%; lower row: dichloromethane extract of CNT-PCMs containing 0.05 wt% CNT.

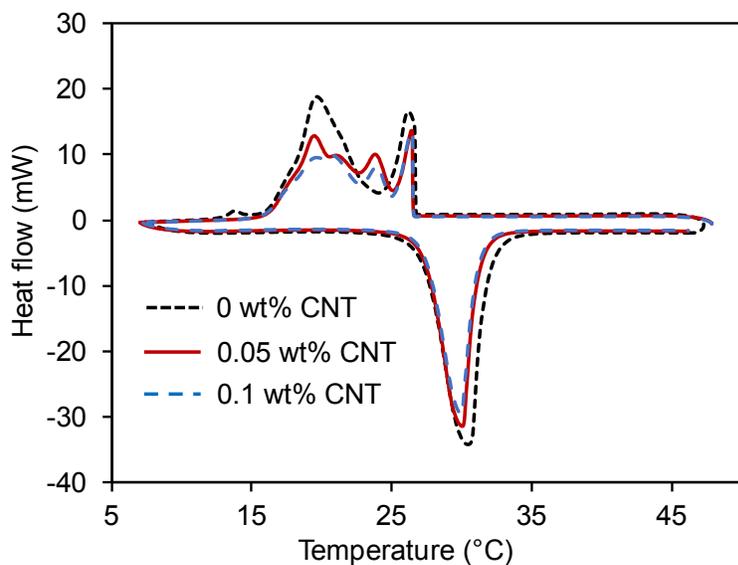


Figure S2. DSC thermograms of CNT-PCM powders. CNT loadings are 0, 0.05 and 0.1 wt%, temperature ramping rate $2\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

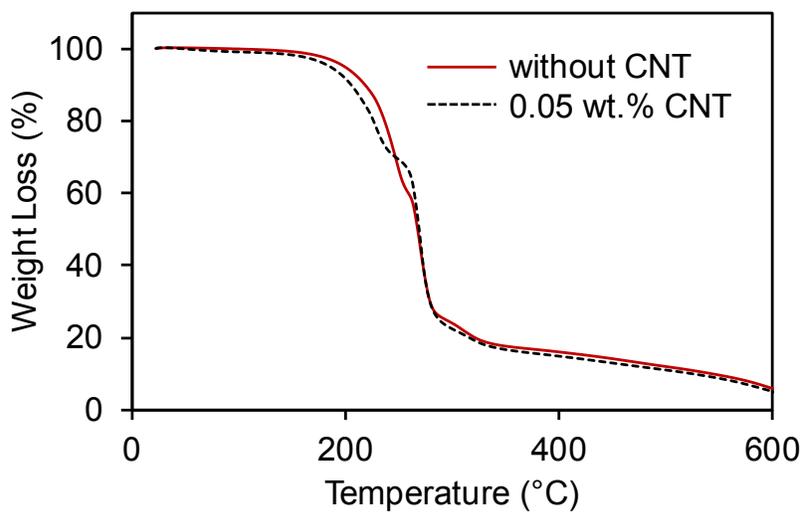


Figure S3. TGA thermogram of melamine-formaldehyde microencapsulated PCMs with 0.05 wt% CNTs (dashed black curve) and without CNTs ($10\text{ K}\cdot\text{min}^{-1}$ scan rate).

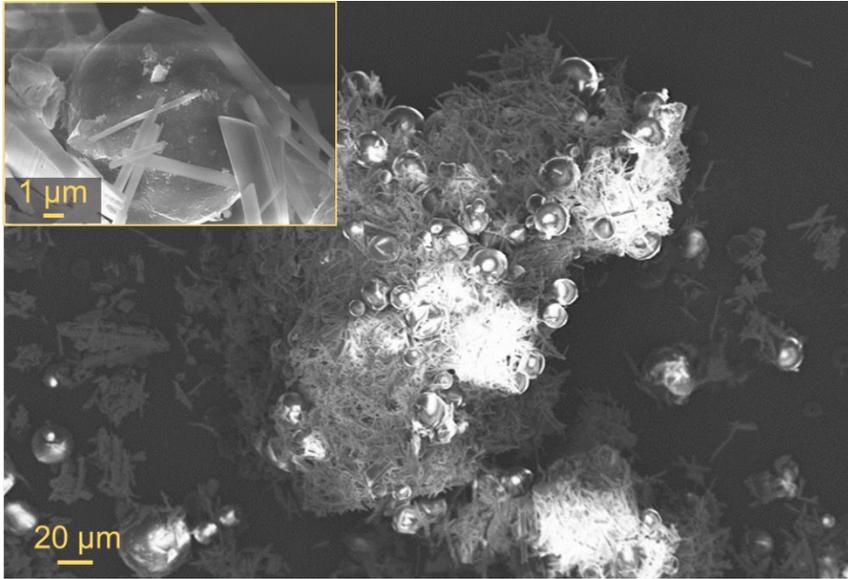


Figure S4. SEM micrograph of PCM loaded plasters showing that the PCM microcapsules are much larger than the gypsum whiskers. The inset zooms-in on a microcapsule. The sample was broken from a plaster board.

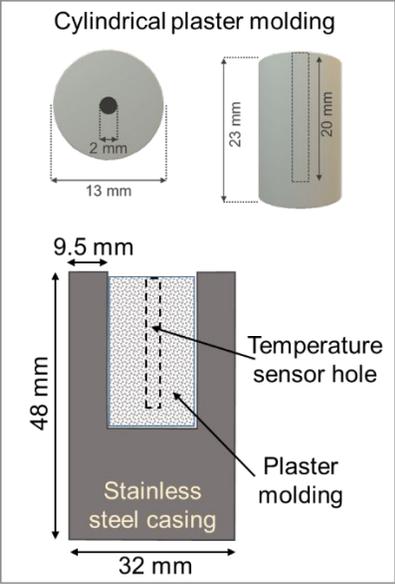


Figure S5. Scheme of the experimental setup for thermal buffering tests

iv. References for the supporting information

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