Cementitious Composites Containing Microencapsulated Phase Change Materials for Sustainable Infrastructure

A thesis submitted in partial satisfaction of the requirements for the degree Master of Science in Mechanical Engineering

by

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This thesis aims to investigate design strategies for concrete construction materials containing microencapsulated phase change materials (PCMs) for energy-efficient buildings and sustainable infrastructure. First, numerical studies based on rigorous finite element simulations were carried out to predict the effective elastic moduli and thermal deformation coefficient of composites consisting of spherical core-shell microcapsules in a continuous matrix, and to identify effective medium approximations (EMAs) capable of accurately estimating these effective properties. Next, experiments studying the thermal behavior of small-scale test cells were conducted to evaluate the performance of microencapsulated PCM-composite building envelope materials. Scaling analysis was used to show how these small-scale test cells, conveniently placed in an environmental chamber, could represent the thermal behavior of time- and space-intensive full-scale outdoor test structures. Furthermore, a thermal model of a room with a PCM-composite envelope was used to examine the energy and cost savings potential of PCM-composite walls in the presence of an active indoor temperature control scheme. A model predictive control (MPC) algorithm that could preemptively account for melting and freezing of the PCM was developed. However, it did not significantly increase the energy and cost savings compared with a traditional proportional control scheme. Finally, temperature evolutions within microencapsulated PCM-composite concrete pavement sections were studied numerically. The inclusion of microencapsulated PCM within the
pavement section was found to reduce early-age temperature rise and corresponding spatial temperature gradients induced by cement hydration, thereby reducing the risk of early-age thermal cracking. Overall, the results of this thesis will be useful in the design of composite concrete containing microencapsulated phase change materials for sustainable infrastructure projects, including energy-efficient building envelopes and road pavements with enhanced lifetime.
The thesis of Benjamin Alexander Young is approved.

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NOMENCLATURE

A cross-sectional area, m²
B hydration rate parameter
Bi Biot number
C material/stiffness tensor, GPa
Cc cement content, kg/m³
Cd centroidal distance between two proximal capsules, µm
Cr heat capacity ratio or cooling cost reduction
c electricity cost, $/kWh
D diameter, µm
E Young’s modulus, GPa
Ea activation energy, J/mol
Fo Fourier number
G shear modulus, GPa
ΔH heat of hydration, J/kg
h convective heat transfer coefficient, W/m².K
hsf latent heat of fusion, J/kg
I identity tensor
K bulk modulus, GPa
Kp proportional control constant, W/°C
k thermal conductivity, W/m.K
L unit cell length or wall/pavement section thickness, m
Ls soil section thickness, m
̂n unit normal vector
N number of unit cells or number of time steps
Nu Nusselt number
p number of spherical capsules in a unit cell
Q total heat transfer, J or kWh
\( q'' \) heat flux, W/m\(^2\)
\( q_s'' \) incident solar radiation flux, W/m\(^2\)
\( q_c \) rate of heat removal by HVAC system, W
\( \dot{q} \) heat generation rate, W/m\(^3\)
\( R \) universal gas constant, J/mol.K
\( Re \) Reynolds number
\( t \) time, s or h
\( t_{eq} \) equivalent age, s or h
\( T \) temperature, °C
\( T_a \) inside air temperature, °C
\( T_p \) pavement temperature, °C
\( T_{pc} \) PCM phase change temperature, °C
\( T_{sa} \) sol-air temperature, °C
\( T_{sl} \) soil temperature, °C
\( T_{\infty} \) outdoor or chamber temperature, °C
\( T_{max}, T_{min} \) maximum and minimum outdoor temperatures, °C
\( T_{ref} \) reference or zero-strain temperature, °C
\( T_w \) Wall temperature, °C
\( \mathbf{u} \) displacement vector, m
\( u \) displacement in x-direction, m
\( v \) displacement in y-direction, m
\( w \) displacement in z-direction, m
\( V \) volume, m\(^3\)
\( x, y, z \) spatial coordinates, m
\( w/c \) water-to-cement ratio, mass basis

**Greek symbols**

\( \alpha \) thermal diffusivity, m\(^2\)/s, or thermal deformation coefficient, \( \mu \varepsilon /{\circ} \mathrm{C} \)
\( \Delta T_{pc} \) phase change temperature window, °C
\( \Delta x \) nodal spacing or mesh size, m
\[ \varepsilon \]  total hemispherical emissivity  
\[ \epsilon \]  strain tensor  
\[ \lambda, \mu \]  Lame's first and second parameters, GPa  
\[ \nu \]  Poisson's ratio  
\[ \phi_j \]  volume fraction of component \( j \) in composite  
\[ \phi_{c+s} \]  volume fraction of core-shell microcapsules, \( \phi_{c+s} = \phi_c + \phi_s \)  
\[ \rho_j \]  density of material \( j \) in composite, \( \text{kg/m}^3 \)  
\[ \sigma \]  Stefan-Boltzmann constant, \( \text{W/m}^2\cdot\text{K}^4 \)  
\[ \sigma \]  stress tensor, GPa  
\[ \tau \]  characteristic hydration time or oscillation period, s or h  
\[ \theta \]  wall orientation angle or degree of hydration  
\[ \theta_\infty \]  ultimate degree of hydration

**Subscripts**

- \( a \)  refers to air  
- \( c \)  refers to core material in composite  
- \( c + s \)  refers to core-shell microcapsule  
- \( eff \)  refers to effective properties  
- \( j \)  refers to material \( j \) in composite or face \( j \) of unit cell  
- \( l \)  refers to liquid phase  
- \( ls \)  refers to limestone  
- \( m \)  refers to matrix material in composite  
- \( p \)  refers to inclusion  
- \( q \)  refers to quartz  
- \( s \)  refers to solid phase or shell material in composite  
- \( sl \)  refers to soil

**Superscripts**

- \( T \)  denotes matrix/vector transpose  
- \( * \)  denotes dimensionless quantity
1.1 Phase change materials in cementitious composites

Phase change materials (PCMs) are energy storage materials that can store large amounts of thermal energy thanks to the latent heat associated with their melting and solidification [10–12]. PCMs are typically classified as organic, inorganic, or eutectic [11, 12]. Organic PCMs are often comprised of paraffin wax blends, but also include fatty acids and alcohols [11, 12]. Advantages of organic, paraffin-based PCMs include: (i) low cost, (ii) chemical stability, and (iii) non-corrosiveness [11]. By blending paraffins with different alkane chain lengths, manufacturers are able to produce PCMs over a wide range of specified melting temperatures [13].

While PCMs are used in a broad range of applications, this study focuses on their use within cementitious composites as a means to significantly increase the thermal mass of concrete, i.e., its capacity to store thermal energy). This increased thermal mass is beneficial to the energy-saving performance of concrete building envelope materials, as well as to the longevity of concrete road pavements, for example. Several methods of incorporating PCMs into concrete exist [14]. Microencapsulation is a process by which PCMs are encapsulated within polymeric (e.g., high-density polyethylene or melamine-formaldehyde) shells with diameters ranging from 1 µm to 1 mm (i) to prevent the leakage of liquid PCM and reaction with the cementitious matrix, and (ii) to minimize the risk of flammability for organic PCMs [11, 14–17]. Figure 1.1 shows an SEM image of PCM microcapsules (MPCM24D, Microtek Labs, Inc.) encapsulated in melamine-formaldehyde [18]. PCMs can also be macroencapsulated in larger containers such as cylindrical tubes, however, this can lead to incomplete
melting and solidification of the PCM and result in undesirable augmentation of heat transfer by natural convection within the PCM [12, 19]. Therefore, microencapsulation is the preferred method of integrating PCMs into cementitious systems.

While the addition of microencapsulated PCMs to concrete may offer substantial benefit in terms of thermal performance, the microencapsulated PCMs typically demonstrate thermomechanical properties inferior to the cement paste matrix, including compressive strength [20, 21], elastic modulus [20, 21], and thermal deformation coefficient [22]. As a result, the inclusion of microencapsulated PCMs in concrete worsens its thermomechanical properties, thereby placing limits on the allowable dosage of PCM. The ability to predict the extent of such degradation, and therefore to determine such dosage limits, is crucial to the design of PCM-composite concrete.

The present study focuses on predicting the effect of microencapsulated PCMs or other particulate inclusions on the effective elastic moduli and thermal deformation coefficient of three-component composites through numerical simulation, experimental measurements, and effective medium approximations.
1.2 Improving building energy efficiency

In the United States, residential and commercial buildings are responsible for around 41% of primary energy consumption, as shown in Figure 1.2 [1]. Building energy consumption is expected to further increase by 10% through 2035 [1]. Furthermore, the state of California has mandated that all new residential and commercial buildings qualify as zero-net energy (ZNE) buildings by 2020 and 2030, respectively [23]. Around half of the energy consumed in buildings can be attributed to the operation of heating, ventilation and air conditioning (HVAC) systems [1]. Therefore, reducing the amount of energy required for space heating and cooling in buildings would have a significant impact on energy consumption and CO$_2$ emissions.

One way to curb heating and cooling energy consumption in buildings would be to increase the thermal mass of building envelopes. Conventional concrete has a large thermal mass and thus is attractive as a building envelope material [24]. Because of this, and because concrete is already used heavily in the construction industry, it is a very practical host for
microencapsulated PCMs in building envelopes. By incorporating PCMs into the concrete, the PCM’s latent heat storage capacity can be exploited to further increase envelope thermal mass and reduce the thermal loads on the building [10, 12, 25, 26]. For example, the PCM could absorb incident heat during a hot day as it melts, and release heat back to the environment at night as it solidifies, therefore reducing the energy required to cool the inside air.

Numerous studies have investigated the benefits of adding PCMs to building envelope materials, as reviewed in Refs. [27–29]. Many of these studies considered large experimental building structures or “cubicles” with PCM-composite envelopes [7, 30–34]. The thermal behavior represented by the structure’s indoor temperature evolution or inner wall heat flux with and without PCM-composite envelopes were compared. The results establish the potential of PCM composite envelopes to dampen undesirable indoor temperature fluctuations or reduce the amount of energy required for space heating and cooling within the structures. These experimental demonstrations [7, 30–34] provide valuable assessments of PCM-composite envelope performance. However, constructing these structures is time-intensive and also requires a large amount of available outdoor space. As a result, such full-scale experimental studies are difficult to conduct, particularly in urban areas. One aim of the present study is to demonstrate, through scaling analysis, how the thermal behavior of PCM-composite building envelopes can be accurately captured with small-scale experiments.

In addition, many studies have used numerical modeling to predict the reduction in magnitude of heating and cooling loads that PCM-composite walls provide compared with conventional walls [27]. For example, Thiele et al. [25, 26] used a transient thermal model of a PCM-concrete composite wall to evaluate the diurnal reduction in heating and cooling loads (i.e., heat flux through the wall) afforded by adding microencapsulated PCM to the wall. PCMs were found to be most effective in reducing heating and cooling loads in “moderate” climates—i.e., those in which the ambient temperature fluctuates above and below the thermal comfort range over a diurnal cycle. Importantly, it was also established that a PCM with melting temperature near the desired indoor temperature provides the largest possible thermal load reduction, irrespective of the outdoor climate conditions [25, 26]. Furthermore,
the PCM’s latent heat can time-shift the peak heat load past the mid-day period of high energy demand, resulting in additional electricity cost savings when time-of-use pricing is in effect [26]. While such numerical studies have presented valuable insights toward the design of PCM-composite building envelopes, most of these studies do not consider the presence of an active heating or cooling system that supplies or removes thermal energy from the indoor air. Rather, they either allow the temperature of the indoor air to vary freely or assume that the building temperature control system is “perfect” (i.e., maintains the indoor temperature at some specified constant value). It is unclear whether the reduction in heating/cooling load afforded by PCM-composite walls, as predicted by the aforementioned studies, corresponds to similar energy and cost reduction in the presence of an active heating or cooling system operated using conventional temperature control schemes. Furthermore, one wonders if a more advanced control scheme could provide additional energy and cost savings, perhaps by anticipating heat storage and release due to PCM melting and solidification.

The present study uses a simple thermal model of a room controlled with traditional feedback temperature control methods, namely (i) on/off control or (ii) proportional control, or an adapted model predictive control (MPC) scheme to examine the potential energy and cost benefits of a PCM-composite wall compared with a conventional concrete wall, and to determine whether these energy and cost savings depend on the control method used.

1.3 Enhancing life of concrete pavements

Another application of PCM-composite concrete is in road pavements and bridge decks. Indeed, the quality of American roads was given a grade of “D” by the American Society of Civil Engineers in 2013 [35]. A major contributor to road deterioration is thermal cracking in concrete pavements, which can be divided into two categories: (i) early-age thermal cracking and (ii) thermal fatigue cracking. Early-age cracking occurs as a result of exothermic hydration reactions between ordinary portland cement (OPC) and water within the fresh concrete. Heat release from such reactions causes the internal temperature within the pavement sections to rise, leading to the development of thermal strains and stresses and
possibility to crack. The inclusion of microencapsulated PCMs into concrete has been suggested as a means of reducing early-age temperature rise and mitigating the corresponding cracking risk [17, 36]. The PCM’s latent heat can be exploited to absorb a portion of the heat released by cement hydration, thereby lowering the extent of temperature rise within the section. Furthermore, the heat is then released upon PCM solidification, slowing the rate of temperature decrease in the section to mitigate the risk of shrinkage cracking.

While the use of PCMs in concrete pavements is a promising approach to reduce cracking risk, such an application has yet to be rigorously explored through modeling. The effect of PCM dosage on early-age temperature rise in cementitious materials has been studied [17,36], however, the thermal behavior of full-sized PCM-containing pavement sections exposed to realistic climate conditions has not been modeled. It remains unclear how much of an effect the inclusion of PCMs has in reducing early-age temperature rise within fresh pavement sections, and how this reduction in temperature rise is influenced by environmental factors and the effective thermal properties of the PCM-composite concrete.

The present study aims to quantify this effect and its dependence on climate conditions and PCM properties, and to develop design rules that can inform the best selection of microencapsulated PCMs for reducing the probability of early-age pavement cracking.

1.4 Objectives and scope

The overall goal of this research is to provide insights which facilitate the design of cementitious materials with improved thermomechanical properties via the inclusion of microencapsulated PCMs. Figure 1.3 illustrates how each chapter of the thesis contributes to this overall goal. Chapter 2 provides a brief background on thermomechanical properties of solids and numerical modeling of PCM-composite concrete. Chapter 3 provides a numerical study on the effective elastic moduli of core-shell-matrix composites, such as concrete containing microencapsulated PCMs. Similarly, Chapter 4 investigates the effect of core-shell inclusions on the effective thermal deformation coefficient of cementitious composites. Chapter 5 presents the results of reduced-scale experiments evaluating the performance of
PCM-composite building envelope materials, along with a scaling analysis demonstrating how the reduced-scale test cells can be representative of the thermal behavior of full-scale building structures. Chapter 6 evaluates how the energy and cost savings associated with PCM-composite building envelopes are affected by the indoor air temperature control scheme within a building. Finally, Chapter 7 presents a numerical study on early-age temperature evolutions within PCM-composite pavement sections.
CHAPTER 2

Background

2.1 Thermomechanical properties of solids

Linear elastic constitutive relationships for an isotropic material are given by [37]

\[ \sigma = C : \epsilon \] (2.1)

where \( \sigma \) and \( \epsilon \) are the stress and strain tensors, respectively, and \( C \) is the fourth-order stiffness tensor. The latter is a property of the material and depends on its microstructure and temperature. The same expression can be written in component form as,

\[ \sigma_{ij} = C_{ijkl} \epsilon_{kl} \] (2.2)

where summation is implied over repeated indices, and their ranges are given as \{i, j, k, l\} \( \in \) \{1, 2, 3\}. For homogeneous and isotropic materials, the tensor \( C \) is given by

\[ C_{ijkl} = \lambda \delta_{ij} \delta_{kl} + \mu ( \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} ) \] (2.3)

where \( \lambda \) and \( \mu \) are the Lamé parameters, and \( \delta_{\alpha\beta} \) denotes a Kronecker delta. The material tensor in Equation (2.3) can be also be expressed in terms of other well known elastic moduli, using the following identities

\[ \lambda = \frac{E \nu}{(1 + \nu)(1 - 2\nu)} = K - \frac{2}{3}G, \quad \mu = \frac{E}{2(1 + \nu)} = G \] (2.4)

where \( E, K, \) and \( G \) are, respectively, the Young’s, bulk, and shear moduli, while \( \nu \) is the Poisson’s ratio.

Furthermore, the constitutive law can be modified to account for the effect of thermal strain as follows [38],

\[ \sigma = C : (\epsilon - \epsilon_T) \quad \text{or} \quad \sigma_{ij} = C_{ijkl}(\epsilon_{kl} - \epsilon_{T,kl}) \] (2.5)
where \( \varepsilon \) and \( \varepsilon_T \) denote the total and thermal strain tensors, respectively. For an isotropic material, the thermal strain \( \varepsilon_T \) is related to the imposed temperature change \( \Delta T \) according to [38],

\[
\varepsilon_T = (\alpha \Delta T) I \quad \text{or} \quad \varepsilon_{T,ij} = \alpha \Delta T \delta_{ij}
\]  

(2.6)

where \( \alpha \) is the thermal deformation coefficient and \( \Delta T \) is defined with respect to some reference or zero-strain temperature \( T_{\text{ref}} \), i.e., \( \Delta T = T - T_{\text{ref}} \) [38]. Note that in a homogeneous material that is not mechanically restrained, \( \varepsilon = \varepsilon_T \) and the stress field is identically zero throughout the material. On the other hand, if it is fully restrained then \( \varepsilon = 0 \) and a stress is induced for \( \Delta T \neq 0 \).

### 2.2 Thermal modeling of PCM-containing cementitious composites

The thermal behavior of composites consisting of spherical inclusions embedded in a continuous matrix, such as concrete with microencapsulated PCM inclusions, was shown to be accurately predicted by simulating an equivalent homogeneous material with appropriate effective thermal properties [25,39]. Such an approach allows for a large reduction in the computation time associated with simulating heat transfer in PCM-composite concrete domains. Heat transfer in the effective homogeneous material can often be treated as one-dimensional, as opposed to the three-dimensional geometry that arises when considering spherical capsules inclusions in a matrix. Based on robust thermodynamic arguments, the effective volumetric heat capacity of the composite was computed as a volume-weighted average of the different heat capacities [25],

\[
(\rho c_p)_{\text{eff}}(T) = \phi_c (\rho c_p)_c(T) + \phi_s (\rho c_p)_s + (1 - \phi_c - \phi_s) (\rho c_p)_m
\]  

(2.7)

where \( \phi_c \) and \( \phi_s \) are the volume fractions of the core and shell components of the microencapsulated PCM, respectively. The effective thermal conductivity of the composite was then
computed using Felske’s model as [40],

\[
k_{\text{eff}} = \frac{k_m(1 - \phi_c - \phi_s)}{(2 + \phi_c + \phi_s) \left[ 3 + 2 \frac{\phi_s}{\phi_c} + \frac{\phi_s k_c}{\phi_c k_m} \right] + (1 - \phi_c - \phi_s) \left[ 3 + \frac{\phi_s}{\phi_c} k_c + 2 \frac{\phi_s}{\phi_c} k_s \right]}.
\]  

(2.8)

To accurately capture the effect of phase change on temperature development in PCM-concrete composites, the effective heat capacity method [10] can be used to describe the PCM’s specific heat \( c_{p,c}(T) \) as a rectangular step function of temperature, i.e.,

\[
c_{p,c}(T) = \begin{cases} 
  c_{p,c,s} & \text{for } T < T_{pc} - \Delta T_{pc}/2 \\
  c_{p,c,s} + \frac{h_{sf}}{\Delta T_{pc}} & \text{for } T_{pc} - \Delta T_{pc}/2 \leq T \leq T_{pc} + \Delta T_{pc}/2 \\
  c_{p,c,l} & \text{for } T > T_{pc} + \Delta T_{pc}/2
\end{cases}
\]  

(2.9)

where \( c_{p,c,s} \) and \( c_{p,c,l} \) are the specific heats (in J/kg.K) of the PCM in the solid and liquid states, respectively, \( h_{sf} \) is its latent heat of fusion (in J/kg), \( T_{pc} \) is the PCM’s melting temperature, and \( \Delta T_{pc} \) is the melting temperature window over which phase change occurs. It should be noted that the use of a step function or Gaussian function to describe phase change behavior results in little, if any difference in terms of simulated thermal behavior [6]. The effective heat capacity method allows one to easily parameterize and examine the influences of different PCM properties including: \( h_{sf}, T_{pc}, \) or \( \Delta T_{pc} \). This method was previously validated against an exact solution for the 1D Stefan problem of heat conduction in a paraffin slab undergoing phase change [6, 25].
CHAPTER 3

Effective Elastic Moduli of Core-Shell-Matrix Composites

3.1 Background

Effective medium approximations (EMAs) have been formulated to predict the effective elastic moduli of three-component core-shell-matrix composites. Various expressions of EMAs developed for $E_{\text{eff}}$, $\nu_{\text{eff}}$, $G_{\text{eff}}$, and $K_{\text{eff}}$ as functions of the elastic moduli of the core (subscript $c$), the shell (subscript $s$), and the matrix (subscript $m$) and of their respective volume fractions, denoted by $\phi_c$, $\phi_s$, and $\phi_m$, are discussed in the next section. Some EMAs use the core-shell volume fraction defined as $\phi_{c+s} = \phi_c + \phi_s$ [2, 41].

3.1.1 Two-component EMAs

Numerous EMAs have been developed to predict the effective elastic moduli of two-component composite materials consisting of particles embedded in a continuous matrix, as reviewed in Ref. [42]. Voigt [43] and Reuss [44] proposed upper and lower bounds for the effective elastic moduli of n-component composites using the parallel and series models, respectively. However, these models are both based on a simple two-dimensional geometry consisting of continuous layered fibers. In addition, the bounds do not typically give a close prediction of the effective elastic moduli of composites with spherical geometry. Another set of bounds was developed by Hashin and Shtrikman [45]. The authors used variational principles in elasticity without any assumption on the composite geometry. These bounds gave a “good” estimate of the effective elastic moduli $E_{\text{eff}}$ and $\nu_{\text{eff}}$ when the ratios between the moduli of
constituent components were “not too large” [45].

Christensen and Lo [46] developed a generalized self-consistent method (GSCM) by representing a two-component composite as a three-component composite consisting of the same concentric core and shell phases surrounded by the equivalent homogeneous effective medium having the effective mechanical properties of the two-phase composite. Hobbs [4] developed an EMA for the effective Young’s modulus $E_{\text{eff}}$ of two-component composites which solely depended on the core volume fraction $\phi_c$ and on the Young’s moduli of the core and matrix $E_c$ and $E_m$, expressed as

$$E_{\text{eff}} = E_m \left[ 1 + \frac{2\phi_c(E_c - E_m)}{(E_c + E_m) - \phi_c(E_c - E_m)} \right]. \quad (3.1)$$

3.1.2 Three-component EMAs

Qiu and Weng [2] used the formulation given by Christensen and Lo [46] to develop upper and lower bounds for the effective shear modulus $G_{\text{eff},+}$ and $G_{\text{eff},-}$ of three-component composites given by

$$G_{\text{eff},+} = G_m + \phi_c(G_c - G_m) \left( b_1^{(e)} - \frac{21}{5(1 - 2\nu_c)} b_2^{(e)} \right) +$$

$$\phi_s(G_s - G_m) \left( b_3^{(e)} - \frac{21}{5(1 - 2\nu_s)} \frac{\phi_{c+s}^{5/3} - \phi_c^{5/3}}{\phi_s \phi_{c+s}^{2/3}} b_4^{(e)} \right), \quad (3.2)$$

$$G_{\text{eff},-} = \left[ \frac{1}{G_m} + \phi_c \left( \frac{1}{G_c} - \frac{1}{G_m} \right) \left( b_1^{(\sigma)} - \frac{21}{5(1 - 2\nu_c)} b_2^{(\sigma)} \right) \frac{G_c}{G_m} + \right.$$

$$\phi_s \left( \frac{1}{G_s} - \frac{1}{G_m} \right) \left( b_3^{(\sigma)} - \frac{21}{5(1 - 2\nu_s)} \frac{\phi_{c+s}^{5/3} - \phi_c^{5/3}}{\phi_s \phi_{c+s}^{2/3}} b_4^{(\sigma)} \right) \frac{G_s}{G_m} \right]^{-1}. \quad (3.3)$$

where $b_i^{(e)}$ and $b_i^{(\sigma)}$ are constants dependent on the elastic moduli of individual components and whose expressions can be found in Ref. [2]. In most cases, the authors found that these bounds were “tighter than” the Hashin-Shtrikman bounds [45]. They also derived an analytical model for the effective bulk modulus $K_{\text{eff}}$ of a three-component composite [2] using Hashin’s expression for two-component composites represented by a single homogeneous particle embedded in a matrix [47]. The authors first applied Hashin’s solution to determine
the effective bulk modulus of an effective core-shell particle $K_{\text{eff},p}$. Then, they developed an exact solution of the effective bulk modulus of the three-component composite by again using Hashin’s solution with $K_{\text{eff},p}$ as the core phase. The exact solution for $K_{\text{eff}}$ was given by [2]

$$
K_{\text{eff}} = K_m + \frac{(K_m + \frac{4}{3}G_m) \left[ A_{12} + B_{12} \left( K_c + \frac{4}{3}G_s \right) \right]}{-A_{12} - \frac{4}{3} \phi_c (G_m - G_s) + (K_c + \frac{4}{3}G_s) \left( \frac{K_c + \frac{4}{3}G_m}{K_c - K_s} - B_{12} \right)}
$$

(3.4)

where the parameters $A_{12}$ and $B_{12}$ are defined as

$$
A_{12} = \phi_c \left( K_m + \frac{4}{3}G_s \right) \quad \text{and} \quad B_{12} = \phi_{c+s} \frac{K_s - K_m}{K_c - K_s}.
$$

(3.5)

Note that the authors did not compare predictions of their model with numerical or experimental results.

Herve and Zaoui [41] extended Christensen and Lo’s model [46] to develop analytical solutions for an $(n+1)$-component sphere consisting of $n$ concentric layers surrounding a core to yield an expression for the effective shear modulus $G_{\text{eff}}$. They also derived an expression for the effective bulk modulus $K_{\text{eff}}$ which was the same as Equation (3.4) derived by Qiu and Weng [2]. Here, the authors assumed that all components were isotropic and linearly elastic and that there was continuous contact at the interfaces between layers. However, they did not validate the expression derived for the elastic moduli with numerical predictions or experimental measurements.

Dunn and Ledbetter [48] used Hori and Nemat-Nasser’s analysis of the average elastic fields in a double inclusion, consisting of two concentric inclusions in an infinite matrix, to develop an analytical expression for the effective stiffness tensor $C_{\text{eff}}$ of three-component core-shell-matrix composites. The predictions of their model agreed well with the experimentally measured effective Young’s modulus $E_{\text{eff}}$ and Poisson’s ratio $\nu_{\text{eff}}$ of mullite/Al$_2$O$_3$ particles embedded in an aluminum matrix for core-shell particle volume fractions $\phi_{c+s}$ ranging from 0 to 0.3. Note that the experimental samples did not correspond to the core-shell particle modeled since the Al$_2$O$_3$ particles were randomly dispersed in spherical mullite particles.

Yang [50] also used Hori and Nemat-Nasser’s double inclusion method [49] to represent spherical concentric core and shell as an effective particle. The author then used the Mori-
Tanaka method [51] to determine the effective stiffness tensor \( C_{\text{eff}} \) of the two-component composite formed by an effective particle embedded in a matrix. Yang [50] compared the effective Young’s modulus predicted by the model with experimental measurements of concrete, where sand, the interfacial transition zone (ITZ), and mortar were modeled as the core, shell, and matrix materials, respectively. The mechanical properties of the ITZ were unknown so an exact comparison between analytical and experimental results could not be performed. Instead, Yang [50] determined that, for a given shell thickness and core volume fraction \( \phi_c \) ranging from 0 to 0.5, the experimental results were within the bounds predicted by the model for shell to matrix Young’s modulus ratios \( E_s/E_m \) ranging from 0.2 to 0.7.

Garboczi and Berryman [3] used differential effective medium theory (D-EMT) to develop an analytical expression for the effective bulk modulus \( K_{\text{eff}} \) and shear modulus \( G_{\text{eff}} \) of microcapsules randomly distributed in a matrix. First, the core and shell were represented as an effective particle using the generalized self-consistent method [46]. The effective bulk modulus \( K_{\text{eff}} \) for the three-component composite was given by [3]

\[
K_{\text{eff}} = \frac{K_m}{\phi_m^k} \quad (3.6)
\]

where the power \( k \) is expressed as [3]

\[
k = \frac{(K_m + \frac{4}{3}G_m)(K_{\text{eff,p}} - K_m)}{K_m (K_{\text{eff,p}} + \frac{4}{3}G_m)} \quad (3.7)
\]

Here, the bulk modulus of the effective core-shell particle \( K_{\text{eff,p}} \) was given by [3]

\[
K_{\text{eff,p}} = K_s + \frac{\phi_{c/s}(K_c - K_s)}{1 + (1 - \phi_{c/s}) \frac{K_c - K_s}{K_s + \frac{4}{3}G_s}} \quad (3.8)
\]

where \( \phi_{c/s} = \phi_c/\phi_{c/s} \). In addition, the effective shear modulus \( G_{\text{eff}} \) was expressed as [3]

\[
G_{\text{eff}} = \frac{G_m}{\phi_m^g} \quad (3.9)
\]

where the power \( g \) was given by [3]

\[
g = \frac{5(K_m + \frac{4}{3}G_m)(G_{\text{eff,p}} - G_m)}{3G_m (K_m + \frac{8}{9}G_m) + 2G_{\text{eff,p}}(K_m + 2G_m)} \quad (3.10)
\]
Here, the shear modulus of the effective core-shell particle $G_{\text{eff,p}}$ was retrieved by solving the quadratic equation [3]

$$A \left( \frac{G_{\text{eff,p}}}{G_s} \right)^2 + 2B \left( \frac{G_{\text{eff,p}}}{G_s} \right) + C = 0$$  \hspace{1cm} (3.11)

where $A$, $B$, and $C$ are constants depending on the radii and elastic moduli of the core and shell components. Their expressions can be found in Ref. [3]. The authors found that the predictions of their model were in good agreement with those obtained from two- and three-dimensional (2D and 3D) numerical simulations of monodisperse and polydisperse microcapsules randomly distributed in a matrix. However, the only material property that was varied in the numerical simulations was the shell Young’s modulus $E_s$. Thus, the validity of this model has not been established for a wide range of core, shell, and matrix mechanical properties.

Li et al. [52] developed an expression for the effective Young’s modulus $E_{\text{eff}}$ of monodisperse and polydisperse particles randomly distributed in a matrix. To derive this expression, they extended the generalized self-consistent method [46] to represent a spherical inclusion, shell, and matrix as a four-phase sphere consisting of a core-shell-matrix particle embedded in an infinite equivalent medium. The effective Young’s modulus was dependent on the effective Poisson’s ratio $\nu_{\text{eff}}$ of the three-component composite. Using the parallel model to predict $\nu_{\text{eff}}$, the authors found good agreement between the predictions of their model and experimental measurements of the effective Young’s modulus of concrete for core volume fractions between 0.4 and 0.8.

Overall, numerous studies [2–4, 41, 43–45, 48, 50, 52] have derived EMAs analytically to predict the effective mechanical properties of core-shell particles embedded in a matrix. However, it remains unclear how the predictions of these EMAs differ from one another and which one is the most accurate. Moreover, most EMAs were typically obtained analytically by considering a single core-shell capsule in an infinite matrix as a representative elementary volume of the three-component composite material. None of these studies investigated whether the effective mechanical properties depend on packing arrangement or particle size distribution. Furthermore, the studies presenting EMAs did not specify their range of applicability for constituent material properties and volume fractions. What’s more, they often
were not validated against experiments or detailed numerical simulations.

The present study aims to perform detailed numerical simulations of three-component core-shell-matrix composites under elastic deformation to elucidate the effect of the composite’s morphology and the constituent’s mechanical properties on the effective Young’s modulus and Poisson’s ratio. It also aims to identify EMAs capable of accurately predicting the effective Young’s modulus and Poisson’s ratio of three-component composites over a wide range of composite morphologies, volume fractions, Young’s moduli, and Poisson’s ratios of the core, shell, and matrix.

3.2 Analysis

3.2.1 Schematics and assumptions

The deformation of composite materials consisting of (i) matrix containing monodisperse spherical microcapsules with simple cubic (SC), body-centered cubic (BCC), or face-centered cubic (FCC) packing arrangements and of (ii) monodisperse and polydisperse microcapsules randomly distributed throughout the matrix was simulated numerically. Figure 3.1 shows a quarter of a simulated unit cell with (a) SC, (b) BCC, and (c) FCC packing arrangements along with the associated Cartesian coordinate system. In addition, a microstructural stochastic packing algorithm [53] was used to create geometric models of monodisperse and polydisperse microcapsules randomly distributed in a matrix. Spherical microcapsules were placed at random locations in a 3D representative volume of arbitrary size until the desired core and shell volume fractions were achieved. Microstructural generation and positioning was conducted such that the minimum centroidal distance $C_D$ between two proximal microcapsules was always greater than the sum of their radii $r_1$ and $r_2$, i.e., $C_D > r_1 + r_2$ [53].

Figure 3.2 shows examples of simulated (a) monodisperse and (b) polydisperse microcapsules randomly distributed in a continuous matrix. Here, the representative elementary volume was a cube 75 $\mu$m in length.

To make the problem mathematically tractable, the core, shell, and matrix materials
Figure 3.1: Schematics of core-shell particles with an (a) SC, (b) BCC, and (c) FCC packing.
were assumed to be isotropic, homogeneous, and linearly elastic with constant mechanical properties. Additionally, the interfaces between components were assumed to be continuous, i.e., no sliding or gapping was allowed. Finally, body forces were assumed to be negligible.

3.2.2 Governing equations and boundary conditions

The linear elastic boundary value problem in each component of the composite material is defined through the (i) differential equilibrium equations, (ii) the strain-displacement relationships, and (iii) the constitutive relations given in Equation (2.1).

First, in the absence of body forces, the differential equilibrium equation in any component is expressed as [37],

$$
\nabla \cdot \sigma = 0 \quad \text{or} \quad \sigma_{ij,j} = 0.
$$

(3.12)

Second, the strain-displacement relation in any component is given by,

$$
\epsilon = \frac{1}{2}[\nabla u + \nabla^T u] \quad \text{or} \quad \epsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}).
$$

(3.13)

where \( u = [u, v, w]^T \) is the displacement vector. Finally, the constitutive law for each constituent is given by

$$
\sigma = C_I : \epsilon
$$

(3.14)

where the subscript \( I = \{c, s, m\} \) denotes the material tensor for either the core, the shell, or the matrix.

Combining Equations (3.12) to (3.14) results in governing equations expressed solely in terms of the displacement field. These equations are referred to as Navier’s equations, which, for the present case, are given by

$$
(\lambda_I + \mu_I) \nabla(\nabla \cdot u_I) + \mu_I \nabla^2 u_I = 0.
$$

(3.15)

where \( \lambda_I \) and \( \mu_I \) are the Lamè’s parameters for each constituent.

In order to fully define the problem at hand, boundary conditions must also be prescribed for the unit-cell domain shown in Figure 3.1. To do so, six boundary conditions are required, which were selected in order to model the elastic deformation of a computational domain of
Figure 3.2: Schematics of unit cells used for numerical simulations with (a) monodisperse microcapsules, $\phi_c = 0.097$, and $\phi_s = 0.041$ as well as with (b) polydisperse microcapsules, $\phi_c = 0.095$, and $\phi_s = 0.041$. 
length \( L \) in the \( y \)-direction. The displacement in the \( y \)-direction (i.e., \( v \)) was set equal to \( \Delta L \) on the face of the unit cell at \( y = L \) while the opposing face (\( y = 0 \)) was fixed in the \( y \)-direction such that,

\[
v_i(x, L, z) = \Delta L \quad \text{and} \quad v_i(x, 0, z) = 0. \tag{3.16}
\]

By virtue of symmetry, the unit cell faces normal to the \( x \)- and \( z \)-directions were immobile in the directions perpendicular to the imposed uniform strain. Therefore, the displacements in the \( x \)- and \( z \)-directions (i.e., \( u \) and \( w \)) vanished, i.e.,

\[
u_i(0, y, z) = 0, \quad u_i(L, y, z) = 0, \quad w_i(x, y, 0) = 0, \quad \text{and} \quad w_i(x, y, L) = 0. \tag{3.17}
\]

Finally, continuous/welded contact between the cores and the inner shells and between the outer shell and the matrix implied displacement continuity across their interfaces.

### 3.2.3 Data processing

Equations (3.13) and (3.14) were used to obtain the local strains, and subsequently stresses, throughout the unit cells from the displacement vector \( \mathbf{u} \). The stress and strain components were not uniform throughout the heterogeneous structure, and thus were volume-averaged to obtain the average stresses. Because the direct stress components—namely, \( \sigma_{11} = \sigma_x \), \( \sigma_{22} = \sigma_y \), and \( \sigma_{33} = \sigma_z \)—and their strain counterparts alone are adequate to extract the effective moduli, only their volume averages were computed through the formulae

\[
\bar{\sigma}_j = \frac{1}{V} \int_0^H \int_0^L \int_0^H \sigma_i(x, y, z) dx dy dz \quad \text{and} \quad \bar{\epsilon}_j = \frac{1}{V} \int_0^H \int_0^L \int_0^H \epsilon_i(x, y, z) dx dy dz \tag{3.18}
\]

for each subscript \( J \in \{x, y, z\} \), where the unit-cell volume is \( V = LH^2 \). The volume-averaged stresses and strains were then used to compute the effective Young’s modulus \( E_{\text{eff}} \) and the effective Poisson’s ratio \( \nu_{\text{eff}} \) by solving

\[
\bar{\sigma}_x = \frac{E_{\text{eff}}}{(1 + \nu_{\text{eff}})(1 - 2\nu_{\text{eff}})}[(1 - \nu_{\text{eff}})\bar{\epsilon}_x + \nu_{\text{eff}}\bar{\epsilon}_y + \nu_{\text{eff}}\bar{\epsilon}_z] \quad \text{and} \tag{3.19}
\]

\[
\bar{\sigma}_y = \frac{E_{\text{eff}}}{(1 + \nu_{\text{eff}})(1 - 2\nu_{\text{eff}})}[\nu_{\text{eff}}\bar{\epsilon}_x + (1 - \nu_{\text{eff}})\bar{\epsilon}_y + \nu_{\text{eff}}\bar{\epsilon}_z]. \tag{3.20}
\]

Note that we numerically verified that \( \bar{\sigma}_x = \bar{\sigma}_z \) and \( \bar{\epsilon}_x = \bar{\epsilon}_z \) for all cases considered in this study. This was expected by virtue of symmetry in the geometry and of the imposed boundary conditions.
Finally, for randomly distributed arrangements, a displacement was successively imposed along the x-, y-, or z-direction. The predicted values of $E_{\text{eff}}$ and $\nu_{\text{eff}}$ were found to be independent of the direction of prescribed displacement. This established that the unit cell of randomly distributed microcapsules was isotropic and constituted a representative elementary volume (REV) of the composite structure.

3.2.4 Method of solution

The finite element method was used to solve the governing Equations (3.15) over the REV domain that was discretized with an adequately refined mesh using the boundary conditions given by Equations (3.16)-(3.17). The volume-averaged stresses and strains were used to retrieve the effective Young’s modulus $E_{\text{eff}}$ and the effective Poisson’s ratio $\nu_{\text{eff}}$ from Equations (3.19)-(3.20). Mesh convergence was verified such that the relative difference in the effective Young’s modulus and Poisson’s ratio was less than 0.5% when the minimum element size was reduced by a factor of 10. A minimum element size of 0.2 $\mu$m and a maximum element growth rate of 1.5 gave numerically converged results.

The method of solution was validated by considering the aforementioned three-component composite geometry with each component having identical material properties. The numerically predicted effective Young’s modulus and Poisson’s ratio were found to be identical to the values of $E$ and $\nu$ imposed for each component.

3.3 Results and discussion

3.3.1 Effect of geometric parameters

The following sections discuss the effects of geometric parameters, namely, the number of simulated unit cells $N$, the core and shell diameters $D_c$ and $D_s$, the unit cell length $L$, and the core and shell volume fractions $\phi_c$ and $\phi_s$ on the effective Young’s modulus $E_{\text{eff}}$ and the effective Poisson’s ratio $\nu_{\text{eff}}$ of the three-component composites considered. The effects of both microcapsule spatial and size distributions on $E_{\text{eff}}$ and $\nu_{\text{eff}}$ were also discussed. In the
baseline case, the core, shell, and matrix Young’s moduli were taken as $E_c = 55.7$ MPa [54], $E_s = 6.3$ GPa [55], and $E_m = 16.75$ GPa [56], while their Poisson’s ratios were $\nu_c = 0.499$ [57], $\nu_s = 0.34$ [55], and $\nu_m = 0.2$ [56], respectively. These properties corresponded to a three-component PCM composite consisting of microencapsulated paraffin wax with a polymeric shell embedded in a cement matrix.

3.3.1.1 Effect of number of unit cells

Figure 3.3 plots (a) the effective Young’s modulus $E_{\text{eff}}$ and (b) the effective Poisson’s ratio $\nu_{\text{eff}}$ retrieved from numerical simulations of three-component composites as functions of the number of unit cells $N$ ranging from 1 to 20 repeated in the direction of applied uniaxial strain and containing monodisperse core-shell particles packed in either SC, BCC, or FCC arrangements. Two different sets of core and shell volume fractions were considered, namely (i) $\phi_c = 0.05$ and $\phi_s = 0.0165$ and (ii) $\phi_c = 0.25$ and $\phi_s = 0.1$. In all cases, the core and shell diameters $D_c$ and $D_s$ were taken as 16 $\mu$m and 18 $\mu$m, respectively. First, Figure 3.3 indicates that $E_{\text{eff}}$ and $\nu_{\text{eff}}$ were independent of the number of unit cells considered. Therefore, simulating one unit cell was sufficient to predict the effective Young’s modulus and Poisson’s ratio for SC, BCC, or FCC packing arrangements, as expected by virtue of symmetry. Second, the effective Young’s modulus $E_{\text{eff}}$ and Poisson’s ratio $\nu_{\text{eff}}$ for BCC and FCC packing arrangements were nearly identical for the volume fractions $\phi_c$ and $\phi_s$ considered. For small core and shell volume fractions of 0.05 and 0.0165, respectively, the predicted $E_{\text{eff}}$ and $\nu_{\text{eff}}$ for the SC packing arrangement were similar to those of the BCC and FCC packings. However, $E_{\text{eff}}$ and $\nu_{\text{eff}}$ were respectively larger and smaller for SC packing compared with BCC and FCC packings for larger core and shell volume fractions $\phi_c$ and $\phi_s$ of 0.25 and 0.1.

3.3.1.2 Effect of core and shell diameters and unit cell size

Figures 3.4 plots (a) the effective Young’s modulus $E_{\text{eff}}$ and (b) the effective Poisson’s ratio $\nu_{\text{eff}}$ retrieved using numerical simulations of three-component composites as functions of
Figure 3.3: (a) Effective Young’s modulus $E_{\text{eff}}$ and (b) effective Poisson’s ratio $\nu_{\text{eff}}$ of a core-shell-matrix composite as functions of the number of unit cells $N$ stacked in the direction of applied uniaxial strain. Results were obtained from numerical simulations of SC, BCC, and FCC packing structures and two combinations of core and shell volume fractions, $\phi_c$ and $\phi_s$, are shown. Here, $D_c = 16$ $\mu$m, $D_s = 18$ $\mu$m, $E_c = 55.7$ MPa, $E_s = 6.3$ GPa, $E_m = 16.75$ GPa, $\nu_c = 0.499$, $\nu_s = 0.34$, and $\nu_m = 0.2$ (baseline case).
core volume fraction $\phi_c$ ranging from 0.05 to 0.4 for core-shell particles packed in an FCC arrangement in a continuous matrix. The mechanical properties of each component were those of the baseline case. The shell volume fraction $\phi_s$ was held constant and equal to 0.1. The core volume fraction $\phi_c$ was varied by either adjusting the core diameter $D_c$ and keeping the unit cell length $L$ constant and equal to 100 $\mu$m or by varying $L$ while $D_c$ was constant and equal to 16 $\mu$m. Similarly, Figures 3.4c and 3.4d, respectively, plot the effective Young’s modulus $E_{\text{eff}}$ and the effective Poisson’s ratio $\nu_{\text{eff}}$ for an FCC packing arrangement as functions of shell volume fraction $\phi_s$ ranging from 0.05 to 0.4 achieved by varying either $L$ or $D_s$. Here, the core volume fraction $\phi_c$ was held constant and equal to 0.1. Overall, Figure 3.4 establishes that for given core and shell volume fractions, $E_{\text{eff}}$ and $\nu_{\text{eff}}$ were independent of $D_c$, $D_s$, and $L$. They indicate that $E_{\text{eff}}$ and $\nu_{\text{eff}}$ depended only on the volume fractions $\phi_c$ and $\phi_s$ for given values of $E_c$, $E_s$, $E_m$, $\nu_c$, $\nu_s$, and $\nu_m$. This was verified to hold true also for BCC and SC packing arrangements (not shown).

### 3.3.1.3 Effect of size distribution and packing arrangement

Table 3.1 reports numerical predictions of the effective Young’s modulus $E_{\text{eff}}$ and effective Poisson’s ratio $\nu_{\text{eff}}$ of three-component composite structures consisting of various core and shell volume fractions of monodisperse and polydisperse microcapsules randomly distributed in a continuous matrix with a unit cell length $L = 75 \mu$m (Figure 3.2). It also shows the values of $E_{\text{eff}}$ and $\nu_{\text{eff}}$ for equivalent composites consisting of monodisperse microcapsules with BCC and FCC packing arrangements having nearly identical core and shell volume fractions $\phi_c$ and $\phi_s$. Here also, the mechanical properties of each constituent were those of the baseline case. Table 3.1 indicates that, for given core and shell volume fractions and constituent elastic moduli, numerical predictions of $E_{\text{eff}}$ and $\nu_{\text{eff}}$ of the different core-shell-matrix composites with randomly distributed monodisperse and polydisperse microcapsules agreed within 1%. Similarly, predictions of $E_{\text{eff}}$ and $\nu_{\text{eff}}$ for FCC and BCC packing arrangements fell within 1% of each other and within a few percents of those obtained for randomly distributed monodisperse and polydisperse microcapsules. These results establish that $E_{\text{eff}}$ and $\nu_{\text{eff}}$ were independent of spatial and size distributions. In other words, BCC and FCC packing arrangements
Figure 3.4: (a) Effective Young’s modulus $E_{\text{eff}}$ and (b) effective Poisson’s ratio $\nu_{\text{eff}}$ of a core-shell-matrix composite as functions of the core volume fraction $\phi_c$ for constant shell volume fraction $\phi_s = 0.1$. (c) Effective Young’s modulus and (d) effective Poisson’s ratio $\nu_{\text{eff}}$ as functions of the shell volume fraction $\phi_s$ for constant $\phi_c = 0.1$. The core-shell particles were arranged in FCC packing. The core, shell, and matrix Young’s moduli and Poisson’s ratios were those of the baseline case.
Table 3.1: Effective Young’s modulus $E_{\text{eff}}$ and effective Poisson’s ratio $\nu_{\text{eff}}$ of three-phase composites consisting of $p$ microcapsules either monodisperse or polydisperse and either in ordered packing arrangements or randomly distributed in a continuous matrix with unit cell length $L$. Here, $E_c = 55.7$ MPa, $E_s = 6.3$ GPa, $E_m = 16.75$ GPa, $\nu_c = 0.499$, $\nu_s = 0.34$, and $\nu_m = 0.2$.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Packing</th>
<th>Size distribution</th>
<th>$p$</th>
<th>$L$ ($\mu$m)</th>
<th>$\phi_c$</th>
<th>$\phi_s$</th>
<th>$E_{\text{eff}}$ (GPa)</th>
<th>$\nu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Random</td>
<td>Monodisperse</td>
<td>19</td>
<td>75</td>
<td>0.097</td>
<td>0.041</td>
<td>13.77</td>
<td>0.25</td>
</tr>
<tr>
<td>2</td>
<td>Random</td>
<td>Polydisperse</td>
<td>22</td>
<td>75</td>
<td>0.095</td>
<td>0.041</td>
<td>13.83</td>
<td>0.25</td>
</tr>
<tr>
<td>3</td>
<td>FCC</td>
<td>Monodisperse</td>
<td>4</td>
<td>100</td>
<td>0.100</td>
<td>0.043</td>
<td>13.51</td>
<td>0.25</td>
</tr>
<tr>
<td>4</td>
<td>BCC</td>
<td>Monodisperse</td>
<td>2</td>
<td>100</td>
<td>0.100</td>
<td>0.043</td>
<td>13.50</td>
<td>0.25</td>
</tr>
<tr>
<td>5</td>
<td>Random</td>
<td>Monodisperse</td>
<td>39</td>
<td>75</td>
<td>0.200</td>
<td>0.046</td>
<td>11.41</td>
<td>0.29</td>
</tr>
<tr>
<td>6</td>
<td>Random</td>
<td>Polydisperse</td>
<td>38</td>
<td>75</td>
<td>0.200</td>
<td>0.046</td>
<td>11.56</td>
<td>0.29</td>
</tr>
<tr>
<td>7</td>
<td>FCC</td>
<td>Monodisperse</td>
<td>4</td>
<td>100</td>
<td>0.200</td>
<td>0.043</td>
<td>11.14</td>
<td>0.30</td>
</tr>
<tr>
<td>8</td>
<td>BCC</td>
<td>Monodisperse</td>
<td>2</td>
<td>100</td>
<td>0.200</td>
<td>0.043</td>
<td>11.12</td>
<td>0.30</td>
</tr>
</tbody>
</table>

were representative of the elastic behavior of monodisperse or polydisperse microcapsules randomly distributed in a matrix. This result is interesting in that simulating deformation in BCC or FCC unit cells is significantly less time consuming and less computationally intensive than any representative elementary volume with randomly distributed microcapsules.

### 3.3.1.4 Effect of core and shell volume fractions

Figure 3.5 plots (a) the effective Young’s modulus $E_{\text{eff}}$ and (b) the effective Poisson’s ratio $\nu_{\text{eff}}$ of a three-component core-shell-matrix composite as functions of core volume fraction $\phi_c$ ranging from 0 to 0.3 for a constant shell volume fraction $\phi_s$ of 0.043. The microcapsules were either monodisperse or polydisperse and either packed in SC, BCC, or FCC arrangements or randomly distributed in the matrix (Table 3.1). Figure 3.5 establishes that the effective Young’s modulus $E_{\text{eff}}$ decreased with increasing core volume fraction $\phi_c$. This was due to the fact that the Young’s modulus of the core $E_c$ was significantly smaller than that of the matrix $E_m$. Similarly, the effective Poisson’s ratio $\nu_{\text{eff}}$ increased with core volume fraction $\phi_c$ since the Poisson’s ratio of the core $\nu_c$ was much larger than that of the shell and of the matrix. Figure 3.5 illustrates that the predictions of the effective Young’s modulus and Poisson’s
ratio were identical for monodisperse spheres in BCC or FCC packing structures and for randomly distributed mono- and poly-dispersed microcapsules, as previously observed in Table 3.1. Here also, predictions for SC packing differed from other spatial distributions.

Figure 3.6 plots (a) the effective Young’s modulus $E_{\text{eff}}$ and (b) the effective Poisson’s ratio $\nu_{\text{eff}}$ as functions of shell volume fraction $\phi_s$ ranging from 0.05 to 0.4 with a constant core volume fraction $\phi_c$ of 0.2. Here also, $E_{\text{eff}}$ decreased with increasing shell volume fraction because the Young’s modulus of the shell $E_s$ was smaller than that of the matrix. Similarly, $\nu_{\text{eff}}$ increased with increasing shell volume fraction because the Poisson’s ratio of the shell $\nu_s$ was larger than that of the matrix. Again, the numerical predictions for BCC and FCC packing arrangements and randomly distributed microcapsules were identical but differed from those for SC packing.

Figures 3.5 and 3.6 also plot the effective Young’s modulus and Poisson’s ratio as a function of core and shell volume fractions predicted by several EMAs found in the literature [2–4, 43–45, 48, 52]. Note that, for the sake of clarity, only the EMAs giving the best predictions were shown. Among the three-component EMAs, the D-EMT model [3], i.e., Equations (3.6) and (3.9), the Qiu and Weng [2] upper bound, i.e., Equations (3.2) and (3.4), and the model by Dunn and Ledbetter [48] gave the best agreement with numerical predictions of $E_{\text{eff}}$ and $\nu_{\text{eff}}$ for BCC and FCC packing arrangements and randomly distributed monodisperse and polydisperse microcapsules. However, for SC packing, none of the EMAs considered agreed well with numerical predictions. In addition, predictions of the effective Young’s modulus by the EMA developed by Hobbs [4] for two-component systems and given by Equation (3.1) fell within 2% of those obtained numerically for BCC and FCC packing arrangements for the cases considered by ignoring the presence of the shell. This led to acceptable results because the shell volume fraction $\phi_s$ was small and $E_s$ was similar to $E_m$. 

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Figure 3.5: (a) Effective Young’s modulus $E_{\text{eff}}$ and (b) effective Poisson’s ratio $\nu_{\text{eff}}$ of a core-shell-matrix composite as functions of the core volume fraction $\phi_c$ for constant shell volume fraction $\phi_s = 0.043$. Results were obtained from simulations of SC, BCC, and FCC packing structures as well as for randomly distributed monodisperse and polydisperse structures. Predictions of the best EMAs are also shown. Here, $E_c$, $E_s$, $E_m$, $\nu_s$, and $\nu_m$ were those of the baseline case.
Figure 3.6: (a) Effective Young’s modulus $E_{eff}$ and (b) effective Poisson’s ratio $\nu_{eff}$ of a core-shell-matrix composite as functions of the volume fraction of shell material $\phi_s$ with constant core volume fraction $\phi_c = 0.2$. Results were obtained from numerical simulations of SC, BCC, and FCC packing structures as well as for randomly distributed monodisperse and polydisperse structures. Predictions of the best EMAs are also shown. Here, the elastic moduli of each phase were those of the baseline case.
3.3.2 Effect of constituent elastic moduli

3.3.2.1 Effect of constituent Young’s moduli

Figures 3.7a-3.7d plot the ratio $E_{\text{eff}}/E_m$ of monodisperse core-shell particles packed in SC, BCC, or FCC structures as a function of the ratio $E_c/E_m$ ranging from $10^{-4}$ to $10^4$ for ratios $E_s/E_m$ equal to 0.1, 1, 10, and 100, respectively. The ratio $E_{\text{eff}}/E_m$ is shown for two values of matrix Young’s moduli $E_m$, namely 1 and 10 GPa. Then, the shell Young’s modulus $E_s$ was adjusted to achieve the desired $E_s/E_m$ ratio. In all cases, the core and shell volume fractions $\phi_c$ and $\phi_s$ were 0.3 and 0.1, respectively. Here also, the Poisson’s ratios of the core, shell, and matrix were $\nu_c = 0.499$, $\nu_s = 0.34$, and $\nu_m = 0.2$, respectively. Figure 3.7 indicates that numerical predictions of $E_{\text{eff}}/E_m$ were identical for BCC and FCC packings. Furthermore, the ratio $E_{\text{eff}}/E_m$ was dependent only on the ratios $E_c/E_m$ and $E_s/E_m$, rather than on the Young’s moduli of each constituent phase $E_c$, $E_s$, and $E_m$ individually. It is interesting to note that the ratio $E_{\text{eff}}/E_m$ showed little dependence on $E_c/E_m$ in the limiting cases when $E_c/E_m$ was very small (soft core) or very large (hard core). This suggests that for microencapsulated PCM-concrete composites with a soft core, a variance in the Young’s modulus $E_c$ of the PCM has little effect on $E_{\text{eff}}$.

Figures 3.7a-3.7d also plot the EMAs for $E_{\text{eff}}$ that gave the best agreement with numerical results, namely, the upper bound of the Qiu and Weng model [2], i.e., Equations (3.2) and (3.4) and the D-EMT model [3], i.e., Equations (3.6) and (3.9). The predictions by the upper bound of the Qiu and Weng model of $E_{\text{eff}}/E_m$ agreed the most closely with numerical predictions of $E_{\text{eff}}$ for microcapsules with BCC or FCC packings across the ranges of $E_c/E_m$ and $E_s/E_m$ considered. For cases when $E_c$ was smaller than $E_m$ ($E_c/E_m < 1$), such as for microencapsulated PCM in concrete, predictions from the D-EMT EMA were in better agreement with numerical predictions than those by the Qiu and Weng model. Finally, Figure 3.7 also shows the Hobbs model [Equation (3.1)] [4] for the case when $E_s/E_m = 1$. In this case, the predictions of the EMA proposed by Hobbs [4] fell within 3% of those for BCC and FCC packing arrangements.

Figure 3.8 plots the effective Poisson’s ratio $\nu_{\text{eff}}$ of monodisperse microcapsules arranged
Figure 3.7: Ratio $E_{eff}/E_m$ of a core-shell-matrix composite for SC, BCC, or FCC packings as a function of the ratio $E_c/E_m$ for ratio $E_s/E_m$ equal to (a) 0.1, (b) 1, (c) 10, and (d) 100. Predictions of EMAs are also shown including the upper Qiu and Weng bound [2], the D-EMT EMA [3], and the Hobbs model [4] (for $E_s = E_m$). Here, $\phi_c = 0.3$, $\phi_s = 0.1$, $\nu_c = 0.499$, $\nu_s = 0.34$, and $\nu_m = 0.2$. 
in SC, BCC, or FCC packings as a function of the ratio $E_c/E_m$ for cases corresponding to those shown in Figure 3.7. It indicates that (i) the numerical predictions of $\nu_{\text{eff}}$ were equivalent for BCC and FCC packing arrangements and (ii) the effective Poisson’s ratio $\nu_{\text{eff}}$ was also dependent only on ratios $E_c/E_m$ and $E_s/E_m$, rather than on $E_c$, $E_s$, and $E_m$ independently. Interestingly, $\nu_{\text{eff}}$ appeared to reach a maximum when the ratio $E_c/E_m$ was between 0.01 and 1 for all values of $E_s/E_m$ considered. This suggests that for composites with $E_c < E_m$, $\nu_{\text{eff}}$ may become undesirably large for certain values of $E_c$. When $E_c/E_m$ was very small or very large, $\nu_{\text{eff}}$ did not show significant dependence on $E_c/E_m$. Figure 3.8 also shows the predictions of the EMAs for $\nu_{\text{eff}}$ that agreed the most with numerical predictions [2,3,45]. Overall, the effective Poisson’s ratio predicted using the D-EMT EMA [3] fell within 5% of that predicted numerically for BCC or FCC packing, for the ranges of $E_c/E_m$ and $E_s/E_m$ considered.

### 3.3.2.2 Effect of constituent Poisson’s ratios

In all the previous results, $\nu_c$, $\nu_s$, and $\nu_m$ were kept constant and corresponded to the baseline case. This section assesses their effects on $E_{\text{eff}}$ and $\nu_{\text{eff}}$. Figures 3.9a and 3.9b plot the effective Young’s modulus $E_{\text{eff}}$ of a composite containing microcapsules with SC, BCC, or FCC packings as a function of the ratio $\nu_c/\nu_m$ ranging from (a) 0 to 5.0 or (b) 0 to 2.5 for ratios $\nu_s/\nu_m$ of 0.5 and 2 and for matrix Poisson’s ratios $\nu_m$ of 0.1 and 0.2, respectively. Similarly, Figures 3.9c and 3.9d plot the corresponding ratio $\nu_{\text{eff}}/\nu_m$ of a core-shell matrix composite as a function of the ratio $\nu_c/\nu_m$. The core and shell volume fractions $\phi_c$ and $\phi_s$ were constant and equal to 0.3 and 0.1, respectively. The core, shell, and matrix Young’s moduli were taken as $E_c = 55.7$ MPa, $E_s = 6.3$ GPa, and $E_m = 16.75$ GPa, respectively. Figure 3.9 indicates that the effective Young’s modulus $E_{\text{eff}}$ was generally independent of the core, shell, and matrix Poisson’s ratios for a given packing arrangement except as the core Poisson’s ratio $\nu_c$ approached the theoretical limit of 0.5 when $E_{\text{eff}}$ increased slightly. Here also, predictions by the D-EMT model [3] for both $E_{\text{eff}}$ and $\nu_{\text{eff}}$ were in good agreement with the numerical predictions for FCC and BCC packing arrangements. Moreover, unlike the ratio $E_{\text{eff}}/E_m$, the ratio $\nu_{\text{eff}}/\nu_m$ depended on the constituent Poisson’s ratios and not solely...
Figure 3.8: Effective Poisson’s ratio $\nu_{\text{eff}}$ of a core-shell-matrix composite for SC, BCC, or FCC packing as a function of the ratio $E_c/E_m$ for the ratio $E_s/E_m$ of (a) 0.1, (b) 1, (c) 10, and (d) 100. Predictions of the upper Qiu and Weng bound [2] and the D-EMT EMA [3] are also shown. Here, $\phi_c = 0.3$, $\phi_s = 0.1$, $\nu_c = 0.499$, $\nu_s = 0.34$, and $\nu_m = 0.2$. 

$E_c/Em = 0.1$

$E_c/Em = 1$

$E_c/Em = 10$

$E_c/Em = 100$
on the ratios $\nu_c/\nu_m$ and $\nu_s/\nu_m$. However, the effective Poisson’s ratio $\nu_{\text{eff}}$ was generally independent of the core Poisson’s ratio.

### 3.4 Conclusions

This study performed detailed 3D numerical simulations of the elastic deformation of three-component composites consisting of monodisperse or polydisperse microcapsules ordered in SC, BCC, or FCC packing or randomly distributed in a continuous matrix. It demonstrated that the effective Young’s modulus $E_{\text{eff}}$ and effective Poisson’s ratio $\nu_{\text{eff}}$ were identical for BCC, FCC, and randomly distributed microcapsule packing arrangements over a wide range of core and shell volume fractions and constituent mechanical properties. The ratio $E_{\text{eff}}/E_m$ was found to be a function of the core and shell volume fractions $\phi_c$ and $\phi_s$ and of the ratios $E_c/E_m$ and $E_s/E_m$. However, it was generally independent of $\nu_m$ and of the Poisson’s ratios $\nu_c/\nu_m$ and $\nu_s/\nu_m$. The effective Poisson’s ratio $\nu_{\text{eff}}$ was found to be a function of $\phi_c$ and $\phi_s$, the ratios $E_c/E_m$ and $E_s/E_m$, and the shell and matrix Poisson’s ratios $\nu_s$ and $\nu_m$. The upper bound of the EMA by Qiu and Weng [2] predicted accurately the numerical results of $E_{\text{eff}}$ for BCC and FCC packings and randomly distributed microcapsules. The D-EMT EMA developed by Garboczi and Berryman [3] gave excellent predictions of $E_{\text{eff}}$ for cases when $E_c/E_m$ was less than 1. Additionally, the EMA developed by Hobbs [4] for two-component composites gave accurate predictions of $E_{\text{eff}}$ when the shell Young’s modulus $E_s$ was similar to that of the matrix $E_m$. Finally, the D-EMT EMA gave the best agreement with numerical predictions of the effective Poisson’s ratio for BCC and FCC packing arrangements in the range of parameters considered. These results can be used to inform the selection of materials for PCM composites for building applications and for other three-phase core-shell-matrix composites such as self-healing polymer composites. In the meantime, efforts are underway to confront these numerical results with experimental measurements for concrete containing microencapsulated PCMs.
Figure 3.9: Effective Young’s modulus $E_{\text{eff}}$ and the ratio $\nu_{\text{eff}}/\nu_m$ of a core-shell-matrix composite packed in a SC, BCC, or FCC arrangement as a function of the ratio $\nu_c/\nu_m$ for (a, c) $\nu_m = 0.1$ and (b, d) $\nu_m = 0.2$. The upper Qiu and Weng bound [2] and the D-EMT EMA [3] are also included. Here, $\phi_c = 0.3$, $\phi_s = 0.1$, $E_c = 55.7$ MPa, $E_s = 6.3$ GPa, and $E_m = 16.75$ GPa.
CHAPTER 4

A General Method for Retrieving Thermal Deformation Properties of Microencapsulated Phase Change Materials or Other Particulate Inclusions in Cementitious Composites

4.1 Background

This study considers three simple effective medium approximations (EMAs) that can be applied to predict the effective thermal deformation coefficient $\alpha_{eff}$ of composites consisting of two or more constituents. The parallel model, also known as the rule-of-mixtures (ROM) [43], can be used to estimate the effective thermal deformation coefficient of a composite material with $N$ components as a simple volume-weighted average over the constituent thermal deformation coefficients, i.e. [43],

$$\alpha_{eff} = \sum_{n=1}^{N} \phi_n \alpha_n$$ (4.1)

where $\phi_n$ and $\alpha_n$ are the volume fraction and thermal deformation coefficient of constituent material $n$, respectively. Turner [58] suggested that the ROM be adjusted to weigh each component $n$ by their respective volume fraction $\phi_n$ and bulk modulus $K_n$, such that

$$\alpha_{eff} = \frac{\sum_{n=1}^{N} \phi_n K_n \alpha_n}{\sum_{n=1}^{N} \phi_n K_n}.$$ (4.2)

Schapery [59] derived an EMA which gave upper and lower bounds for the effective thermal deformation coefficient $\alpha_{eff}$ of composites with $N$ components based on energy

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conservation considerations. In this case, $\alpha_{\text{eff}}$ was expressed as an average of upper and lower bounds such that,

$$\alpha_{\text{eff}} = \overline{\alpha} + \left( \frac{K_\alpha}{K} - \overline{\alpha} \right) \frac{1}{K_L} \frac{1}{K} - \frac{1}{K_{\text{eff}}} \frac{1}{K} \pm \Delta\alpha. \quad (4.3)$$

Here, the overline denotes a volume-weighted average over the constituents, i.e. [59],

$$\overline{\alpha} = \sum_{n=1}^{N} \phi_n \alpha_n, \quad \overline{K} = \sum_{n=1}^{N} \phi_n K_n, \quad \text{and} \quad \overline{K_\alpha} = \sum_{n=1}^{N} \phi_n K_n \alpha_n. \quad (4.4)$$

In addition, $K_L$ is given by,

$$K_L = \left( \sum_{n=1}^{N} \frac{\phi_n}{K_n} \right)^{-1} \quad (4.5)$$

and the effective bulk modulus $K_{\text{eff}}$ can be estimated as the average of $K_L$ and $\overline{K}$, i.e.,

$$K_{\text{eff}} = (K_L + \overline{K})/2. \quad \text{Finally, the deviation} \Delta\alpha \text{in} \alpha_{\text{eff}} \text{from the average was expressed as [59],}$$

$$\Delta\alpha = \left( \frac{1}{K_{\text{eff}}} - \frac{1}{K} \right)^{1/2} \left( \frac{1}{K_L} - \frac{1}{K_{\text{eff}}} \right)^{1/2} \times$$

$$\left[ \left( \frac{K_\alpha}{K} \right)^2 - \frac{K_\alpha}{K} \right] \left( \frac{1}{K_L} - \frac{1}{K_n} \right) - \left( \frac{K_\alpha}{K} - \overline{\alpha} \right)^2 \right]^{1/2}. \quad (4.6)$$

Note that each of the aforementioned EMAs was developed for a linearly elastic composite featuring isotropic constitutive materials with arbitrary geometry. The effective thermal deformation coefficient predicted by each EMA depends only on the volume fractions and thermomechanical properties of the constituent materials but is independent of their spatial distribution. They can also be extended to a composite made of any number of constituents. As such, these EMAs are easily applied to cementitious and other composite materials with more than one type of inclusion, including both fine aggregates (e.g., quartz sand) and soft inclusions (e.g., microencapsulated PCM), as well as coarse aggregates that would be present in a typical concrete pavement. In addition, several other EMAs have been developed specifically for two-component composites—further details can be found in Ref. [60].
4.2 Materials and methods

4.2.1 Materials

An ASTM C150 [61] compliant Type I/II ordinary portland cement (OPC) was mixed with deionized (DI) water to prepare cement pastes (matrix only) and mortars (matrix + inclusions) in accordance with ASTM C192 [62]. The OPC had a nominal mass-based mineralogical composition of: 56.5% Ca\textsubscript{3}SiO\textsubscript{5}, 18.0% Ca\textsubscript{2}SiO\textsubscript{4}, 11.4% Ca\textsubscript{4}Al\textsubscript{2}Fe\textsubscript{2}O\textsubscript{10}, 6.3% Ca\textsubscript{3}Al\textsubscript{2}O\textsubscript{6}, 4.6% CaCO\textsubscript{3}, and 1.1% CaSO\textsubscript{4}\cdot2H\textsubscript{2}O. ASTM C778 [63] compliant graded quartz sand and microencapsulated PCM inclusions (MPCM24D, Microtek Laboratories) were used as inclusions within the cement mortars. The microencapsulated PCMs consisted of a paraffin core encapsulated within a melamine-formaldehyde (MF) shell. The microencapsulated PCMs were received in the form of dry powders. The corresponding peak melting temperature and enthalpy of phase change of microencapsulated PCMs were 27.8°C and 161.2 ± 0.5 kJ/kg representing the average value over three melting and solidification cycles.

Cementitious mortars were prepared with various volume fractions (i.e., dosages) of microencapsulated PCM and/or quartz inclusions at a water-to-cement ratio (w/c, mass basis) of 0.45. For mortars containing microencapsulated PCM inclusions only, the inclusions were dosed for three different volume fractions, namely, 5, 10 and 20 vol.%. For mortars containing quartz inclusions only, the quartz dosages were 10, 20, and 50 vol.%. For mortars containing mixed inclusions, the total inclusion volume fraction was fixed at 50 vol.%, where the microencapsulated PCM inclusions comprised 10, 15, or 20 vol.%. The microencapsulated PCMs were mixed with the anhydrous OPC by hand prior to the addition of DI water to ensure random and uniform distribution in the mortar. To enhance the fluidity of the fresh mixtures, a commercially available water-reducing admixture (MasterGlenium 7500, BASF Corporation) was added at a dosage on the order of 0-to-1.5 wt.% by mass of cement, depending on the type and dosage of inclusions present.
4.2.2 Experimental methods

Thermal deformation coefficient measurements were carried out using prismatic specimens with various mixture proportions, as described above. The specimens were cast in 2.54 cm x 2.54 cm x 28.50 cm molds in accordance with ASTM C157 [64] and cured under 100% relative humidity for the first 24 hours at 25°C. Following demolding after 24 hours, the specimens were sealed with aluminum tape and cured in sealed bags at 25°C for 28 days. Then, the length of each specimen was measured at 25°C and the specimens were transferred to an environmental chamber (KB024-DA, Darwin Chambers Company) at 45°C, and stored for 2 hours until they reached thermal equilibrium. The fractional length change (i.e., the linear thermal strain) $\Delta L/L_0$ due to temperature change $\Delta T = 45°C - 25°C$ was measured with a length comparator, as illustrated in Figure 4.1. Then, the thermal deformation coefficient of the specimens was calculated according to,

$$\alpha_{eff} = \frac{\Delta L}{L_0 \Delta T}. \quad (4.7)$$

In addition, elastic thermal strain within the specimens was verified by also calculating $\alpha_{eff}$ based on a temperature change from 5°C to 45°C and verifying that the measured $\alpha_{eff}$ was independent of the imposed temperature change. It was also confirmed that the specimens recovered their initial length when returned to their initial temperature of 25°C. Such elastic stress-strain behavior implies that the thermal deformation coefficient of cementitious composites would remain constant across the range of diurnal temperature variations that would be experienced by a concrete pavement. However, when the concrete’s temperature falls below 0°C, its thermomechanical behavior is complicated by melting and freezing of water within its pores [65] and thus cannot be treated as simple elastic deformation.

4.3 Analysis

4.3.1 Schematic and assumptions

Figure 4.2 illustrates the computational cubic unit cells of length $L$ utilized in this study, along with the associated coordinate system. Free thermal deformation was simulated nu-
Figure 4.1: Photograph of the experimental setup used to measure the effective thermal deformation coefficient of cementitious composites containing microencapsulated PCMs and/or quartz sand inclusions.
merically in domains with ordered monodisperse packing arrangements, namely (a) body-centered cubic (BCC), (b) simple cubic (SC), or (c) face-centered cubic (FCC) or in domains with randomly distributed (d) monodisperse or (e) polydisperse microcapsules. The core and shell volume fractions $\phi_c$ and $\phi_s$ can be expressed in terms of the average core and shell diameters $\bar{D}_c$ and $\bar{D}_s$ and the unit cell length $L$ according to,

$$\phi_c = \frac{N_p \pi \bar{D}_c^3}{6L^3} \quad \text{and} \quad \phi_s = \frac{N_p \pi (\bar{D}_s^3 - \bar{D}_c^3)}{6L^3}$$  \hspace{1cm} (4.8)

where $N_p$ is the number of core-shell particles contained within the unit cell.

A stochastic packing algorithm [53] was used to generate the size and location of randomly distributed monodisperse and polydisperse microcapsules within unit cells of edge length $L = 75 \mu m$ (Figure 4.2d-4.2e). The algorithm placed microcapsules at random locations within the unit cell until the desired core volume fraction $\phi_c$ was achieved within 0.5%. It ensured that the minimum centroidal distance between two sphere centers $C_D$ was greater than the sum of their radii $r_1 + r_2$ [53]. The packing algorithm considered a particle size distribution with average shell diameter $\bar{D}_s = 18 \mu m$ as well as 10th and 95th percentile shell diameters equal to 9 $\mu m$ and 33 $\mu m$, respectively [53]. All microcapsules had a shell thickness of 1 $\mu m$, i.e., $(D_s - D_c)/2 = 1 \mu m$ [53]. Previously, we used the same microstructures to predict the effective thermal conductivity [39] and elastic moduli [66] of three-component composites. The size and location of the microcapsules can be found in supplementary material.

To make the problem mathematically tractable, it was assumed that (i) all materials were linearly elastic and isotropic, (ii) body forces were negligible, and (iii) continuous contact was maintained at the material interfaces, i.e., no sliding or gapping was allowed.

4.3.2 Governing equations and boundary conditions

The stress field in each component was governed by the steady-state differential equilibrium equation [37],

$$\nabla \cdot \sigma_n = 0 \hspace{1cm} (4.9)$$

where $\sigma_n$ is the local stress tensor in component $n$ referring to the core (subscript $c$), shell (subscript $s$), or matrix (subscript $m$). The stress $\sigma_n$ and strain $\varepsilon_n$ tensors were related
Figure 4.2: Schematic of computational cells with various particle size distributions and packing arrangements used in numerical simulations of free thermal deformation in three-component composites consisting of spherical microcapsules in a continuous matrix, namely, (a) body-centered cubic (BCC), (b) simple cubic (SC), (c) face-centered cubic (FCC), (d) randomly distributed monodisperse microcapsules, and (e) randomly distributed polydisperse microcapsules.
according to the constitutive law given by Equation (2.5). Here, the temperature rise $\Delta T$ was imposed by fixing the temperature at each face of the cube at $T = T_{ref} + \Delta T$ such that solving the steady-state heat diffusion equation resulted in a spatially uniform temperature $T$ throughout the domain. Additionally, the strain-displacement relation in each component was given by [37],

$$\varepsilon_n = \frac{1}{2} [\nabla u_n + (\nabla u_n)^T]$$  (4.10)

where $u_n = [u_n, v_n, w_n]^T$ is the displacement vector in component $n$.

In order to fully define the problem, boundary conditions on each of the cube’s six faces, denoted by index $j$, were prescribed to represent free volumetric thermal deformation. For ordered packing arrangements (Figures 4.2a-4.2c), the faces at $x = 0$ ($j = 1$), $y = 0$ ($j = 2$), and $z = 0$ ($j = 3$) were fixed by virtue of symmetry, i.e.,

$$u_n \cdot \hat{n}_j = 0 \quad \text{for} \quad j = 1, 2, \text{ or } 3$$  (4.11)

where $\hat{n}_j$ denotes the unit normal vector to face $j$. The remaining faces were allowed to expand freely. As such, the traction force on these faces vanished [37],

$$\sigma_n \cdot \hat{n}_j = 0 \quad \text{for} \quad j = 4, 5, \text{ or } 6.$$  (4.12)

Moreover, for unit cells with randomly distributed microcapsules (Figures 4.2d-4.2e), all six faces were allowed to expand freely, i.e.,

$$\sigma_n \cdot \hat{n}_j = 0 \quad \text{for} \quad j = 1, 2, \ldots, \text{ or } 6.$$  (4.13)

### 4.3.3 Data processing

Solving the governing Equations (2.5), (4.9) and (4.10) along with their corresponding boundary conditions yields the displacement field $u_n(x, y, z)$ in each component of the composite volume initially at $V_0$. Then, the corresponding change in volume $\Delta V$ of the deformed body for a temperature change of $\Delta T$ was used to compute the effective thermal deformation coefficient $\alpha_{eff}$ (in $\mu\varepsilon/^{\circ}\text{C}$, neglecting higher-order strain terms) according to [38],

$$\alpha_{eff} = \frac{1}{3} \frac{\Delta V}{V_0 \Delta T}.$$  (4.14)
4.3.4 Method of solution

The governing Equations (2.5), (4.9), and (4.10) along with the corresponding boundary conditions [Equations (4.11)-(4.13)] were solved using the finite element method with the commercially available finite element solver COMSOL Multiphysics®. Computation was performed on a single CPU with two 2.6 GHz processors and 8 GB RAM. Numerical convergence was verified such that the predicted value of \( \alpha_{\text{eff}} \) did not change by more than 0.5% when the minimum element size was decreased by a factor of 2. Numerical convergence was reached using a minimum element size of 0.2 \( \mu \)m and a maximum element growth rate of 1.5. The number of finite elements in the computational domain ranged from 66,252 to 534,108. In addition, it was verified that the predicted \( \alpha_{\text{eff}} \) was independent of the imposed temperature difference \( \Delta T \) for 5°C < \( \Delta T \) < 30°C.

4.4 Results and discussion

4.4.1 Numerical simulations

This section uses numerical simulations of free thermal deformation to elucidate the effect of geometric parameters as well as constituent material properties on the effective thermal deformation coefficient \( \alpha_{\text{eff}} \) of three-component composites consisting of spherical microcapsules in a continuous matrix. Table 4.1 outlines the baseline case values of thermal deformation coefficient \( \alpha \), Young’s modulus \( E \), Poisson’s ratio \( \nu \), and bulk modulus \( K \) used in the simulations. These properties were chosen to represent a composite consisting of microencapsulated PCM inclusions in a cementitious matrix [22, 66–68]. Note that the bulk modulus \( K \) is related to the Young’s modulus \( E \) and Poisson’s ratio \( \nu \) according to [37],

\[
K = \frac{E}{3(1-2\nu)}. \tag{4.15}
\]
Table 4.1: Baseline case values of thermal deformation coefficient $\alpha$, Young’s modulus $E$, Poisson’s ratio $\nu$, and bulk modulus $K$ of the core, shell, and matrix materials used in numerical thermal deformation simulations.

<table>
<thead>
<tr>
<th>Material</th>
<th>Subscript</th>
<th>$\alpha$ ($\mu\varepsilon/^\circ C$)</th>
<th>$E$ (GPa)</th>
<th>$\nu$</th>
<th>$K$ (GPa)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core</td>
<td>c</td>
<td>109</td>
<td>0.056</td>
<td>0.499</td>
<td>9.3</td>
<td>[22,66]</td>
</tr>
<tr>
<td>Shell</td>
<td>s</td>
<td>50</td>
<td>6.3</td>
<td>0.34</td>
<td>6.6</td>
<td>[66,67]</td>
</tr>
<tr>
<td>Matrix</td>
<td>m</td>
<td>11</td>
<td>22.1</td>
<td>0.15</td>
<td>10</td>
<td>[68]</td>
</tr>
</tbody>
</table>

4.4.1.1 Effect of computational domain size

Figure 4.3 plots the numerically predicted effective thermal deformation coefficient $\alpha_{eff}$ as a function of the total number of simulated BCC, FCC, or SC unit cells $N$ in the cubic computational domain for $N = 1, 8 (2 \times 2 \times 2)$, or $27 (3 \times 3 \times 3)$. Here, unit cells with three sets of core and shell volume fractions $\phi_c$ and $\phi_s$ were simulated. Figure 4.3 establishes that $\alpha_{eff}$ was independent of the number of unit cells simulated. The predicted $\alpha_{eff}$ was also nearly identical for each ordered packing arrangement (BCC, FCC, or SC). Indeed, the maximum relative difference between $\alpha_{eff}$ for any two different domain sizes or packing arrangements was less than 2%. Note that these small variations in $\alpha_{eff}$ were expected due to the absence of periodicity in the imposed boundary conditions. Based on this result, a domain consisting of a single unit cell with BCC packing was used for all further simulations of domains featuring ordered microcapsules.

4.4.1.2 Effect of core and shell volume fractions

Figure 4.4 plots the numerically predicted effective thermal deformation coefficient $\alpha_{eff}$ as a function of the core-shell volume fraction $\phi_{c+s} = \phi_c + \phi_s$ ranging from 0 to 0.5. The thermomechanical properties of each constituent material were those of the baseline case (Table 4.1). Here, the ratio of core to core-shell volume fractions $\phi_c/\phi_{c+s}$ was held constant and equal to either 0.5 or 0.85. The corresponding core and shell volume fractions $\phi_c$ and $\phi_s$
Figure 4.3: Effective thermal deformation coefficient $\alpha_{\text{eff}}$ of three-component composites consisting of spherical microcapsules in a continuous matrix predicted numerically as a function of the number $N$ of BCC, FCC, or SC unit cells in the cubic computational domain. The thermomechanical properties of the core, shell, and matrix materials are listed in Table 4.1.
were imposed by fixing either (i) the core diameter $D_c$, (ii) the shell diameter $D_s$, or (iii) the unit cell length $L$ in Equation (4.8). Figure 4.4 shows that the effective thermal deformation coefficient $\alpha_{eff}$ increased linearly with increasing core-shell volume fraction $\phi_{c+s}$. This was due to the fact that both the core thermal deformation coefficient $\alpha_c$ and the shell thermal deformation coefficient $\alpha_s$ were larger than that of the matrix $\alpha_m$. In addition, for given core and shell volume fractions, $\alpha_{eff}$ was the same regardless of which geometric parameter $D_c$, $D_s$, or $L$ was fixed.

Moreover, Figure 4.4 also shows predictions from (i) the ROM or parallel model [Equation (4.1)], (ii) Turner’s model [Equation (4.2)], and (iii) the average of the upper and lower bounds of Schapery’s model [Equation (4.3)]. Excellent agreement was found between the numerical predictions of $\alpha_{eff}$ and predictions from Schapery’s model. The ROM and Turner’s model overestimated and underestimated the numerical predictions, respectively.

### 4.4.1.3 Effect of size and spatial distributions

Table 4.2 reports the effective thermal deformation coefficient $\alpha_{eff}$ predicted numerically using computational domains with different core and shell volume fractions $\phi_c$ and $\phi_s$ and with either ordered monodisperse or randomly distributed monodisperse or polydisperse microcapsules. Note that very similar values of $\alpha_{eff}$ were obtained for Cases 1-3 ($\phi_c \approx 0.1$, $\phi_s \approx 0.04$) and also for Cases 4-5 ($\phi_c \approx 0.2$, $\phi_s \approx 0.05$). Thus, for a given $\phi_c$ and $\phi_s$, $\alpha_{eff}$ did not depend on the packing arrangement (i.e., ordered or random) or microcapsule size distribution (i.e., monodisperse or polydisperse). In other words, a single unit cell with BCC packing was representative of the thermal elastic behavior of cells with randomly distributed monodisperse or polydisperse microcapsules. In light of these results, a computational domain consisting of a single unit cell with BCC packing was utilized for the remainder of this study.
Figure 4.4: Numerically predicted effective thermal deformation coefficient $\alpha_{\text{eff}}$ as a function of the core-shell volume fraction $\phi_{c+s} = \phi_c + \phi_s$ for the baseline case (Table 4.1). Here, the ratio $\phi_c/\phi_{c+s}$ was held constant and equal to 0.5 or 0.85 and the corresponding core and shell volume fractions $\phi_c$ and $\phi_s$ were imposed by fixing either (i) the core diameter $D_c$, (ii) the shell diameter $D_s$, or (iii) the unit cell length $L$. 

$D_c = 10 \, \mu m$
$D_s = 12 \, \mu m$
$L = 75 \, \mu m$

$\alpha_{\text{eff}}$ (µε/°C)
Table 4.2: Numerically predicted effective thermal deformation coefficient $\alpha_{\text{eff}}$ of composites consisting of ordered monodisperse or randomly distributed monodisperse or polydisperse core-shell microcapsules in a continuous matrix for the baseline case (Table 4.1).

<table>
<thead>
<tr>
<th>Case</th>
<th>Packing</th>
<th>Size distribution</th>
<th>$N_p$</th>
<th>$L$ (µm)</th>
<th>$\phi_c$</th>
<th>$\phi_s$</th>
<th>$\alpha_{\text{eff}}$ (µε/°C)</th>
<th>$\alpha_{\text{eff}}$ (µε/°C)</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BCC</td>
<td>Monodisperse</td>
<td>2</td>
<td>22.2</td>
<td>0.096</td>
<td>0.041</td>
<td>21.2</td>
<td>21.2</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Random</td>
<td>Monodisperse</td>
<td>19</td>
<td>75</td>
<td>0.097</td>
<td>0.041</td>
<td>21.0</td>
<td>21.3</td>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
<td>Random</td>
<td>Polydisperse</td>
<td>22</td>
<td>75</td>
<td>0.095</td>
<td>0.041</td>
<td>20.9</td>
<td>21.1</td>
<td>1.1</td>
</tr>
<tr>
<td>4</td>
<td>BCC</td>
<td>Monodisperse</td>
<td>2</td>
<td>17.4</td>
<td>0.2</td>
<td>0.046</td>
<td>31.3</td>
<td>31.2</td>
<td>0.2</td>
</tr>
<tr>
<td>5</td>
<td>Random</td>
<td>Polydisperse</td>
<td>38</td>
<td>75</td>
<td>0.2</td>
<td>0.046</td>
<td>31.7</td>
<td>31.2</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Moreover, predictions from Schapery’s model [Equation (4.3)] were again in excellent agreement with the numerically predicted \( \alpha_{eff} \) and differed by less than 2% for all cases considered in Table 4.2.

### 4.4.1.4 Effect of constituent thermal deformation coefficients

Figure 4.5 plots the numerically predicted effective thermal deformation coefficient \( \alpha_{eff} \) as a function of (a) the core thermal deformation coefficient \( \alpha_c \), (b) the shell thermal deformation coefficient \( \alpha_s \), and (c) the matrix thermal deformation coefficient \( \alpha_m \) ranging from 0 to 500 \( \mu \varepsilon/\degree C \) for core volume fraction \( \phi_c = 0.2 \) and shell volume fraction \( \phi_s = 0.15 \). Each plot shows two different sets of values \( \alpha_c, \alpha_s, \) or \( \alpha_m \) between 5 and 400 \( \mu \varepsilon/\degree C \) in an effort to explore a wide range of variation in constituent thermal deformation coefficients. Figure 4.5 shows that \( \alpha_{eff} \) increased linearly with each constituent’s thermal deformation coefficient.

Moreover, Figure 4.5 shows predictions by the ROM, Turner, and Schapery models. Here also, excellent agreement was observed between the Schapery model and the numerical predictions over the wide range of constituent thermal deformation coefficients considered, with a relative error not exceeding 3%.

### 4.4.2 Experimental measurements and property retrieval

This section presents a general method to retrieve the thermal deformation coefficient of particulate inclusions that are difficult to measure directly by combining Schapery’s model [Equation (4.3)], previously validated numerically, with the measured effective thermal deformation coefficient. Here, the thermal deformation coefficient \( \alpha_p \) of the inclusions was retrieved by least-square fitting the experimentally measured effective thermal deformation coefficient for different inclusion volume fractions \( \phi_i \) to Schapery’s model by minimizing the sum-of-squares error \( \delta \) given by,

\[
\delta = \sum_{i=1}^{M} [\alpha_{eff,exp}(\phi_i) - \alpha_{eff,Schapery}(\phi_i)]^2. \tag{4.16}
\]
Figure 4.5: Numerically predicted effective thermal deformation coefficient $\alpha_{eff}$ as a function of (a) core thermal deformation coefficient $\alpha_c$, (b) shell thermal deformation coefficient $\alpha_s$, or (c) matrix thermal deformation coefficient $\alpha_m$ ranging from 0 to 500 $\mu\varepsilon/^{\circ}C$. The core and shell volume fractions were $\phi_c = 0.2$ and $\phi_s = 0.15$. 
4.4.2.1 Validation

The suggested method for retrieving the inclusion thermal deformation coefficient was validated by demonstrating its use on experimental data presented by Walker et al. [5] for cement pastes with crushed limestone inclusions with volume fraction $\phi_{ls}$ ranging from 0 to 0.6. Additionally, the authors directly measured the thermal deformation coefficient of the cement paste alone as $\alpha_m = 9.72 \, \mu\varepsilon/{}^\circ\text{C}$, and that of the limestone as $\alpha_{ls} = 4.4 \, \mu\varepsilon/{}^\circ\text{C}$ by sawing specimens from the parent stone [5]. Here, the elastic modulus and Poisson’s ratio of the limestone were taken as 31 GPa and 0.25, respectively [69]. Figure 4.6 plots the experimentally measured effective thermal deformation coefficient $\alpha_{\text{eff}}$ as a function of limestone volume fraction $\phi_{ls}$ [5]. The error bars correspond to an uncertainty of $\pm 5\%$. Figure 4.6 also shows the best fit obtained with the Schapery model, corresponding to a retrieved value of $\alpha_{ls} = 4.3 \, \mu\varepsilon/{}^\circ\text{C}$. This value of $\alpha_{ls}$ agrees very well with that measured directly by the authors, thus demonstrating that our suggested approach can be used to obtain accurate estimates of inclusion thermal expansion coefficients.

4.4.2.2 Thermal deformation coefficient of PCM microcapsules

Figure 4.7a plots the experimentally measured effective thermal deformation coefficient $\alpha_{\text{eff}}$ of cement paste with microencapsulated PCM specimens as a function of microencapsulated PCM volume fraction $\phi_{c+s}$ ranging from 0 to 0.3. The error bars correspond to one standard deviation or 68% confidence interval of three measurements. Figure 4.7a shows that $\alpha_{\text{eff}}$ slightly increased with increasing $\phi_{c+s}$, confirming that the thermal deformation coefficient of the PCM microcapsules was indeed larger than that of the cementitious matrix. The latter was measured to be $\alpha_m = 14.1 \, \mu\varepsilon/{}^\circ\text{C}$, corresponding to $\phi_{c+s} = 0$. The thermal deformation coefficient $\alpha_{c+s}$ of the PCM microcapsules was retrieved by least-square fitting the experimental measurements of $\alpha_{\text{eff}}$ with Schapery’s model, as outlined previously. In this case, the retrieved value of $\alpha_{c+s}$ was $42 \, \mu\varepsilon/{}^\circ\text{C}$. Interestingly, this value was similar to the thermal deformation coefficient of the MF shell, reported in the literature as $\alpha_s = 50 \, \mu\varepsilon/{}^\circ\text{C}$ [67].
Figure 4.6: Effective thermal deformation coefficient $\alpha_{\text{eff}}$ of cement pastes with crushed limestone inclusions as a function of limestone volume fraction $\phi_{ls}$ ranging from 0 to 0.6 measured by Walker et al. [5] and predicted by Schapery’s model using the retrieved value of $\alpha_{ls} = 4.3 \ \mu \varepsilon/^{\circ}C$. 
Figure 4.7: Experimentally measured thermal deformation coefficient $\alpha_{eff}$ of cement pastes containing (a) microencapsulated PCM with $\phi_{c+s}$ ranging from 0 to 0.25, (b) quartz sand with $\phi_q$ ranging from 0 to 0.6, or (c) both microencapsulated PCM and quartz sand with $\phi_{c+s}$ ranging from 0 to 0.25 and $\phi_q + \phi_{c+s} = 0.5$. 

Schapery, $\alpha_{c+s} = 42 \, \mu \epsilon/\degree C$

Schapery, $\alpha_{q} = 3.87 \, \mu \epsilon/\degree C$
The PCM microencapsulation process is often carried out at elevated temperatures around 100°C [70]. During subsequent cooling, the paraffinous core contracts more than the shell, i.e., $\alpha_c >> \alpha_s$ (see Table 4.1), leaving some empty space in the PCM microcapsules at room temperature. Then, upon subsequent heating, the thermal deformation coefficient $\alpha_c$ of the core material has negligible impact on the thermal deformation coefficient $\alpha_{c+s}$ of the core-shell microcapsule, as the core is allowed to expand freely without exerting any stress on the shell. Therefore, the thermal deformation coefficient of the PCM microcapsule $\alpha_{c+s}$ is expected to be similar to that of the shell material for temperatures below 100°C.

### 4.4.2.3 Thermal deformation coefficient of quartz sand inclusions

Figure 4.7b plots the experimentally measured effective thermal deformation coefficient $\alpha_{eff}$ of cement mortar (i.e., cement paste with quartz sand inclusions) as a function of quartz inclusion volume fraction $\phi_q$ ranging from 0 to 0.5. In this case, the low thermal deformation coefficient of the quartz sand caused $\alpha_{eff}$ to decrease with increasing quartz volume fraction $\phi_q$. Here again, the thermal deformation coefficient of the quartz inclusions $\alpha_q$ was determined by least-square fitting the experimental measurements to the Schapery model. The elastic modulus $E_q$ and Poisson’s ratio $\nu_q$ of quartz were taken, from the literature, as 73 GPa and 0.17, respectively [71]. Here, the resulting value of $\alpha_q$ was 3.9 $\mu\varepsilon/^\circ C$. Note that a wide range of thermal deformation coefficient values for quartz are reported in the literature, ranging from 0.5 $\mu\varepsilon/^\circ C$ for silica (amorphous) [72] to 9.3 $\mu\varepsilon/^\circ C$ for quartzite [73].

### 4.4.2.4 Mixed inclusion measurements

Figure 4.7c plots the experimentally measured effective thermal deformation coefficient $\alpha_{eff}$ of microencapsulated PCM-mortar composite specimens with both PCM and quartz sand inclusions as a function of PCM volume fraction $\phi_{c+s}$ ranging from 0 to 0.5. Here, the total inclusion volume fraction was kept constant for all specimens such that $\phi_q + \phi_{c+s} = 0.5$. In particular, note that $\alpha_{eff}$ for a specimen with $\phi_{c+s} = 0.2$ and $\phi_q = 0.3$ was measured to be 14.0 $\mu\varepsilon/^\circ C$ while that of the cementitious matrix was measured earlier as $\alpha_m = 14.1 \mu\varepsilon/^\circ C$. 

55
Thus, the effect of adding 20 vol.% microencapsulated PCM was “offset” by the addition of 30 vol.% quartz. Finally, Figure 4.7c shows the predictions of $\alpha_{eff}$ by Schapery’s model using the values of $\alpha_c+s$ and $\alpha_q$ retrieved from previous experiments (Figures 4.7a-4.7b). Excellent agreement was found between $\alpha_{eff}$ predicted by the Schapery model and measured experimentally. These results demonstrate the ability of Schapery’s model to account for the combined, independent effects of both inclusions on the effective thermal deformation coefficient of the mortars.

### 4.4.2.5 Design rule for thermal deformation equivalence in PCM-mortar composites

As shown in Figure 4.7, the addition of PCM microcapsules tends to increase the effective thermal deformation coefficient of the composite while the addition of quartz sand tends to decrease it. Therefore, one could “compensate” for the increase in $\alpha_{eff}$ caused by the addition of PCM microcapsules by adding an appropriate amount of quartz sand to maintain the ratio $\alpha_{eff}/\alpha_m$ below some threshold. Figure 4.8 plots the required quartz sand volume fraction $\phi_q$ corresponding to a ratio $\alpha_{eff}/\alpha_m$ equal to 1.25, 1, or 0.75, as a function of microencapsulated PCM volume fraction $\phi_{c+s}$ ranging from 0 to 0.3. Here, Schapery’s model was used with the retrieved values of $\alpha_c+s$ and $\alpha_q$ to determine $\phi_q$ for each $\alpha_{eff}/\alpha_m$ and $\phi_{c+s}$. Note that for a desired ratio $\alpha_{eff}/\alpha_m < 0.75$, PCM volume fractions above $\sim0.25$ are not feasible as they require a minimum total inclusion volume fraction $\phi_{c+s} + \phi_q$ of 0.85 or higher. Also, for an allowable ratio of $\alpha_{eff}/\alpha_m = 1.25$, no quartz sand is required for PCM volume fraction $\phi_{c+s}$ below 0.125.

### 4.5 Conclusion

This paper examined the effect of microencapsulated PCMs and other particulate inclusions on the thermal deformation behavior of cementitious composites, and presented a convenient approach to estimate the thermal deformation coefficient of inclusions based on measured effective properties. The effective thermal deformation coefficient of three-component core-
Figure 4.8: Required quartz sand volume fraction $\phi_q$ to ensure that the ratio $\alpha_{\text{eff}}/\alpha_m$ of a PCM-mortar composite remains equal to 1.25, 1, or 0.75, plotted as a function of microencapsulated PCM volume fraction $\phi_{c+s}$ ranging from 0 to 0.3.
shell-matrix composites was first predicted numerically using finite element simulations of free thermal deformation. It was found to be a function of only the constituents’ volume fractions and thermomechanical properties. Predictions from the effective medium approximation developed by Schapery were found to agree well with the numerical results over a wide range of constituent thermal deformation coefficients. Moreover, the effective thermal deformation coefficient of cementitious microencapsulated PCM-composites was measured experimentally for cement paste and cement mortar with various volume fractions of quartz sand and microencapsulated PCM. The experimental measurements were used in conjunction with Schapery’s model to retrieve the thermal deformation coefficient of PCM microcapsules and of quartz sand grains. The thermal deformation coefficient of the PCM microcapsules was found to be near that of the shell material, due to the fact that the capsules might not be completely filled with PCM, thus leaving space inside for the PCM core to expand. Schapery’s model was shown to predict accurately the effective thermal deformation coefficient of cementitious composite samples with a mixture of microencapsulated PCM and quartz sand inclusions based on the previously retrieved properties. Finally, a design rule was suggested for determining the amount of quartz sand required to offset the effect of the PCM microcapsules in increasing the thermal deformation coefficient of PCM-mortar composites. These results could be useful in modeling the thermal deformation behavior of pavement sections featuring microencapsulated PCMs for crack resistance.
CHAPTER 5

Reduced-scale Experiments to Evaluate Performance of Composite Building Envelopes Containing Phase Change Materials

5.1 Background

Numerous experimental studies have been conducted to compare the thermal behavior of test rooms with and without PCM-composite envelopes. Cabeza et al. [7] constructed a pair of large outdoor cubicles (2 m x 2 m x 3 m) with a conventional concrete envelope or with a composite concrete envelope containing 5 wt.% microencapsulated PCM with a melting temperature around 26\degree C in the south, west, and roof walls. The cubicles were subjected to the climate of Puigverd de Lleida, Spain over a period of three summer months. The authors found that the cubicle containing PCM featured smaller interior wall temperature fluctuations and smaller inner wall heat flux (heat load). Castell et al. [30] performed similar experiments on concrete and alveolar brick cubicles with and without macroencapsulated PCM. Here, the authors included an active cooling system within the cubicles. They found that the inclusion of PCM decreased the cooling energy requirement by about 15% over a summer season.

Zhang et al. [31] constructed two 1.83 m x 1.83 m x 1.22 m test rooms featuring wooden frame walls without and with PCM featuring a melting temperature window between 20\degree C and 30\degree C. The PCM was macroencapsulated in copper tubes embedded in the insulation layer of the wall. The test rooms were exposed to summer conditions in Lawrence, Kansas, and the indoor temperature of the test rooms was controlled by an air conditioning system.
The authors found that the space cooling energy requirement for a summer day was reduced by 8.6% for a wall with 10% PCM by weight and by 10.8% for a wall with 20% PCM by weight.

Kuznik and Virgone [32] constructed an experimental setup consisting of a large test room (3.1 m x 3.1 m x 2.5 m) adjacent to a climatic chamber on one side. An array of heat lamps was also used to simulate incident solar radiation. The outdoor temperature and solar radiation flux corresponding to a summer, mid-season, and a winter day were imposed at the outer surface of the test room wall. The authors found that when the test room walls were modified to include an additional 5 mm-thick wallboard layer with 60 wt.% microencapsulated PCM with melting temperature around 20°C, the amplitude of the indoor temperature oscillation was reduced by 21-27% for all days simulated. They also found that the maximum indoor temperature was reduced by up to 4°C in the summer.

Fang and Zhang [33] constructed three test cells with dimensions 0.7 m x 0.7 m x 0.7 m. Each test cell had five ordinary gypsum board walls and a ceiling wall containing either 0, 20, or 50 wt.% of impregnated PCM with a melting temperature around 23°C. The authors used a tungsten heat lamp placed at various vertical distances above the top wall to simulate solar radiation. In the experiments, the lamp was switched on and the resulting transient change in the interior test cell temperature was recorded. The maximum temperature attained by the interior air was reduced by 5°C and 9°C for wall panels containing 20 wt.% and 50 wt.% of PCM, respectively. Note that the authors did not measure the response of the test cells to periodic exterior temperature fluctuations.

Overall, previous experimental studies of diurnal thermal response of building enclosures with envelopes made of PCM-composite walls have been limited to full-scale test rooms placed in various actual or simulated outdoor climates. Unfortunately, such experiments are time-consuming and resource-intensive to build, operate, and optimize. The objective of the present study is to demonstrate that a reduced-scale test cell subjected to faster temperature fluctuations in a controlled environmental chamber can be used in place of a full-scale outdoor setup.
5.2 Materials and methods

5.2.1 Experimental setup

Two concrete wall panels 45 cm in length and width and 2.54 cm in thickness were fabricated for this study, namely (i) a plain mortar wall panel consisting of 45% cement paste and 55% quartz inclusions by volume and (ii) a PCM-composite wall panel consisting of 45% cement paste, 45% quartz, and 10% microencapsulated PCM by volume (MPCM24D, Microtek Laboratories, Inc.). The PCM microcapsules consisted of a paraffin-based core material enclosed in a melamine-formaldehyde (MF) shell. The melting temperature $T_{pc}$ of the PCM was around 24$^\circ$C and the latent heat of fusion was 160 kJ/kg [6].

The wall panels were fabricated using commercially available Type I/II ordinary portland cement and deionized (DI) water. For the PCM-composite panel, the desired microencapsulated PCM volume fraction $\phi_{c+s} = 0.1$ was achieved by measuring and adding the appropriate mass based on the density of the PCM microcapsules $\rho_{c+s}$ taken as 900 kg/m$^3$ [18]. The mortars were prepared according to ASTM C305 [74], and the water-to-cement (w/c) ratio on a mass basis was 0.45. A commercial viscosity-modifying admixture (MasterMatrix VMA 450, BASF Corporation) was added at 0.1% of the total mortar mass to minimize segregation of inclusions and maintain a homogeneous distribution of PCM microcapsules and quartz inclusions in the specimen. An acrylic plastic mold was used to fabricate the wall panels with the desired dimensions. The wall panels were allowed to cure in sealed conditions for 28 days.

Figure 5.1a shows a photograph of the experimental cubic test cell of length 45 cm. The base and four side walls of the cell were made of 5.08 cm (2 inch) thick CertiFoam® insulation with an R-value of 1.8 (m$^2$ K)/W (DiversiFoam Products, Inc.). The top wall was one of the concrete wall panels previously described. A total of 10 thermocouples were placed at four different locations within the test cell and at three different lateral locations on the inner and outer wall surfaces. To ensure that the interior air was well-mixed and had uniform temperature $T_a(t)$, a small computer fan with a blade diameter of 8 cm (EFX-08-12, SilenX Corporation) was placed inside the test cell and powered at its maximum speed of 1400 ±
The test cell was placed in a programmable freeze-thaw environmental chamber (TH024, Darwin Chambers Company) and subjected to four different sinusoidal chamber temperature cycles of period $\tau = 1.5$ hours such that the chamber temperature $T_o(t)$ was,

$$T_o(t) = \left(\frac{T_{o,\text{max}} - T_{o,\text{min}}}{2}\right) \sin \left(\frac{2\pi t}{1.5}\right) + \frac{T_{o,\text{max}} + T_{o,\text{min}}}{2}$$

(5.1)

where $t$ is in hours, while $T_{o,\text{min}}$ and $T_{o,\text{max}}$ are the minimum and maximum values of $T_o(t)$. The four cycles were defined to explore a wide range of outdoor temperature oscillations with respect to the PCM melting temperature $T_{pc} = 24^\circ$C: (i) Cycle A with $T_{o,\text{min}} = 5^\circ$C, $T_{o,\text{max}} = 20^\circ$C, (ii) Cycle B with $T_{o,\text{min}} = 15^\circ$C, $T_{o,\text{max}} = 40^\circ$C, (iii) Cycle C with $T_{o,\text{min}} = 10^\circ$C, $T_{o,\text{max}} = 30^\circ$C, and (iv) Cycle D with $T_{o,\text{min}} = 5^\circ$C, $T_{o,\text{max}} = 35^\circ$C.

During each experiment, the temperature inside the test cell $T_a(t)$ was recorded as a function of time. Additionally, the inner and outer wall surface temperatures were also recorded. Each experiment was run for at least 12 hours in order to allow the system to reach a periodic steady state and to collect data for several oscillation periods. Experimental data from Cycle A was used to estimate the convective heat transfer coefficients prevailing in the environment chamber, as well as to verify periodic behavior of the inside air temperature. The other three cycles (B-D) were used to compare inside air temperature evolutions for test cells with either a plain mortar or PCM-mortar composite wall.

5.3 Analysis

5.3.1 Schematic and assumptions

Figure 5.1b shows a schematic of the test cell with inside air temperature $T_a(t)$ with a PCM-mortar composite wall placed inside an environmental chamber with temperature $T_o(t)$ along with the associated coordinate system. The top mortar-based wall had thickness $L$
Figure 5.1: (a) Photograph of the experimental test cell with dimensions of 45 cm x 45 cm x 45 cm. Five walls were made of 5.08 cm thick foam insulation while the remaining face was made of a plain mortar or PCM-mortar composite wall panel 2.54 cm in thickness. Thermocouples were placed at three different lateral locations on the inner and outer wall surfaces and at four different locations inside the test cell. (b) Schematic of a test cell with a single PCM-composite wall and five insulated walls placed inside an environmental test chamber. The wall has effective thermal properties $k_{eff}$ and $(\rho c_p)_{eff}$. Both the outer ($x = 0$) and inner ($x = L$) wall surfaces are exposed to convection with the chamber and inside air, respectively.
and effective thermal properties \((\rho c_p)_{eff}(T)\) and \(k_{eff}\). Convective heat transfer took place between the chamber air and the exterior wall surface at \(x = 0\). Likewise, convective heat transfer also took place between the inside air and the interior surface of the wall at \(x = L\). Heat was conducted through the wall in the \(x\)-direction, and the other walls of the cell were treated as perfectly thermally insulated.

To make the problem mathematically tractable, the following assumptions were made: (1) the inside air was assumed to be well-mixed with uniform indoor temperature \(T_a(t)\), (2) heat generation within the test cell was ignored, (3) one-dimensional (1D) heat conduction normal to the wall surfaces prevailed, (4) all material properties were constant and isotropic except for the temperature-dependent specific heat \(c_{p,c+s}(T)\) of the PCM, (5) the PCM specific heat in the solid and liquid phases was the same (i.e., \(c_{p,c+s,s} = c_{p,c+s,l}\)), and (6) all walls other than the mortar or PCM-composite wall were assumed to be perfectly insulated. To justify this final assumption, it was verified that the predicted inside air temperature \(T_a(t)\) did not differ by more than 0.2°C when heat transfer through the foam base and side walls was accounted for.

### 5.3.2 Governing equations

The temperature in the composite wall \(T_w(x,t)\) was governed by the 1D transient heat diffusion equation [75],

\[
\frac{\partial T_w}{\partial t} = \alpha_{eff}(T_w) \frac{\partial^2 T_w}{\partial x^2} \tag{5.2}
\]

where \(\alpha_{eff}(T) = k_{eff}/(\rho c_p)_{eff}(T)\) is the effective thermal diffusivity of the wall. Additionally, the energy conservation equation for the inside air can be expressed as,

\[
(\rho c_p)_a V_a \frac{dT_a}{dt} = h_i A_w [T_w(L,t) - T_a(t)] \tag{5.3}
\]

where \(V_a\) is the volume of air in the test cell, \(A_w\) is the surface area of the plain mortar or PCM-mortar wall and \(h_i\) is the convective heat transfer coefficient between the inner wall surface \((x = L)\) and the inside air. Experimentally, these dimensions were \(V_a = 0.04 \text{ m}^3\), \(A_w = 0.12 \text{ m}^2\), and \(L = 2.54 \text{ cm}\).
5.3.3 Initial and boundary conditions

The inside air and the wall were assumed to have an initial uniform temperature $T_i$ at $t = 0$, i.e.,

$$T_w(x,0) = T_a(0) = T_i.$$  (5.4)

Additionally, two convective heat flux boundary conditions for solving Equation (5.2) were imposed at the inner ($x = L$) and outer ($x = 0$) wall surfaces so that

$$-k_{eff} \frac{\partial T_w}{\partial x}(0,t) = h_o [T_o(t) - T_w(0,t)] \quad \text{and} \quad -k_{eff} \frac{\partial T_w}{\partial x}(L,t) = h_i [T_w(L,t) - T_a(t)].$$  (5.5)

Note that the governing Equations (5.2) and (5.3) are coupled by virtue of the fact that the convective heat flux at the inner wall surface ($x = L$) is dependent on both the inner wall surface temperature $T_w(L,t)$ and the inside air temperature $T_a(t)$.

5.3.4 Constitutive relationships

Table 5.1 summarizes the density $\rho$ and specific heat $c_p$ of cement paste, quartz, microencapsulated PCM (MPCM24D), and air used in the simulations. The effective volumetric heat capacity of the composite wall panel was predicted by a volume-weighted average as,

$$(\rho c_p)_{eff}(T) = \phi_{c+s}(\rho c_p)_{c+s}(T) + \phi_q(\rho c_p)q + (1 - \phi_{c+s} - \phi_q)(\rho c_p)m$$  (5.6)

where the subscripts $c+s$, $q$, and $m$ refer to microencapsulated PCM, quartz, and cement paste, respectively. Figure 5.2 plots the experimentally measured specific heat $c_{p,c+s}(T)$ of MPCM24D PCM microcapsules as a function of temperature for a ramp rate of $1^\circ C/min$, previously reported in [6]. Based on these measurements, the latent heat of fusion $h_{sf}$ of the PCM was determined to be 160 kJ/kg. The multitude of peaks in the DSC curves can be attributed to the presence of impurities (i.e., constituents with different molecular weights) within the commercial PCM [6]. Note that $c_{p,c+s}(T)$ differs slightly depending on whether the sample is heated or cooled. Here, the data from the heating curve was used in Equation (5.6) to simulate the experiments. Finally, the effective thermal conductivity $k_{eff}$ of the mortar and PCM-composite wall panels was obtained from experimental measurements using the
Table 5.1: Density $\rho$ and specific heat $c_p$ of cement paste, quartz, MPCM24D, and air.

<table>
<thead>
<tr>
<th>Material</th>
<th>Subscript</th>
<th>$\rho$ (kg/m$^3$)</th>
<th>$c_p$ (J/(kg K))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement paste</td>
<td>m</td>
<td>1965</td>
<td>1530</td>
<td>[76]</td>
</tr>
<tr>
<td>Quartz</td>
<td>q</td>
<td>2650</td>
<td>745</td>
<td>[75]</td>
</tr>
<tr>
<td>MPCM24D</td>
<td>c+s</td>
<td>900</td>
<td>$c_{p,c+s}(T)$</td>
<td>[6]</td>
</tr>
<tr>
<td>Air</td>
<td>a</td>
<td>1.2</td>
<td>1005</td>
<td>[75]</td>
</tr>
</tbody>
</table>

guarded hot-plate method [77]. Here, $k_{\text{eff}}$ was taken as $1.77 \pm 0.27$ W/(m K) for the plain mortar wall panel and as $1.46 \pm 0.22$ W/(m K) for the composite wall panel with 10 vol.% of PCM where the experimental uncertainty represents one standard deviation [77].

5.3.5 Method of solution

The governing Equations (5.2) and (5.3) were solved along with the corresponding boundary and initial conditions using an explicit finite difference method. Convergence criteria was defined such that the inside air and wall temperature spatiotemporal evolutions differed by no more than 1% when the nodal spacing $\Delta x$ or the time step $\Delta t$ was reduced by a factor of 2. A numerically converged solution was achieved using a nodal spacing $\Delta x = 2.5$ mm and a time step $\Delta t = 5$ s. The finite element code used to solve the transient heat diffusion equation in the wall with phase change was validated against an exact solution of the Stefan problem for transient 1D heat conduction through a paraffin slab [25,78].

5.3.6 Scaling analysis

In order to non-dimensionalize the governing equations, the following dimensionless variables were introduced,

$$x^* = \frac{x}{L}, \quad t^* = Fo = \frac{\alpha_{\text{eff},s} t}{L^2},$$

$$T_{w}^*(x^*, t^*) = \frac{T_w(x,t) - T_{o,\text{min}}}{T_{o,\text{max}} - T_{o,\text{min}}}, \quad \text{and} \quad T_a^*(t^*) = \frac{T_a(t) - T_{o,\text{min}}}{T_{o,\text{max}} - T_{o,\text{min}}}. \quad (5.7)$$
Figure 5.2: Specific heat $c_{p,c+s}(T)$ of MPCM24D PCM microcapsules measured by DSC as a function of temperature with a temperature ramp rate of $1^\circ$C/min [6]. The data from the heating curve was used to determine $(\rho c_p)_{\text{eff}}(T)$ for numerical simulations of the test cell experiments.
Here, $\alpha_{eff,s}$ is the effective thermal diffusivity of the wall based on the PCM solid phase specific heat $c_{p,c+s,s}$. Substituting Equations (5.7) into Equation (5.2) yields,

$$\frac{1}{\alpha_{eff}(T^*)} \frac{\partial T_w^*}{\partial t^*} = \frac{\partial^2 T_w^*}{\partial x^*^2}. \quad (5.8)$$

The dimensionless thermal diffusivity $\alpha_{eff}(T^*)$ can be expressed based on the effective heat capacity method and assuming $c_{p,c+s,s} = c_{p,c+s,l}$ [Assumption (5)] as,

$$\frac{1}{\alpha_{eff}(T^*)} = \frac{(\rho c_p)_{eff}(T^*)}{(\rho c_p)_{eff,s}} = \begin{cases} 
1 & \text{for } T^* < T^*_{pc} - \Delta T^*_{pc}/2 \\
1 + \frac{\rho_{c+s}h_{sf}^*}{\Delta T^*_{pc}} & \text{for } T^*_{pc} - \Delta T^*_{pc}/2 \leq T^* \leq T^*_{pc} + \Delta T^*_{pc}/2 \\
1 & \text{for } T^* > T^*_{pc} + \Delta T^*_{pc}/2 
\end{cases} \quad (5.9)$$

where the dimensionless PCM melting temperature $T^*_{pc}$ and melting temperature window $\Delta T^*_{pc}$ are defined as

$$T^*_{pc} = \frac{T_{pc} - T_{o,min}}{T_{o,max} - T_{o,min}} \quad \text{and} \quad \Delta T^*_{pc} = \frac{\Delta T_{pc}}{T_{o,max} - T_{o,min}}. \quad (5.10)$$

Here, the dimensionless latent heat of fusion $h_{sf}^*$ is defined as

$$h_{sf}^* = \frac{\rho_{c+s}h_{sf}}{(\rho c_p)_{eff,s}(T^*_{o,max} - T^*_{o,min})}. \quad (5.11)$$

Additionally, the boundary conditions at the outer ($x^* = 0$) and inner ($x^* = 1$) wall surfaces given by Equation (5.5) can be rewritten in dimensionless form as,

$$\frac{\partial T_w^*}{\partial x^*}(0,t^*) = -Bi_o[T^*_o(t^*) - T^*_w(0,t^*)] \quad \text{and} \quad \frac{\partial T_w^*}{\partial x^*}(1,t^*) = -Bi_i[T^*_w(1,t^*) - T^*_a(t^*)] \quad (5.12)$$

where $Bi_o = h_o/(Lk_{eff})$ and $Bi_i = h_i/(Lk_{eff})$ are the Biot numbers associated with the outside and inside convective thermal resistances, respectively.

Moreover, the energy conservation Equation (5.3) for the inside temperature $T_a(t)$ can be non-dimensionalized by substituting the appropriate dimensionless variables of Equation (5.7) to yield,

$$\frac{dT_a^*}{dt^*} = Bi_i C_r [T^*_w(1,t^*) - T^*_a(t^*)]. \quad (5.13)$$

Note that the product of dimensionless numbers $Bi_i$ and $C_r$ on the right side of Equation (5.13) is defined as,

$$Bi_i C_r = \left( \frac{h_i L}{k_{eff}} \right) \left( \frac{(\rho c_p)_{eff,s} A_w L}{(\rho c_p)_a V_a} \right) \quad (5.14)$$
where $C_r$ represents the ratio of the total heat capacity of the wall to that of the inside air.

Additionally, the sinusoidal outside temperature variation can be rewritten in dimensionless form by introducing a dimensionless oscillation period $\tau^* = \tau \alpha_{\text{eff}}/L^2$ representing the ratio of the oscillation period $\tau$ to the characteristic time for heat diffusion through the wall $L^2/\alpha_{\text{eff}}$. Then, the dimensionless outside temperature $T_o^*(t^*)$ can be expressed as,

$$T_o^*(t^*) = \frac{T_o(t) - T_{o,\text{min}}}{T_{o,\text{max}} - T_{o,\text{min}}} = 0.5 \left[ 1 + \sin \left( \frac{2\pi t^*}{\tau^*} \right) \right]. \quad (5.15)$$

In summary, the seven dimensionless numbers $Bi_i, Bi_o, C_r, \tau^*, T_{pc}^*, \Delta T_{pc}^*$, and $h_{sf}^*$ govern the behavior of $T_w(x,t)$ and $T_a(t)$. In practice, given two enclosures with different geometries and PCM phase change properties subjected to different sinusoidal outside temperature fluctuations, the transient dimensionless wall and inside air temperatures $T_w^*(x^*,t^*)$ and $T_a^*(t^*)$ will be identical provided that the dimensionless numbers $Bi_i, Bi_o, C_r, \tau^*, T_{pc}^*, \Delta T_{pc}^*$, and $h_{sf}^*$ are identical.

This scaling analysis can be easily extended to situations when (i) solar radiation is incident on one or more faces of the envelope and (ii) heat is transferred through more than one wall.

### 5.4 Results and discussion

#### 5.4.1 Verification of periodic steady-state

Figure 5.3a plots the inside air temperature $T_a(t)$ experimentally measured as a function of time during Cycle A with 1.5-hour period for a test cells with a plain mortar wall panel. It also plots the imposed chamber temperature $T_o(t)$ as a function of time. In addition, Figure 5.3b plots the 5th, 7th, and 9th periods of $T_a(t)$ and $T_o(t)$ for a test cell with a plain mortar wall. It is evident that the three cycles are superimposed on the same plot, establishing that the temperature $T_a(t)$ inside the test cell behaved periodically with the same frequency as that of $T_o(t)$ after 5 cycles. Then, the system had reached a periodic steady-state and the effect of the initial conditions vanished. Thus, for the remainder of this study, only a single oscillation period after the fifth cycle is considered.
Figure 5.3: (a) Experimentally measured chamber temperature $T_o(t)$ and inside air temperature $T_a(t)$ as functions of time $t$ for a test cell with a plain mortar wall subjected to chamber temperature Cycle A. (b) Superimposed plots of $T_o(t)$ and $T_a(t)$ for the 5th, 7th, and 9th oscillation periods.
5.4.2 Convective heat transfer coefficient estimation

In order to validate numerical predictions against experimental measurements, one needs to use as inputs to the model the convective heat transfer coefficients $h_i$ and $h_o$ prevailing experimentally. These parameters were estimated by finding the values of $h_i$ and $h_o$ that minimized the sum-of-squared error $\delta$ between the experimentally measured and numerically predicted inside air temperature over a single oscillation period for a test cell Cycle A and with a plain mortar wall. The sum-of-squared error $\delta$ can be expressed as,

$$\delta = \sum_{k=1}^{N} (T_{\text{exp},k} - T_{\text{num},k})^2$$ (5.16)

where $T_{\text{exp},k}$ and $T_{\text{num},k}$ are the experimentally measured and numerically predicted inside air temperatures, respectively, at time step $k$, and $N$ represents the number of time steps in a single oscillation period. The resulting values for $h_i$ and $h_o$ were 13 W/(m$^2$ K) and 20 W/(m$^2$ K), respectively.

5.4.3 Comparison between experiments and numerical simulations

Figure 5.4 plots the experimentally measured and numerically predicted inside air temperature $T_a(t)$ and imposed outside temperature $T_o(t)$ for the test cell with either a plain mortar or a PCM-mortar composite wall over one oscillation period for (a-b) Cycle B, (c-d) Cycle C, and (e-f) Cycle D. Here, the experimentally measured minimum and maximum values of $T_o(t)$ were used as inputs to the numerical model. For all cycles, these values were about $0.6^\circ C$ larger than the input values to the chamber temperature controller. Figure 5.4 shows that, for Cycle B, the presence of PCM in the wall panel did not reduce the amplitude of the inside air temperature oscillations. Also, the presence of PCM did not delay the inside air temperature in reaching its maximum. Indeed, the outside temperature oscillated between 15 and 45$^\circ C$ for Cycle B, while PCM melting/freezing took place between around 17 and 25$^\circ C$ (Figure 5.2). In these conditions, the temperature in most of the PCM-mortar wall remained above the melting temperature window. Thus, most of the PCM in the wall remained liquid. As a result, the increased thermal mass of the PCM wall during phase change
was not exploited during this cycle.

On the other hand, Figures 5.4c-5.4f show a significant reduction in the amplitude of $T_a(t)$ for Cycles C and D when using a PCM-mortar composite wall panel compared with a plain mortar wall panel. Additionally, $T_a(t)$ reached its maximum at a later time for the PCM wall panel. This amplitude reduction and phase shift were due to melting and solidification of the PCM embedded in the wall. In fact, $T_a(t)$ oscillated between 10°C and 30°C and between 5°C and 35°C for Cycles C and D, respectively, encompassing the PCM phase change temperature window of 17-25°C.

Moreover, Figures 5.4 shows good qualitative agreement between experimental measurements and numerical predictions. However, the effect of the PCM in delaying the maximum inside air temperature was more pronounced in the numerical simulations than in the experiments. This discrepancy between the experimentally measured and numerically predicted inside air temperature evolutions could be partially attributed to uncertainty in the material properties used by the numerical model, including possible differences between the thermophysical properties of the cement paste in the plain mortar and PCM-mortar wall panels. Indeed, when PCM melting and freezing did not take place in most of the wall for Cycle B (Figure 5.4a-b), the inside air temperature actually reached its maximum sooner when the PCM-composite wall was used, indicating that the thermal mass of the cement paste matrix in the PCM-composite wall was slightly lower than in the plain mortar wall. Also, while both convective heat transfer coefficients $h_i$ and $h_o$ were treated as constants by the model, they were not necessarily constant in the experiments. In practice, it would be difficult to measure the transient behavior of these coefficients.

Overall, Figure 5.4 establishes that the numerical model could predict the thermal behavior of the test cells, with some minor discrepancies.

### 5.4.4 Scaling analysis

This section presents numerical validation of the scaling analysis. Here, the wall material considered was the composite PCM-mortar wall with 10 vol.% PCM. For the purpose of
Figure 5.4: Experimentally measured and numerically predicted inside air temperature $T_a(t)$ for test cells with either a plain mortar or PCM-mortar wall subjected to chamber temperature $T_o(t)$ corresponding to (a-b) Cycle B, (c-d) Cycle C, and (e-f) Cycle D.
scaling analysis and for parameterizing the problem, the temperature-dependent specific heat \( c_{p,c+s}(T) \) of the microencapsulated PCM was estimated using the effective heat capacity method [Equation (2.9)]. The PCM specific heat outside the phase change temperature window was taken as \( c_{p,c+s,s} = c_{p,c+s,l} = 1900 \text{ J/(kg K)} \) [13]. Table 5.2 outlines several cases considering various values of (i) test cell dimensions, (ii) outside minimum \( T_{o,min} \) and maximum \( T_{o,max} \) temperatures, (iii) oscillation period \( \tau \), (iv) convective heat transfer coefficients \( h_o \) and \( h_i \), (v) PCM melting temperature \( T_{pc} \), (vi) PCM melting temperature window \( \Delta T_{pc} \), and (vii) latent heat of fusion \( h_{sf} \). The values of the seven dimensionless numbers governing the temperatures in the wall and in the test cell were identical in all cases and equal to \( Bi_o = 0.592, Bi_i = 0.278, Cr = 126, \tau^* = 5.07, T_{pc}^* = 0.7, \Delta T_{pc}^* = 0.5, \) and \( h_{sf}^* = 2.99 \). The geometry of Case 1 corresponds to the reduced-scale experimental test cell presented previously and subjected to chamber temperature Cycle C with a period \( \tau \) of 1.5 hours. Cases 2-4 and Cases 5-7 represent two large-scale enclosures with different dimensions and a period \( \tau \) of 24 hours corresponding to actual outdoor diurnal cycles. Finally, Case 8 represents a medium-scale enclosure with a period of 12 hours. The maximum \( T_{o,max} \) and minimum \( T_{o,min} \) outside temperatures were chosen to represent different climates. For example, Cases 3 and 4 correspond to a cold winter day and a hot summer day, respectively.
Table 5.2: Cases used for numerical validation of the scaling analysis. Case 1 corresponds to the experimental test cell subjected to chamber temperature Cycle C, while the other cases correspond to various full-scale enclosures. The values of the dimensionless numbers were, in all cases, $Bi_o = 0.592$, $Bi_i = 0.278$, $Cr = 126$, $\tau^* = 5.07$, $T_{pc}^* = 0.7$, $h_{sf}^* = 2.99$, and $\Delta T_{pc}^* = 0.5$.

<table>
<thead>
<tr>
<th>Case</th>
<th>Type</th>
<th>$L$ (m)</th>
<th>$A_w$ (m$^2$)</th>
<th>$V_a$ (m$^3$)</th>
<th>$T_{o,min}$ (°C)</th>
<th>$T_{o,max}$ (°C)</th>
<th>$h_o$ (W/(m$^2$ K))</th>
<th>$h_i$ (W/(m$^2$ K))</th>
<th>$T_{pc}$ (°C)</th>
<th>$\Delta T_{pc}$ (°C)</th>
<th>$h_{sf}$ (kJ/kg)</th>
<th>$\tau$ (hr)</th>
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<td>0.16</td>
<td>0.064</td>
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</tr>
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<td>Large-scale #1</td>
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<td>48</td>
<td>10</td>
<td>30</td>
<td>8.5</td>
<td>4</td>
<td>24</td>
<td>10</td>
<td>160</td>
<td>24</td>
</tr>
<tr>
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<td>48</td>
<td>0</td>
<td>10</td>
<td>8.5</td>
<td>4</td>
<td>7</td>
<td>5</td>
<td>80</td>
<td>24</td>
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<td>48</td>
<td>20</td>
<td>45</td>
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<td>4</td>
<td>37.5</td>
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<td>12.5</td>
<td>200</td>
<td>24</td>
</tr>
<tr>
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<td>0.102</td>
<td>20</td>
<td>32</td>
<td>5</td>
<td>25</td>
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<td>7</td>
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<td>32</td>
<td>30</td>
<td>40</td>
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<td>4</td>
<td>37</td>
<td>5</td>
<td>80</td>
<td>24</td>
</tr>
<tr>
<td>8</td>
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<td>11.31</td>
<td>15</td>
<td>35</td>
<td>12.02</td>
<td>5.66</td>
<td>29</td>
<td>10</td>
<td>160</td>
<td>12</td>
</tr>
</tbody>
</table>
5.4.4.1 Wall temperature profiles

Figures 5.5a and 5.5b plot the wall temperature $T_w(x, t)$ as a function of the distance $x$ from the outer wall surface ranging from 0 to 0.102 m at time (a) $t = \tau/4$ and (b) $t = 3\tau/4$ for Cases 1-8 (Table 5.2). As expected, the temperature profiles at both times varied significantly among cases due to the differences in wall thickness, convective heat transfer coefficients, and outside temperatures. Figures 5.5c and 5.5d plot the corresponding dimensionless wall temperature $T^*_w(x^*, t^*)$ as a function of the dimensionless distance $x^* = x/L$ ranging from 0 to 1 at dimensionless time $t^*$ equals to $\tau^*/4$ and $3\tau^*/4$, respectively. It is evident that all the dimensionless temperature profiles at both times were identical for the eight cases considered. Similar results were obtained at any other time during the cycle. These results establish the validity of the scaling analysis for the wall temperature $T_w(x, t)$.

5.4.4.2 Inside air temperature

Figure 5.6a plots the inside air temperature $T_a(t)$ as a function of time $t$ ranging from 0 to 24 hours for Cases 1-8 (Table 5.2). Here also, $T_a(t)$ varied significantly among cases due to the significant differences in dimensions, period $\tau$, outdoor temperature $T_o(t)$, and PCM properties. Figure 5.6b plots the dimensionless inside temperature $T^*_a(t^*)$ as a function of the dimensionless time $t^*$ ranging from 0 to 5.07 corresponding to a single oscillation period. Once again, the dimensionless inside temperatures $T^*_a(t)$ collapsed on a single line for all cases considered.

Figures 5.5 and 5.6 establish that scaling analysis of the experimentally-validated thermal model identified the seven dimensionless numbers governing the spatiotemporal behavior of $T_w(x, t)$ and $T_a(t)$. They indicate that the reduced-scale experimental test cell (Case 1) with a diurnal period of 1.5 hours can be used to experimentally simulate the thermal behavior of large-scale enclosures (Cases 2-7) subjected to various daily outdoor temperature cycles.
Figure 5.5: Wall temperature $T_w(x, t)$ as a function of the spatial distance $x$ for Cases 1-8 summarized in Table 5.2 shown at (a) $t = \tau/4$ and (b) $t = 3\tau/4$. Also shown is the dimensionless wall temperature $T_w^*(x^*, t^*)$ as a function of the dimensionless distance $x^*$ for (c). $t^* = \tau^*/4$ and (d) $t^* = 3\tau^*/4$. 
Figure 5.6: (a) Inside temperature $T_a(t)$ as function of time $t$ along with (b) dimensionless inside temperature $T_a^*(t^*)$ as a function of the dimensionless time $t^*$ for Cases 1-8 summarized in Table 5.2.
5.4.5 Application to a real full-scale experimental setup

For illustration purposes, this section applies scaling analysis to two full-scale experimental outdoor 2 m x 2 m x 3 m cubicles with 12 cm-thick concrete walls constructed by Cabeza et al. [7]. In one cubicle, the north and east walls were made of plain concrete while the ceiling, south, and west walls were made of concrete with 5 wt.% microencapsulated PCM. The PCM was reported to have latent heat $h_{sf} = 110$ kJ/kg and melting temperature $T_{pc} = 26^\circ$C [7]. The other cubicle was a reference structure for which all walls and ceiling were made of plain concrete. The cubicles were subjected to the outdoor environment of Lleida, Spain in the summer of 2005. Figure 5.7a plots the outdoor temperature $T_o(t)$ and horizontal solar radiation flux $q''_{s,5}(t)$ as recorded during the experiment on June 6th, 2005 [7]. Here, the minimum and maximum outdoor temperatures were $T_{o,min} \approx 11^\circ$C and $T_{o,max} \approx 30^\circ$C.

Moreover, in simulating the experimental structures, the dimensionless energy conservation equation for the inside air given by Equation (5.13) was modified to account for heat transfer through all four side walls and the ceiling such that,

$$\frac{dT^*_a}{dt^*} = \sum_{j=1}^{5} B_i_{i,j} C_{r,j} [T^*_{w,j}(1,t^*) - T^*_a(t^*)]$$ (5.17)

where the subscript $j$ refers to the four walls and ceiling. Because the walls and ceiling had different compositions and boundary conditions, the dimensionless heat diffusion equation (5.8) for the wall temperatures $T^*_w(x^*,t^*)$ was solved for each wall separately. In addition, the boundary condition at each outer wall surface, given by Equation (5.12), was modified to include the effect of the incident solar radiation flux $q''_{s,j}(t)$, i.e.,

$$\frac{\partial T^*_w}{\partial x^*}(0,t^*) = -B_{i_{o,j}} [T^*_o(t^*) - T^*_w(0,t^*)] - \alpha_s q''_{s,j}(t^*)$$ (5.18)

where the dimensionless solar radiation flux $q''_{s,j}(t^*)$ was defined as,

$$q''_{s,j}(t) = \frac{q''_{s,j}(t)L_j}{k_{eff,j}(T_{o,max} - T_{o,min})}.$$ (5.19)

Here, incident solar radiation was ignored except on the ceiling ($j = 5$) and south wall ($j = 4$), i.e., $q''_{s,j}(t) = 0$ for $j \in \{1, 2, 3\}$. The following relationship was used to estimate the solar
Table 5.3: Thermal conductivity $k$, density $\rho$, and specific heat $c_p$ used in numerical simulation of experiments conducted on full-scale cubicles by Cabeza et al. [7].

<table>
<thead>
<tr>
<th>Material</th>
<th>Subscript</th>
<th>$k$ (W/(m K))</th>
<th>$\rho$ (kg/m$^3$)</th>
<th>$c_p$ (J/(kg K))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concrete</td>
<td>m</td>
<td>1.4</td>
<td>2300</td>
<td>880</td>
<td>[75]</td>
</tr>
<tr>
<td>PCM</td>
<td>c</td>
<td>0.21</td>
<td>900</td>
<td>1900</td>
<td>[13]</td>
</tr>
<tr>
<td>Melamine-formate (MF)</td>
<td>s</td>
<td>0.42</td>
<td>1500</td>
<td>1670</td>
<td>[81]</td>
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</table>

The indoor convective heat transfer coefficient $h_i$ was taken as 7.7 W/(m$^2$ K) based on the ISO standard [8]. The outdoor convective heat transfer coefficient $h_o$ was estimated using the correlation developed by Defraeye et al. [82] for a leeward exterior building wall given by,

$$h_o = 2.27U_\infty^{0.83}$$ (5.21)

$$80$$
where \( U_\infty \) is the wind speed (in m/s) and \( h_o \) is in W/(m\(^2\) K). Here, \( U_\infty \) was taken as 6 m/s based on the average value for a summer in the region of Lleida [83], resulting in \( h_o = 10.0 \) W/(m\(^2\) K). Note that the actual value of \( h_o \) prevailing experimentally would vary with time based on the speed and direction of the wind. The wind speed reported by Cabeza et al. [7] on a different day fluctuated between 0 and 20 m/s, but featured an average value of less than 10 m/s. Finally, the total hemispherical solar absorptivity of the wall surfaces \( \alpha_s \) was taken as 0.6 corresponding to unpainted concrete [75].

Table 5.4 summarizes the dimensions, convective heat transfer coefficients \( h_o \) and \( h_i \), and oscillation period \( \tau \) corresponding to the experimental setup used in Ref. [7] as well as those for the equivalent reduced-scale model. The dimensions of the reduced-scale model were chosen such that the dimensionless numbers \( Bi_{i,j} \), \( Bi_{o,j} \), and \( C_{r,j} \) for each wall were identical to those estimated for the outdoor building structures. Specifically, the Biot numbers for the PCM-composite side walls (\( j \in \{3, 4\} \)) and ceiling (\( j = 5 \)) were \( Bi_{i,3\leq j \leq 5} = 0.76 \) and \( Bi_{o,3\leq j \leq 5} = 0.99 \). They were of the same order of magnitude as those reported for our experimental apparatus discussed previously in Section 5.2. Likewise, the values of \( C_{r,3\leq j \leq 4} = 99.5 \) for the PCM-composite side walls and \( C_{r,5} = 66.4 \) for the ceiling were similar in magnitude to \( C_r = 126 \) for our test cell. The plain concrete walls (\( j \in \{1, 2\} \)) had \( Bi_{i,1\leq j \leq 2} = 0.66 \), \( Bi_{o,1\leq j \leq 2} = 0.85 \), and \( C_{r,1\leq j \leq 2} = 100.7 \). On the other hand, the values of \( T_{pc} \), \( \Delta T_{pc} \), and \( h_{sf} \), \( T_o,\text{min} \), and \( T_o,\text{max} \) were the same for the reduced-scale model as for the full-scale experiment, and such that \( T_{pc}^* = 0.79 \), \( \Delta T_{pc}^* = 0.42 \), and \( h_{sf}^* = 2.6 \) in both cases. Finally, the dimensionless period \( \tau^* \) based on the thermal diffusivity of the PCM-composite walls was equal to 3.64 in both cases.
Table 5.4: Parameters corresponding to the experimental cubicles studied by Cabeza et al. [7] and those corresponding to a reduced-scale model with identical dimensionless numbers $Bi_{o,j}$, $Bi_{i,j}$, $C_{r,j}$, $\tau_j$, $T_{pc}^*$, $\Delta T_{pc}^*$, $h_{sf}^*$, and $q''_{s,j}^*(t^*)$.

<table>
<thead>
<tr>
<th>Type</th>
<th>$L$ (m)</th>
<th>Width (m)</th>
<th>Depth (m)</th>
<th>Height (m)</th>
<th>$h_o$ (W/(m$^2$ K))</th>
<th>$h_i$ (W/(m$^2$ K))</th>
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</tr>
<tr>
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<td>0.5</td>
<td>0.75</td>
<td>40</td>
<td>30.8</td>
<td>1.5</td>
</tr>
</tbody>
</table>
The measured outdoor temperature $T_o(t)$ and solar irradiation $q_s''(t)$ in the full-scale setup of Ref. [7] were scaled to have an oscillation period $\tau = 1.5$ hours in the reduced-scale model, as illustrated in Figure 5.7b. Additionally, the magnitude of the imposed solar radiation flux on both the roof and south wall was scaled such that the dimensionless radiation flux $q_s''(t^*)$ given by Equation (5.19) was identical for both cases. These scaled profiles were used as the boundary conditions for the reduced-scale model.

Figure 5.7c plots the interior (i.e., $x = L$) south-wall temperature $T_{w,4}(L, t)$ as a function of time $t$ ranging from 0 to 24 hours measured experimentally [7] and predicted numerically using the previously described reduced-scale model for structures with and without PCM-composite walls. Additionally, Figure 5.7d plots the corresponding dimensionless interior ($x^* = 1$) south-wall surface temperature $T_{w,4}^*(1, t^*)$ as a function of dimensionless time $t^*$ over one oscillation period. It shows good agreement between the values of $T_{w,4}^*(1, t^*)$ measured experimentally and those predicted numerically. The underprediction of the maximum value of $T_{w,4}^*(1, t^*)$ can be attributed to uncertainty in (i) the wall material properties, (ii) the experimental outdoor convective heat transfer coefficient $h_o$, and (iii) a possible underprediction of the south wall solar radiation flux. However, the effect of PCM in reducing the magnitude of the inner south-wall temperature fluctuation was accurately captured by the scaled model.

These results illustrate the ability of scaling analysis to represent the thermal behavior of a realistic full-scale structure with a reduced-scale model. Therefore, rather than constructing a full-scale structure to evaluate the thermal performance of various building envelope materials, including those containing PCM, one could simply determine the eight dimensionless numbers governing the thermal behavior of the building envelope, and then design a reduced-scale model with identical dimensionless numbers to be conveniently tested in a laboratory environmental chamber.
Figure 5.7: (a) Outdoor temperature $T_o(t)$ and horizontal solar radiation flux $q''_{s,5}(t)$ corresponding to June 6th, 2005 in Lleida, Spain, measured by Cabeza et al. [7] during their experimental study of full-scale test cells with and without PCM-composite walls and (b) higher-frequency $T_o(t)$ and $q''_{s,5}(t)$ used as inputs to the reduced-scale numerical model. (c) South-wall temperature $T_w,4(L,t)$ and (d) dimensionless south-wall temperature $T_w^*(1,t^*)$ measured experimentally and predicted numerically using the reduced-scale model of the experimental structures.
5.5 Conclusion

This study presented an approach to experimentally evaluate the performance of PCM-composite building envelope materials without requiring a significant amount of time, material, or space. First, a transient thermal model accounting for the thermal coupling between PCM-composite wall and inside air temperatures of an enclosure was outlined. Then, the thermal model was validated against experimental temperature measurements on a reduced-scale test cell subjected to sinusoidal outdoor temperature oscillations. Scaling analysis of the coupled energy conservation equations and their boundary conditions was developed and identified seven (eight if accounting for incident solar radiation) relevant dimensionless numbers governing the thermal behavior of the test cell including melting and solidification of the PCM. This scaling analysis was validated with a previously developed numerical simulation tool. The application of the scaling analysis to experimental results from a full-scale outdoor structure was then illustrated [7]. The results demonstrated that a full-scale enclosure exposed to a realistic outdoor climate can be represented by a reduced-scale test cell in an environmental chamber.
CHAPTER 6

Temperature Control Schemes for Buildings with PCM-composite Envelopes

6.1 Background

Temperature control schemes in buildings can be divided into traditional feedback control methods, e.g., on/off or proportional control, and more advanced strategies such as model predictive control (MPC). Classical control schemes are the most widely used to regulate the indoor air temperature in buildings due to their simplicity and ease of implementation [84,85]. As illustrated in Figure 6.1a, a feedback temperature control system uses the measured difference between the indoor set point temperature $T_s$ and the actual indoor air temperature $T_a(t)$ to determine a control signal. For example, in the case of cooling a room, the control signal could be the rate of heat removal from the indoor air $q_c$ (in Watts). The resulting indoor temperature $T_a(t + \Delta t)$ is then determined by the control input $q_c(t)$ as well as disturbances to the system (e.g., outdoor temperature $T_o(t)$).

An on/off temperature controller is a simple device that maintains the indoor temperature within a specified temperature range, i.e., within the range $T_s \pm \Delta T_s$ where $T_s$ is the indoor set point temperature and $\Delta T_s$ is the allowed deviation. For example, an on/off cooling scheme would turn on the air conditioner when $T_a > T_s + \Delta T_s$, and turn it off when $T_a < T_s - \Delta T_s$. Note that the control signal $q_c$ is not dependent on the magnitude of $T_a - T_s$.

Proportional (P) controllers are also commonly used for building temperature control [84]. In a proportional temperature control scheme, the control signal is proportional to the difference between the current indoor temperature $T_a$ and the set point $T_s$. In the case of
cooling a room, the heat removal rate $q_c(t)$ would be determined according to,

$$q_c(t) = \begin{cases} 
K_p[T_a(t) - T_s] & \text{for } T_a > T_s \\
0 & \text{for } T_a \leq T_s 
\end{cases}$$

(6.1)

where the constant of proportionality $K_p$ is expressed in W/$^\circ$C. Note that $K_p$ should be tuned appropriately depending on the parameters of the system.

Model predictive control (MPC) is an advanced control strategy that uses a mathematical model of the system along with future disturbance predictions (e.g., outdoor temperature $T_o(t)$) in order to determine optimal control input, as depicted in Figure 6.1b. At specified intervals, the MPC controller solves an optimization problem to determine the optimal vector of control inputs $\mathbf{q}_c = [q_c(1), q_c(2), ..., q_c(N)]$ that minimizes the accumulation of an objective or cost function $J(t)$ over a prediction horizon of length $\hat{t}$. The number of time steps on the prediction horizon $N$ is then $N = \hat{t}/\Delta t_p$, where $\Delta t_p$ is the time step between predictions. The general form of the MPC optimization problem for cooling a room can then be expressed as,

$$\min_{\mathbf{q}_c} \sum_{k=1}^{N} J(k), \quad \mathbf{q}_c = [q_c(1), ..., q_c(N)]^T$$

(6.2)

where the subscript $k \in \{1, ..., N\}$ denotes discrete times within the prediction horizon. The optimization problem is also subject to constraints on $q_c(t)$ or the system state $\mathbf{x}(t)$. Once the optimal control vector is found, the first element $q_c(1)$ is applied as the control input. This process is then repeated at scheduled intervals.

Recently, the use of MPC in HVAC control systems has been suggested as a means of managing disturbances such as time-varying set points or heat generation from room occupancy [84, 86]. Such disturbances are not well handled by traditional feedback control methods, as they cannot act preemptively to accommodate them. Similarly, the storage and release of heat in PCM-composite building envelopes due to melting and solidification of the PCM might lead to over-heating or over-cooling when a traditional feedback control method is used. Here, we seek to determine whether an adaptive MPC scheme that predicts the onset of PCM melting and solidification within the building envelope can reduce cooling energy
Figure 6.1: Block diagram representation of (a) classical feedback control and (b) model predictive control schemes for temperature control of a room.
and cost requirements for indoor temperature control compared with traditional feedback control methods.

6.2 Analysis

6.2.1 Schematic and assumptions

Figure 6.2 shows a schematic of a room with dimensions 6 m x 6 m x 2.5 m and with a PCM-composite wall of thickness $L = 10$ cm, area $A_w = 15$ m$^2$, and effective thermal properties $k_{eff}$ and $(\rho c_p)_{eff}$. The outer ($x = 0$) and inner ($x = L$) wall surfaces exchanged heat by virtue of convection with the outdoor air at temperature $T_o(t)$ and inside air at temperature $T_a(t)$, respectively, with convective heat transfer coefficients $h_o$ and $h_i$. An HVAC system controlled the indoor air temperature $T_a(t)$ by removing heat at a rate $q_c(t)$. Additionally, an insulation layer of thickness $L_{ins} = 5$ cm and thermal conductivity $k_{ins} = 0.03$ [75] was added at the interior wall such that the overall thermal resistance (R-value) of the envelope was near the value of 1.3 (m$^2$ K)/W recommended by ASHRAE for building envelopes in Southern California [87].

To make the problem mathematically tractable, it was assumed that (i) all walls other than the PCM-composite wall were thermally insulated, (ii) the indoor air was well-mixed with spatially uniform temperature $T_a(t)$, (iii) the PCM specific heat was the same in the solid and liquid phases (i.e., $c_{p,c,s} = c_{p,c,l}$), (iv) there was no heat generation within the room, and (v) transient thermal energy storage within the insulation layer was negligible due to its small thermal mass compared with the cementitious PCM-composite wall.

6.2.2 Governing equations

The temperature inside the PCM-composite wall was governed by the transient 1D heat diffusion equation [75],

$$(\rho c_p)_{eff}(T_w) \frac{\partial T_w}{\partial t} = k_{eff} \frac{\partial^2 T_w}{\partial x^2}$$

(6.3)
Figure 6.2: Schematic of a room with indoor air temperature $T_a(t)$ and an envelope consisting of a PCM-composite wall layer of thickness $L = 10$ cm and an insulation layer of thickness $L_{ins} = 5$ cm. The dimensions of the room were $6$ m x $6$ m x $2.5$ m while the indoor and outdoor convective heat transfer coefficients were $h_i = 7.7$ W/(m$^2$ K) and $h_o = 25$ W/(m$^2$ K), respectively [8]. The indoor temperature $T_a(t)$ is controlled by an HVAC system which removes heat at a rate $q_c(t)$. 

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while the rate of change of the indoor air temperature $T_a(t)$ can be expressed using an energy balance as,

$$(\rho c_p) a V_a \frac{\partial T_a}{\partial t} = U_i A_w [T_w(L,t) - T_a(t)] - q_c(t)$$

(6.4)

where $V_a$ is the volume of air inside the room and $q_c(t)$ is the heat removal rate determined by the temperature controller. Here also, the effective indoor heat transfer coefficient $U_i$ accounts for both the convective resistance and conductive resistance from the insulation layer, i.e.,

$$U_i = \left( \frac{1}{h_i} + \frac{L_{ins}}{k_{ins}} \right)^{-1}. \quad (6.5)$$

6.2.3 Initial and boundary conditions

The indoor air and the PCM-composite wall were assumed to be at some initial temperature $T_{init}$ at $t = 0$, i.e.,

$$T_a(0) = T_w(x,0) = T_{init}.$$  \hspace{1cm} (6.6)

Additionally, two boundary conditions were required to solve the heat diffusion equation in the composite wall. Convective heat flux boundary conditions were imposed at the outer ($x = 0$) and inner ($x = L$) wall surfaces such that,

$$-k_{eff} \frac{\partial T_w}{\partial x}(0,t) = h_o[T_o(t) - T_w(0,t)] \quad \text{and} \quad -k_{eff} \frac{\partial T_w}{\partial x}(L,t) = U_i[T_w(L,t) - T_a(t)]. \quad (6.7)$$

6.2.4 Control schemes

6.2.4.1 Traditional control schemes

Here, the on/off control scheme considered was defined with respect to a “thermal comfort” range between $21^\circ$C and $23^\circ$C. In other words, the setpoint temperature was $T_s = 22^\circ$C with an allowed deviation of $\Delta T_s = \pm 1^\circ$C. When the air conditioner was on, $q_c(t)$ was constant and equal to 500 W.

For proportional control, the set point was taken as $T_s = 23^\circ$C (the upper bound of the comfort range) in an effort to reduce cooling energy consumption. The proportionality constant $K_p$ was taken as 2000 W/$^\circ$C. Here also, $q_c(t)$ was not allowed to exceed 500 W.
6.2.4.2 Model predictive control

The present study considered two model predictive control (MPC) schemes with different objective functions. In both cases, the prediction horizon $\hat{t}$ was 2 hours and the prediction time step $\Delta t_p$ was 6 minutes. The first was an energy-minimizing MPC (EMPC) scheme that sought to minimize the total cooling energy consumption over the prediction horizon $\hat{t}$.

The optimization problem in this case can be expressed as,

$$\min_{q_c} \sum_{k=1}^{N} q_c(k), \quad q_c = [q_c(1), ..., q_c(N)]^T. \quad (6.8)$$

The second was a cost-minimizing (CMPC) scheme that sought to minimize the total cooling energy cost, i.e.,

$$\min_{q_c} \sum_{k=1}^{N} q_c(k)c(k), \quad q_c = [q_c(1), ..., q_c(N)]^T \quad (6.9)$$

where $c(k)$ is the predicted cost of electricity at time step $k$. Here, it was assumed to follow the summer time-of-use (TOU) electricity pricing schedule adopted by Southern California Edison in 2015 [88],

$$c(t) = \begin{cases} $0.34$/kWh & \text{for } 12:00 \text{ pm} < t < 6:00 \text{ pm} \\ $0.14$/kWh & \text{otherwise} \end{cases}. \quad (6.10)$$

Both MPC optimization problems were subject to the same constraints. First, the indoor temperature $T_a(t)$ must remain within the allowed range, i.e.,

$$T_s - \Delta T_s \leq T_a(k) \leq T_s + \Delta T_s \quad \text{for} \quad k \in \{1, ..., N\}. \quad (6.11)$$

Here, $T_s = 22^\circ$C and $\Delta T_s = 1^\circ$C were the same as for the on/off control scheme discussed previously. Second, the cooling power $q_c$ must remain between 0 and some maximum value $q_{c,max}$ such that,

$$0 \leq q_c(k) \leq q_{c,max} \quad \text{for} \quad k \in \{1, ..., N\}. \quad (6.12)$$

Finally, a constraint was placed on the maximum amount that $q_c$ can vary between successive time steps. This can be expressed as,

$$|q_c(k+1) - q_c(k)| \leq \Delta q_{c,max} \quad \text{for} \quad k \in \{1, ..., N - 1\}. \quad (6.13)$$
Figure 6.3: Schematic of the simplified “2-node” model used by the MPC scheme to predict $T_a(t)$ over the prediction horizon. The simplified model includes three dependent variables, namely (i) indoor air temperature $T_a(t)$, (ii) inner wall temperature $T_{w,i}(t)$, and (iii) outer wall temperature $T_{w,o}(t)$.

Here, $\Delta q_{c,max}$ was taken as 50 W.

In order to solve the optimization problem, a simple mathematical model of the system is required to predict future values of $T_a(t)$ given a potential vector of control inputs $q_c$. To accomplish this, a simplified “2-node” model of the PCM-composite wall was used, as depicted in Figure 6.3. This simplified model features a small number of dependent (state) variables (outer wall temperature $T_{w,o}(t)$, inner wall temperature $T_{w,i}(t)$, and indoor air temperature $T_a(t)$) while still being able to account for transient thermal energy storage within the wall. It should also be noted that in both optimization problems given by (6.8) and (6.9), the objective function is linear with respect to the control vector $q_c$. This linearity would allow the optimization problem to be solved efficiently through linear programming (LP). However, due to the nonlinearity introduced to the heat diffusion Equation (6.3) by the temperature-dependent heat capacity of the PCM $(\rho c_p)_{eff}(T)$, the constraint on
the indoor temperature \( T_a \) given by (6.11) is not linear in \( q_c \). The MPC model was fully linearized using an iterative procedure in which the wall temperature \( T_w(x, t) \) was predicted assuming that \( T_a(t) = T_s \). This approximation was made under the reasoning that \( T_a(t) \) is not expected to deviate from \( T_s \) by more than 1°C due to constraint (6.11). Then, the resulting wall temperature was used to approximate \( (\rho c_p)_{eff,i}(t) \) and \( (\rho c_p)_{eff,o}(t) \) as functions of time rather than temperature over the prediction horizon. In effect, this approach models PCM melting and solidification as a time-varying forcing function. Consequently, the 2-node model becomes a linear time-variant system which can be described using the state-space method as,

\[
x(k + 1) = A(k)x(k) + Bq_c(k) + E(k)T_o(k)
\]  

(6.14)

where the vector \( x(k) \) represents the state of the system at time step \( k \) and whose components are the three dependent variables, i.e.,

\[
x(k) = \begin{bmatrix} T_a(k) \\ T_{w,i}(k) \\ T_{w,o}(k) \end{bmatrix}.
\]  

(6.15)

Expressions for \( A(k) \), \( B \), and \( E(k) \) can be derived based on energy conservation in each wall node and in the indoor air and are given by,

\[
A(k) = \begin{bmatrix} 1 - \frac{U_i A_w \Delta t_p}{(\rho c_p)_{eff} V_a} & \frac{U_i A_w \Delta t_p}{(\rho c_p)_{eff} V_a} & 0 \\ 2F_{o,i}(k)B_{i,i} & 1 - 2F_{o,i}(k) - 2B_{i,i}F_{o,i}(k) & 2F_{o,i}(k) \\ 0 & 2F_{o,o}(k) & 1 - 2F_{o,o}(k) - 2B_{i,o}F_{o,o}(k) \end{bmatrix},
\]  

(6.16)

\[
B = \begin{bmatrix} \frac{\Delta t_p}{(\rho c_p)_{eff} V_a} \\ 0 \\ 0 \end{bmatrix}, \quad \text{and} \quad E(k) = \begin{bmatrix} 0 \\ 0 \\ 2F_{o,o}(k)B_{i,o} \end{bmatrix}.
\]  

Here, the dimensionless Biot numbers are defined as,

\[
B_{i,i} = \frac{U_i L}{k_{eff}} \quad \text{and} \quad B_{i,o} = \frac{h_o L}{k_{eff}}
\]  

(6.17)

and the Fourier numbers are defined as,

\[
F_{o,i}(k) = \frac{k_{eff} \Delta t_p}{(\rho c_p)_{eff,i}(k)L^2} \quad \text{and} \quad F_{o,o}(k) = \frac{k_{eff} \Delta t_p}{(\rho c_p)_{eff,o}(k)L^2}
\]  

(6.18)
where the subscripts $i$ and $o$ refer to the inner and outer wall nodes, respectively.

Finally, the future values of the indoor air temperature $[T_a(1), ..., T_a(N)]^T$ can then be determined as a function of the control vector $q_c = [q_c(1), ..., q_c(N)]^T$ and predicted outdoor temperature $[T_o(1), ..., T_o(N)]^T$ according to,

$$
\begin{pmatrix}
  T_a(1) \\
  T_a(2) \\
  T_a(3) \\
  \vdots \\
  T_a(N)
\end{pmatrix}
= \begin{pmatrix}
  CA_1 \\
  CA_2 A_1 \\
  CA_3 A_2 A_1 \\
  \vdots \\
  C \prod_{k=1}^{N} A_k
\end{pmatrix} x(0)
+ \begin{pmatrix}
  CB \\
  CA_2 B \\
  CA_3 A_2 B \\
  \vdots \\
  C \prod_{k=2}^{N} A_k B
\end{pmatrix}
\begin{pmatrix}
  q_c(1) \\
  q_c(2) \\
  q_c(3) \\
  \vdots \\
  q_c(N)
\end{pmatrix}
+ \begin{pmatrix}
  CE_1 \\
  CA_2 E_1 \\
  CA_3 A_2 E_1 \\
  \vdots \\
  C \prod_{k=2}^{N} A_k E_1
\end{pmatrix}
\begin{pmatrix}
  T_o(1) \\
  T_o(2) \\
  T_o(3) \\
  \vdots \\
  T_o(N)
\end{pmatrix}
$$

(6.19)

where the vector $x(0)$ represents the current state and $C$ is defined such that $T_a(k) = C x(k)$, i.e., $C = [1 0 0]$.

### 6.2.5 Constitutive relationships

Table 6.1 summarizes the thermophysical properties of PCM, melamine-formaldehyde (MF), concrete, and air used in the simulations. The PCM had latent heat of fusion $h_{sf} = 160$ kJ/kg, melting temperature $T_{pc} = 24^\circ C$, and melting temperature window $\Delta T_{pc} = 10^\circ C$ [6]. The effective volumetric heat capacity of the composite material $(\rho c_p)_{eff}(T)$ was determined using the effective heat capacity method and the volume weighted average given by Equation (2.7). The Felske model [Equation (2.8)] was used to determine the effective thermal conductivity $k_{eff}$.
Table 6.1: Density $\rho$, specific heat capacity $c_p$, and thermal conductivity $k$ of PCM, melamine-formaldehyde (MF), concrete, and air used in the thermal model.

<table>
<thead>
<tr>
<th>Material</th>
<th>Subscript</th>
<th>$\rho$ (kg/m$^3$)</th>
<th>$c_p$ (J/(kg K))</th>
<th>$k$ (W/(m K))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCM</td>
<td>$c$</td>
<td>900</td>
<td>1900</td>
<td>0.21</td>
<td>[13]</td>
</tr>
<tr>
<td>MF</td>
<td>$s$</td>
<td>1500</td>
<td>1670</td>
<td>0.42</td>
<td>[81]</td>
</tr>
<tr>
<td>Concrete</td>
<td>$m$</td>
<td>2300</td>
<td>880</td>
<td>1.4</td>
<td>[75]</td>
</tr>
<tr>
<td>Air</td>
<td>$a$</td>
<td>1.2</td>
<td>1005</td>
<td>N/A</td>
<td>[75]</td>
</tr>
</tbody>
</table>

The outdoor temperature $T_o(t)$ was approximated as a sine function of the form,

$$T_o(t) = \frac{1}{2}(T_{\text{max}} - T_{\text{min}}) \sin \left( \frac{2\pi t}{24} \right) + \frac{1}{2}(T_{\text{max}} + T_{\text{min}})$$  \hspace{1cm} (6.20)

where $t$ is in hours and $t = 0$ corresponds to 6:00 am such that the maximum $T_o(t)$ occurs at 12:00 pm. Here, $T_{\text{max}}$ and $T_{\text{min}}$ were taken as 32°C and 16°C, respectively, to represent a typical summer day in California Climate Zone 9 (Los Angeles, CA) [89]. The indoor and outdoor convective heat transfer coefficients were taken as $h_i = 7.7$ W/(m$^2$ K) and $h_o = 25$ W/(m$^2$ K), in accordance with ISO standards [8].

6.2.6 Method of solution

Equations (6.3) and (6.4) were solved along with the corresponding boundary conditions using the finite difference method with a fixed time step $\Delta t = 20$ s and nodal spacing $\Delta x = 1$ cm. Numerical convergence was verified such that the resulting indoor air temperature $T_a(t)$ differed by no more than 1% when the time step or nodal spacing was reduced by a factor of 2. For simulations involving model predictive control, the optimization was carried out using MATLAB’s optimization toolbox. The simulation tool used to solve for the temperature profile in the PCM-composite wall was validated against an exact solution for the Stefan problem of 1D transient heat conduction in a paraffin slab with phase change [78]. In order to eliminate the effect of initial conditions and ensure that the solution had reached a cyclic steady-state, simulations were conducted for a preceding time of 4 days before data was...
6.2.7 Data processing

The total amount of energy removed by the HVAC system \( Q_c \) was obtained by integrating the cooling power \( q_c(t) \) over the 24-hour simulation period,

\[
Q_c = \int_0^{24h} q_c(t) dt.
\]  
(6.21)

Similarly, the total cooling cost was obtained by integrating the product of \( q_c(t) \) and the time-dependent electricity cost \( c(t) \),

\[
C_c = \int_0^{24h} q_c(t) c(t) dt.
\]  
(6.22)

Finally, the cooling energy reduction \( Q_r \) and cost reduction \( C_r \) were computed as the percent reduction in total cooling energy consumption \( Q_c \) or cost \( C_c \) for a room with a PCM-composite wall compared with a plain concrete wall, i.e.,

\[
Q_r = \frac{Q_{c,\text{concrete}} - Q_{c,\text{PCM}}}{Q_{c,\text{concrete}}} \quad \text{and} \quad C_r = \frac{C_{c,\text{concrete}} - C_{c,\text{PCM}}}{C_{c,\text{concrete}}}.
\]  
(6.23)

6.3 Results and Discussion

6.3.1 Evolution of indoor temperature and heat removal rate

6.3.1.1 Traditional control schemes

Figure 6.4 plots the numerically predicted (a) indoor air temperature \( T_a(t) \) and (b) heat removal rate \( q_c(t) \) as functions of time over a single day for a room cooled with an on/off control scheme and with either (i) a plain concrete wall or (ii) PCM-composite wall with microencapsulated PCM volume fraction \( \phi_{c+s} = 0.2 \). Also shown in Figure 6.4b is the time-dependent electricity rate described by Equation (6.10). To ensure that the indoor temperature \( T_a(t) \) did not exceed the upper bound of the thermal comfort range (23°C), the controller employed several on/off cycles between around 12:00 pm and 12:00 am. Specifically, 9 on/off cycles occurred for a room with a plain concrete wall, while only 7 were required for a room with
a PCM-composite wall. Also, the first on/off cycle took place around 2 hours later for the room with a PCM-composite wall compared to that with a plain concrete wall. Note that because only cooling was considered, the indoor air temperature was allowed to drop below the thermal comfort range. Indeed, for a room with a plain concrete wall, $T_a(t)$ was below the lower thermal comfort bound of $21^\circ$C before 9:00 am and after 2:00 am the following night. However, the indoor temperature of the room with a PCM-composite wall did not drop below the thermal comfort range at any point during the 24-hour period, due to the increased thermal mass of the wall afforded by PCM solidification at night.

Similarly, Figure 6.4 also plots the (c) indoor air temperature $T_a(t)$ and (d) heat removal rate $q_c(t)$ as functions of time over a single day for a room cooled with a proportional control scheme. In this case, the temperature controller kept the indoor air temperature very near the set point temperature of $T_s = 23^\circ$C, i.e., the top of the thermal comfort range, between 12:00 pm and 12:00 am. Here again, the presence of PCM in the wall prevented the indoor temperature from dropping below the thermal comfort range during the night. Additionally, Figure 6.4d shows that the peak of the heat removal rate $q_c(t)$ was reduced in magnitude and time-shifted by around 3 hours for a PCM-composite wall compared to a plain concrete wall. While the majority of cooling took place within the period of peak electricity cost (12:00 pm to 6:00 pm) for a plain concrete wall, only about half of the cooling took place within this period for a PCM-composite wall.

6.3.1.2 Model predictive control

Figure 6.5 plots the (a) indoor air temperature $T_a(t)$ and (b) heat removal rate $q_c(t)$ as functions of time for a room cooled with an energy minimizing MPC (EMPC) control scheme. Here again, simulated temperatures and heat removal rates are shown for a room with either a plain concrete wall or a PCM-composite wall. Figures 6.5a and 6.5b show that the room controlled with an EMPC scheme featured indoor temperature $T_a(t)$ and heat removal rate $q_c(t)$ very similar to that observed when a proportional control scheme was used (Figure 6.4c-6.4d), for both the plain concrete and PCM-composite walls. In other
Figure 6.4: Indoor temperature $T_i(t)$ and heat removal rate $q_c(t)$ as functions of time for a room with a plain concrete or PCM-composite wall cooled with on/off or proportional control.
words, the optimal control strategy for minimizing energy consumption was simply to keep the indoor temperature at the top of the comfort range, as was accomplished with the proportional control scheme. This suggests that melting and solidification of the PCM in the wall did not induce any special control action. Indeed, PCM phase change is a gradual process that might be adequately handled by traditional feedback control.

Figure 6.5 also plots (c) indoor air temperature $T_a(t)$ and (d) heat removal rate $q_c(t)$ as functions of time for a room with either a plain concrete or PCM-composite wall cooled with a cost-minimizing MPC (CMPC) scheme. While the evolution of $T_a(t)$ and $q_c(t)$ was overall similar to those resulting from the use of an EMPC scheme (Figures 6.5a and 6.5b), they differed in the time preceding the jump in electricity cost at 12:00 pm. Here, the CMPC controller appeared to “pre-cool” the room in an effort to reduce the amount of cooling required during the peak energy pricing period. Interestingly, this pre-cooling effect was much more substantial for a room with a plain concrete wall than one with a PCM-composite wall.

### 6.3.2 Total diurnal energy consumption and cost

Table 6.2 reports the numerically predicted total diurnal cooling energy consumption $E_c$ and cost $C_c$ corresponding to the simulations shown previously in Figures 6.4 and 6.5. Also shown are the percent cooling energy reduction $Q_r$ and cost reduction $C_r$ attributed to the PCM-composite wall for each control scheme considered. As expected, the on/off control scheme was the least energy- and cost-efficient as it continually cycled the indoor air temperature $T_a(t)$ between the upper and lower bounds of the comfort range. The proportional, EMPC, and CMPC control schemes had lower energy and cost requirements by virtue of the fact that they kept the indoor air temperature near the top of the comfort range when cooling was required. The percent reduction in cooling energy consumption $Q_r$ afforded by the PCM-composite wall ranged from around 25% to 35% depending on the control scheme. Because of the PCM’s ability to partially time-shift the cooling load past the period of high energy cost, the percent cost reduction $C_r$ afforded by the PCM-composite wall exceeded
Figure 6.5: Indoor temperature $T_i(t)$ and heat removal rate $q_c(t)$ as functions of time for a room with a plain concrete or PCM-composite wall cooled with energy-minimizing or cost-minimizing model predictive control (MPC) schemes.
the energy reduction $Q_r$ and ranged from around 31% to 44%. Neither the EMPC nor the CMPC control schemes appeared to offer significant energy or cost savings compared with the proportional control scheme. The ability of the CMPC controller to pre-cool the room in anticipation of the electricity price increase only saved a very small fraction of the total diurnal cooling cost.
Table 6.2: Diurnal cooling energy consumption $Q_c$ and cost $C_c$ for a room with either a plain concrete or PCM-composite wall cooled with various control schemes. Also shown is the percent reduction in diurnal cooling energy consumption $Q_r$ and cost $C_r$ afforded by the PCM-composite wall compared with the plain concrete wall.

<table>
<thead>
<tr>
<th>Control scheme</th>
<th>$Q_c$ (kWh)</th>
<th>$C_c$ ($0.01$)</th>
<th>$Q_r$</th>
<th>$C_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Plain concrete</td>
<td>$\phi_{c+s} = 0.2$</td>
<td>Plain concrete</td>
<td>$\phi_{c+s} = 0.2$</td>
</tr>
<tr>
<td>On/off</td>
<td>0.639</td>
<td>0.475</td>
<td>17.61</td>
<td>12.09</td>
</tr>
<tr>
<td>Proportional</td>
<td>0.525</td>
<td>0.348</td>
<td>14.80</td>
<td>8.24</td>
</tr>
<tr>
<td>EMPC</td>
<td>0.531</td>
<td>0.352</td>
<td>14.97</td>
<td>8.35</td>
</tr>
<tr>
<td>CMPC</td>
<td>0.549</td>
<td>0.355</td>
<td>14.23</td>
<td>8.24</td>
</tr>
</tbody>
</table>
6.4 Conclusion

This study examined the diurnal energy and cost requirements associated with cooling a room with a PCM-composite envelope using various indoor temperature control schemes. It found that the diurnal cooling energy consumption was reduced by 25-33% when the envelope contained 20 vol.% PCM compared with a plain concrete envelope. Additionally, a cooling cost reduction of 31-44% was observed due to the time-shift in peak cooling load afforded by the melting of the PCM during the hot portion of the day. Also, the PCM’s ability to increased thermal inertia of the envelope prevent the indoor temperature from dropping below the thermal comfort range at night. A model predictive control (MPC) scheme was developed which could predict PCM melting and solidification in the wall. However, this advanced control scheme did not appear to offer significant energy or cost savings compared with a traditional proportional control scheme, suggesting that PCM melting and solidification is appropriately handled by traditional feedback control methods. These results can be used in the design of energy-efficient buildings featuring PCM-composite envelopes.
CHAPTER 7

Early-age Temperature Evolutions in Concrete Pavements Containing Microencapsulated Phase Change Materials

7.1 Background

Several studies have developed thermal models to predict transient temperature evolutions in pavement sections exposed to the outdoor environment [90–101]. These models have been developed for both mature concrete sections [90–97] as well as for early-age concrete, for time periods following concrete placement until seven days [98–101], when heat generation resulting from cement hydration reactions is a significant contributor to thermal behavior. Since the subgrade can serve as a heat-sink, such models describe transient temperature evolutions both within the pavement section, and within an underlying soil layer [96].

To assess the effects of cement hydration on early-age temperature evolutions, it is crucial to account for the degree of hydration (i.e., extent of reaction) of the cement [102, 103]. In general, this quantity depends on both time and the temperature history at a given location, since the reaction rate increases with temperature [56]. Hansen and Pederson [104] proposed that the effects of both time and temperature can be accounted for via an “equivalent age” $t_{eq}(x,t)$ defined as,

$$ t_{eq}(x,t) = \int_0^t \exp \left[ -\frac{E_a}{R} \left( \frac{1}{T(x,t)} - \frac{1}{T_{ref}} \right) \right] dt \quad (7.1) $$

where $E_a$ is the activation energy, $R = 8.314 \, \text{J/mol.K}$ is the ideal gas constant, and $T_{ref}$ is the reference temperature. The equivalent age concept, based on the Arrhenius formalism
of assuming reaction rate has an exponential relationship with temperature, has been widely applied to predict the degree of hydration and strength development in concrete [99–101, 105–109]. The degree of hydration $\theta(t_{eq})$ can be approximated as a function of the equivalent age as [101, 109],

$$\theta(t_{eq}) = \theta_\infty \exp \left[ - \left( \frac{\tau}{t_{eq}} \right)^B \right]$$

(7.2)

where the parameters $\theta_\infty$, $B$, and $\tau$ are assessed by fitting Equation (7.2) to experimental data of $\theta(t_{eq})$.

### 7.2 Materials and methods

#### 7.2.1 Material synthesis

A microencapsulated phase change material (MPCM24D, Microtek Laboratories Inc.) consisting of a paraffinous core encapsulated within a melamine-formaldehyde (MF) shell was used. The PCM featured a melting temperature around 24°C. An ASTM C150 [61] compliant Type I/II ordinary portland cement (OPC) was used. The OPC featured a nominal composition of: 57.8% C$_3$S, 18.2% C$_2$S, 5.5% C$_3$A and 9.1% C$_4$AF as determined by X-ray fluorescence (XRF). The cementitious composites were mixed in accordance with ASTM C305 [110]. First, cement pastes were prepared by mixing OPC with deionized (DI) water at water-to-cement ratios (w/c, mass basis) of 0.45 and 0.55. Microencapsulated PCM was added to the anhydrous OPC and mixed by hand prior to the addition of DI water. The cementitious composites containing PCM were prepared for microencapsulated PCM volume fractions $\phi_{c+s} = 0.05$ and 0.10. The desired microencapsulated PCM volume fraction $\phi_{c+s}$ was achieved by adding the required mass of microencapsulated PCM to the mixture based on its density $\rho_{c+s} = 900$ kg/m$^3$ [111].

#### 7.2.2 Experimental procedures

An isothermal calorimeter (Tam Air, TA Instruments) was used to measure the thermal power (i.e., heat flow in W) and the heat of hydration of cementitious composites for different
w/c and PCM volume fractions. The measurements were performed as described in ASTM C1702 [105] for 7 days. The testing temperature of the isothermal calorimeter was set to 15, 30, or 45°C in order to observe different reaction rates and states of the PCM (i.e., solid or liquid). Reference specimens of DI water were prepared with equivalent thermal mass to the cementitious composites and used to measure the baseline heat flow signal. The baseline signal was subtracted from the measured heat flow of the cementitious composites. All mixture ingredients were conditioned to the relevant test temperature (15, 30, or 45°C) before mixing. Immediately after mixing, approximately 10 g of each cementitious specimen was loaded into a 20 mL glass ampoule, sealed, and then placed into the calorimeter block.

7.3 Analysis

7.3.1 Schematic and assumptions

Figure 7.1 illustrates the simulated pavement section of thickness \( L = 0.25 \) m similar to that of a typical U.S. highway pavement [9] and soil section of thickness \( L_s = 2 \) m along with the associated coordinate system. The pavement section had effective properties \( k_{\text{eff}} \) and \((\rho c_p)_{\text{eff}}(T_p)\) and experienced a local rate of heat generation per unit volume \( \dot{q}(x, t) \). The soil layer had a thermal conductivity \( k_{\text{sl}} \) and volumetric heat capacity \((\rho c_p)_{\text{sl}}\). The upper surface of the pavement \((x = 0)\) was exposed to convection with the ambient air at temperature \( T_\infty \) with convective heat transfer coefficient \( h \). It was also exposed to solar radiation flux \( q''_s(t) \) (in W/m²), and exchanged thermal radiation with the sky at temperature \( T_{\text{sky}} \). The pavement surface had a total hemispherical solar absorptivity \( \alpha_s \) and a total hemispherical emissivity \( \varepsilon \). The bottom of the soil section \((x = L + L_s)\) was assumed to be at a constant temperature \( T_g \).

To make the problem mathematically tractable, it was assumed that: (i) one-dimensional (1D) heat conduction in the \( x \)-direction prevailed, (ii) all the material properties were constant and isotropic except for the temperature-dependent specific heat of the PCM, (iii) the PCM’s specific heat was the same in the solid and liquid states, i.e., \( c_{p,c,s} = c_{p,c,l} \), (iv) the
Figure 7.1: A schematic of simulated pavement and soil sections of thickness $L = 0.25$ m, corresponding to a typical highway pavement in the U.S. [9], and $L_s = 2$ m, respectively. The upper surface of the pavement ($x = 0$) was exposed to convective heat transfer and thermal radiation exchanges with the outdoor environment, while the bottom of the soil section ($x = L + L_s$) was held at a constant temperature $T_g$. 
convective heat transfer coefficient $h$ at the pavement surface remained constant, (v) radiation exchange between the pavement and the sky was unobstructed and from a small surface to large surroundings, and, (vi) evaporative cooling at the pavement surface was negligible.

### 7.3.2 Governing equations

The temperature in the pavement section $T_p(x, t)$ was governed by the 1D transient heat diffusion equation with heat generation [75],

$$
(\rho c_p)_{eff}(T_p) \frac{\partial T_p}{\partial t} = k_{eff} \frac{\partial^2 T_p}{\partial x^2} + \dot{q}(x, t)
$$

where $\dot{q}(x, t)$ is the local rate of heat generation per unit volume (in W/m$^3$). Similarly, the soil temperature $T_{sl}(x, t)$ was also governed by the transient heat diffusion equation but without heat generation, i.e.,

$$
(\rho c_p)_{sl} \frac{\partial T_{sl}}{\partial t} = k_{sl} \frac{\partial^2 T_{sl}}{\partial x^2}.
$$

Additionally, the pavement equivalent age $t_{eq}(x, t)$ can be expressed in differential form as,

$$
\frac{\partial t_{eq}}{\partial t} = \exp \left[ -\frac{E_a}{R} \left( \frac{1}{T_p(x, t)} - \frac{1}{T_{ref}} \right) \right].
$$

### 7.3.3 Initial and boundary conditions

At time $t = 0$, the temperature in the pavement section was taken to be uniform and equal to an initial temperature $T_{init}$, i.e.,

$$
T_p(x, 0) = T_{init}.
$$

Additionally, the soil section was assumed to have a uniform initial temperature equal to the ground temperature $T_g$,

$$
T_{sl}(x, 0) = T_g.
$$

To account for the fact that some hydration had taken place before the concrete was placed, the pavement was assumed to be at an initial equivalent age $t_{eq}(x, 0) = 0.5$ hours though in practice, due to the time elapsed during transportation, this number may be slightly higher. A heat flux boundary condition was imposed at the upper pavement surface ($x = 0$) to
include the effects of convective heat transfer, absorption of incident solar radiation, and thermal emission. Both convection and incident solar radiation can be accounted for by introducing the sol-air temperature $T_{sa}(t)$ as $[112]$,

$$T_{sa}(t) = T_\infty(t) + \frac{\alpha_s q_s''(t)}{h}$$  \hspace{1cm} (7.8)

where $\alpha_s$ is the pavement’s total hemispherical solar absorptivity, $q_s''(t)$ is the incident solar radiation flux, and $h$ is the convective heat transfer coefficient between the pavement surface and the outdoor air at $T_\infty$. Then, the heat flux at $x = 0$ can be expressed as,

$$-k_{eff} \frac{\partial T_p}{\partial x} = h[T_{sa}(t) - T_p(0,t)] - \varepsilon \sigma [T_p(0,t)^4 - T_{sky}^4]$$  \hspace{1cm} (7.9)

where $\varepsilon$ is the total hemispherical emissivity of the pavement surface, $\sigma = 5.67 \times 10^{-8}$ W/m$^2$.K$^4$ is the Stefan-Boltzmann constant, and $T_{sky}$ is the average sky temperature, taken as $2^\circ$C $[75]$. The bottom surface of the soil section ($x = L + L_s$) remained at $T_g$, i.e.,

$$T_{sl}(L + L_s, t) = T_g.$$  \hspace{1cm} (7.10)

Finally, the temperature and heat flux were continuous across the pavement-soil interface such that

$$T_p(L, t) = T_{sl}(L, t) \quad \text{and} \quad k_{eff} \frac{\partial T_p}{\partial x} = k_{sl} \frac{\partial T_{sl}}{\partial x}(L, t).$$  \hspace{1cm} (7.11)

### 7.3.4 Heat generation rate

The total heat released per unit volume of the concrete from exothermic cement-water reactions at a given location can be written in terms of the degree of hydration $\theta(t_{eq})$ and equivalent age $t_{eq}(x, t)$ as $[101]$,

$$Q(t_{eq}) = C_c \Delta H \theta(t_{eq})$$  \hspace{1cm} (7.12)

where $\Delta H$ is enthalpy of reaction (in J/kg) and $C_c$ is the cement content, i.e., the mass of cement per unit volume of the concrete (in kg/m$^3$). The enthalpy of reaction of cement can be calculated as the mass-averaged enthalpy of reaction (with water) of each mineralogical phase,

$$\Delta H = m_{C_3S} \Delta H_{C_3S} + m_{C_2S} \Delta H_{C_2S} + m_{C_3A} \Delta H_{C_3A} + m_{C_4AF} \Delta H_{C_4AF}$$  \hspace{1cm} (7.13)
where $m_i$ and $\Delta H_i$ are the mass fraction and enthalpy of reaction, respectively, of each constituent in cement, namely $C_3S$, $C_2S$, $C_3A$, and $C_4AF$ [113,114]. The mass fraction of each constituent was obtained by X-ray fluorescence measurements. The resulting $\Delta H$ was calculated as 475 kJ/kg for the cement used in this study. Then, by combining Equations (7.1) and (7.2) along with Equation (7.12) the instantaneous rate of heat generation $\dot{q}(x,t)$ (in W/m$^3$) can be expressed as [101],

$$
\dot{q}(x,t) = \frac{C_c \Delta H \theta \infty B}{t_{eq}(x,t)} \left( \frac{\tau}{t_{eq}(x,t)} \right)^B \exp \left[ - \left( \frac{\tau}{t_{eq}(x,t)} \right)^B \right] \times \exp \left[ - \frac{E_a}{R} \left( \frac{1}{T_p(x,t)} - \frac{1}{T_{ref}} \right) \right].
$$

(7.14)

### 7.3.5 Constitutive relationships

Table 5.1 summarizes the thermal conductivity $k$, density $\rho$, and specific heat $c_p$ of concrete, melamine-formaldehyde shell (MF), PCM core, and soil used in the simulations. The PCM’s latent heat of fusion was taken as $h_{sf} = 180$ kJ/kg [115]. The effective volumetric heat capacity of the pavement section was calculated using a volume average as in Equation (2.7), while the effective thermal conductivity was determined using Equation (2.8) [40]. The effective heat capacity method outlined by Equation (2.9) was used to determine the PCM’s specific heat $c_{pc}(T)$ as a function of its temperature. The cement content $C_c$ was taken as 586 kg/m$^3$ corresponding to laboratory formulated mortars with a total inclusion (fine aggregate) volume fraction of 55%. Note that in a typical concrete, the inclusion volume fraction can be as high as 75% [116], which would result in a lower cement content.

Convective heat transfer at the upper pavement surface was modeled as laminar forced convection over a flat plate using the correlation for the surfaced-averaged Nusselt number [75],

$$
\overline{Nu}_L = \frac{hL_c}{k} = 0.664Re_L^{1/2}Pr^{1/3}
$$

(7.15)

where $Re_L = u_\infty L_c/\nu$ is the Reynolds number based on the wind velocity $u_\infty$ and $Pr$ is the fluid Prandtl number. The thermal conductivity $k_a$, kinematic viscosity $\nu_a$, and Prandtl number $Pr_a$ of air at 27°C were taken as 0.03 W/m.K, $1.58 \times 10^{-5}$ m$^2$/s, and 0.707.
respectively [75]. Here, the characteristic length $L_c$ was taken as 1.5 m to represent the area-to-perimeter ratio [94] for a pavement section of “infinite” length and typical width of 3 m [117], while the average wind speed $u_\infty$ was taken as 2.5 m/s [89]. The resulting convective heat transfer coefficient $h$ obtained from Equation (7.15) was 5 W/m$^2$.K. Note that this value is close to that of 3.6 W/m$^2$.K predicted by the correlation suggested by Wolfe et al. [118] based on experimental measurements of the convective heat transfer coefficient at a pavement surface.

The sol-air temperature $T_{sa}(t)$ imposed in Equation (7.9) was obtained from Climate Consultant for California Climate Zone 9 (Los Angeles, CA) [89]. Figure 7.2 plots the outdoor air temperature $T_\infty(t)$ and the sol-air temperature $T_{sa}(t)$ corresponding to: (a) September 24$^{th}$ and (b) March 2$^{nd}$ in Los Angeles, CA. These days were selected because they were the hottest and coldest days, respectively, based on historically averaged weather data. The ground temperature $T_g$ was imposed as 19$^\circ$C [89]. The initial temperature of the pavement section was $T_{init} = 40^\circ$C. Finally, the total hemispherical solar absorptivity of the pavement $\alpha_s$ was taken as 0.6, while its total hemispherical emissivity was 0.9, as reported in the literature for plain concrete [75].

7.3.6 Method of solution

The transient 1D governing Equations (7.3)-(7.5) were solved along with the corresponding boundary and initial conditions using a semi-implicit finite difference method [75]. The solution was considered to be numerically converged when the resulting pavement temperature (i.e., at any time or spatial location) differed by no more than 1% after reducing the nodal spacing $\Delta x$ or the time step $\Delta t$ by a factor of 2. A nodal spacing $\Delta x = 5.8$ mm and time step $\Delta t = 300$ s were sufficient to provide a converged solution.
Figure 7.2: The outdoor air temperature $T_{\infty}(t)$ and sol-air temperature $T_{sa}(t)$ corresponding to (a) September 24th and (b) March 2nd in Los Angeles, CA.
7.3.7 Data processing

Two criteria were defined to evaluate the thermal performance of the pavement section. First, the maximum pavement temperature $T_{\text{max}}(t)$ was defined for each instant as,

$$T_{\text{max}}(t) = \max_{x}[T_p(x,t)]. \quad (7.16)$$

Second, the maximum temperature gradient $T_{x,\text{max}}(t)$ was defined for each instant as,

$$T_{x,\text{max}}(t) = \max_{x} \left[ \frac{\partial T_p}{\partial x}(x,t) \right]. \quad (7.17)$$

Finally, the overall maximum (peak) temperature and temperature gradient attained within the pavement section during the 24-hour simulation period were also recorded and defined as,

$$T_{\text{peak}} = \max_{x,t}[T_{\text{max}}(t)] \quad \text{and} \quad T_{x,\text{peak}} = \max_{x,t}[T_{x,\text{max}}(t)]. \quad (7.18)$$

7.4 Results and discussion

7.4.1 Isothermal calorimetry

Figure 7.3a displays heat flow as a function of time from the time of initial mixing of cement and water measured at different temperatures, namely 15, 30, and 45°C, and with PCM volume fraction $\phi_{c+s}$ equal to 0 or 10%. Expectedly, increasing the temperature accelerated cement hydration, manifesting as a shortened induction period and elevated maximum heat flow. The addition of PCMs was observed to have no influence on the kinetics of reactions [17]. This indicates that the PCM microcapsules induced no acceleratory filler effect on cement hydration; either on account of their small specific surface area or on account of featuring surface properties unfavorable for C-S-H nucleation [119]. To further evaluate the effects of PCM on the degree of hydration, Figure 7.3b plots the time-dependent degree of hydration $\theta(t)$ for cementitious specimens with $w/c = 0.45$ or 0.55 and PCM volume fraction $\phi_{c+s}$ of 0, 5, or 10%. At a fixed temperature (i.e., $T = 30^\circ C$), $\theta(t)$ did not show significant dependence on either $w/c$ or $\phi_{c+s}$. It should be noted that the lack of dependence on $w/c$
is expected when sufficient space for the formation of hydration products, and water are available, i.e., for \( \text{w/c} > 0.42 \) [114].

The activation energy of cement hydration was calculated using an Arrhenius approach via the equivalent age concept expressed in Equation (7.1) and assuming a uniform temperature in the sample. The activation energy \( E_a \) was estimated from the slope of the degree of hydration \( \theta \) versus \( 1000/T \) plot, for reaction times corresponding to 6, 12, 18, 24 hours at 30\(^\circ\)C. Particular attention was paid to the first 24 equivalent hours of hydration when reactions are most sensitive to the effects of temperature. For example, Figure 7.4a shows the activation energy as a function of PCM dosage for mixtures at both \( \text{w/c} = 0.45 \) and 0.55. It indicates that the activation energy had little dependence on \( \phi_{c+s} \). The average activation energy for cement hydration was therefore taken as 31.9 kJ/mol.

Figure 7.4 displays the measured degree of hydration \( \theta(t_{eq}) \) as a function of equivalent age \( t_{eq} \) for varying \( \text{w/c} \) and \( \phi_{c+s} \) for a reference temperature \( T_{ref} = 30^\circ\)C (chosen arbitrarily). Also shown is the resulting degree of hydration “master curve” obtained by fitting Equation (7.2) to all experimental data. The curve fit parameters that produced the best fit were \( \theta_\infty = 0.495 \), \( B = 0.9 \), and \( \tau = 11.4 \) hours. The small variation of experimental measurements from the master curve indicates that the PCM microcapsules do not influence degree of hydration, and broadly function as inert inclusions. Overall, these results indicate that the master curve can be used to describe \( \theta(t_{eq}) \) for any PCM volume fraction \( \phi_{c+s} \) between 0 and 10\% and \( \text{w/c} \) between 0.45 and 0.55, so long as the activation energy is known. Thus, the values of \( \theta_\infty = 0.495 \), \( B = 0.9 \), and \( \tau = 11.4 \) hours as determined from fitting the experimentally measured isothermal calorimetry data were used in Equation (7.14) to determine the instantaneous rate of heat generation in the numerical model.

### 7.4.2 Pavement temperature evolutions

Figure 7.5 plots the predicted maximum temperature \( T_{max}(t) \) and maximum local temperature gradient \( T_{x,max}(t) \) developed within a pavement section exposed to the sol-air temperature corresponding to September 24\(^{th}\) in Los Angeles, CA, for a placement time of either
Figure 7.3: Representative heat flow profiles for cement pastes (w/c = 0.55) with and without PCM cured at different temperatures, and, (b) the degree of hydration (reaction) of the cementitious specimens as a function of time.
Figure 7.4: (a) The activation energy of cement hydration as a function of PCM volume fraction, and, (b) the degree of cement hydration $\theta(t_{eq})$ as a function of equivalent age $t_{eq}$. The master curve applies to all mixtures regardless of PCM dosage and w/c.
12 pm (a-b) or 6 pm (c-d) for: (i) a plain concrete pavement or (ii) a pavement with 10 vol.% microencapsulated PCM. The PCM melting temperature $T_{pc}$ was fixed at 45°C, and the melting temperature window $\Delta T_{pc}$ was fixed at 8°C, i.e., PCM melting/freezing took place between 41°C and 49°C. The choice of PCM melting temperature was made such that the entire phase change temperature window fell between the initial pavement temperature $T_{init} = 40°C$ and the maximum temperature attained by the plain concrete section, which was around 55-60°C. Figure 7.5a shows that for a placement time of 12 pm, a single large peak in the pavement temperature was observed around 6 hours after placement. This can be attributed to the peak of heat generation from hydration occurring near the same time as the peak outdoor temperature and solar irradiation. By contrast, for a placement time of 6 pm (Figure 7.5c), there were two separate peaks in $T_{max}(t)$ corresponding to (i) the peak of heat generation, and (ii) the peak outdoor temperature and solar irradiation of the following day - wherein the subsequent peak was in fact more substantial than the hydration heat peak. In each case, both the maximum temperature and maximum local temperature gradient reached their peak values within the first 24 hours of placement.

Figure 7.5 indicates that for both placement times considered, the peak temperature was around 5°C lower for the PCM-containing pavement section as compared to the plain concrete section. However, the addition of 10 vol.% PCM adversely affected the maximum temperature gradient (Figures 7.5b and 7.5d), compared with the plain concrete section. This is because the PCM microcapsules, on account of their low thermal conductivity, acted as thermal insulators, thereby preventing the dissipation of heat through the pavement surface and the subgrade. Indeed, the inclusion of 10 vol.% PCM with thermal conductivity $k_c = 0.21$ W/m.K reduced the thermal conductivity of the pavement section from $k_m = 1.4$ W/m.K to $k_{eff} = 1.2$ W/m.K, i.e., a reduction of around 15%.

To distinguish the effects of the PCM’s latent heat capacity from that of the reduced thermal conductivity, Figure 7.5 also shows the maximum temperature $T_{max}(t)$ and temperature gradient $T_{x,max}(t)$ obtained from simulating a pavement section with 10 vol.% PCM, but with an effective thermal conductivity equal to that of the plain concrete $k_m$. In this case, the maximum temperature gradient was reduced by up to 16% or 11% compared with
Figure 7.5: The maximum temperature $T_{\text{max}}(t)$ and local temperature gradient $T_{x,\text{max}}(t)$ developed within pavement sections exposed to outdoor temperature and solar irradiation corresponding to September 24th in Los Angeles, CA placed at either (a-b) 12 pm or (c-d) 6 pm. The results shown are for a plain concrete pavement section and sections with 10 vol.% microencapsulated PCM. The PCM’s melting temperature $T_{pc}$ was 45°C and the melting temperature window $\Delta T_{pc}$ was 8°C. The initial pavement temperature was taken as $T_{\text{init}} = 40°C$. 
that of the plain concrete section for placement times of 12 pm and 6 pm, respectively. To continue examining the benefits of PCM latent heat and given the limited effect of the thermal conductivity difference on the maximum temperature within the section (see Figure 7.5a), the PCM-composite pavement section was treated as having an effective thermal conductivity $k_{eff}$ equal to the plain concrete value of $k_m = 1.4$ W/m.K for the remainder of this study. In practice, this could be achieved by: (i) selecting a PCM with a larger thermal conductivity, (ii) selecting a PCM encapsulated within a higher thermal conductivity shell structure [120, 121], (iii) impregnating PCM directly into porous aggregates [122], and/or, (iv) adding inclusions with large(r) thermal conductivity, such as quartz sand or graphite, to compensate for the loss in thermal conductivity caused by the addition of PCM microcapsules. These results also suggest that inorganic PCMs, which tend to have larger thermal conductivities than organic PCMs [123] - only if chemical passivity can be ensured - may be better suited for use in pavement sections.

Table 7.1 shows the peak temperature $T_{peak}$ and temperature gradient $T_{x,peak}$ attained within the first 24 hours of placement for plain concrete or PCM-composite pavement sections exposed to outdoor weather conditions corresponding to either September 24th or March 2nd in Los Angeles, CA. Four different placement times (12 am, 6 am, 12 pm, and 6 pm) were investigated. Table 7.1 indicates that the inclusion of 10 vol.% PCM reduced the peak temperature $T_{peak}$ in all cases. In particular, the inclusion of PCM reduced the peak temperature the most on September 24th for placement times of 6 am and 12 pm. The peak temperature gradient attained within the pavement was also lower for the PCM-composite pavement section in all cases considered. Here again, the addition of PCM was most beneficial in the September 24th case for placement times of 6 am and 12 pm, reducing the peak temperature gradient by 14% and 16%, respectively. Overall, these results establish that including PCM in pavement sections poured in climates such as that of Los Angeles, CA can provide a noticeable benefit in reducing the peak temperature and temperature gradient developed within the pavement at early-ages; so long as the effective thermal conductivity of the pavement is not substantially reduced.
Table 7.1: The peak temperature $T_{peak}$ and temperature gradient $T_{x,peak}$ developed within the first 24 hours after placement for plain concrete or PCM-composite pavement sections exposed to outdoor temperature and solar irradiation corresponding to September 24th or March 2nd in Los Angeles, CA.

<table>
<thead>
<tr>
<th>Day</th>
<th>Placement time</th>
<th>$T_{peak}$ ($^\circ$C)</th>
<th>$T_{x,peak}$ ($^\circ$C/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>September 24th</td>
<td>12 am</td>
<td>60</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>6 am</td>
<td>66</td>
<td>230</td>
</tr>
<tr>
<td></td>
<td>12 pm</td>
<td>61</td>
<td>234</td>
</tr>
<tr>
<td></td>
<td>6 pm</td>
<td>55</td>
<td>181</td>
</tr>
<tr>
<td>March 2nd</td>
<td>12 am</td>
<td>47</td>
<td>196</td>
</tr>
<tr>
<td></td>
<td>6 am</td>
<td>52</td>
<td>203</td>
</tr>
<tr>
<td></td>
<td>12 pm</td>
<td>50</td>
<td>205</td>
</tr>
<tr>
<td></td>
<td>6 pm</td>
<td>47</td>
<td>194</td>
</tr>
</tbody>
</table>

7.4.3 Parametric study

The following section presents a parametric study aimed at elucidating the effects of various material and mixture parameters on the thermal performance of a PCM-composite pavement section, namely (i) PCM melting temperature $T_{pc}$ and melting temperature window $\Delta T_{pc}$, (ii) PCM volume fraction $\phi_{c+s}$, (iii) PCM latent heat of fusion $h_{sf}$, and (iv) the initial placement temperature of the concrete $T_{init}$. Here, the effective thermal conductivity $k_{eff}$ of the composite pavement section was again assumed to be equal to 1.4 W/m.K corresponding to that of a plain concrete section.

7.4.3.1 Effect of PCM melting temperature and melting temperature window

Figure 7.6 plots the peak pavement temperature $T_{peak}$ and peak temperature gradient $T_{x,peak}$ within a PCM-composite pavement section for PCM volume fraction $\phi_{c+s} = 0.1$ as a function of the PCM’s melting temperature $T_{pc}$ ranging from 40°C to 50°C. The outdoor weather conditions corresponded either to (a-b) September 24th or (c-d) March 2nd in Los Angeles, CA. The placement time was 6 am in both cases. Different values of PCM melting temperature window $\Delta T_{pc}$ ranging from 2°C to 8°C were also considered. For reference, the
peak temperature and peak temperature gradient attained within a plain concrete pavement section exposed to the same climate conditions are also shown. Figure 6 shows that $T_{\text{peak}}$ and $T_{x,\text{peak}}$ did not show a significant dependence on the width of the melting temperature window $\Delta T_{pc}$, provided that the window is fully encompassed. Figures 7.6a and 7.6c also show that for both cases considered, the peak temperature was reduced the most when the lower bound of the PCM phase change window was near the pavement’s initial temperature $T_{\text{init}} = 40^\circ\text{C}$. In other words, the optimal PCM melting temperature was,

$$T_{pc,\text{opt}} = T_{\text{init}} + \frac{\Delta T_{pc}}{2}. \quad (7.19)$$

Figures 7.6b and 7.6d indicate that selection of the PCM melting temperature near this optimum also provides the largest possible reduction in peak temperature gradient.

**7.4.3.2 Effect of PCM volume fraction and latent heat of fusion**

Figure 7.7 plots (a) the peak temperature $T_{\text{peak}}$ and (b) the peak temperature gradient $T_{x,\text{peak}}$ attained within a PCM-composite pavement section as a function of the PCM volume fraction $\phi_{c+s}$ and its latent heat of fusion $h_{sf}$. Figure 7.7a establishes that the peak temperature decreased with increasing PCM volume fraction, and decreased more sharply with increasing PCM latent heat. Figure 7.7b shows that the peak temperature gradient also decreased with increasing PCM volume fraction when $h_{sf}$ was between 100 and 200 kJ/kg. However, for $h_{sf} = 300$ or 450 kJ/kg, $T_{x,\text{peak}}$ was no longer reduced by further increases in the PCM dosage once $\phi_{c+s}$ reached 0.2, suggesting that there is a limit to which the temperature gradient can be reduced by latent heat storage alone.

Figure 7.7 also plots (c) $T_{\text{peak}}$ and (d) $T_{x,\text{peak}}$ as functions of the product $\phi_{c+s}h_{sf}$, which represents the total latent heat storage capacity of the composite. It establishes that the reduction in temperature and temperature gradient afforded by PCM additions depended on this product, rather than $\phi_{c+s}$ or $h_{sf}$ individually. Note that this would not be the case if the effective thermal conductivity of the pavement was allowed to change with PCM dosage. Also, since the addition of PCMs can negatively impact the mechanical properties (e.g. compressive strength and elastic modulus) of cementitious composites [21, 124] - it
Figure 7.6: The effect of PCM melting temperature $T_{pc}$ and melting temperature window $\Delta T_{pc}$ on the peak temperature $T_{peak}$ and the local temperature gradient $T_{x,peak}$ attained within a composite pavement section placed at 6 am on (a-b) September 24th or (c-d) March 2nd. The PCM volume fraction was $\phi_{c+s} = 0.1$ and its latent heat of fusion was $h_{sf} = 180 \text{ kJ/kg.}$
Figure 7.7: The effect of (a-b) microencapsulated PCM volume fraction $\phi_{c+s}$ and PCM latent heat of fusion $h_{sf}$ as well as (c-d) the product $\phi_{c+s} h_{sf}$ on the peak temperature and temperature gradient attained within a composite pavement section placed on September 24th at 6 am. Here, the PCM’s melting temperature was $T_{pc} = 45^\circ C$ and the melting temperature window was $\Delta T_{pc} = 8^\circ C$. 
is beneficial to increase the amount of latent heat storage capacity in the composite by increasing $h_{sf}$ rather than $\phi_{c+s}$, as also noted by Šavija and Schlangen [125].

7.4.3.3 Effect of the concrete’s placement temperature

Figure 7.8 plots (a) the peak pavement temperature $T_{\text{peak}}$ and (b) the peak temperature gradient $T_{x,\text{peak}}$ attained within a plain concrete or PCM-composite pavement section as a function of the initial placement temperature $T_{\text{init}}$ ranging from 20°C to 40°C. Here, the PCM melting temperature varied along with the initial temperature such that the criterion in Equation (7.19) was satisfied. As would be expected, the peak temperature decreased linearly with decreasing initial temperature of the concrete. The difference in $T_{\text{peak}}$ between the plain concrete and PCM-containing pavements remained similar for each placement temperature considered, indicating that the peak temperature reduction afforded by PCM additions is independent of the concrete’s initial temperature. On the other hand, the peak temperature gradient was lowest for an initial temperature $T_{\text{init}} = 24$°C and the difference in $T_{x,\text{peak}}$ between plain concrete and PCM-containing sections decreased with decreasing $T_{\text{init}}$.

Taken together, these results suggest that in conjunction with adding PCM, cooling the mixture prior to placement would be the most effective means to mitigate thermal cracking. A simple (and well-known) method of this nature is to add ice to the concrete mixture; whose effectiveness is ensured by the large latent heat associated with melting the ice as well as the large sensible heat capacity of water [56, 116]. It should be noted that the optimal choice of the PCM’s melting temperature corresponding to $T_{\text{init}} = 24$°C, according to Equation (7.19), is $T_{pc} = 28$°C. Importantly, a PCM with this melting temperature may also inhibit temperature cycling at later ages, where the pavement temperature evolution is largely dictated by the outdoor air temperature. Therefore, the benefit of lowering the initial pavement temperature is twofold: (i) it reduces the maximum temperature and temperature gradient developed within the pavement at early-ages, and (ii) it allows the use of a PCM with a lower melting temperature that could offer benefits associated with reducing thermal
Figure 7.8: (a) Peak temperature $T_{peak}$ and (b) peak temperature gradient $T_{x,peak}$ within a plain concrete or PCM-dosed pavement section as a function of the initial temperature $T_{init}$. Here, the PCM volume fraction was $\phi_{c+s} = 0.1$, the latent heat of fusion was $h_{sf} = 180$ kJ/kg, and the melting temperature window was $\Delta T_{pc} = 8^\circ C$. The melting temperature $T_{pc}$ was chosen in each case such that $T_{pc} = T_{init} + \Delta T_{pc}/2$. 
7.4.4 Comparison of PCM with high thermal conductivity inclusions

Based on the results presented earlier in Section 7.4.2, it may be speculated if adding inclusions with a high thermal conductivity (i.e., in an effort to dissipate heat at a higher rate) would be more beneficial to early-age performance than the inclusion of microencapsulated PCM. To investigate this possibility, Figure 7.9 plots the maximum temperature $T_{max}(t)$ within pavement sections made of (i) plain concrete, (ii) concrete with 10 vol.% graphite aggregates, or (iii) concrete with 10 vol.% PCM. Here, the density $\rho$ and specific heat $c_p$ of the graphite used were 2210 kg/m$^3$ and 709 J/kg.K, respectively [75]. The thermal conductivity of the graphite was taken as 20 W/m.K [126]. Figure 7.9 shows that the peak temperature was reduced only slightly by the inclusion of graphite inclusions, whereas the inclusion of PCM reduced the peak temperature by nearly 5°C. Therefore, while high thermal conductivity inclusions may increase heat dissipation and/or reduce temperature gradients within the section, they do not show the benefit afforded by the PCM’s latent heat storage i.e., in limiting the hydration heat induced temperature rise at early-ages.

7.5 Summary and conclusions

This study developed a transient thermal model to predict early-age temperature evolutions within (concrete) pavement sections containing microencapsulated PCMs. Experimental calorimetry data was used to describe the degree of hydration of the cementitious matrix as a function of temperature and time. The degree of hydration data was then used to determine the local rate of heat generation and its influence on pavement temperature evolutions. The inclusion of 10 vol.% microencapsulated PCM within the pavement was shown to induce noticeable reductions in the temperature developed within the first 24 hours of placement. Additionally, the addition of PCM also reduced local temperature gradients developed within the pavement section so long as the effective thermal conductivity of the pavement was not reduced. Finally, a parametric study was carried out to assess the effects of different parame-
Figure 7.9: Maximum temperature $T_{\text{max}}(t)$ developed within pavement sections made of plain concrete, concrete with graphite inclusions, or concrete with microencapsulated PCM exposed to outdoor temperature and solar irradiation corresponding to September 24th in Los Angeles, CA and placed at 6 am.
ters including: melting temperature, latent heat of fusion, and initial pavement temperature, and to suggest a selection criterion for the appropriate choice of PCM melting temperature. These results inform the design and proportioning of PCM-dosed concrete (pavement) mixtures that feature improved resistance to thermal cracking.
CHAPTER 8

Conclusion

This thesis examined the inclusion of microencapsulated phase change materials (PCMs) within concrete construction materials. The effective elastic moduli and thermal deformation coefficient of such composites—i.e., those consisting of spherical capsules within a continuous matrix—were predicted using rigorous numerical simulations of elastic and thermoelastic deformation. Effective medium approximations (EMAs) were identified that could conveniently and accurately predict these effective properties based on the volume fractions (dosages) and thermomechanical properties of the constituent materials. Next, reduced-scale experiments were conducted to evaluate the thermal performance of building walls containing microencapsulated PCMs. Scaling analysis was used to show that such convenient reduced-scale experiments can represent the thermal behavior of full-scale building structures with microencapsulated PCM-concrete composite walls. Furthermore, a thermal model of a room with a microencapsulated PCM-concrete composite wall was developed to simulate the diurnal energy consumption and cost associated with controlling the room’s temperature on a warm day. It was found that including 20% microencapsulated PCM by volume within the concrete wall reduced the diurnal cooling energy consumption by around 20%, and reduced the associated electricity cost by 30%. However, the use of an advanced model predictive control (MPC) scheme that could predict melting and freezing of the PCM for controlling the indoor temperature did not result in significant energy or cost savings compared with a traditional proportional control scheme. Finally, the inclusion of microencapsulated PCM within concrete pavement sections was investigated. Numerical simulations of early-age temperature evolutions showed that including microencapsulated PCM within concrete pavements can significantly reduce the temperature rise caused by cement hydration.
reactions within the first few days following placement, thus reducing the risk of thermal cracking. Overall, the results of this thesis provide insights that could be instrumental in the design of composite concrete with embedded microencapsulated PCMs for use in buildings with improved energy efficiency or road pavements with increased durability.
REFERENCES


