

Caio Vinicius Santos Cartaxo

Development of microencapsulated phase change materials for energy efficiency applications

Dissertação de Mestrado

Dissertation presented to the Programa de Pós–graduação em Engenharia Mecânica of PUC-Rio in partial fulfillment of the requirements for the degree of Mestre em Engenharia Mecânica.

Advisor : Prof. Márcio da Silveira Carvalho Co-advisor: Dr. Amanda da Costa e Silva de Noronha Pessoa

> Rio de Janeiro February 2025



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Abstract

Cartaxo, Caio Vinicius Santos; Carvalho, Márcio da Silveira (Advisor); Pessoa, Amanda da Costa e Silva de Noronha (Co-Advisor). **Development of microencapsulated phase change materials for energy efficiency applications**. Rio de Janeiro, 2025. 71p. Dissertação de mestrado – Departamento de Engenharia Mecânica, Pontifícia Universidade Católica do Rio de Janeiro.

One way to reduce CO2 emissions is to decrease energy consumption in buildings. A promising approach to achieve this goal is the use of phase change materials (PCMs) as thermal energy storage systems for thermoregulation applications. However, the integration of PCMs into building components is a challenge. Microencapsulation of PCMs has shown promising results as a passive form to improve the thermal performance of building materials, reducing the wasted energy with thermal comfort. In this context, this work focuses on two different aspects of microencapsulated phase change materials. The first is a numerical investigation of the internal temperature behavior of building walls with a thin layer of concrete with capsules. A one-dimensional transient method is proposed, in which the presence of the microcapsules is modeled through a concentration function and the phase change process is modeled by the effective heat capacity method. The effects of the position of the PCM layer, concentration, PCM melting temperature, and phase change enthalpy on the internal temperature profile of the wall were evaluated. In addition, we fabricated microencapsulated PCMs using poly(dimethylsiloxane) (PDMS) as the shell material and calcium chloride hexahydrate (CaCl2 \cdot 6H2O) as the PCM core. The preparation was carried out using glass capillary microfluidic devices to ensure the production of monodisperse microcapsules with adjustable geometrical properties such as size and shell thickness. The study shows a direct relationship between the position and concentration on the internal temperature as well as the reduction of the internal temperature of the walls. We were able to fabricate and store PDMS/CaCl2 · 6H2O microcapsules with tunable properties. Finally, preliminary thermal efficiency tests were conducted which showed that this shell/core combination was not ideal for these applications. However, based on the promising results of the numerical model, new combinations will be developed and tested in future work.

Keywords

Phase Change Materials; Microencapsulation; Finite Element Method; Heat Transfer; Energy Efficiency.

Resumo

Cartaxo, Caio Vinicius Santos; Carvalho, Márcio da Silveira; Pessoa, Amanda da Costa e Silva de Noronha. **Desenvolvimento de material de mudança de fase microencapsulado para aplicações em eficiência energética**. Rio de Janeiro, 2025. 71p. Dissertação de Mestrado – Departamento de Engenharia Mecânica, Pontifícia Universidade Católica do Rio de Janeiro.

Uma abordagem promissora para reduzir as emissões de CO2 e diminuir o consumo de energia em edificações é o uso de materiais de mudança de fase (PCMs) como sistemas de armazenamento de energia térmica para aplicações de conforto térmico. No entanto, a incorporação de PCMs em materiais de construção ainda é um desafio. O microencapsulamento de PCMs tem mostrado resultados promissores como forma passiva de melhorar o desempenho térmico dos materiais de construção, reduzindo o gasto com sistemas de refrigeração. Nesse contexto, este trabalho se concentra em dois aspectos diferentes dos materiais de mudança de fase microencapsulados. O primeiro é uma investigação numérica do comportamento da temperatura interna de paredes de construções com uma fina camada de concreto com cápsulas. E proposta uma metodologia transiente unidimensional, com a presença das microcápsulas sendo simulada por uma função de concentração e o processo de mudança de fase com o método de capacidade térmica efetiva. O estudo mostra os efeitos da posição da camada de PCM, da concentração, da temperatura de fusão do PCM e da entalpia no perfil de temperatura interna da parede. Além disso, foi produzido PCMs microencapsulados usando poli(dimetilsiloxano) (PDMS) como material de casca e cloreto de cálcio hexa-hidratado (CaCl2 · 6H2O) como núcleo de PCM. A produção foi realizada usando dispositivos microfluídicos para garantir a produção de microcápsulas monodispersas com propriedades geométricas ajustáveis. O estudo mostra uma relação direta entre a posição e a concentração na temperatura interna, bem como a redução da temperatura interna das paredes. Microcápsulas de PDMS/CaCl2 · 6H2O foram produzidas. Por fim, foram realizados testes preliminares de eficiência térmica, demonstrando que essa combinação de casca/núcleo não era ideal para essas aplicações no entanto, devido aos resultados promissores apresentados pelo modelo numérico, novas combinações serão desenvolvidas e testadas em trabalhos futuros.

Palavras-chave

Materiais de Mudança de Fase; Microencapsulamento; Método de Elementos Finitos; Transferência de Calor; Eficiência Energética.

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List of Abreviations and Symbols

PCM – Phase Change Material

MPCM – Microencapsulated Phase Change Material

PDMS – poly(dimethylsiloxane)

EPE – Empresa de Pesquisas Energéticas

IEA – International Energy Agency

HVAC – Heating, Ventilating and Air Conditioning

GFEM – Galerkin's Finite Element Method

ODE – Ordinary Differential Equation

W/O - Water-in-oil

O/W – Oil-in-water

W/O/W – Water-in-oil-in-water

O/W/O - Oil-in-water-in-oil

- ρ Specific mass [kg/m³]
- ξ Capsule concentration [%]
- α Wall absorptance [%]
- η Elementary coordinate
- P Generic physical property
- G(t) Time dependent solar irradiation $\left[\frac{W}{m^2}\right]$
- $T_{\infty_1}(t)$ Time dependent outside temperature [°C]
- T_{∞_2} Inside temperature [°C]
- T_{min} Minimum temperature [°C]
- T_{max} Maximum temperature [°C]
- T_0 Initial temperature of the wall [°C]
- ΔT phase change transition temperature interval [°C]
- T_c Center temperature of phase change [°C]
- T Temperature [°C]
- t Time [s]
- u Internal energy $\left[\frac{J}{kq}\right]$
- l Distance between capillaries
- L Wall thickness [m]
- δ PCM layer thickness [m]
- δ^* Dimensionless PCM layer thickness
- h_{in} Inside convective coefficient $\left[\frac{W}{m^2 K}\right]$
- h_{out} Outside convective coefficient $\left[\frac{W}{m^2 K}\right]$
- k Generic thermal conductivity
- k_c Thermal conductivity of concrete $\left[\frac{W}{m_c K}\right]$
- k_{pcm_s} Thermal conductivity of solid state PCM $[\frac{W}{m.K}]$
- k_{pcm_l} Thermal conductivity of liquid state PCM $\left[\frac{W}{m_l}\right]$
- C_p^c Concrete specific heat $\left[\frac{J}{ka}\right]$
- $C_{p_s}^{pcm}$ Specific heat of solid state PCM $\left[\frac{J}{kq}\right]$
- $C_{p_l}^{pcm}$ Specific heat of liquid state PCM $\left[\frac{J}{ka}\right]$
- C_L Latent heat of fusion of PCM $\left[\frac{kJ}{ka}\right]$
- D_i Microcapsule inner diameter $[\mu m]$
- D_o Microcapsule outer diameter $[\mu m]$
- δ_c Capsule shell tickness $[\mu m]$
- Q_i Inner phase flow rate [ml/h]
- Q_m Middle phase flow rate [ml/h]
- Q_o Outer phase flow rate [ml/h]
- h_e Element size

Introduction

1.1

Motivation

Society's increasing demand for energy contributes directly to the climate change we are experiencing today. There is a direct link between economic growth, energy use, and CO_2 emissions, with energy production responsible for more than 40% of global CO_2 emissions (IEA, 2022). Society's growing awareness of climate change is driving several sectors of the economy to find solutions to mitigate its effects in a way that minimizes the impact on national development. These include carbon capture systems, improving the affordability of renewable energy generation, and focusing on increasing energy use efficiency.

Buildings are responsible for approximately a third of global energy consumption and for almost 30% of the world's CO_2 emissions (González et al., 2022). Most energy is used for comfort applications, including heating, ventilation, and air conditioning (HVAC) systems (Yang et al., 2014). According to a technical report by the Energy Research Company (EPE) (Ferreira and Soares, 2018), more than 35% of the Brazilian energy consumption in cities comes from the use of HVAC systems. Although the Brazilian electric matrix is predominantly renewable (Fig. 1.1), there is a significant impact on the country's CO_2 emissions.

The development of more efficient alternatives to improve thermal management systems is a scientific challenge. The use of thermal energy storage (TES) systems appears to be promising in these building applications (Heier et al., 2015).

Thermal energy storage systems are an ingenious way to capture, store, and release heat after some time. Storage can be subdivided into physical storage, such as sensible and latent heat storage, or chemical storage, also



Figure 1.1: Electric matrix: Brazil x World comparison. Data sourced from: https://www.iea.org/data-and-statistics/data-tools/energy-statistics-data-browser

known as reactive storage. With the use of phase change materials (PCMs), latent heat presents the best compromise between storage density and cost among all alternatives (Abhat, 1983; Mohamed et al., 2017).

1.2

Phase Change Materials and Their Applications in Thermal Energy Systems

Phase change materials are substances that exploit the solid-solid, solidliquid, or liquid-gas isothermal phase change process to store energy in the form of heat, being capable of releasing that energy when the material goes through the reverse process. Figure 1.2 presents the relationship between temperature and stored energy for a PCM, highlighting one of its most significant advantages, their ability to absorb heat nearly at constant temperature, which allows them to be considered for several thermal comfort applications. PCMs can be classified into three main categories, Organic, Inorganic, and Eutectic (Fig. 1.3).

In general, inorganic PCMs are less expensive and have a higher energy



Figure 1.2: Latent energy storage for solid-liquid phase change. Adapted from Amaral et al. (2017).



Figure 1.3: PCM types. Adapted from Mohamed et al. (2017).

storage capacity per unit of volume than their organic counterparts; however, they are corrosive and susceptible to phase separation and supercooling (Dixit et al., 2022). The supercooling can significantly impact the long-term usability of salt hydrates, reducing their effectiveness in heat storage.

Metallic PCMs do not present the aforementioned disadvantages, but they have a much higher phase change temperature, which limits their suitability for thermal comfort applications.

Organic PCMs stand out for their chemical and thermal stability; however, they are flammable and present a lower thermal conductivity when compared with inorganic counterparts. Despite these limitations, they are the most commonly used type of PCM in the literature.

Research interest in TES systems using PCMs can be traced back to the early 1940s, when the melting behavior of pure substances was analyzed in the context of ice storage applications (London and Seban, 1943).

The use of TES systems in combination with with solar thermal energy is a widely researched topic (Garg HP, 1985). Solar hot water systems are a cost-effective method of providing hot water. The incorporation of PCMs into these systems aims to maximize the higher radiation hours, by using the solidliquid phase change within heat exchangers to store thermal energy, which is subsequently released, increasing efficiency and usability (Prakash et al., 1985; Ecevit et al., 1990; Bansal and Buddhi, 1992; Douvi et al., 2021).

Based on the same physical principle, high-temperature PCMs are often used in concentrating solar power plants. These power plants generate electricity by heating water using solar concentrating panels and store heat using molten salts (>300°C) or metallic alloys (>500°C) (Tamme et al., 2003; Kenisarin, 2010; Nomura and Akiyama, 2017).

The use of PCMs as thermal regulators has become a predominant trend, spanning various industries and sectors. One of these is related to the thermal management of electric batteries, with Li-ion batteries being particularly temperature-sensitive, and having an optimal operating temperature range of 15°C to 40°C (Farag et al., 2017). It has been shown that the integration of PCMs as thermal regulators increases the safety and efficiency of Li-ion batteries (Javani et al., 2014; Luo et al., 2022).

Another application that is related to thermoregulation is the use of PCMs in buildings. This application can have two different goals: thermal storage from natural sources or from artificial sources. The integration of PCMs into buildings can have three mechanisms: i - walls, floors, or ceilings; ii - other building components; iii - thermal storage units (Sharma et al., 2009). Numerous researchers have investigated the potential of PCM wall boards to improve thermal comfort. While PCMs show promising results from a thermal management perspective, the high costs associated with manufacturing and the challenges of installing them into wall boards, such as leaks and undesirable interactions with the bulk material have made their practical application unfeasible (Peippo et al., 1991; Feldman et al., 1991; Stovall and Tomlinson, 1995; Neeper, 2000; Qureshi et al., 2011; Evola and Marletta, 2014).

With the progress of microencapsulation technologies, the development of microencapsulated PCMs (MPCMs) has opened up new perspectives for the use of PCMs in various applications and overcome most of the disadvantages of the previous incorporation process (Schossig et al., 2005).

1.3

Microencapsulated Phase Change Materials



Figure 1.4: PCM microcapsule structure.

Microencapsulation of PCM is a technique in which a phase change material is encolsed in a hard shell, with a size of 1 to 1000 μ m (see Fig. 1.4). This isolation from the bulk material brings several advantages for the incorporation of PCMs into various thermal management applications, allowing them to be incorporated into heat exchanger slurries, textilew, building materials, etc. They also prevent any unwanted chemical interaction with the external medium, as the PCM could be flammable or corrosive. Finally, the size of the capsules increases the efficiency of the heat transfer process and thus the efficiency in storing and releasing thermal energy (Tyagi et al., 2011; Ismail et al., 2023).

The first applications of microencapsulated PCMs focused on working fluids for heat exchangers and date back to the early 1980s. At that time, researchers were faced with technical limitations regarding the strength of the capsules, which had to withstand the phase change process and mixing in the slurries (Mulligan et al., 1996). Hart and Thornton (1982) were among the first to show promising results in capsule production with slurry application in mind. Throughout the 1990s, research focused on understanding the thermal and mechanical behavior of fluids within microcapsules (Charunyakorn et al., 1991; Goel et al., 1994) and showed promising results for applications in the aerospace industry (Mulligan et al., 1996; Fossett et al., 1998). The promising results have meant that the study of slurries is still in vogue today, with new materials being developed and the application of MPCM slurries being expanded (Sabbah et al., 2009; Yu et al., 2019; Xu et al., 2022). Another application of microencapsulated PCMs that emerged in the 1990s was textiles with passive thermal management, where the capsules are blended into the textile fibers to buffer the effects of temperature fluctuations and avoid abrupt fluctuations in body temperature (Shim et al., 2001). Although the thermal performance shows relevant results, the use of capsules in clothing is associated with some disadvantages such as withstanding the laundering process, reduction of elasticity, and weight increase (Shin et al., 2005).

Research into the application of microencapsulated PCMs for thermal management in buildings began in the early 2000s, with the work of Schossig et al. (2005), in which the authors performed a parametric study to identify the best scenarios and conducted experiments on 50 x 50 cm wall samples. They obtained promising results, with a maximum temperature reduction of about 2 °C. Figure 1.5 shows a schematic representation of the main objectives of using microencapsulated PCMs in buildings. The high thermal energy stored by PCMs is used to maintain the indoor environment within an interval of comfort temperature.



Figure 1.5: Schematics of PCM incorporated into concrete. Reproduction from Sharma et al. (2022)

Cabeza et al. (2007) presented an experimental work in which two concrete cubicles were compared: one made of conventional concrete and the other with 5% (v/v) of a commercial microencapsulated PCM. The authors monitored the phase change cycles (melting-freezing) of the MPCM and inferred a strong correlation between PCM efficiency and weather seasons. Hunger et al. (2009) studied the thermal and mechanical properties of selfcompacted concrete with different percentages of capsules, and found that energy savings of up to 12% can be expected when 5% (v/v) of capsules are added to the concrete. However, the concrete showed a loss of compressive strength, which could be attributed to the destroyed shells of PCM, which negatively interfered with the concrete matrix. As a solution, the researchers proposed the production of stronger shells, which could resist strong alkaline conditions.

Shortly afterwards, the first review articles on this topic were published, covering applications, technologies for capsule fabrication, research on new PCMs, and numerical modeling of the phase change process (Sharma et al., 2009; Zhao and Zhang, 2011; Tyagi et al., 2011; Dutil et al., 2011; Kalnæs and Jelle, 2015).

Li et al. (2019) proposed a year-round approach to wallboard with microencapsulated PCM. To take advantage of all seasons, three different microencapsulated PCMs with fusion temperatures of 12, 18, and 29°C were incorporated into the wallboard. They compared two different layouts, a hybrid one, where all capsules are mixed, and one where the capsules are arranged in layers. The authors showed that the capsules in different layers delayed the heat transfer from outdoor to indoor and released the stored energy quickly.

Soares et al. (2021) conducted an extensive numerical validation study, using three numerical models for phase change processes in heat transfer problems: effective heat capacity, additional heat source, and enthalpy method. 3-D simulations were performed using Ansys software and compared with experimental results. The results showed that the three different approaches were able to achieve good agreement with the experimental data.

The development of thermal energy storage systems based on microencapsulated PCMs still presents some challenges, such as new shell-PCM combinations leading to stronger and more stable microcapsules, as well as better control of the microencapsulation process and optimization of the concentration and configuration of the PCM in the walls.

1.4

Objectives

This dissertation is mainly divided into two areas of research on microencapsulated phase change materials. The first is a numerical investigation of the effectiveness of MPCMs in building materials, using a one-dimensional model to evaluate the reduction in room temperature through the use of microencapsulated PCMs in building assemblies. A parametric analysis of the effects of microcapsule concentration, phase change temperature of the PCM, and the position of the PCM layer within the wall is presented. The results allow the optimization of the wall configuration with the aim of lowering the room temperature.

The second line of research focuses on the production of monodispersed microencapsulated PCM using microfluidics, which allows a precise control of the capsule's geometry (size and shell thickness) and flexibility in the materials used.

Numerical Model

2.1

Differential Equation of Heat Diffusion

Ozisik (1993) textbook presents a thorough derivation of the heat diffusion equation in both integral and differential forms. We will pick up from there, and start with the vector form of the transient heat conduction equation (Eq. 2-1). Where k is the conductivity, ρ is the density, and c is the heat capacity.

$$\nabla \cdot (k\nabla T) = \rho c \frac{\partial T}{\partial t} \tag{2-1}$$

Assuming a one-dimensional transient problem, with a heterogeneous wall containing a PCM layer ,i.e., the thermal properties vary with position and the PCM properties depend on temperature, the equation can be written as

$$\rho(x,T)C_p(x,T)\frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(k(x,T)\frac{\partial T(x,t)}{\partial x}\right)$$
(2-2)

2.2

Mathematical Model

The domain of interest is a layer of uniformly dispersed PCM microcapsules sandwiched between two concrete walls, as shown in Fig. 2.1, where L is the wall thickness and δ is the thickness of the layer with dispersed microencapsulated PCM. The external side of the wall is at X = 0 and takes solar radiation and convection into account. The internal boundary is at X = L and has natural convection.

The volumetric concentration of PCM-containing microcapsules within



Figure 2.1: Model schematics

the layer δ is ξ . The physical properties (ρ, C_p, k) of this portion of the wall are given by a weighted average between the bulk material and the microcapsules, as shown in Eq. 2-3.

$$P(\xi) = \xi P_{capsules} + (1 - \xi) P_{bulk}$$
(2-3)

The radiation model used in this study is based on historical measurements of solar irradiation as documented by Wang and Liu (1988), where G(t) is the amount of energy received per square meter of surface. This model conceptualizes daily solar radiation as a half-period of a sinusoidal curve with a peak at 12 hours and minimum values at 6 and 18 hours. α is the absorptance coefficient of the wall, this parameter varies from 0 to 1 and depends on the latitude, longitude, and wall color. Wang and Liu (1988) also propose the use of a wall absorptance coefficient of 0.15, which is used in this work.

$$G(t) = G_{max} sin\left(\frac{\pi}{43200}(t - 21600)\right)$$
(2-4)

The time-dependent external temperature, $T_{\infty 1}(t)$ is modeled by a sine function, with the highest temperature, T_{max} , occurring at 12 hours and the lowest temperatures, T_{min} , at 0 hours (midnight).

$$T_{\infty 1}(t) = T_{min} + (T_{max} - T_{min})sin\left(\frac{\pi}{86400}t\right)$$
(2-5)

The latent heat model is based on the work of Jin et al. (2018), who compared the two most commonly used methods for modeling phase change processes: the effective heat capacity method and the enthalpy method. In the present work, the first method is used to model the phase change process. In this modeling approach, the specific heat is a function of position and temperature, as in Eqs. (2.6) - (2.9), where C_p^c is the specific heat of the concrete, $C_{p_s}^{p_cm}$ and $C_{p_l}^{p_cm}$ are the specific heat of the PCM as a solid and a liquid, respectively, T_c is the center temperature of the phase change, ΔT is the phase transition temperature interval, and C_L is the latent heat of the PCM.

$$\begin{cases} C_p^c & \text{for } 0 < x < \frac{L}{2} - \frac{\delta}{2} \text{ and } \frac{L}{2} + \frac{\delta}{2} < x < L \text{ for any } T(x,t) \end{cases}$$

$$(2-6)$$

$$f_{op} = \int_{-\infty}^{-\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{$$



Figure 2.2: Graphical representation of effective heat capacity by temperature.

Figure 2.2 shows how the heat capacity of the PCM microcapsules varies with temperature. During the phase change process, the heat capacity is much higher than that of the PCM material in its liquid and solid states.

The approach for thermal conductivity is analogous. In both cases, the Heaviside functions are represented by sigmoid functions due to the discontinuous nature of the Heaviside function. Sigmoid functions model the steps in a continuous, differentiable function, and thus avoid numerical problems when solving the partial differential equation.

$$\begin{cases} k_c & \text{for } 0 < x < \frac{L}{2} - \frac{\delta}{2} \text{ and } \frac{L}{2} + \frac{\delta}{2} < x < L \text{ for any } T(x,t) \\ \text{for } \frac{L}{2} & \delta < x < \frac{L}{2} + \frac{\delta}{2} \text{ and } T(x,t) < T \end{cases}$$

$$(2-10)$$

$$\begin{cases} k_{pcm_s} & \text{for } \frac{L}{2} - \frac{o}{2} < x < \frac{L}{2} + \frac{o}{2} \text{ and } T(x,t) < T_c \\ \frac{k_{pcm_s} + k_{pcm_l}}{2} & \text{for } \frac{L}{2} - \frac{\delta}{2} < x < \frac{L}{2} + \frac{\delta}{2} \text{ and } T(x,t) - \Delta T < T(x,t) < T(x,t) + \Delta T \text{ (2-12)} \\ k_{pcm_l} & \text{for } \frac{L}{2} - \frac{\delta}{2} < x < \frac{L}{2} + \frac{\delta}{2} \text{ and } T(x,t) > T_c \end{cases}$$

$$(2-11)$$

where k_c is the concrete conductivity, k_{pcm_s} is the thermal conductivity of the solid PCM and k_{pcm_l} is that of the liquid PCM.

To summarize, the governing equation for this proposed problem is the one-dimensional transient heat equation, with boundary conditions of convection and radiation on the outside wall and natural convection on the inside one. Temperature and position-dependent conductivity, density, and heat capacity are also considered.

$$\rho(x,\xi,T)C_p(x,\xi,T)\frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(k(x,\xi,T)\frac{\partial T(x,t)}{\partial x}\right)$$
(2-14)

With the following initial and boundary conditions:

$$\int T(x,0) = T_0$$
 (2-15)

$$-k(x)\frac{\partial T(0,t)}{\partial x} = h_{out}(T_{\infty_1}(t) - T(x,t)) + \alpha G(t)$$
(2-16)

$$\sum_{n=1}^{\infty} -k(x)\frac{\partial T(L,t)}{\partial x} = h_{in}(T(x,t) - T_{\infty_2})$$
(2-17)

where T_0 is the initial temperature of the wall, $T_{\infty_1}(t)$ is the outside temperature function, dependent of maximum and minimum temperatures, T_{∞_2} (20°C) is the inside temperature, and h_{out} and h_{in} are the outside and the inside convective coefficient, respectively.

The main dimensionless groups that govern the problem are the Biot number, which relates the thermal resistance by conduction inside a material and the thermal resistance for convection at the material surface;

$$Bi_{out} = \frac{h_{out}L}{k_c} \tag{2-18}$$

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$$Bi_{in} = \frac{h_{in}L}{k_c} \tag{2-19}$$

the dimensionless phase change temperature and phase change enthalpy;

$$\Theta_f = \frac{T_c}{T_{\infty_2}} \tag{2-20}$$

$$H^* = \frac{C_L - (C_s^{pcm} \Delta T)}{C_s^{pcm} \Delta T}$$
(2-21)

and the dimensionless numbers related to the geometry of the problem.

$$x^* = \frac{x}{L} \tag{2-22}$$

$$\delta^* = \frac{\delta}{L} \tag{2-23}$$

2.3

Numerical Solution

It is not the goal of this work to go into every detail of the numerical method used to solve the problem, but to present the basics of the solution procedure. The non-linear differential equations were solved using Galerkin's Finite Element Method (GFEM).

The GFEM finds an approximate solution of a differential equation in a finite dimension subspace. This solution can be expressed as a linear combination of basis functions of the subspace (ϕ_j) .

$$u_h(x) = \sum_{i=1}^{N} c_j \phi_j(x)$$
 (2-24)

where c_j 's are the expansion coefficients, the unknowns of the discretized problem. They can be calculated by setting the weighted residuals to zero. In the Galerkin's formulation, the weight functions and the basis functions are equal.

$$R_i = \int_{\Omega} R(x)\phi_i(x)dx = 0 \tag{2-25}$$

Starting from Eq. 2-14, we derive the weighted residuals, which are given in Eq. 2-29. The time dependence is discretized using the finite difference method, which we will discuss later in this chapter.

$$T(x,t) = \sum_{j=1}^{N} T_j(t)\phi_j(x)$$
(2-26)

$$\frac{\partial T(x,t)}{\partial x} = \sum_{j=1}^{N} T_j(t) \frac{\partial \phi_j(x)}{\partial x}$$
(2-27)

$$R(x) = \rho C_p \frac{\partial T}{\partial t} - \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right)$$
(2-28)

$$R_{i} = \int_{0}^{L} \phi_{i}(x) \left[\rho C_{p} \frac{\partial T}{\partial t} - \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) \right] dx \qquad (2-29)$$

Splitting Eq. 2-29 into two integrals and integrating by parts we will have

$$R_{i} = \int_{0}^{L} \phi_{i} \rho C_{p} \frac{\partial T}{\partial t} dx + \int_{0}^{L} k \frac{\partial \phi_{i}}{\partial x} \frac{\partial T(x,t)}{\partial x} dx - \left[\phi_{i}(x) k \frac{\partial T(x,t)}{\partial x} \Big|_{x=L} - \phi_{i}(x) k \frac{\partial T(x,t)}{\partial x} \Big|_{x=0} \right]$$
(2-30)

The two last terms of the equation are the boundary conditions of the problem, and therefore only appear in the first and the last nodes of the problem. Therefore, the final equations of the weighted residuals, using Eqs. 2-20 and 2-21 are:

$$R_{i} = \sum_{j=1}^{N} \rho C_{p} \frac{dT_{j}(t)}{dt} \int_{0}^{L} \phi_{i}(x)\phi_{j}(x) dx + \sum_{j=1}^{N} kT_{j}(t) \int_{0}^{L} \frac{\partial \phi_{i}(x)}{\partial x} \frac{\partial \phi_{j}(x)}{\partial x} dx + \phi_{i}(0)h_{out}(T_{\infty_{1}}(t) - T_{x=0}) + \alpha G(t) \quad \text{for } i = 1$$

$$(2-31)$$

$$R_{i} = \sum_{j=1}^{N} \rho C_{p} \frac{dT_{j}(t)}{dt} \int_{0}^{L} \phi_{i}(x) \phi_{j}(x) dx + \sum_{j=1}^{N} kT_{j}(t) \int_{0}^{L} \frac{\partial \phi_{i}(x)}{\partial x} \frac{\partial \phi_{j}(x)}{\partial x} dx \quad \text{for } i = 2, \dots, N-1$$

$$(2-32)$$

$$R_{i} = \sum_{j=1}^{N} \rho C_{p} \frac{dT_{j}(t)}{dt} \int_{0}^{L} \phi_{i}(x)\phi_{j}(x) dx + \sum_{j=1}^{N} kT_{j}(t) \int_{0}^{L} \frac{\partial \phi_{i}(x)}{\partial x} \frac{\partial \phi_{j}(x)}{\partial x} dx + \phi_{i}(L)h_{in}(T_{x=L} - T_{\infty_{2}}) \quad \text{for } i = N$$

$$(2-33)$$

The system of ordinary differential equations can be written in matrix form as:

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$$\frac{\partial \underline{T}}{\partial t} = \underline{\underline{M}}^{-1} \underline{\underline{A}} \, \underline{T} \tag{2-34}$$

where,

$$M_{ij} = \int \phi_i \phi_j dx \tag{2-35}$$

$$A_{ij} = \int \frac{\partial \phi_i}{\partial x} \frac{\partial \phi_j}{\partial x}$$
(2-36)

The domain (Ω) is divided into elements with the same structure (see Fig. 2.3). Each element is connected by nodes, the basis and weight functions are first-order Lagrange polynomials. This method aims to simplify the calculation of the integrals and make several terms of $\underline{\underline{A}}$ equal to zero.

$$\phi_i(x_j) = \delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases}$$
(2-37)
(2-38)

Defining an element coordinate system (η) where, in every element, the nodes have the same coordinates: the first node at $\eta = -1$ and the second at $\eta = 1$. Therefore, the basis functions in elementary point of view and its derivatives are presented in Eq. 2-39 and Eq. 2-40.



Figure 2.3: Element structure

$$\phi_1 = \frac{(1-\eta)}{2} \quad and \quad \frac{\partial\phi_1}{\partial\eta} = -\frac{1}{2} \tag{2-39}$$

$$\phi_2 = \frac{(1+\eta)}{2} \quad and \quad \frac{\partial\phi_2}{\partial\eta} = \frac{1}{2} \tag{2-40}$$

If we perform a coordinate change from a global coordinate system in Eq. 2-38 to the elementary point of view, we obtain:

$$R_{i}^{(e)} = \sum_{j=1}^{N} \frac{dT_{j}(t)}{dt} \int_{-1}^{1} \rho C_{p} \phi_{i}(x) \phi_{j}(x) \frac{h_{e}}{2} d\eta + \sum_{j=1}^{N} T_{j}(t) \int_{-1}^{1} -k(x) \frac{\partial \phi_{i}(x)}{\partial \eta} \frac{\partial \phi_{j}(x)}{\partial \eta} \frac{2}{h_{e}} d\eta$$
(2-41)

where h_e is the size of the element in the global coordinate system. Using the Euler explicit finite difference method to discretize the time dependence, the final equation of the problem is:

$$R_{i}^{(e)} = \sum_{j=1}^{N} \frac{T_{j}^{k} - T_{j}^{k-1}}{\Delta t} \int_{-1}^{1} \rho C_{p} \phi_{i}(x) \phi_{j}(x) \frac{h_{e}}{2} d\eta + \sum_{j=1}^{N} T_{j}^{k} \int_{-1}^{1} -k(x) \frac{\partial \phi_{i}(x)}{\partial \eta} \frac{\partial \phi_{j}(x)}{\partial \eta} \frac{2}{h_{e}} d\eta$$
(2-42)

The integrals were solved using the Gaussian quadrature method. The system of ODE's was solved using Newton's method.

2.4

Results and Discussions

2.4.1

Mesh Validation

A mesh validation test was performed to observe the convergence of the results with increasing refinement of the mesh. The test was performed by varying the number of elements and thus h_e from 10 to 300 elements. Since the domain is limited to 0.15m, the size of each element ranges from 15mm to 0.5mm. Figure 2.4 shows the temporal evolution of the internal temperature of the wall predicted with the different meshes. The temperature profile of all curves (except the curve with 10 elements) tends to overlap after the first heat cycle.

In Fig. 2.4 one can see a good convergence of the results with a mesh with 100 elements. This is also illustrated by Tab. 2.1 where the mean difference between the most refined case and the case with 100 elements is around 0.07°C.

| Number of elements | Mean difference $[^\circ\mathrm{C}]$ |
|--------------------|--------------------------------------|
| 10 | 0,8428 |
| 30 | $0,\!1453$ |
| 100 | 0,0636 |
| 150 | 0,0153 |
| 200 | 0,0001 |
| 300 | 0 |
| | |

Table 2.1: Mean difference compared to 300 elements.



Figure 2.4: Mesh analysis detail (from 11.5 to 36 hours).

2.4.2

Parametric Study

The simulations include three days (72 hours) of heating and cooling cycles according to the models proposed in the previous section. The room and the wall have an initial temperature of 23°C and the temperature profiles are all from $x^* = 1$, i.e., the inner surface of the wall. The external conditions of the problem: external temperature, peak irradiation energy, irradiation time interval, and absorptance, are proposed to emulate a summer day in Rio de Janeiro. The first analysis deals with the influence of the concentration of MPCMs at different positions of the layer containing the MPCMs. Five different layer positions were analyzed, from the exterior plaster, $x^* = 0$, to the interior plaster, $x^* = 1$. In all cases δ is set to 5 mm ($\delta^* = 0.034$), and the phase change temperature (T_c) is 28°C ($\Theta_f = 1.22$).



Figure 2.5: Temperature profile of the interior surface of the wall with the MPCM layer placed at the exterior plaster $(x^* = 0)$.

Figure 2.5 shows the evolution of the inner wall temperature during 3 days for different capsule concentrations with the MPCM layer at $x^* = 0$, on the outer wall. After the first cycle, when the initial cold condition is still dominant, the effect of the use of PCM actually leads to an increase in the inner wall temperature. This behavior can be explained by the fact that the PCM layer is confronted with a higher heat flux, due to direct solar irradiation, reaching temperatures well above the phase change temperature, so that it cannot store heat efficiently. Increasing the capsule concentration only exacerbated this behavior. The results show a consistent increase in internal temperature with increasing capsule concentration. If the PCM layer must be used at this location, a different material, with a higher phase change temperature would be more suitable.

The effect of the presence of PCM can be observed in the temperature curves as a change in the slope of the curve. As the material changes phase, the temperature rise is slowed down. This is clear in the first cycle of Fig 2.5. As expected, the higher the concentration, the longer the period of slower temperature rise.

Figures 2.6 to 2.9 present the predicted internal wall temperature as

a function of capsule concentration for different layer positions, e.g. $x^* = 1/4$, 1/2, 3/4 and 1, respectively. The temperature evolution changes with the position of the PCM layer. As the PCM layer is further away from the outer wall, it takes more time for the temperature of the layer to reach the phase change temperature. At this point, the conductive heat that reaches the PCM layer is used to change the phase of the internal content of the capsules.

From Fig. 2.5 to Fig. 2.9, moving the PCM layer further from the outside wall leads to an increase of the PCM performance in reducing the internal wall temperature. This result is consistent with the fact that, for that specific phase change temperature, the heat flux in which the PCM have to deal with must be optimized for its thermophysical characteristics. The diffusive nature of the heat conduction led to an absorption of energy by the concrete wall before it reaches the PCM layer, and, the larger the concrete layer before the PCM, more heat is stored through sensible heat optimizing the heat flux that is received by the PCM layer and thus making the PCM more efficient.

In the best scenario (see Fig. 2.9), with a capsule concentration of 40% in a 5mm layer, a reduction of almost 4°C in the peak temperature of the first heating cycle was achieved. This result shows the potential of the PCM microcapsules for thermal management applications.

These results show good agreement with other works in the literature, where the peak temperature reduction goes from 2°C to 4°C with less than 5% of capsules within the wall (Cabeza et al., 2007). The results also show concordance with the literature in the overall shape of the curves, a sinusoidallike pseudo-permanent regime, where the amplitude of the wave is reduced by the use of PCMs, with a lower peak temperature but a higher minimum temperature.

In all cases, during the phase change process, the noticeable change in slope is shortly followed by a return to a derivative similar to the case without PCM. In the case at $\xi = 0.4$ in Fig. 2.8 ($x^* = 3/4$) and at $\xi = 0.3$ and 0.4 in Fig. 2.9 ($x^* = 1$), a different behavior of the curves can be observed, with a pseudo-plateau of temperature around 28°C during the first heating cycle. This phenomenon occurs because of the low intensity of the heat flux arriving at the PCM layer, where the amount of energy is not able to fully melt the PCM, and the energy loss during the low temperatures of the night is not able to completely solidify the PCM again.

When placing the MPCM layer in the internal wall, the use of only 20% of capsules within the layer of PCM is able to reduce the maximum internal



Figure 2.6: Temperature profile of the internal wall with the MPCM layer placed at $x^* = \frac{1}{4}$.



Figure 2.7: Temperature profile of the internal wall with the MPCM layer placed at $x^* = \frac{1}{2}$.



Figure 2.8: Temperature profile of the internal wall with the MPCM layer placed at $x^* = \frac{3}{4}$.



Figure 2.9: Temperature profile of the internal wall with the MPCM layer placed at internal plaster $(x^* = 1)$.



Figure 2.10: Temperature profile of the internal wall for different positions with ξ fixed at 0.2.

wall temperature by about 2 °C (see Tab. 2.2), highlighting the intrinsic relationship between the layer positioning (see Fig. 2.10) and high energy storage density of PCM. Therefore, the optimal use of MPCMs in buildings is basically an optimization work, with several dependent variables, such as: external temperature profile, sun irradiation, wall absorptance, thermophysical properties of the construction materials, and all of them will interfere in the best position for placement and the best PCM choice.

| | $\xi = 0$ | $\xi = 0.1$ | $\xi = 0.2$ | $\xi = 0.3$ | $\xi = 0.4$ |
|----------------------|-----------|-------------|-------------|-------------|-------------|
| Max temperature [°C] | 31,79 | 30,90 | 29,75 | 28,34 | 28,10 |
| Min temperature [°C] | 27,73 | $28,\!08$ | 27,75 | $27,\!62$ | $27,\!55$ |

Table 2.2: Maximum and minimum temperatures of each concentration for the internal plaster.

Figures 2.11 and 2.12 presents the inner wall temperature as a function of the phase change temperature for PCM layer located at $x^* = 0$ and $x^* = 1$, respectively, with $\xi = 0.2$. Observing Fig. 2.11, the results corroborates for the previous statements where a higher phase change temperature would lead to a lower peak temperature at the external plaster. However, the peak temperature



Figure 2.11: Internal temperature profile with PCM layer at $x^* = 0$ with center phase change temperature variation.

reduction is paired with the highest minimum temperature among the cases, demonstrating that is better to have a lower phase change temperature in a more suitable position than the opposite.

The overall best performance is obtained with a phase change temperature of 30 °C ($\Theta_f = 1.3$), which leads to a reduction of the maximum temperature in the second and third cycle of approximately 2.5 °C, when compared with the case without PCMs, corroborating to the use of this position ($x^* = 1$) to place the PCM layer when the external conditions are similar to a summer day at Rio de Janeiro.

The final parametric study analyzes the influence of the phase change enthalpy of the PCM, i.e., the amount of energy that the PCM can store or release during the solid/liquid phase transition. The values chosen for the simulations are based on the difference between an organic paraffin based PCM and a salt hydrate inorganic PCM.

The result is consistent because the main difference expected by changing only the enthalpy is the duration of the phase change energy storage region (the change in the slope) on the temperature profile graphic. Figures 2.13 and



Figure 2.12: Internal temperature profile with PCM layer at $x^* = 1$ with center phase change temperature variation.



Figure 2.13: Internal temperature profile with with PCM layer at $x^* = 0$ with different enthalpies.



Figure 2.14: Internal temperature profile with with PCM layer at $x^* = 1$ with different enthalpies.

2.14 presents this behavior.

When the PCM layer is located in the outer wall $(x^* = 0)$, due to the higher heat flux, the difference between the cases are smaller but still noticeable. The effect is stronger when the PCM layer is located in the inner wall $(x^* = 1)$, where we are able to see clearly how the process of storage ends earlier with $C_L = 170 \text{ kj/kg}$ $(H^* = 84)$ when compared with the C_L 220 kj/kg $(H^* = 109)$ case.

Microencapsulation

3.1

Literature Review

3.1.1

Emulsions

Emulsions are dispersions of a liquid suspended in small spherical droplets as a continuous phase of another immiscible liquid. Typically, one component is aqueous, while the other is oily. A system that contains three immiscible phases is referred to as double emulsion. These systems are formed by small droplets of liquid contained in a larger droplet of another liquid, which are dispersed within a continuous phase. They can be divided into two types, oil-in-water-in-oil (O/W/O) and water-in-oil-in-water (W/O/W) (Iqbal et al., 2015). Both systems are illustrated in Fig. 3.1





The process of emulsification, or the formation of emulsions, is a dynamic

and non-spontaneous phenomenon that requires energy input to form the droplets. The process requires a certain amount of mechanical energy to disperse the liquid into these droplets, which can be achieved through various techniques, such as shaking, mixing, stirring, the use of porous membranes, or ultrasound (Akbari and Nour, 2018).

Emulsion stability refers to the ability of an emulsion to resist physicochemical alterations over time (McClements, 2007). Emulsions are thermodynamically unstable due to the tendency of liquid/liquid mixtures to minimize the interfacial area between immiscible phases (Kilpatrick, 2012), leading to drop coalescence and phase separation. The stability of emulsions can be enhanced through the addition of emulsifying agents, which are typically surfactants. These are adsorbed to the oil-water interface, weakening the interfacial forces and allowing liquids to partially mix by reducing droplet size or forming a mechanical barrier between the phases (Goodarzi and Zendehboudi, 2019).

3.1.2

Microencapsulation

Microcapsules are formed by a core substance enclosed by a shell (see Fig. 1.4), that protects the core from interaction with the surrounding medium (Dubey, 2009; Sris and Prabha, 2012).

Microencapsulation enables a functional barrier between the core and the external environment. This barrier can be engineered to rupture under specific conditions or to withstand the internal phase. The size of these microcapsules varies from one micron to a few millimeters and can be classified into two categories: (i) mono-core or mononuclear, presenting a single core enclosed by a shell, (ii) poly-core or polynuclear, with more than one core in the same shell structure, as illustrated in Fig. 3.2.



Figure 3.2: Different capsule structures, where the blue colored is the continuous phase and the cream colored is the dispersed phase. (a) Mono-core microcapsule and; (b) Poly-core microcapsule.

The first commercial application for microcapsules dates back to the early 1950s, when Green (1953) developed a copying paper technology that used pressure as a rupture trigger. From there, microencapsulation led to the development of new products and technologies in a wide range of industrial sectors, from cosmetics to thermal control in buildings.

In the biomedical field, microcapsules can be used as containers for bioadsorbents and enzymes that act as artificial cells (Chang, 2005). In the cosmetic industry, vitamins, skin care agents, anti-aging products, and other actives, are encapsulated to protect the active ingredient present in a carrier phase, designed to rupture upon contact with the human skin (Cheng et al., 2008). The food industry also developed an interest in microencapsulation technology, as capsules can solve problems related to environmentally unstable ingredients such as vitamins, colorants, probiotics, and conservants (Schrooyen et al., 2001; Madene et al., 2006).

In the petroleum industry, the use of microcapsules has shown advances in enhanced oil recovery applications, in which microcapsules can be used as fluid mobility agents to redistribute flow through porous media (Ribeiro, 2019). Microcapsules can also carry surfactants, taking advantage of their tunable release properties to deliver their payload only in the porous media, clearing the flow path and increasing the volume of oil recovered (Abbaspourrad et al., 2013; Zhang et al., 2020).

There are several methods to produce microcapsules, each one with different advantages and drawbacks. Microfluidic systems offer a route for the fabrication of monodisperse microcapsules with control over their structure and geometric properties. Through microfluidic devices, microencapsulation can be achieved by the formation of double emulsion templates, which undergo to a gelation/solidification process of the middle phase in order to form the solid shell and thus, the microcapsule (Datta et al., 2014).

3.2

Materials and Methods

3.2.1

PCM Selection

The correct selection of PCM across several options of melting temperature and chemical compositions (see Fig. 1.3) is crucial for the design of thermal energy storage systems and the microencapsulation process (Cabeza et al., 2024). If the melting temperature is too high for the intended application, the material will not go through the phase change process, absorbing heat only in the sensible region, not taking advantage of the latent heat, which is two to three orders of magnitude higher than the sensible heat. Conversely, if the melting temperature is too low, it will undergo the phase change process too early, absorbing energy in a non-optimal range of temperature, reducing the effectiveness of the PCM in temperature regulation.

The second point outlined, the influence on the microencapsulation process, is related to the chemical composition of the PCM. The double emulsion template, which will form the microcapsule after the curing process, could be either O/W/O or W/O/W, therefore, the miscibility of the PCM to water or oil will determine the geometric parameters of the microfluidic device, the required glass capillaries' surface treatment and the selection of the shell material.

Several works have already compiled the main PCMs that are used for microencapsulation purposes, such as Su et al. (2015); Ismail et al. (2023); Chaudhari et al. (2024). Following a review of the criteria and possibilities of encapsulation, two PCMs emerged as potential candidates for microencapsulation. (i) An oil-miscible organic paraffin, n-octadecane (C_8H_{18}) which has a solid-liquid phase change temperature of 28°C and phase change enthalpy of 240 $\frac{kJ}{kg}$. (ii) A water-miscible inorganic salt hydrate, calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) which has phase change temperature of 29°C and a phase change enthalpy of 190 $\frac{kJ}{kg}$.

As pointed out by Mohamed et al. (2017) and Dixit et al. (2022), salt hydrates tend to present supercooling. This is a natural phenomenon whereby a PCM in a liquid state can reach temperatures below the theoretical melting temperature and remain in a metastable state where a plethora of factors could trigger solidification (see Fig.3.3). The temperature at which the solidification process initiates is known as the nucleation temperature (Shamseddine et al., 2022). For TES systems, supercooling is seen as a drawback because it prevents the release or the absorption of energy through latent heat.



Figure 3.3: Supercooling during solidification process.

The microencapsulation of n-Octadecane is a more explored topic in the literature, where a plethora of encapsulations methods and shell materials are used (Fan et al., 2005; Lone et al., 2013; Yu et al., 2014; Methaapanon et al., 2020). The use of $CaCl_2 \cdot 6H_2O$ as MPCM is still underexplored, mainly due to the aforementioned drawbacks (Yang and Kim, 2018; Dey and Ganguly, 2023) with gaps that concerns to encapsulation technics and shell materials. This, alongside the other advantages of salt hydrates pointed in the first chapter guided the decision to work with the $CaCl_2 \cdot 6H_2O$.



Figure 3.4: Nucleation of $CaCl_2 \cdot 6H_2O$ with 1 wt.% of $SrCl_2 \cdot 6H_2O$ captured using an inverted microscope (DMi8, Leica Microsystem, Germany).

As $CaCl_2 \cdot 6H_2O$ was chosen, a reduction in the supercooling phenomena is desired. Thakkar et al. (2022) proposed the addition of strontium chloride hexahydrate $(SrCl_2 \cdot 6H_2O)$, a nucleating agent, to improve chemical stability and mitigate supercooling phenomena. The proportion used is wt. 1% of $SrCl_2 \cdot 6H_2O$. A time course of nucleation and grain growth of the resulting salt hydrate is shown in Fig. 3.4.

3.2.2

Polydimethylsiloxane Microcapsules

The capsules were produced using the double emulsion template proposed by Utada et al. (2005). After the emulsion formation, the middle phase goes through a curing process, whereby the polymeric phase reticulates and forms the capsule shell. In this work, the double emulsion template is composed of $CaCl_2 \cdot 6H_2O$ as the inner phase, polydimethylsiloxane (PDMS) as the middle phase, and poly(vinyl alcohol) (PVA) as the outer phase.

The preparation of the internal phase samples starts with $CaCl_2 \cdot 6H_2O$ 99% (Sigma-AldrichTM) in solid state, as crystals, which are melted using a hot plate (Corning PC-420D, USA) at 35°C until complete melting. Subsequently, 1 wt.% of $SrCl_2 \cdot 6H_2O$ 99% (Sigma-AldrichTM) was added to the base salt and magnetic stirred for 2 hours at 35°C, until complete solubilization of the strontium chloride was achieved.

Polydimethylsiloxane (PDMS) (Sylgard 184 elastomer kit, Dow Corning) was used as middle phase. This PDMS uses a curing agent that increases the rate of reticulation with temperature. The preparation of the sample consists in vigorous mixing the PDMS with the curing agent by mechanical agitation for 2 minutes with a glass rod, this process generates undesired bubbles that interfere in the flow, so, after mixed, the PDMS is placed in vacuum chamber for 30 minutes, ensuring that it is completely free of bubbles. To enable visualization through fluorescence, Oil Glo 22 (Spectroline, Spectronics Corporation, USA) was added. Three different PDMS:crosslinker ratios were tested to produce the PCM microcapsules, 10:1, 5:1 and 2:1 and the results will be discussed later on this work.

The carrier phase is a 10 wt% PVA (MW 13000–23000 Da, 87–89 % hydrolyzed, from Sigma AldrichTM) solution, prepared using a hot plate at 80 °C for 40 minutes for complete solubilization. After that, the solution is left under magnetic stirring overnight at room temperature and, finally, filtered

using a 5 μm membrane.

3.2.3

Fluid Characterization

Figure 3.5 presents the flow curves of the PCMs selected in the previous section. Fluids were characterized using a stress-controlled rheometer (DHR-3, TA instruments, USA) with concentrical cylider geometry for $CaCl_2 \cdot 6H_2O$ and cone plate geometry for n-Octadecane. The fluids shown a Newtonian behavior, i.e., the viscosity is independent of the shear rate. The values obtained for the n-ocadecane are in agreement with those found in the literature (Abdi et al., 2020). For the $CaCl_2 \cdot 6H_2O$, there is a gap in the literature about the mechanical behavior of it, since it is difficult to find reliable information of its flow curves without and with the addition of $SrCl_2 \cdot 6H_2O$.



Figure 3.5: Flow curves of the selected PCMs at 30°C.

As this PDMS is a polymeric material whose solidification is triggered by mixing with a crosslinking agent and accelerated by temperature, the mechanical behavior of the polymeric shell depends on the proportion of crosslinker, temperature exposure and time after mixing. Figure 3.6 shows the influence of temperature in the reticulation time of PDMS with a crosslinker proportion of 5:1. The increase in viscosity indicates the action of the crosslinker, curing the PDMS. The results of temperature comparison shows that PDMS cure is significantly accelerated by the increase in temperature.



Figure 3.6: Viscosity of the polymeric phase with crosslinker proportion of 5:1 wt, for different temperatures and shear rate fixed at $10s^{-1}$.

3.2.4

Microfluidic Device

The production of the double emulsion templates is achieved using a three-dimensional coaxial microfluidic device in a configuration proposed by Utada et al. (2005). The device is built on a glass slide, where two cylindrical glass capillaries were placed on opposite sides of a square capillary.

- 1. The process starts with two cylindrical glass-capillaries (World Precision Instruments Inc., USA) exhibiting inner and outer diameters of 0.58mm and 1mm, respectively. They are tapered to an inner diameter of 20μ m by a micropipette puller (P-1000 Sutter Instruments Co., USA), which simultaneously heats and pulls them.
- 2. Then, the tips are manually sanded to the desired final inner diameter. The called injection capillary (left capillary in Fig 3.7) has a smaller inner tip diameter(ϕ_i), of 150 μ m and the collection capillary (right capillary in Fig 3.7) has a larger inner tip diameter(ϕ_c), of 580 μ m.
- 3. Both injection and collection capillaries are surface treated for one hour. The injection capillary is treated with the commercial hydrophobic rain repellent Glass Shield (Inove Pack do Brasil, Brazil). The collection



Figure 3.7: Detailed view of the center portion of the device. Adapted from Michelon et al. (2019).

capillary is treated with a hydrophilic polyelectrolyte solution, composed of 1 wt% of poly (acrylamide-co-diallydimethyl-ammonium chloride) (Sigma-Aldrich, USA) and 2M NaCl.

- Meanwhile, a square capillary with an inner dimension of 1.05 mm (Atlantic Internal Technology Inc., USA) is fixed to a glass slide with epoxy resin.
- 5. Once the chemical treatment has been completed, both capillaries are inserted at the opposite ends of the square capillary, coaxially aligned at a distance of 225 μm , using Epoxy.
- 6. Two stainless steel blunt dispensing needles of inner and outer diameter of 0.66 mm and 0.91 mm respectively (model 304, McMaster-Carr, USA) were placed at the junctions between capillaries and fixed in place with Epoxy resin. The final device is shown in Fig. 3.8.

To produce the desired W/O/W templates, the inner phase flows through the injection capillary, while the middle and outer phases flows in opposite directions at the interstice between the cylindrical capillary and the square capillary. (see Fig. 3.7)

Stable flow conditions in all three phases are essential for the correct formation of the W/O/W droplets, even bubbles or dirt could potentially impede the correct formation of the double emulsion. It is noteworthy that due the handmade nature of the devices, malfunctions may occur, mainly due to misalignment, non-conformity's at the inner diameters obtained after the sanding process or poor chemical treatment of the capillaries. These aforementioned error sources directly impacts the flow regime.



Figure 3.8: Coaxial glass-capillary device used to produce the PDMS-PCM templates.

3.2.5

Production Setup and Collection

Figure 3.9 presents the experimental setup for PCM microcapsule fabrication. The production of the double emulsion templates (W/O/W) was monitored using a high-speed camera (IL5-S, Fastec Imaging Corporation, USA) attached to an inverted microscope (DMi8, Leica Microsystem, Germany). The flow rates of the inner(Q_i), middle(Q_m), and outer(Q_o) phases were controlled by three syringe pumps (Pump 11, Harvard Apparatus, USA).

Given that the inner phase is the PCM and the room was maintained at 22°C, a solution had to be developed to heat the syringe containing the PCM and keep it a in liquid state. A water bath (Polyscience, USA) was used to pump hot water through a copper serpentine that encircles the syringe (see Fig. 3.10), maintaining the temperature between 35 °C and 40 °C. The syringes are connected to the capillary device by flexible tubes with an outer diameter of 0.052" and an inner diameter of 0.034". The fluids flow through these three tubes and, after saturating the microfluidic device, flow through the collection tube, which is attached to the capillary outlet. These connections are detailed in Fig. 3.8.

After leaving the microfluidic device (see Fig. 3.11(a)), the formed double emulsion passes through a 3.75 m tube, immersed in a water bath (see Fig.



Figure 3.9: Experimental setup for capsules production, including: (a) inverted microscope with a high-speed camera; (b) three syringe pumps; (c) water bath; (d) hot plate; (e) collecting vial; (f) computer

3.11(b)) with temperature fixed at 50 °C using a hot plate (Corning PC-420D, USA). This bath aims to accelerate the curing process of the PDMS shell. The main objective of this post-production bath is to reduce the possibility of the capsules to absorb free water from the environment due to the very high osmotic pressure inside the capsule. If the capsule absorbs water, it will change the concentration of the salt hydrate and thus change the melting temperature. This issue will be discussed in depth in the next section.

Finally, the capsules are collected in 20 ml vials (Fig. 3.11(c)) that initially contains Mili-Q water, the water is drained as soon as possible and substituted by the stock solution. The vials are placed in a tube rotator (Scilogex, USA) to avoid the coalescence of the freshly produced capsules, and remain there for one week, allowing complete reticulation of the polymeric shell.

3.2.6

Microcapsule Production and Characterization

For a fixed geometry of the microfluidic device, the operability window and the fine tune of capsules dimensions are dictated by the flow rates of the inner, middle, and outer phases (Chen et al., 2012; Michelon et al., 2019). The shell thickness is correlated to the ratio between the middle and inner phases flow rates (Q_m/Q_i) , the higher this ratio is, the thicker the capsule, thus, more PDMS is in the shell. The outer phase flow rate (Q_o) is related to the overall



Figure 3.10: First water bath setup (Polyscience, USA). (a) Serpentine encircling the PCM syringe.

size of the capsule, the greater this flow, the smaller the diameter of the capsule and the faster they are produced.

To successfully produce monodispersed W/O/W templates, a dripping regime, as shown in Fig. 3.12, is desired. This regime occurs when the ratio between the viscous shear stress of the surrounding fluid, responsible by the droplet break up, and the interfacial tension of the fluids, reaches a critical value where both interfaces break simultaneously at the same location (Baroud et al., 2010).

After production and recovery, every batch of microcapsules is characterized in terms of shell thickness (δ_c) and inner (D_i), outer diameters (D_o), as shown in Eq. 3-1. The measurement process begins with micrographs using a confocal fluorescence microscopy(TCS SP8 DMi8, Leica Microsystems, Germany). The images are processed using the software ImageJ (FIJI), at least 50 different capsules from each batch are measured.

$$\delta_c = \frac{D_o - D_i}{2} \tag{3-1}$$

3.3 Results and Discussion



Figure 3.11: Ongoing production of the capsules. (a) Passing through the microfluidic device; (b) Inside the 50°C bath; (c) Entering the collecting vial.



Figure 3.12: 2D diagram of the flow of the inner, middle and outer phases inside the device.

3.3.1

Stock Solution Development

To a better understanding of the issues faced with the initial stock solution, a breaf review in osmotic pressure and osmolality is needed. When two solutions are separated by a semi-porous membrane and its solute concentration is not equal, the water molecules tend to migrate from the higher concentrated solution to the lower one. This phenomenon is called osmosis. The strength of the process is measured by the osmotic pressure. Osmolality is a measurement of the concentration of solute per one kilogram of water of solution (Rasouli, 2016). So, the higher the osmolality, the higher this osmotic pressure is.

In the microcapsules field, osmotic pressure is one among different mechanisms that can be engineered to release the capsule payload (see Fig. 3.13) (Esser-Kahn et al., 2011; Zhang et al., 2017; Pessoa et al., 2024). As the goal of this work is not to target deliver an active, the osmotic pressure presented a challenge into development of a stock solution.



Figure 3.13: Schematics of osmotic pressure capsule burst mechanism. Adapted from Esser-Kahn et al. (2011).

To demonstrate this phenomenon, the microcapsules produced using the proposed methodology and materials, were collected in water and stayed 24 h in the tube rotator. As shown in Fig. 3.14, the microcapsules presented geometrical instabilities when submitted to the aqueous medium. The microcapsules swelled, achieved significantly higher diameters and some of them even burst. These results indicate that the PDMS shell allows the osmotic flow of water to permeate from the outer to the inner phase of the capsules.

After assessing that the osmotic pressure would be the cause of the instabilities seen in Fig. 3.14, $CaCl_2 \cdot 6H_2O$ osmolality was calculated to be about 14000 mOsmol/kg. With this number in mind, a stock solution with the same osmolality should be developed to match the osmotic pressure between the inside and outside of the capsule.



Figure 3.14: Microscopy of MPCM capsules 24 hours after production, stored in Milli-Q water.

A solution of 34.7 wt. % (5 M) of $CaCl_2$ anhydrous was prepared and the osmolality was was fine-tuned to a value of 14050 mOsmol/kg using a freezing point osmometer (K-7400S, Knauer, Germany).

With the osmotic pressure between the phases balanced, a production collecting the capsules directly in the $CaCl^2$ anhydrous presented incompatibilities between the carrier phase (PVA) and the stock solution. When the PVA gets mixed with the salt solution, it starts a process of gelification, damaging the capsules. This complication was solved with an intermediate collection phase, using Milli-Q water to rapidly wash the capsules before transferring them to the stock solution.

Figure 3.15 presents a confocal microscopy of the capsules that were produced and stored following the methodology. In contrast to the results observed for water-stocked capsules (Fig. 3.14), monodisperse microcapsules were achieved 24 hours after the production. Their stability was monitored over a period of 3 weeks, and, as shown in Fig. 3.16, inner and outer diameters remained stable.



Figure 3.15: Confocal fluorescence micrographs of the $CaCl_2 \cdot 6H_2O + SrCl_2 \cdot 6H_2O$ microcapsules 24 hours after production, stocked in $CaCl_2$ anhydrous 14000 mOsmol/kg solution.



Figure 3.16: Microcapsule average geometric parameters after 1, 7 and 21 days.

3.3.2

Capsule Production

3.3.2.1

Effect of PDMS/Crosslinker ratio

The microcapsules containing PCMs have to achieve an optimal balance between stiffness and elasticity, since the phase change process is accompanied by a variation of the internal volume. Therefore, during the research on optimal conditions to produce the capsules, one important parameter investigated was the ideal proportion between PDMS and its curing agent. The proportion of crosslinker not only affects the polymer viscosity, it but also changes the behavior of the fluid and the mechanical properties of the shell. Lower PDMS:crosslinker ratios, i. e., a higher crosslinker density, stiffer shells are produced, with the drawback of increased fragility. Conversely, an elevated ratio yields a less rigid and more elastic shell (Nascimento et al., 2017). Thus, PCM microcapsules were produced with three different PDMS to curing agent ratios: 10:1, 5:1, and 2:1.



Figure 3.17: Confocal fluorescence microscopy of 2:1 ratio capsules. (a) Thin capsules; (b) Thick capsules.



Figure 3.18: Inverted microscope images of 10:1 ratio capsules. (a) Thin capsules; (b) Thick capsules.

The 2:1 ratio exhibited an unstable flow behavior within the glass capillary, with a low encapsulation efficiency, with the presence of separated droplets from the various phases, yet failing to form the W/O/W template. It is worth mentioning that the capsules were formed only under extremely high



Figure 3.19: Inverted microscope images of 5:1 ratio capsules. (a) Thin capsules; (b) Thick capsules.

flow rates, with a total flow rate of 60 ml/h. As illustrated in Fig. 3.17, the majority of the capsules exhibited an absence of discernible internal phases, accompanied by a high polydispersity in size and the formation of satellite droplets.

From an encapsulation efficiency perspective, the 10:1 ratio presented a slightly better performance than the 2:1, but it is hard to stabilize the flow to an ideal intermittent dripping regime. The best case scenario was achieved with a total flow rate of 9 ml/h, producing capsules with around 650 μ m. Both thick and thin capsules also present a wide variety of diameters and satellite capsules (see Fig. 3.18).

Finally, the optimal condition was determined to be 5:1 ratio capsules, which exhibited excellent flow stability, reproducible results, and capacity to adjust the geometrical properties of the capsules, such as size and shell thickness, by changing the flow rate of the phases. Figure 3.19 shows geometrical consistency among the capsules.

3.3.2.2

Production of Capsules with Different Thicknesses

In this work, from a dimensional perspective, two different capsules were produced and from now on they will be referred as thinner and thicker capsules. To achieve this variation in shell tickness, two different sets of flow rates were used and are presented in Tab. 3.1.

Figure 3.20 presents images made with the high speed camera attached to the inverted microscope, enabling the observation of a stable production regime. The reflecting sphere at the core of the W/O/W templates is the

| | Inner Flow | Middle Flow | Outer Flow |
|--------------|-------------|-------------|-------------|
| | Rate [mL/h] | Rate [mL/h] | Rate [mL/h] |
| Thin Tick | $2 \\ 2$ | $2 \\ 3$ | 10 10 |

Table 3.1: Flow conditions used to produce thin and thick capsules.

PCM, encircled by a pinkish fluid which is the PDMS dyed with the fluorophore agent, Oil Glo 22. It is possible to observe even before characterization that the volume of the surrounding PDMS is greater in thicker capsule production(Fig. 3.20(b)). At this moment, the productivity of the setup was also evaluated. With the thin capsule production parameters, a rate of 690 capsules per minute was achieved. The thick ones yielded a rate of 780 capsules per minute, which can be attributed to the higher total flow rate of the setup, which was 15 mL/h, against 14mL/h.



Figure 3.20: Image from the high speed camera of (a) thin and (b) thick microcapsule production.

Figures 3.21(a) and 3.21(b) presents microcapsules of two different thicknesses fabricated using microfluidics. This approach successfully achieved geometric stability and demonstrated the capability to regulate dimensional parameters by changing flow conditions. Table 3.2 shows the mean values of relevant geometric dimensions of more than 40 different capsules. The minimal



Figure 3.21: Micrograph of the capsules using a confocal fluorescence microscopy.

dispersion observed among the samples attests to the efficacy of the employed methodology in producing monodisperse PCM/PDMS microcapsules.

| | Diameter $[\mu m]$ | Thickness $[\mu m]$ | $\delta_c/D_o~[\%]$ |
|------|--------------------|---------------------|---------------------|
| Thin | 655 ± 10 | 38 ± 4 | 5,80 |
| Tick | 633 ± 6 | 51 ± 4 | 8,06 |

Table 3.2: Average geometrical properties of different samples of thin and thick capsules produced under the Tab. 3.1 flow rates.

3.3.3

Preliminary Thermal Efficiency Tests

Prior to conducting experiments with capsules in concrete, preliminary validation tests were conducted to assess the capsule's response to temperature variations. The objective of these tests was to gain insight into the behavior of the MPCM and the capsule's shell under conditions of phase change stress.

The preliminary test consisted of heating the capsules evenly using a water bath. The vial containing the microcapsules was placed inside a becker with water being maintained at 40 °C by a hot plate. The vial was kept inside the bath until the internal temperature matched the outside water temperature. Figure 3.22 shows confocal fluorescence microscopy of the capsules before the heating cycle.



Figure 3.22: Micrographs of the capsules before the heating cycle using an confocal fluorescent microscope(Leica, Germany). (a) Brightfield channel; (b) Fluorescence channel

Observing Fig. 3.23, the PDMS shell did not withstand the internal payload during the phase change process. Figures 3.23(a) and 3.23(c) show apparent diffusion of the internal phase through the shell, this possibility is raised due to the change in the color, the PCM usually appears darker in the images. In Fig 3.23(b), it is possible to observe that some capsules got deformed, creating a weak spot in the shell, that is likely to burst at some point.

At Fig. 3.23(d), another issue is presented, as the capsules start to agglomerate after the heat cycle, hindering the clear visualization of the capsules. Moreover, some of the capsules appear to be empty, which may indicate that the PCM has leaked.



Figure 3.23: Capsules after the heating cycle.

Although PDMS/PCM microcapsules with different geometrical properties were successfully produced using microfluidic devices, their suitability to thermal efficiency applications may be limited, due to leakage of the internal phase and the instabilities observed during thermal cycling. Another capsule system must be investigated aiming to achieve stable and robust PCM microcapsules for building applications.

Final Remarks and Suggestions for Future Works

The aim of this dissertation was to evaluate two different aspects of microencapsulated phase change materials with a focus on building applications: (i) numerical simulation of the efficiency of using microencapsulated PCM in concrete walls; (ii) design and fabrication of PCM microcapsules using microfluidic devices.

The simulation focused on understanding the internal temperature behavior of a concrete wall with a thin layer of a mixture of concrete and capsules, considering the environmental conditions of a summer day in Rio de Janeiro. For this purpose, a one-dimensional transient model was used, taking into account solar radiation and convection on the outer surface of the wall, and natural convection on the inner surface of the wall. The method used to simulate the presence of the capsule was a concentration function. The results showed good agreement with what has been reported in the scientific literature, demonstrating that the the concentration function is able to accurately emulate the presence of capsules within a wall.

A direct correlation between the position of the layer and the efficiency of the PCM in lowering the internal temperature was demonstrated. The further closer to the inner surface of the wall and away from the outer surface of the wall, the most efficient the PCM is. In the best case, the indor temperature could be reduced by almost 12%, which shows that the use of PCM in buildings could be really beneficial from an energy efficiency point of view.

Experimentally, capsules of $CaCl_2 \cdot 6H_2O + 1$ wt % $SrCl_2 \cdot 6H_2O$ were successfully produced. The control and tunability of their geometric parameters were achieved by changing the ratio of the inner and middle flow rates, which emphasizes the advantageous use of microfluidic devices for microcapsules fabrication. A stock solution for capsules with very high osmotic pressure was developed, which showed good results in stabilizing the capsules over a period of 21 days.

Although the proposed method was capable of producing microencapsu-

The results show the potential of using microencapsulated phase change materials in buildings. From a numerical point of view, future works should aim to improve the solution process, reduce computation times and develop a more accurate 2D model that can account for the heterogeneous distribution of the capsules in the wall. From an experimental point of view, since the production methodology was successful, new pairs of payload and shell materials should be investigated to obtain robust and stable capsules for concrete applications. The main suggestions for future work in this area would be to carry out small-scale heat transfer experiments to compare the results with the numerical model.

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