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A general method for retrieving thermal deformation properties of microencapsulated phase change materials or other particulate inclusions in cementitious composites

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ABSTRACT

This study examined the effects of spherical core-shell particle inclusions, such as microencapsulated phase change materials (PCMs), on the thermal deformation behavior of cement-based composites. First, simulations of volumetric thermal deformation in representative microstructures were carried out, based on the finite element method (FEM), to predict the effective thermal deformation coefficient of the composites. Excellent agreement was found between the effective thermal deformation coefficient predicted by FEM and by the effective medium approximation (EMA) developed by Schapery (1968). Furthermore, the effective thermal deformation coefficient of cementitious composites with either microencapsulated PCM or quartz particulates was measured. The measured effective thermal deformation coefficients together with Schapery's model were used to retrieve the thermal deformation coefficients of the inclusions themselves. The thermal deformation coefficient of PCM microcapsules was estimated to be similar to that of the shell component due to partial filling of the microcapsules. The results show a means for (i) retrieving the thermal deformation properties of functional core-shell inclusions and (ii) for designing cementitious composites with PCMs which find use in the built environment and high-performance composites.

1. Introduction

In 2013, The American Society of Civil Engineers gave the road infrastructure in the United States a grade of "D", and estimated that $67 billion is spent annually on the repair of deficient or damaged road pavements [1]. Substantial damage is caused to concrete pavements due to volume change that results from temperature change—caused by (i) cement hydration reactions at early ages, over the first 7 days following concrete placement, and (ii) ambient temperature change, at later ages (that results in fatigue damage) [2,3]. Microencapsulated phase change materials (PCMs) have been proposed as a means to mitigate thermal damage in concrete pavements [4,5]. Microencapsulated PCMs, a core-shell particulate, are thermal energy storage materials that can store and release latent heat associated with reversible phase transitions between the liquid and solid phases [6]. In concrete pavements, such storage and release of heat can be exploited to: (i) reduce early-age temperature rise and (ii) decrease the amplitude of diurnal temperature oscillations to reduce thermal fatigue damage [4,5].

PCM particulates with a median diameter on the order of 10 to 20 μm are often produced by an interfacial polymerization process wherein a polymer shell (e.g., of melamine-formaldehyde) is used to encapsulate a core material (e.g., alkanes such as paraffin wax). To provide stress-relief over multiple phase change cycles, typically, the PCM microcapsules are only partially filled—as a result, they contain some internal porosity [6]. Due to the presence of this internal porosity, and their small size, it is challenging to characterize the material properties of these core-shell structures. This is especially so in the

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Nomenclature

C	material/stiffness tensor, GPa
D	diameter, μm
E	Young's modulus, GPa
G	shear modulus, GPa
I	identity tensor
K	bulk modulus, GPa
L	unit cell length, μm
M	number of experimental measurements
N	number of unit cells or number of constituent materials in composite
$\hat{\mathbf{n}}_j$	unit normal vector to face j of unit cell
T	temperature, °C
T_{pc}	PCM melting temperature, °C
T_{ref}	reference/zero-strain temperature, °C
u	displacement vector, m
u	x-displacement, m
v	y-displacement, m
w	z-displacement, m
w/c	water/cement ratio, mass basis

Greek symbols

α	thermal deformation coefficient, $\mu\varepsilon$/°C
ϕ_n	volume fraction of material n in composite
ρ	density, kg/m^3
$\boldsymbol{\sigma}$	Cauchy stress tensor, GPa
$\boldsymbol{\varepsilon}$	strain tensor
ν	Poisson's ratio

Subscripts

c	refers to core material in composite
$c+s$	refers to core-shell microcapsule
eff	refers to effective properties
j	refers to face j of unit cell
ls	refers to limestone
m	refers to matrix material in composite
n	refers to constituent material n in composite
p	refers to inclusion
q	refers to quartz
s	refers to shell material in composite

Superscripts

T	denotes matrix/vector transpose

context of thermal deformation behavior when both the core and the shell would expand (or contract), albeit to different extents. This is an issue in applications such as concrete pavements, where it is important to know the thermal deformation coefficients of inclusions that are embedded in the cementitious matrix so as to quantify their influences on the volume stability of the overall solid.

The present study aims to assess the influences of PCM microcapsules on the effective thermal deformation coefficient of cementitious composites by complementary approaches including (i) finite element simulations of volumetric thermal deformation in representative microstructures, (ii) effective medium approximations, and (iii) measurements of linear thermal deformation of prismatic composite specimens. By identifying an effective medium approximation (EMA) capable of accurately estimating the effective thermal deformation coefficient of multicomponent composites consisting of a matrix and core-shell inclusions, a general approach is highlighted (i) for retrieving the thermal deformation coefficient of core-shell microcapsules or other particulate inclusions embedded in a continuous matrix and (ii) for designing cementitious composites with PCMs.

2. Background

2.1. Thermal deformation of solids

The constitutive law for a linearly elastic material considering thermal effects is given by [7],

$$\boldsymbol{\sigma} = \mathbf{C}:(\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_T) \quad \text{or} \quad \sigma_{ij} = C_{ijkl}(\varepsilon_{kl} - \varepsilon_{T,kl}) \tag{1}$$

where $\boldsymbol{\varepsilon}$ and $\boldsymbol{\varepsilon}_T$ denote the total and thermal strain tensors, respectively, and **C** is the stiffness tensor. If the material is isotropic, the components of the stiffness tensor **C** can be expressed in terms of the material's elastic constants according to [8],

$$C_{ijkl} = \lambda\delta_{ij}\delta_{kl} + G(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \tag{2}$$

where the Lamé parameter λ and shear modulus G are related to the Young's modulus E and Poisson's ratio ν according to [8],

$$\lambda = \frac{E\nu}{(1+\nu)(1-2\nu)} \quad \text{and} \quad G = \frac{E}{2(1+\nu)}. \tag{3}$$

For an isotropic material, the thermal strain $\boldsymbol{\varepsilon}_T$ is related to the imposed temperature change ΔT according to [7],

$$\boldsymbol{\varepsilon}_T = (\alpha\Delta T)\mathbf{I} \quad \text{or} \quad \varepsilon_{T,ij} = \alpha\Delta T\delta_{ij} \tag{4}$$

where α is the thermal deformation coefficient and ΔT is defined with respect to some reference or zero-strain temperature T_{ref}, i.e., $\Delta T = T - T_{ref}$ [7]. Note that in a homogeneous material that is not mechanically restrained, $\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_T$ and the stress field is identically zero throughout the material. On the other hand, if it is fully restrained then $\boldsymbol{\varepsilon} = 0$ and a stress is induced for $\Delta T \neq 0$.

2.2. Effective medium approximations

This study considers three simple effective medium approximations (EMAs) that can be applied to predict the effective thermal deformation coefficient α_{eff} of composites consisting of two or more constituents. The parallel model, also known as the rule-of-mixtures (ROM) [9], 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. [9],

$$\alpha_{eff} = \sum_{n=1}^{N}\phi_n\alpha_n \tag{5}$$

where ϕ_n and α_n are the volume fraction and thermal deformation coefficient of constituent material n, respectively. Turner [10] suggested that the ROM be adjusted to weigh each component n by their respective volume fraction ϕ_n and bulk modulus K_n, such that

$$\alpha_{eff} = \frac{\sum_{n=1}^{N}\phi_n K_n\alpha_n}{\sum_{n=1}^{N}\phi_n K_n}. \tag{6}$$

Schapery [11] derived an EMA which gave upper and lower bounds for the effective thermal deformation coefficient α_{eff} of composites with N components based on energy conservation considerations. In this case, α_{eff} was expressed as an average of upper and lower bounds such that,