Development of Correlations of the Charging and Discharging Times of Carboxyl-Functionalized Multi-Walled Carbon Nanotubes (MWCNT-COOH) and Water with and without Polyethylene Glycol in Spherical Encapsulation

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Abstract: This investigation shows the results of a coupled numerical and experimental study on the solidification and melting of spherical capsules and the development of correlations for solidification time and melting time with parameters that impact the complete phase change time of nanofluids and water with and without polyethylene glycol inside plastic spherical capsules. Experiments included the investigation of different configurations of plastic spherical capsule diameters, external temperature, the initial temperature of phase change material (PCM), and PCMs. The PCMs used were water, water with a concentration of polyethylene glycol from 10% to 50%, and multi-wall carbon nanotubes functionalized with carboxylic acid group (COOH-MWCNT) with MWCNT at 0.125, 0.25, 0.5, and 1.0%. The simplified model was validated with available experimental results from the present work and from the literature, showing maximum deviations in the range of 0.25 to 12%. The simulation results showed that the use of nanoparticles in the base fluid increased the velocity of the solidification and melting processes and shortened the time for complete solidification and melting. The correlations for the complete solidification time and complete melting time followed the experimental results, with a maximum deviation of about 6%, which proves an excellent concordance of the correlations with the experiments.

Keywords: solidification and melting of PCM; plastic spherical capsule; carbon nanotubes; storage latent heat; correlations; time to complete phase change

1. Introduction

Recent reported results and new tendencies show that energy exploitation and demand are increasing at a fast rate with the eminent results of increased global warming and emissions of offensive gases. Due to national development and industrialization expansion in most developing countries, recent governmental declarations have indicated flexible commitment regarding the control of emissions and global warming. This implies that tendencies toward energy exploitation are present, but will hopefully exist at smaller rates in the best scenario. Available energy is a measure of wellness and excellent living standard. However, with limited conventional energy sources and clear tendencies of their eminent depletion, the search for renewable versions of dominant technologies to sustainably replace conventional resources is still going on. Solar and wind resources...
are among the favorite candidates, and are widely available and used in most countries. Because of their intermittent nature, they need energy storage systems to ensure their effective and efficient utilization. In the case of solar energy, thermal storage is the most used technique because of its simple technology and efficiency in storing, keeping and recovering energy [1,2].

To reduce energy consumption, mainly carbon dioxide emissions, the use of solar energy and nanofluids combined with latent heat storage has appeared as a very innovative and attractive solution due to advantages such as constant temperature, high storage and heat supply, and repeatable use without degradation [3].

Latent heat thermal energy storage systems have been extensively investigated in recent years. Numerous studies report the loading and unloading techniques of latent heat storage systems with various phase change materials. Most of these studies were carried out in the temperature range for domestic applications from 0 °C to 60 °C. The formulation, modeling and numerical treatment commonly used the enthalpy formulation [4,5] because of its simplicity, easiness of implementation, and adequacy for treating complicated geometries and different boundary conditions.

Energy storage systems using the latent heat concept are preferred due to their higher energy storage capacity per unit volume [6] when compared to sensible heat, and their nearly isothermal behavior during the phase change process. According to MacDevette and Myers [7], the performance of latent heat storage systems is strongly related to the thermal characteristics of phase change materials that are responsible for energy storage and release. In addition to application in latent heat thermo-accumulation systems, phase change materials are also applied in the building sector, heat removal from electronic components, food conservation, and the transport and automotive industry.

Systems that use latent heat have received a lot of attention from researchers in the field [8,9]. A particular application of this energy storage concept is ice banks, used in integrated refrigeration and air conditioning systems. The phase change phenomenon is rooted in geometry. Many research studies have been devoted to investigating, numerically and experimentally, the effects of encapsulation geometrical parameters in cylindrical, spherical and flat capsules [10–14]. Arunachalam [15] conducted an extensive review of container geometry, enhancement techniques, and applications for latent heat storage.

Spherical capsule enclosures are widely used to encapsulate PCMs due to the simplicity of packaging and ease of manufacture. Regin et al. [16] carried out an extensive review of works on the heat transfer characteristics of a thermal energy storage system in PCM capsules. Bedecarrats et al. [17,18] studied the performance of a test plant with phase change thermal energy storage using spherical capsules. Other researchers have numerically and experimentally investigated the phase change process on spherical capsules in a latent heat system [19–23].

In recent years, due to rapid advances in the field of nanotechnology, nanoparticle PCM has been used by researchers to change and/or improve the mechanical, electrical and thermal properties of PCMs. According to Angayarkanni and Philip [24], nanofluids have some characteristics that are completely different from the dispersion of particles of bigger physical scale. Comparing nanofluids with other traditional refrigerants, nanofluids exhibited higher thermal conductivity. Furthermore, nanofluids produce a lower pressure drop, which is quite interesting in heat transfer applications.

Keblinski et al. [25] studied the heat flux with suspended nanoparticles. The results showed that nanofluids have superior thermal conductivity compared to other PCMs. They have also shown that nanofluid technology provides chances for the development of nano-technology-based refrigerant fluid for various engineering innovations and medical applications.

Solangi et al. [26] reported that the main difficulty in preparing a nanofluid is its low stability. The stability of a nanofluid requires uniformity in the dispersion of the nanoparticles in the base fluid. The thermophysical properties vary over time during
practical applications. For selection and applications of nanofluids in the field of heat transfer, consideration must be given to low-cost, long-term stability and excellent fluidity.

Fan and Khodadadi [27] carried out an experimental study to improve thermal conductivity and unidirectional accelerated freezing with CuO/cyclohexane nanofluids. Xiang and Drzal [28] and Yavari et al. [29] dispersed graphene in different solutions and found improvements in thermal conductivity.

Kumar et al. [30] performed an experimental analysis on thermal conductivity with porous aluminum and salt hydrate as a PCM in order to increase the equilibrium of the system and the degree of overcooling.

Melting points below 30 °C have been widely used in the refrigeration of food storage environments. Polyethylene glycol has a melting temperature range of 20–30 °C. Additionally, most of the thermal energy storage studies for the use of waste heat in the air conditioning of buildings work with a heating temperature of 25–35 °C. In this work, nanofluids were used. Considering the focus on domestic applications and the phase change temperature ranges of the other PCMs used, a common working fluid temperature range was chosen and fixed for all the PCMs of the present paper to compare and to give reliability to the experiments. The working range of temperatures adopted for solidification and melting was similar to those of Ismail and Moraes [10] and Lago et al. [31].

In the numerical investigation, a simulation algorithm was built based on the finite difference method with moving mesh. Considering that domains are variable in the solid and liquid regions, the use of a mobile mesh, which adjusts to each time interval, facilitates the numerical calculation since the solid–liquid interface is always located at one of the mesh nodes. The heat transfer process is considered as conductive when the solid and liquid phases are unique, and conductive with phase change when the two phases coexist. The convective effect present in the liquid region of the PCM is treated by means of an effective thermal conductivity coefficient that replaces the value of the liquid conductivity in the energy equation, as in Bedecarrats et al. [17].

Therefore, the purpose of this article is to experimentally and numerically investigate the time to complete the melting and solidification of functionalized carbon nanotubes under conditions of different plastic spherical capsule diameters, including bath temperature and initial PCM temperature, and use the experimental results to develop correlations for thermal applications.

As a contribution to the literature, correlations were developed for the complete solidification. Melting times showed a maximum difference of about 6%, while the correlation of the melting time showed a difference of about 4.8%. The simplified model validated with experimental results represents a valuable contribution for quick estimates of melting and solidification times in thermal storage systems with maximum deviations in the range of 0.25 to 12%. The correlations developed are useful for latent heat thermal storage system projects, as well as for other applications such as the numerical validation of PCM simulation studies in spherical capsules.

2. Experimental Setup

The test equipment used in this study was composed of a solidification bench and a melting bench. Both are shown schematically in Figures 1 and 2. The solidification system was a commercial vapor compression unit with a cooling coil, cooling tank and a pumping circuit, as shown in Figure 1. The conventional refrigeration unit delivered refrigerant to the cooling coil to cool the alcohol to the desired temperature for the test. The cooled alcohol was then fed to the constant temperature bath where the plastic spherical capsule was submersed. A calibrated thermocouple was inserted in the alcohol thermal bath, another one was fixed to the external surface of the capsule, and a third thermocouple was fixed at the center of the plastic spherical capsule to follow the evolution of the temperature at the center of the shell.
Figure 1. The solidification experimental workbench.

Figure 2. The melting experimental workbench.

The size of the thermal bath tank was 350 × 330 × 280 mm. The thermocouple in the tank was placed on the opposite side the heat transfer fluid entering the tank to check that the temperature was the same at the inlet and outlet of the heat transfer fluid. The hysteresis of the temperature controller was 0.3 °C for both cooling load and heating load. The desired temperature evolution was that of the center of the sphere, even so, a thermocouple was placed on the surface of the spherical capsule to analyze the behavior of the temperature profile on the outer surface of the capsule. Thus, the heat transfer model of this domain was based on pure conduction and considered the boundary conditions of convection on the external surface of the plastic spherical capsule. A centrifugal pump and globe valves were used to circulate and control the heat transfer fluid (alcohol) through the circuit.

Figure 2 presents the experimental workbench of the melting process. This heating system consisted of a main tank with dimensions of 350 × 330 × 280 mm where the thermal bath was located and was thermally insulated with a polystyrene sheet. In test main tank, the spherical plastic capsules were lifted on a support. The spherical capsule had two T-type thermocouples located in the center of the plastic spherical capsule and on its outer surface to monitor the shell temperature. Temperature measurements were made in the thermal bath to ensure temperature control and were assisted by a thermostat with an accuracy of ±1 °C and a resolution of 0.1 °C. For heating the thermal bath, there was a tank
with two electrical resistances of 300 W each. Finally, for the circulation and control of the heat transfer fluid through the circuit, pumps and globe valves were used.

Thermocouples were calibrated with certified precision thermometers and were accurate to within ±0.5 °C. Plastic spherical capsules of diameters of 0.055 m, 0.076 m, 0.106 m, and 0.131 m were used with pure water or a mixture of polyethylene glycol and water, or an aqueous solution of COOH-MWCNT, according to the last process test. The investigation carried out was for modular cold storage units for domestic applications. Commercial spherical plastic capsules of size 0.055–0.131 m was investigated because of their abundance, easy acquisition, low cost, and their environmental impact.

Calibrated copper–constantan thermocouples (Type T) with uncertainty ±0.5 °C were used to capture measurements in spherical capsules. A data acquisition system was used to capture temperatures.

The PCMs inside the plastic spherical capsules were pure water, polyethylene glycol concentration (10 to 50%) in water, or concentrations of nanoparticles (nanofluids with MWCNT at 0.125; 0.25; 0.5 and 1.0% m/m) in solution propylene glycol antifreeze of 50% m/m. Table 1 shows standards of the experimental variables. The thermophysical properties of PCMs are shown in Table 2 [31,32].

### Table 1. Standards of the experimental variables.

| Temperature of the thermal bath during solidification | −18 °C, −12 °C, −10 °C, −5 °C |
| Volume flow rate during the solidification | 0.0009 m³/min |
| Temperature of the thermal bath during melting | 26 °C, 28 °C, 30 °C, 32 °C |
| Volume flow rate during the melting | 0.002 m³/min |
| Diameter of plastic spherical capsule | 0.055, 0.076, 0.106, 0.131 m |

### Table 2. Properties of PCMs [31,32].

<table>
<thead>
<tr>
<th>PCM</th>
<th>Density—( \rho ) (g/cm³)</th>
<th>Thermal Conductivity—( k ) (W/m·K)</th>
<th>Specific Heat—( C_p ) (J/kg·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (liquid phase)</td>
<td>0.999</td>
<td>0.56</td>
<td>4210</td>
</tr>
<tr>
<td>Water (solid phase)</td>
<td>0.917</td>
<td>2.25</td>
<td>2040</td>
</tr>
<tr>
<td>Polyethylene glycol</td>
<td>1.128</td>
<td>0.06</td>
<td>-</td>
</tr>
<tr>
<td>Nanofluid (COOH-WMCNT)</td>
<td>0.5 a 3.5</td>
<td>3180 (multi-wall)</td>
<td>-</td>
</tr>
</tbody>
</table>

The carboxyl-functionalized multi-walled carbon nanotubes (MWCNT-COOH) were chosen because they are interesting alternatives for heat transfer applications. Propylene glycol is a fluid widely used in antifreeze solutions within the food industry due to its non-toxic character and low solidification temperature; however, despite being a fluid used for heat transfer, its thermophysical properties impair the efficiency of the process, mainly due to the low thermal conductivity and high viscosity of these fluids. The dispersion of MWCNT-COOH positively influences the thermal conductivity and density of these pure fluids, as well as in aqueous solutions. Nanotubes dispersed in propylene glycol have a heat transfer coefficients greater than 60% compared to water.

The carbon nanotubes were purchased from Timesnano located in the Chinese Academy of Sciences. With these nanoparticles, functionalized nanotubes (COOH-MWCNT) were produced.

The samples were dispersed by the Prob TT13 sonicator of the Sonoplus HD 2200 equipment, which allowed the change in the sonication power in a range of 20 to 200 W with a frequency of 20 kHz. After preliminary tests, the sonication power was adjusted to 100 W (Watts) in 250 mL (milliliters) of fluid for all samples produced with a minimum of 40 min of sonication time for samples with carbon nanotubes. The procedure was carried out in an ice bath supported by a refrigeration system to keep the temperature low, preventing the nanofluid from reaching more than 35 °C at the end of the sonication period.
Visual assessment allowed us to identify whether nanofluids had sufficient stability—indicated by visible sedimentation at 48 h—to characterize their properties at higher particle concentrations. Samples that did not show stability due to van der Walls forces (polar medium/non-polar particle) were subjected to different stabilization methods to evaluate the effects on thermophysical properties. More details on the preparation of this PCM can be found in Freitas’ thesis [32].

3. Mathematical and Numerical Model

During the solidification process inside the plastic spherical capsule submersed in the tank full of working fluid at constant temperature lower than the freezing temperature of the phase change material, the working fluid exchanged energy with the PCM contained in the capsule, initially causing a decrease in its temperature until the moment when the first solidification layer was formed inside the shell. At later stages, solidification of the PCM progressed inside the plastic spherical capsule where the solid and liquid phases coexisted, until the moment when the last fraction of liquid was frozen. Finally, the temperature of the material when solidified was further reduced until the temperature of the entire plastic spherical capsule was the same as that of the working fluid. During the phase change process, there was a solidification front moving from the capsule internal wall towards its center. In the mathematical model, the three steps of the phase change process were considered.

The heat transfer process was considered as conductive when the solid and liquid phases were unique, and conductive with phase change when the two phases coexisted. The convective effect presented in the liquid region of the PCM was treated by means of an effective thermal conductivity coefficient that replaced the liquid conductivity value in the energy equation, as in Bedecarrats et al. [18].

Figure 3 illustrates each of the phases (liquid and solid layer of the phase change material). The thermal resistances $R_s$, $R_c$ and $R_{ext}$ are given by:

$$R_s = \frac{1}{4\pi k_s} \left( \frac{1}{r_{sf}} - \frac{1}{r_{int}} \right)$$

$$R_c = \frac{1}{4\pi k_c} \left( \frac{1}{r_{int}} - \frac{1}{r_{ext}} \right)$$

$$R_{ext} = \frac{1}{4\pi h r_{ext}^2}$$

where $R_s$ is the thermal resistance equivalent to the solid phase, $R_c$ is the thermal resistance equivalent to the spherical capsule, $R_{ext}$ is the thermal resistance equivalent to the external condition, $k_s$ is the thermal conductivity of the solidified material, and $k_c$ is the thermal conductivity of the capsule.

In pure cooling processes, which correspond to the first and third stages of the process, the governing equation of conduction and its respective boundary conditions can be written as:

$$\frac{\partial T_i}{\partial t} = \frac{k_i}{\rho_i c_i} \left( \frac{2}{r} \frac{\partial T_i}{\partial r} + \frac{\partial^2 T_i}{\partial r^2} \right)$$

$$Q = -k \frac{\partial T}{\partial r} = \frac{T - T_{\infty}}{r_{ext} - r_{int}} \left( \frac{r_{int}}{r_{ext} - r_{int}} \right) + \left( \frac{r_{int}}{r_{ext}} \right)^2 \frac{1}{\pi}$$

$$\frac{\partial T_i}{\partial t} = 0, \quad r = 0$$

In Equation (4), $k$, $\rho$ and $c$ are the thermal conductivity, density and specific heat, respectively. However, the values of the variables must correspond with the condition
of the phase change material, i.e., completely liquid in the first stage of the process and completely solid in the third stage. The temperature, time and radial coordinate in the fixed coordinate system are represented by \( T \), \( t \) and \( r \), respectively. In Equation (5), the thermal conductivity of the capsule material and the heat transfer coefficient on the external surface are \( k_c \) and \( h \), respectively.

\[
\frac{\partial T_s}{\partial t} = \frac{k_s}{\rho_s c_s} \left( \frac{2}{r} \frac{\partial T_s}{\partial r} + \frac{\partial^2 T_s}{\partial r^2} \right), \quad r_{sf} < r < r_{int} \tag{7}
\]

Liquid region:

\[
\frac{\partial T_l}{\partial t} = \frac{k_l}{\rho_l c_l} \left( \frac{2}{r} \frac{\partial T_l}{\partial r} + \frac{\partial^2 T_l}{\partial r^2} \right), \quad 0 < r < r_{sf} \tag{8}
\]

Boundary conditions:

\[
-k_s \frac{\partial T_s}{\partial r} = \frac{T_s - T_\infty}{r_{ext} - r_{int}} - \frac{\left( r_{int} \right)}{h} \left( \frac{\partial T_l}{\partial r} \right) \bigg|_{r=r_{int}} \tag{9}
\]

\[
\frac{\partial T_l}{\partial t} = 0, \quad r = 0 \tag{10}
\]

\[
T_s = T_l = T_{mf}, \quad r = r_{sf} \tag{11}
\]

To calculate the position of the interface \( r_{sf} \) at each instant of time, an energy balance is made at the solid–liquid interface to obtain an additional equation. Here, the variable \( L \) represents the latent heat of the phase change material.

Figure 3. Schemes of the phase change processes within plastic spherical capsules: (a) solidification of PCM; (b) melting of PCM.

In the second moment, the phase change occurs through the heat transfer in the system and is characterized by the coexistence of both the liquid and solid phases in two domains, interconnecting the solutions through the boundary condition at the interface. Equations that govern the phenomenon and their respective boundary conditions can be written as:

Solid region:

\[
\frac{\partial T_s}{\partial t} = \frac{k_s}{\rho_s c_s} \left( \frac{2}{r} \frac{\partial T_s}{\partial r} + \frac{\partial^2 T_s}{\partial r^2} \right), \quad r_{sf} < r < r_{int} \tag{7}
\]

Liquid region:

\[
\frac{\partial T_l}{\partial t} = \frac{k_l}{\rho_l c_l} \left( \frac{2}{r} \frac{\partial T_l}{\partial r} + \frac{\partial^2 T_l}{\partial r^2} \right), \quad 0 < r < r_{sf} \tag{8}
\]

Boundary conditions:

\[
-k_s \frac{\partial T_s}{\partial r} = \frac{T_s - T_\infty}{r_{ext} - r_{int}} - \frac{\left( r_{int} \right)}{h} \left( \frac{\partial T_l}{\partial r} \right) \bigg|_{r=r_{int}} \tag{9}
\]

\[
\frac{\partial T_l}{\partial t} = 0, \quad r = 0 \tag{10}
\]

\[
T_s = T_l = T_{mf}, \quad r = r_{sf} \tag{11}
\]
The interface velocity and the rate of solidified mass which can be written as:

\[
\dot{m} = \rho \frac{\partial V}{\partial t}
\]  

(12)

\[
\frac{\partial V}{\partial t} = A \frac{dr_{sf}}{dt}
\]  

(13)

\[
\dot{m} = \rho A \frac{dr_{sf}}{dt}
\]  

(14)

\[
A \left( k_s \frac{\partial T_s}{\partial r} - k_l \frac{\partial T_l}{\partial r} \right) = \left( \rho A \frac{dr_{sf}}{dt} \right) L
\]  

(15)

The energy balance can be written as:

\[
k_s \frac{\partial T_s}{\partial r} - k_l \frac{\partial T_l}{\partial r} = \rho L \frac{dr_{sf}}{dt}, \quad r = r_{sf}
\]  

(16)

Introducing \( s(t) \) as the position variable of the instantaneous interface position, and the following dimensionless parameters,

\[
s(t) = 1 - \frac{r_{sf}}{r_{int}} \quad \text{or} \quad \frac{r_{sf}}{r_{int}} = 1 - s(t)
\]  

(17)

\[
\tau = \frac{at}{r_{int}^2}
\]  

(18)

\[
Bi = \frac{hr_{int}}{k_{sol}}
\]  

(19)

\[
Ste = \frac{C_p(T_f - T_\infty)}{L}
\]  

(20)

one can write:

\[
\tau = \frac{1}{Ste} \left[ \frac{1}{6} + \frac{1}{3Bi} \left( \frac{r_{int}}{r_{ext}} \right)^2 \left( 1 - (1 - s(t))^3 \right) + \frac{k_s}{3k_c} \left( 1 - (1 - s(t))^3 \right) \right] \frac{r_{ext} - r_{int}}{r_{ext}} - \left( 1 - s(t) \right)^2 \times \left[ \frac{1}{2} - \frac{(1-s(t))^2}{3} \right]
\]  

(21)

where \( \tau \) is the dimensionless time.

At the start of the solidification process, \( s(t) \ll 1 \), and Equation (21) above becomes:

\[
\tau = \frac{1}{Ste} \left( 1 - (1 - s(t))^3 \right) \times \left[ \frac{1}{3Bi} \left( \frac{r_{int}}{r_{ext}} \right)^2 + \frac{k_s}{3k_c} \left( \frac{r_{ext} - r_{int}}{r_{ext}} \right) \right]
\]  

(22)

The solidified mass at any instant is calculated from the following Equations:

\[
M_{sol,t} = \left( \frac{4}{3} \pi \left( r_{int} - r_{sf} \right) \right) \rho_s
\]  

(23)

\[
M_{total} = \frac{4}{3} \pi r_{int}^3 \rho_s
\]  

(24)

\[
FM_t = \frac{M_{sol,t}}{M_{total}}
\]  

(25)

The heat convection coefficient on the outer surface of the spherical capsule is obtained from the correlation of the mean Nusselt number (\( Nu \)). For a spherical capsule subject to an external flow with a speed of 1 m/s, whose temperature is different from that of the surface of the capsule, convective currents appear as products of the temperature difference.
The average heat transfer coefficient for this physical situation can be obtained from the correlation [33]:

$$Nu = \frac{hD}{k_{fluid}} = 2 + 0.6Re^{0.5}Pr^{0.33}$$  \hspace{1cm} (26)$$

This mathematical model can be numerically solved with the elaboration of an algorithm based on finite differences and the implicit method. Figure 4 shows the domains that were used in the solidification and melting processes. One domain illustrates the solid zone and the other domain illustrates the liquid zone, and the discretization of these domains occurs individually. In the solidification process, at each time step, the mesh of the solid region expands as the mesh of the liquid region contracts. When the pure solidification process occurs, where there is only one of the phases, a fixed mesh in the domain is used. In the melting process, at each time step, the mesh of the liquid region expands as the mesh of the solid region contracts, and when all the mass has merged, only a fixed mesh in the domain is used. Mesh tests were performed to determine the ideal size, which justified the independence of the numerical simulation results in the physical model studied reliably and with less processing time. The mesh test was performed considering the time of complete solidification and melting, which occurred when the center of the phase change material in the spherical capsule underwent the phase change process. In the mesh calibration test, a mesh of 10, 20, 30, 50, 70, 90 and 100 subdivisions in the radial direction of the sphere were considered, starting from the inner surface to the center, covering the entire surface of the sphere. The permissible margin of error for the value of the difference between solidification and melting times was one percentage point (0.01 or 1%). In the mesh of 90 subdivisions, the error was 0.98%, which was the first value that fit within the defined error margin. From 90 subdivisions, the values of the differences decreased, reaching negligible values when compared with the elapsed time of the process.

![Figure 4. Numerical scheme of the solidification and melting processes within plastic spherical capsules.](image-url)

Figures 5 and 6 show comparative results of numerical predictions of the numerical model and experimental tests performed to validate the model. Experimental curves indicate a degree of overcooling that does not exist in numerical simulations. The degree of overcooling depends on the temperature of the external fluid and the size of the capsule. Figure 5 shows an average deviation of about 7%, while Figure 6 shows an average deviation of about 12%. On the other hand, Figure 7 shows an average deviation of 2%. The calculation of the deviation is given by the following Equation:
\[ \sigma = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n}} \]  

(27)

Figure 5. Numerical and experimental temperature change in the solidification process of the 76 mm diameter plastic spherical capsule.

Figure 6. Numerical and experimental temperature change in the solidification process of the 106 mm diameter plastic spherical capsule.

Figure 7 shows a comparison of the evolution of the temperature at the center of the plastic spherical capsule compared with the experimental results from [10]. The results seem to agree well with the maximum deviation of 1.9%.

Figure 8 compares the numerical prediction from the present work with the experimental results from [10]. The concordance is excellent, showing a maximum deviation of 1.1%.
were 0.050, 0.076, 0.106, and 0.131 m. For the melting process, the bath temperatures of the working fluid were 26 °C, 28 °C, 30 °C, and 32 °C.

4. Results and Discussion

The numerical code presented satisfactory comparative results with the literature, and hence can closely represent the behavior of a physical prototype. The developed code can provide a cheap and validated means of predicting the thermal parameters of the phase change process within a spherical container in comparison with costly experimental tests.

In the solidification process, the cold temperatures of the working fluid used were −5, −10, −12, and −18 °C, while the diameters of the investigated plastic spherical capsules were 0.050, 0.076, 0.106, and 0.131 m. For the melting process, the bath temperatures of the working fluid were 26 °C, 28 °C, 30 °C, and 32 °C.
The PCMs tested were pure water, polyethylene glycol concentration (10 to 50%) in water, and concentrations of nanoparticles (nanofluids with MWCNT at 0.125; 0.25; 0.5; and 1.0% m/m) in a solution of propylene glycol antifreeze of 50% m/m.

4.1. Times for Complete Solidification and Melting

Figure 9 presents the temperature change at the center and on the surface of the spherical capsule filled with water during the solidification process. Figure 9a shows the temperature change at the center of the 131 mm spherical capsule during the solidification process at −18 °C. Figure 9b shows the temperature change at the center of the 50 mm spherical capsule during the solidification process at −12 °C. The time to complete solidification is considered to be the time span between the beginning and end of the constant temperature range. As can be seen in Figure 9a,b, the temperature at the center of the plastic spherical capsule progressively drops as a result of the transfer of heat by conduction and convection in the liquid phase change material within the spherical capsule until it reaches the solidification temperature of zero degrees Celsius. The temperature remains at 0 °C until the entire mass of the PCM is solidified, and then drops again as a consequence of thermal conduction.

![Figure 9](image-url)
Figure 10 presents the temperature change at the center and on the surface of the spherical capsule filled with polyethylene glycol during the solidification process. Figure 10a shows the temperature change at the center of the 131 mm spherical capsule during the solidification process at $-18^\circ$C. Figure 10b shows the temperature change at the center of the 106 mm spherical capsule during the solidification process at $-18^\circ$C. It can be noted in Figure 10a as well as Figure 9a,b that a region of supercooling occurs before the start of the solidification process of the PCM. The overcooling region is the state in which the liquid is below the solid–liquid equilibrium temperature. This overcooling phenomenon is lightly observed in Figures 10b and 11 due to the increased concentration of polyethylene glycol and the use of nanofluids in the spherical capsules causing the increase in thermal diffusivity.

Figure 10. Change in the temperature at the center of the plastic spherical capsule during solidification of polyethylene glycol.
Figure 10. Change in the temperature at the center of the plastic spherical capsule during solidification of polyethylene glycol.

Figure 11. Temperature change in the center of the plastic spherical capsule during solidification of nanofluids.

Figure 12a,b present the temperature change at the center and on the surface of the plastic spherical capsule with water during the melting process. Figure 12a shows the temperature change at the center of the 50 mm spherical capsule during the melting process at 28 °C. Figure 12b shows the temperature change at the center of the 131 mm spherical capsule during the melting process at 28 °C. The time to complete melting was considered to be the time span between the beginning and end of the constant temperature range. As can be seen in Figure 12a,b, there was a gradual increase in temperature in the center of the capsule as a result of the conductive heat transfer mechanism in the solid phase until a melting temperature of zero degree Celsius was reached.

The temperature changes inside the plastic spherical capsules with nanofluids are shown in Figure 13a,b. Figure 13a shows the temperature change at the center of the 50 mm spherical capsule during the melting process at 32 °C. Figure 13b shows the temperature change at the center of the 76 mm spherical capsule during the melting process at 32 °C. As can be seen, the phase change process became faster due to the presence of nanofluids and the melting time decreased by about 40% to 50% when using PCM with nanomaterial. This decrease was due to the enhancement of thermal conductivity, and consequently the heat transfer rate between the PCM and the spherical surface.

4.2. Impact of PCM on the Experimental Times for Complete Solidification and Melting

Figure 14 shows the impact of use of different PCMs on the times for complete solidification. The phase change materials (PCMs) used in the experiments were pure water, water with polyethylene glycol, and propylene glycol with nanofluid. Analyzing the graph in Figure 14, it can be seen that the use of nanofluids decreased the complete solidification time and the use of high concentrations of polyethylene glycol increased the complete solidification time because the thermal conductivity of polyethylene glycol was lower than that of the other PCMs used and its specific mass was greater than that of other PCMs.
Figure 11. Temperature change in the center of the plastic spherical capsule during solidification of nanofluids.

Figure 12a,b present the temperature change at the center and on the surface of the plastic spherical capsule with water during the melting process. Figure 12a shows the temperature change at the center of the 50 mm spherical capsule during the melting process at 28 °C. Figure 12b shows the temperature change at the center of the 131 mm spherical capsule during the melting process at 28 °C. The time to complete melting was considered to be the time span between the beginning and end of the constant temperature range. As can be seen in Figure 12a,b, there was a gradual increase in temperature in the center of the capsule as a result of the conductive heat transfer mechanism in the solid phase until a melting temperature of zero degree Celsius was reached.

Figure 12. Temperature change in the center of the plastic spherical capsule during melting of water.

In addition, one can observe that the rise in the percentage of nanofluids dispersed in the base fluid increased the refrigeration rate of the liquid zone, that is, the existence of nanofluids accelerated the solidification of the base fluid in the capsule. This behavior was due to the increase in the thermal diffusivity of the nanofluid caused by the increase in the concentration of nanoparticles in the base fluid. It is worth highlighting that the decrease in the temperature inside the main tank shortened the time for complete solidification.

Figure 15 also showed that the complete time for the entire mass to melt reduced as the temperature of the thermal bath increased. This effect was caused by an increase in the temperature in the main tank bath which increased the temperature gradient inside the tank and, as a consequence, there was an increase in the flow of heat transfer, which contributed to the reduction in the complete melting time.
nanofluids and the melting time decreased by about 40% to 50% when using PCM with nanomaterial. This decrease was due to the enhancement of thermal conductivity, and consequently the heat transfer rate between the PCM and the spherical surface.

Figure 13. Temperature change in the center of the plastic spherical capsule during melting of nanofluids.

Figure 15 shows the impact of use of different phase change materials on the times for complete melting. As can be seen, the use of the nanofluids shortened the time for complete melting because the thermal diffusivity was higher, which improved heat propagation in the PCM. In addition, increasing the concentration of suspended nanofluids in the base fluid increased its effective density and thermal conductivity, which contributed to the reduction in the time for complete phase change.
contributed to the reduction in the complete melting time. The increase in the thermal bath temperature increased the temperature gradient inside the tank, which lead to an increase in the flow of heat transfer. This effect was caused by the increase in the effective density and thermal conductivity of the nanofluid. It is worth highlighting that the decrease in the temperature of the thermal bath increased. This behavior was due to the increase in the thermal diffusivity of the nanofluid caused by the increase in the concentration of nanoparticles in the base fluid. It is possible to observe that the increase in the thermal diffusivity of the nanofluid caused by the increase in the concentration of nanoparticles in the base fluid increased its effective density and thermal conductivity, which contributed to the reduction in the time for complete phase change.

Figure 14 also showed that the complete time for the entire mass to melt reduced as the diameter of the spherical capsule increased, there was an increase in the time to solidify the entire mass of the PCM, mainly due to the increase in resistance to heat transfer between the PCM and the thermal bath. It is possible to observe that the increase in the thermal diffusivity of the nanofluid caused by the increase in the concentration of nanoparticles in the base fluid increased its effective density and thermal conductivity, which contributed to the reduction in the time for complete phase change.

4.3. Impact of the Plastic Spherical Capsule Dimension on the Time for Complete Solidification and Melting

Figure 16 shows the impact of the change in the size of the capsule on the complete time for physical change from the liquid state of the PCMs to the solid state. As can be seen, as the diameter of the spherical capsule increased, there was an increase in the time to solidify the entire mass of the PCM, mainly due to the increase in resistance to heat transfer between the PCM and the thermal bath. It is possible to observe that the increase in time to solidify the PCM mass became more significant for the diameters of 106 mm and 131 mm. In addition, another point to note is that the lower the bath temperature, the shorter the complete solidification time. This may be related to the increase in temperature gradient which decreased the total thermal resistance, therefore reducing the time to complete solidification.
was perceived, and thus correlations of the thermal parameters were elaborated. Based on measures of correlations between variables, this allowed the prediction of values of variables from the knowledge of values of other variables. The variables estimated in the correlations were the complete solidification time ($t_{\text{complete solidification}}$) and the complete melting time ($t_{\text{complete melting}}$). These times were es-

4.4. Development of Correlations of the Times for Complete Solidification and Melting

The correlation measure is the type of measure that is used when we want to know if several variables have some kind of relationship, so that when one varies, the others vary as well. In this present study, the relationship degree of the experimental variables was perceived, and thus correlations of the thermal parameters were elaborated. Based on measures of correlations between variables, this allowed the prediction of values of variables from the knowledge of values of other variables.

Figure 16. Impact of the dimension of the plastic spherical capsule on the complete solidification time.

Figure 17 shows the impact of the change in the size of the plastic capsule on the complete time for the whole mass of PCM to melt. The complete time for the melting process decreased with spherical capsule size due to the fact that the decrease enhanced heat dissipation to the solid phase change material and hence decreased the melting time. The increase in the thermal bath temperature reduced the complete time for the PCM mass to melt due to the high temperature gradient.

Figure 17. Impact of the dimension of the plastic spherical capsule on the complete melting time.
timated from the knowledge of the diameter of the plastic spherical capsule (D), the percentage of polyethylene glycol in the mixture (W), the percentage of nanofluids (Y), external temperature (T$_{ext}$), and the initial temperature at the center of the spherical capsule (T$_{ini}$). The following equations show the correlations obtained:

Solidification time:

$$t_{\text{completesolidification}} = 12381.12D^{0.58}T_{ini}^{1.28}|T_{ext}|^{-0.49}(1 - W)^{-2.55}(1 - Y)^{125.78}$$  \hspace{1cm} (28)$$

Melting time:

$$t_{\text{completemelting}} = 285435.83D^{0.79}|T_{ini}|^{0.45}T_{ext}^{-0.91}(1 - W)^{-0.91}(1 - Y)^{-10.05}$$  \hspace{1cm} (29)$$

It is worth mentioning that the correlations obtained were validated with a diverse range of experiments and had a high degree of reliability and correlation ($R^2$). To validate the correlations, the parameters from different sets of experimental results were inserted in the correlations and the predicted values were compared with the experimental results, as shown in Figures 18 and 19.

![Figure 18. Comparison of the correlation of the solidification time with experimental data.](image)

![Figure 19. Comparison of the correlation of the melting time with experimental data.](image)
Figure 18 confronts the results of the experimental solidification time and the results of the correlation elaborated for the solidification time, and it is noticed that the curves have an excellent agreement with a maximum average deviation of 6% for lower concentrations of nanofluids.

Figure 19 shows the correlation of melting time. A comparison of the predicted time with the experimental melting time shows a difference of about 5% and an average error of 1.8%. These results confirm that the correlations are suitable for predicting the complete solidification and melting times. Finally, the developed correlations will facilitate the calculation of the complete solidification and melting times of PCMs of system designs with latent heat storage.

5. Conclusions

The present work reports on the results of an experimental and numerical study on the solidification and melting processes of different types of PCM contained in plastic spherical capsules. The simulation results showed that the presence of nanoparticles in the base fluid accelerated the solidification and melting processes and reduced the times for complete solidification and melting. These enhancements were achieved because of the improvements in the thermo-physical properties of the resulting PCM. The simplified model was validated with experimental results from the present work and from the literature, showing an average deviation varying from 0.25% to 12%.

The developed correlations serve as support for future investigations in latent heat storage systems involving the application of nanofluids and plastic spherical capsules. The reduction in the phase change process time is an advantage for the dynamic loading and unloading of the thermal storage system. However, and in counterpoint to the advantage of reduced time, the presence of solid nanoparticles reduces the latent thermal capacity for the same volume. In this case, a compromised decision may be necessary.

Solidification tests indicated that increasing the diameter of the plastic spherical capsule increased the time for complete solidification and melting. The developed correlation for the complete solidification time showed concordance with the experiments with a maximum deviation of 6%, while the validation of the correlation of the time for complete melting showed a difference of about 5% when compared with the experimental results. This confirms the suitability of the proposed correlations for pre-design and evaluation purposes.

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Nomenclature

\[ A \] \quad \text{Correlations constant [-]}
\[ Bi \] \quad \text{Biot number [hr}^{-1}\text{]}\]
\[ C_p \] \quad \text{Specific number [J·kg}^{-1}\text{·K}^{-1}]\]
\[ D \] \quad \text{Plastic spherical capsule diameter [m]}
\[ h \] \quad \text{Convective heat transfer [W·m}^{-2}\text{·K}^{-1}]\]
\[ L \] \quad \text{Latent heat [J·kg}^{-1}]\]
\[ M_{\text{sol}} \] \quad \text{Solidified mass [kg]}
\[ M_{\text{total}} \] \quad \text{Total mass [kg]}
\[ n \] \quad \text{Value numbers}
\[ Q \] \quad \text{Heat flux [W]}
\[ s(t) \] \quad \text{Interface position [m]}
\[ Ste \] \quad \text{Stefan number [C}_p(T_f-T_\infty)/L]\]
\[ T_{\text{ini}} \] \quad \text{Initial temperature at the center of the sphere [°C]}
\[ T_{\text{ext}} \] \quad \text{External surface temperature [°C]}
\[ t_{\text{completesolidification}} \] \quad \text{Complete solidification time [s]}
\[ t_{\text{completemelting}} \] \quad \text{Complete melting time [s]}
\[ W \] \quad \text{Polyethylene glycol fraction [%]}
\[ x_i \] \quad \text{Average of values}
\[ x \] \quad \text{Individual value}
\[ Y \] \quad \text{Nanofluids fraction [%]}

Greek symbols

\[ \alpha \] \quad \text{Thermal diffusivity [m}^2\text{s}^{-1}]\]
\[ \kappa \] \quad \text{Thermal conductivity [W·m}^{-1}\text{·K}^{-1}]\]
\[ \rho \] \quad \text{Density [kg·m}^{-3}]\]
\[ \sigma \] \quad \text{Standard deviation}
\[ \tau \] \quad \text{Dimensionless time}

References


