Numerical modelling of PCMs encapsulated in spherical shells using inverse enthalpy-temperature functions

O G Pop\textsuperscript{a*}, C A Iuga\textsuperscript{b,c}, L. Fechete Tutunaru\textsuperscript{d}, F. Domnita\textsuperscript{a}, M C Balan\textsuperscript{e}

\textsuperscript{a}Department of Building services engineering, Technical University of Cluj-Napoca, Romania.
\textsuperscript{b}Department of Pharmaceutical Analysis, Iuliu Hatieganu University of Medicine and Pharmacy, Cluj-Napoca, Romania.
\textsuperscript{c}Iuliu Hatieganu University of Medicine and Pharmacy, Proteomics and Metabolomics Department, MedFuture Research Center for Advanced Medicine, Louis Pasteur Street 4-6, Cluj-Napoca, 400012, Romania.
\textsuperscript{d}Department of Automotive Engineering and Transports, Technical University of Cluj-Napoca, Romania.
\textsuperscript{e}Department of Mechanical Engineering, Technical University of Cluj-Napoca, Romania

*E-mail: Octavian.Pop@insta.utcluj.ro

Abstract. The study presents a numerical model that uses the enthalpy method in order to solve the moving boundary problem and to predict the thermal behaviour of phase change materials during solidification and melting. The commercially available paraffin RT21 is considered as phase change material, and the thermophysical properties of the paraffin were determined by differential scanning calorimetry. An inverse enthalpy-temperature function was determined based on the results of the differential scanning calorimetry measurements in order to model the phase change process. The model was experimentally validated, and good agreement was found between the computed and measured results.

1. Introduction
Phase change materials (PCMs) have the potential of reducing energy consumption due to their capacity of storing high amounts of thermal energy at relative constant temperature, thus, eliminating the gap between energy availability and peak consumption periods [1]. Mathematical modelling is an important instrument to be employed in simulating the behaviour and in evaluating the efficiency of PCM based regenerative heat exchangers [2]. In [3, 4] it is considered that mathematical modelling should be accompanied by experimental research that generates appropriate data for validation, as confidence in existing models is relatively low. The accuracy of models is significantly influenced by: the variation of the thermophysical properties of the PCMs [5, 6], and the interior natural convection that occurs during melting [7]. The importance of the precision at which the thermophysical properties are determined when generating input data is studied in [5, 6]. Differential scanning calorimetry (DSC) is the main thermo-analytical method employed in order to determine the thermal behaviour of the PCM during phase change. Based on the thermal flux indicated by the DSC the variation of enthalpy or apparent heat capacity is determined and taken into account [8, 9].
The internal heat transfer mechanisms also play an important role in the modelling procedure. The solidification process is characterized by conduction, while melting is dominated by convection [7]. The most common method of modelling natural convection is by incorporating this heat transfer mechanism in an increased effective thermal conductivity [7].

The aim of this study is to present a mathematical model that estimates the enthalpy and temperature profile of PCMs encapsulated in spheres. The model uses inverse enthalpy-temperature functions to predict the thermal behaviour of the PCM during melting and solidification. An experiment is carried out in order to generate data and validate the mathematical model.

2. The mathematical model and enthalpy formulation

The enthalpy method was adopted in order to model the thermal behaviour of the PCM. The PCM undergoes a heat transfer process through forced convection using air as heat transfer fluid. The governing Fourier equation of the enthalpy profile within the spherical capsule is:

$$\rho_{PCM} \frac{\partial H_{PCM}(r,t)}{\partial t} = \frac{\lambda_{PCM}}{r^2} \left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial T_{PCM}(r,t)}{\partial r} \right) \right]$$

where $\rho_{PCM}$ [kg/m$^3$] is the density of the PCM, $H_{PCM}$ [J/kg] is the enthalpy of the PCM, $r$ [m] is the radial coordinate, $t$ [s] is the time, $\lambda_{PCM}$ [W/m·K] is the thermal conductivity of the PCM and $T_{PCM}$ is the temperature of the PCM.

The boundary conditions on the exterior surface of the sphere and at the centre are:

$$m_C c_C \frac{dT_C}{dt} = \alpha \cdot 4 \pi r_C^2 \cdot (T_{air} - T_{C,e}) - \lambda_{PCM} \cdot 4 \pi r_i^2 \cdot \frac{\partial T_{PCM}}{\partial r} \text{ at } r = r_C \text{ and } \frac{\partial T_{PCM}}{\partial r} = 0 \text{ at } r = 0$$

where $m_C$ [kg], $c_C$=840 [J/kg·K], $T_C$ [°C] are the mass, the specific heat capacity, and the temperature of the capsule, respectively, $\alpha$ [W/m$^2$·K] is the coefficient of forced convection calculated as recommended in [10], $r_{C,e}$ [m] and $T_{C,e}$ [°C] are the exterior radius and temperature of the capsule, respectively, $T_{air}$ [°C] is the air temperature and $r_i$ [m] is the inner radius of the capsule.

The explicit scheme was employed to numerically solve the governing equation, by computing the new value of the enthalpy based on the old values of enthalpy and temperature. The exterior boundary condition was solved explicitly neglecting the temperature gradient in the small thickness of the spherical wall. The number of spatial nodal and the time increment were set at 7 and 0.5 s, respectively. The effective thermal conductivity of the PCM in liquid phase during melting was determined using the following correlation $\frac{\lambda_{eff}}{\lambda_{PCM}} = 0.174R_a^{0.323}$ valid for $10^3< R_a<5 \cdot 10^6$ [7]. The Rayleigh number $R_a$ [-] is determined using $\delta$ [m], the gap between the solid front and the spherical wall, as characteristic length. A program, implementing the numerical solution, was developed in Matlab.

3. The thermophysical properties of the PCM and the enthalpy function

RT21 a paraffin wax produced by Rubitherm GmbH was considered in this study as PCM. The thermophysical properties were determined in a Mettler Toledo 822 DSC under dynamic atmosphere at an air flow rate of 25 ml/min. A 10.14 mg sample was sealed in a 40 μL aluminium crucible and scanned in the temperature range of (6-27) °C, at a cooling and heating rate of 0.1 K/min. Figures 1 and 2 present the DSC results. The PCM has the following properties: density in solid/liquid phase $\rho_{PCM}$=880/770 kg/m$^3$, the specific heat capacity $c_{PCM}$=2 kJ/kg·K, the thermal conductivity $\lambda_{PCM}$=0.2 W/m·K, the cinematic viscosity $\nu_{PCM}$= 25.71·10$^{-6}$ m$^2$/s, and the latent heat for solidification/melting $L_{PCM}$ = 136.33/138.00 [kJ/kg]. The start and stop temperatures of the PCM for the solidification process are 23.44 °C and 6.00 °C, respectively. For the melting process the start and stop temperatures are 6.66 °C and 24.13 °C, respectively. At these temperatures the DSC curve separates from the baseline. The enthalpies corresponding to the start/stop temperatures for the solidification process are 181.818/12.228 kJ/kg and for the melting process are 13.445/179.582 kJ/kg. These enthalpies also represent the validity interval of the inverse temperature-enthalpy function.
In order to compute the PCM temperature based on the resulting enthalpy variation, an inverse exponential enthalpy-temperature function was considered. For example, the inverse enthalpy-temperature function for melting is as follows:

\[
T_{PCM} = \begin{cases} 
\frac{H_{PCM}}{C_{PCM}} f_{PCM} & \text{for } T_{PCM} \leq T_{s,m} \\
T_{s,m} + \frac{H_{PCM} - C_{PCM} T_{s,m}}{C_{PCM}} & \text{for } T_{PCM} < T_{s,m} \leq T_{st,m} \\
T_{st,m} & \text{for } T_{PCM} \geq T_{st,m}
\end{cases}
\] (3)

where \(T_{s,m}[\degree C]\) and \(T_{st,m}[\degree C]\) are the melting temperatures at the start and stop points, respectively. In equation (3), \(H_{PCM}\) is expressed in kJ/kg. A similar system can be developed for the solidification process. The coefficients \(y_0, A_1, A_2, C_1, C_2\) are the results of a curve fitting process carried out in OriginLab. The values of the coefficients for solidification/melting are: \(y_0=24.84/30.82, A_1=-8.36/-19.40, A_2=-17.43/-15.14, C_1=-17.08/-19.91\) and \(C_2=-70.05/-216.64\).

4. The experimental setup

An experimental latent heat thermal storage was used to generate data for validation. The setup consists of a cylindrical evacuated double glass wall housing a row of 11 spheres containing RT21, an air-cooling system based on Peltier modules 136 W and cooled with air and water, a DC powered ventilator and a hot air gun. Figures 3 and 4 present the setup in schematic form and in the laboratory, respectively.
5. Results and discussions

Two solidification experiments were carried out: at the air velocities of 0.65 and 0.80 m/s and the mean inlet air temperature after stabilization of 2.20 and 2.13 °C, respectively. Two melting experiments were carried out at the air velocities of 0.75 and 1.02 m/s and the mean inlet air temperatures after stabilization of 44.98 and 38.46 °C, respectively. The numerical values were compared with the measured data. The deviations were evaluated by the following metrics: mean bias error (MBE) and root mean square error (RMSE).

Figures 5 and 6 present the graphical validation of the model for the highest and lowest values of the MBE and RMSE at solidification. The measured air inlet temperature (Θin) is also represented.

The numerical data is in good agreement with the measured values. The best agreement is achieved at the last sphere (ΘS11) as opposed to the first sphere where the highest deviations were observed. Better agreement is achieved at lower air velocities. Figures 7 and 8 present the graphical validation of the model for the highest and lowest values of the MBE and RMSE at melting. The measured air inlet temperature (Θin) is also represented.

The numerical data is in good agreement with the measured values. Figures 9 presents the values of the RMSE and MBE for both solidification and melting. It can be observed that the errors in the case of melting are significantly lower than in the case of solidification for all the considered air velocities.
In the case of solidification, it can be observed that the highest values of the deviations are for the first sphere, near the inlet, and the lowest values are for the last sphere, near the outlet. The errors decrease towards the outlet. No error variation trend can be identified in the case of melting.

6. Conclusions
A mathematical model was developed that employs the enthalpy method in order to estimate the temperature variations of PCM encapsulated in spherical shells. The thermophysical properties of the PCM were determined using the DSC dynamic method. Inverse enthalpy-temperature functions were obtained based on the measured data in order to take into account the thermal behaviour of the PCM during phase change. The model also takes into account natural convection during melting. The model was found to be in good agreement with the measured data. The best agreement was found at melting. Further accuracy analyses for different PCMs and at different air velocities and temperatures will be carried out in future studies. Future research will also be focused on using the mathematical model in order to study the thermal behaviour of latent heat regenerators in different operating conditions.

7. References
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