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BCES
Birmingham Centre for Energy Storage

Thermo-mechanical modelling of encapsulated PCMs for cold and heat storage

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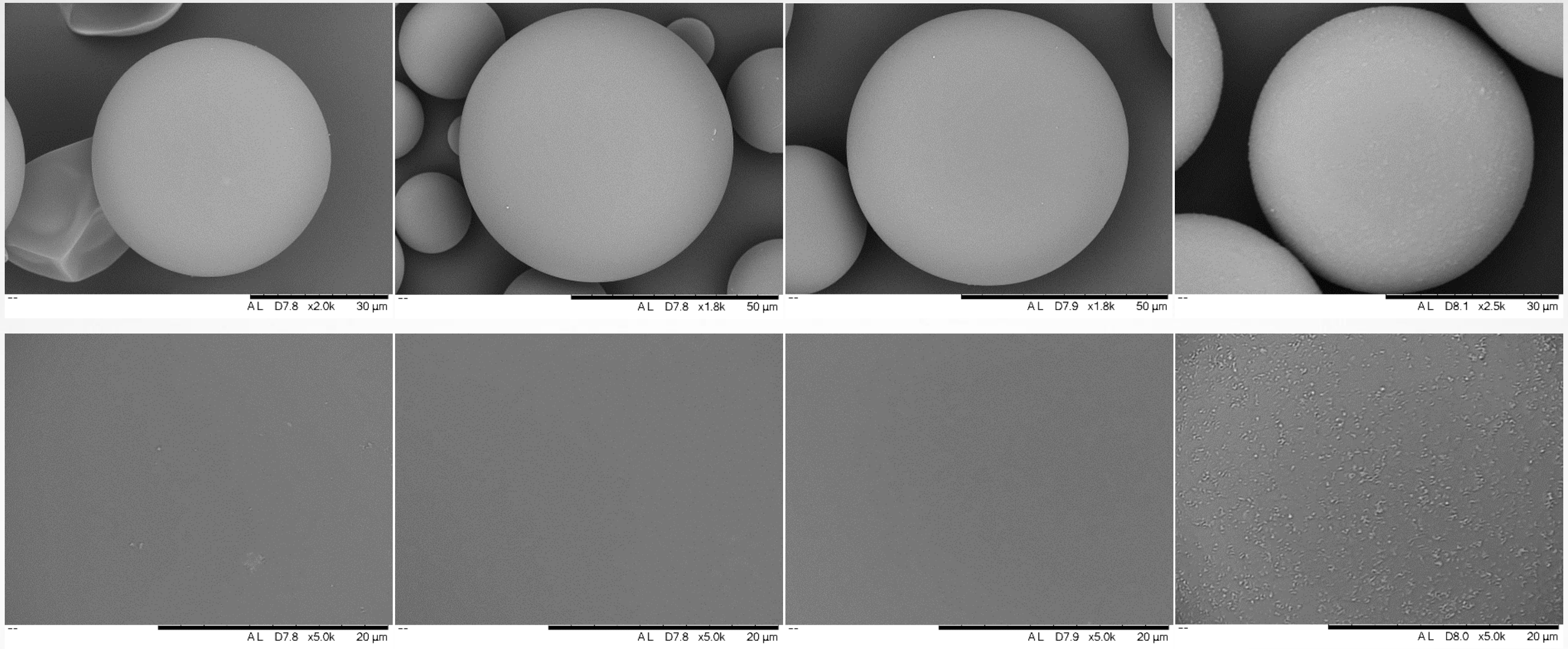
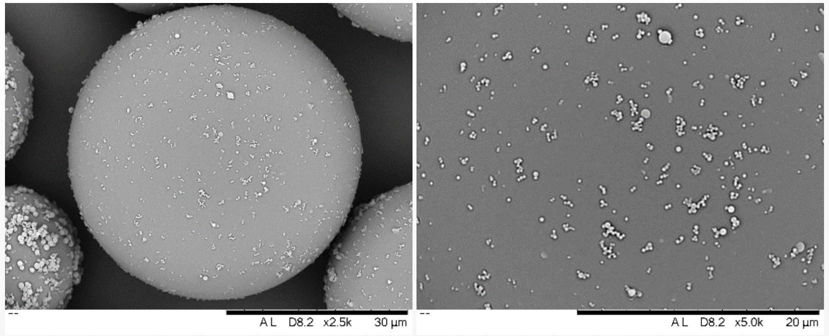
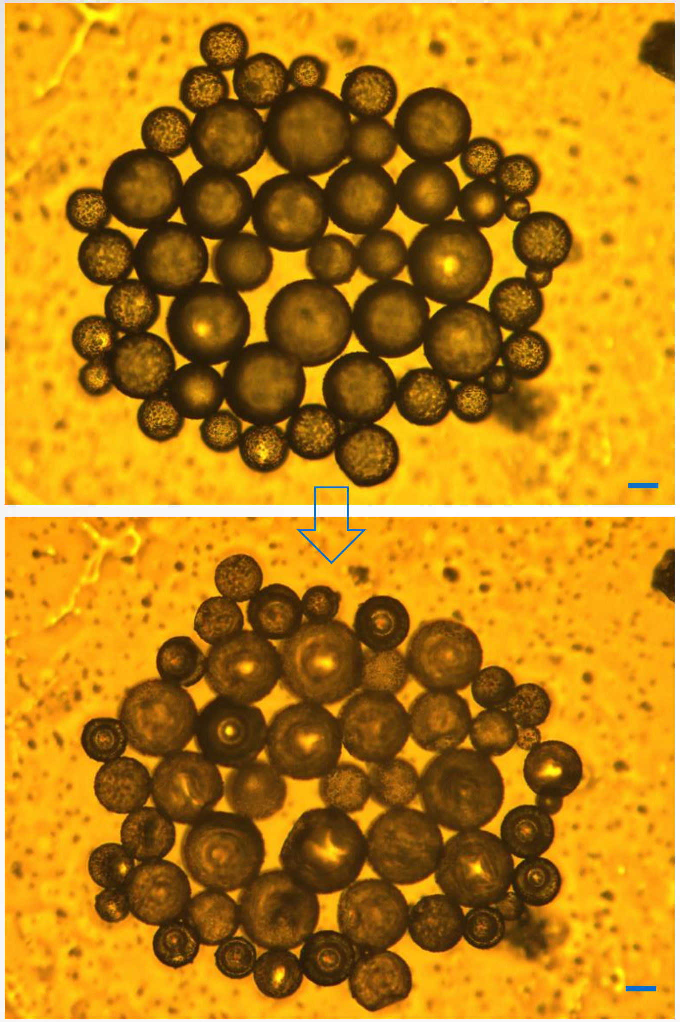
contents

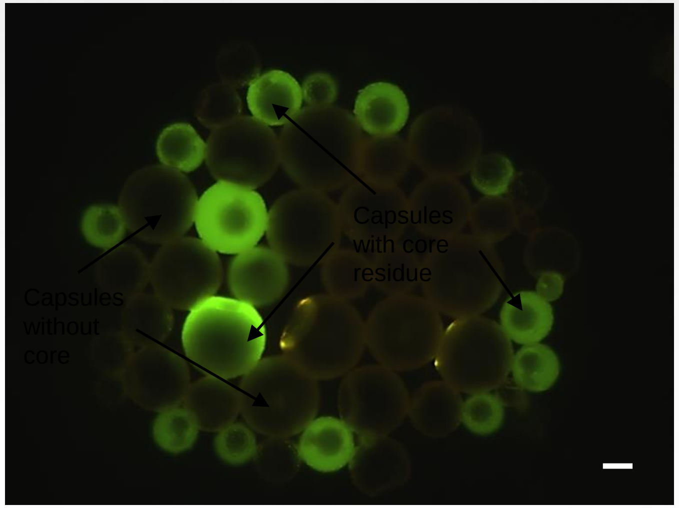
1.1 Problems of microcapsules for cold storage

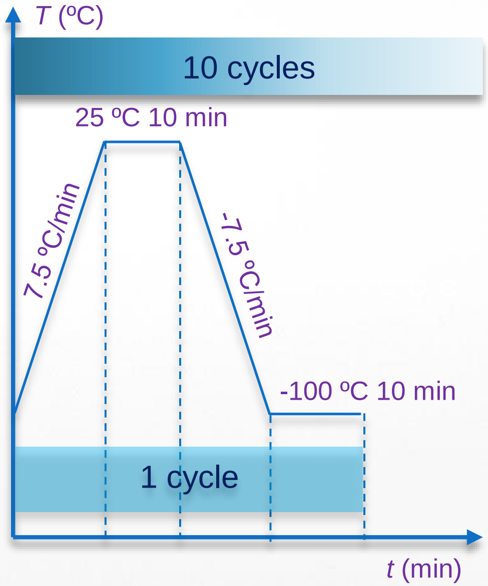




1.1 Problems of microcapsules for cold storage







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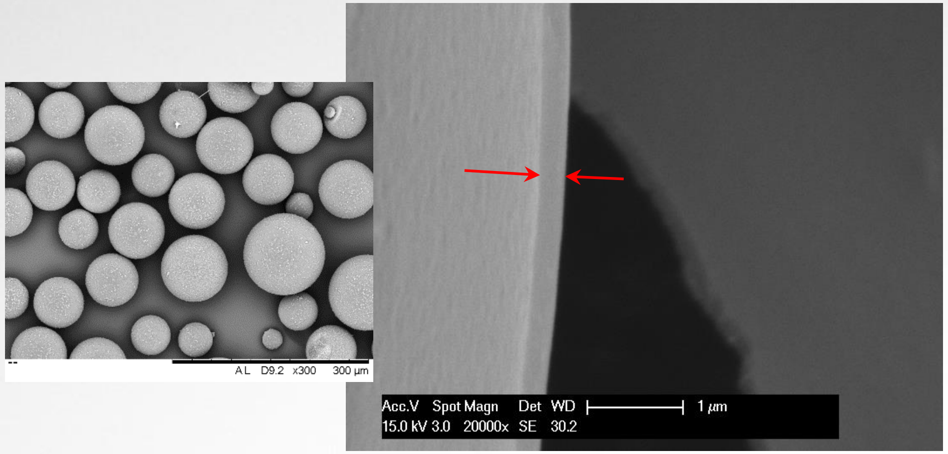
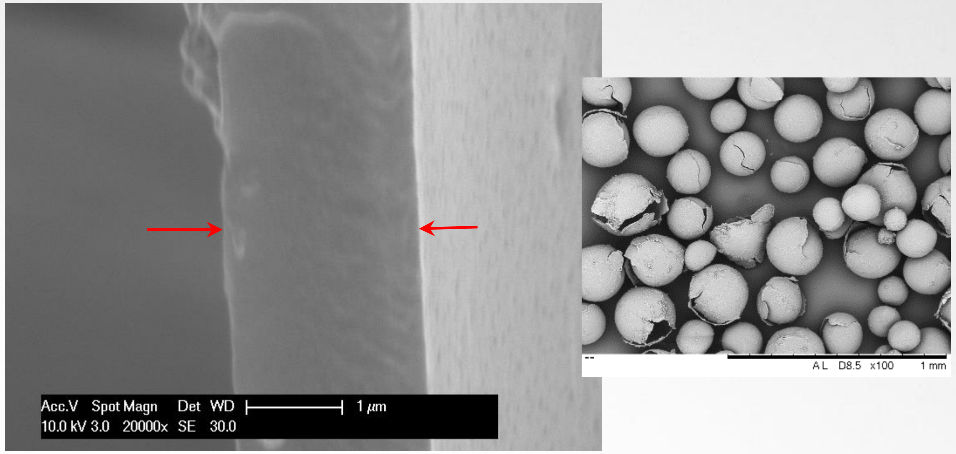
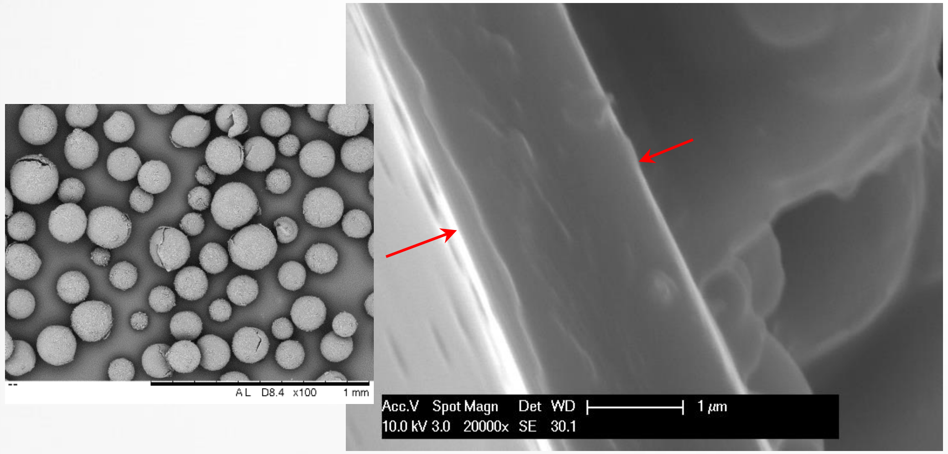
1.1 Problems of microcapsules for cold storage



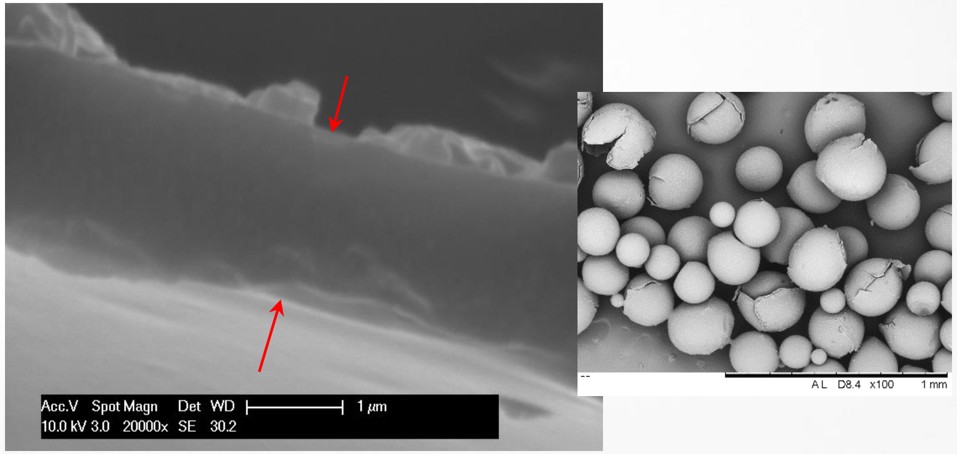
0.2 *wt.*% GA (282±6 nm)



0.05 *wt.*% Larch (1.87±0.03 µm)



0.2 *wt.*% SA (1.84±0.04 µm)



1 *wt.*% Larch (1.63±0.02 µm)

1.1 Problems of microcapsules for cold storage

➢ Morphologies of microcapsules with different shells after thermal cycles

PCM

***m*-Diethylbenzene (-81°C)**

Shell

Pure melamine formaldehy

MF with electroless Cu coa

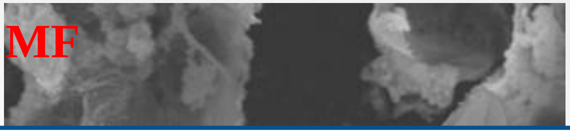
MF with both nano-Al_2O_3 a

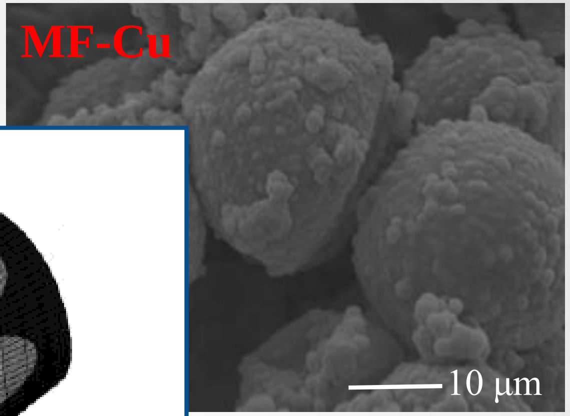
Morphologies

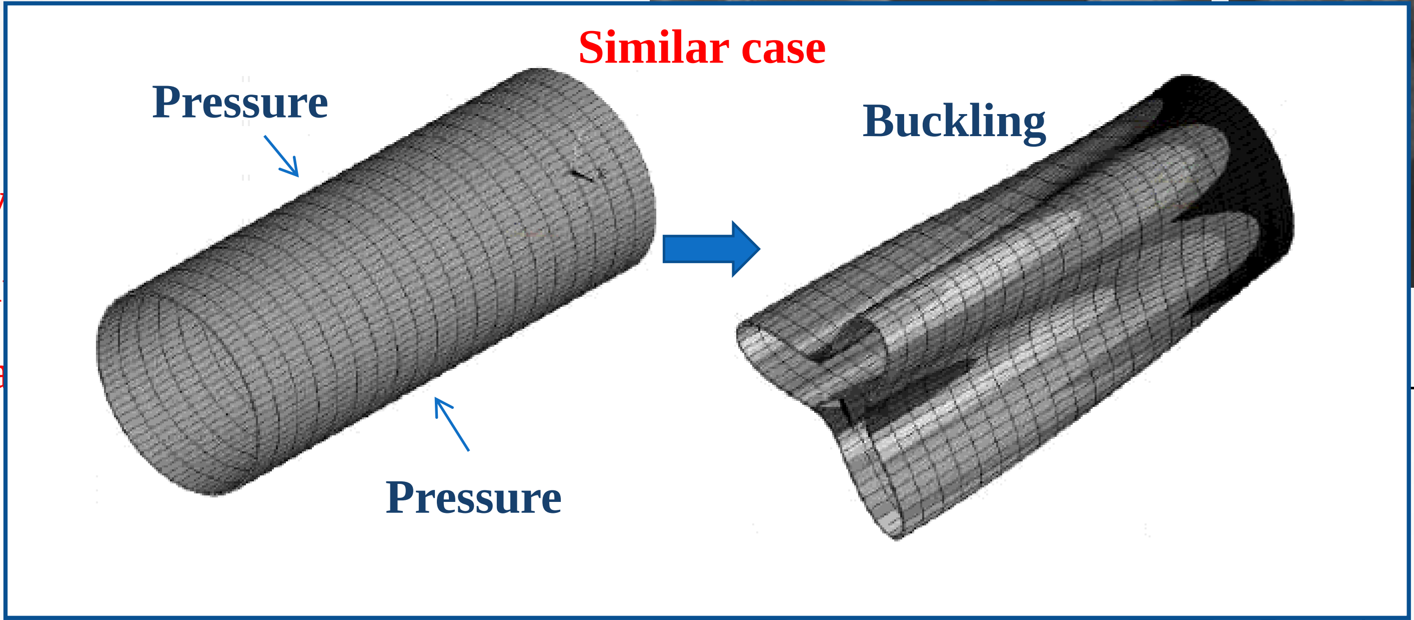
MF: Most are broken

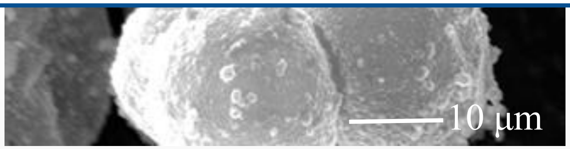
MF-Cu: Some are bulked and some keep spherical shape

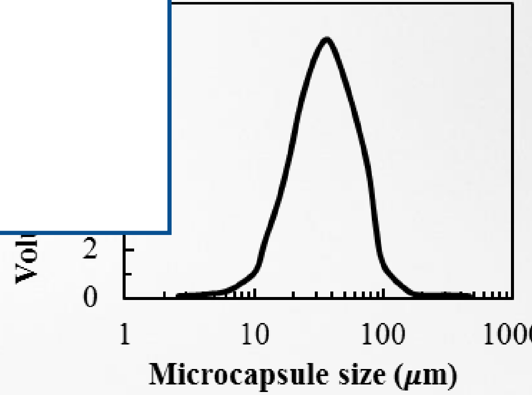
MF-Cu-Al: All keep spherical shape











T decrease → PCM solidification → V shrinkage → P decrease → ΔP increase → Buckling

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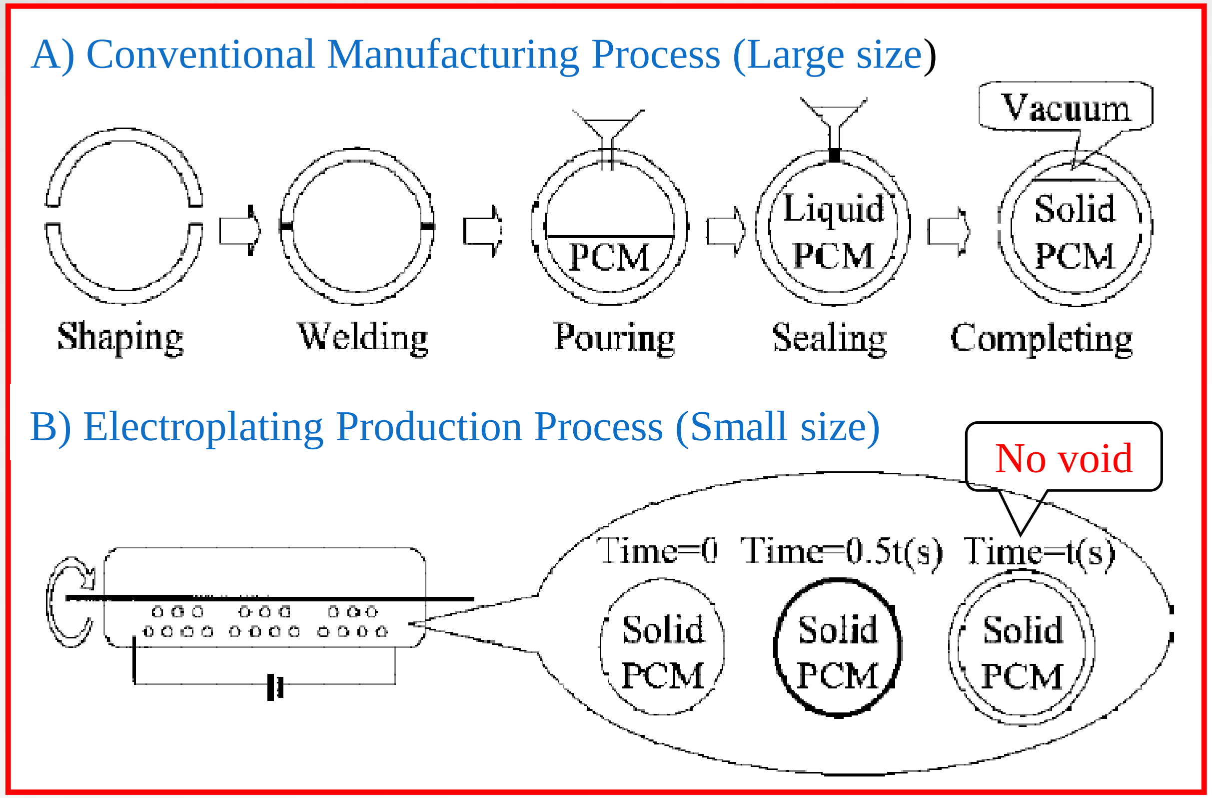
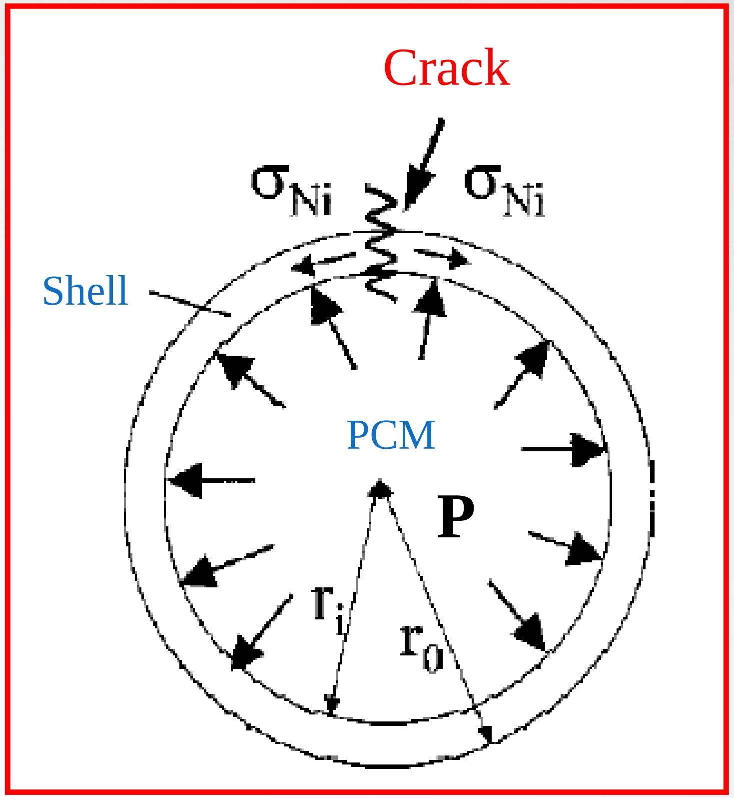
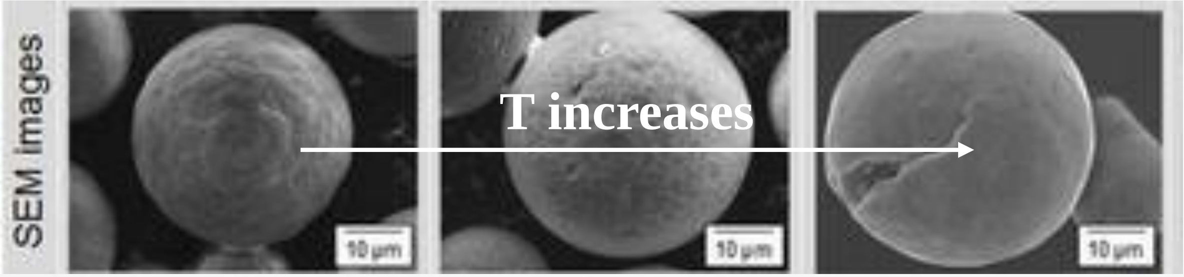
1.2 Problems of capsules for heat storage







↑

P increase ← **V expansion**

↑

T increases → **PCM melting**

T. Nomura et al. Scientific Reports 5 (2015) 9117.

1.3 Purposes of this study

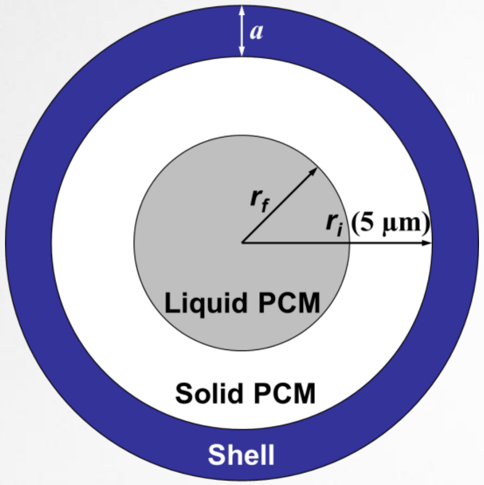
- **Establish thermo-mechanical models of microcapsules for cold and heat storage**
- **Reveal effects of key parameters on internal pressure and mechanical behaviors**
- **Determine the conditions of avoiding buckling or cracking of microcapsules**
- **Ascertain effects of key parameters on phase change dynamic and storage capacity**
- **Tailor key parameters to obtain optimal comprehensive energy storage performance**

contents

2.1 Thermo-mechanical models for cold storage

➢ Geometry and coupled approach

Solidification



Energy conservation equation
(enthalpy method for phase change)
(1D, Non-dimensionalized, FVM)

$f_l(r,t)$ ⇒ $T(r,t)$

Lamé's equation
(couple volume displacement)
(couple pressure inside shell)

$T_f(P)$ ⇑ $H_f(P,\ T_f)$

iterate

P

P (convergence)

Thermodynamic model
(liquid-solid equilibrium condition)

Buckling theory
(critical pressure, deformation)

2.1 Thermo-mechanical models for cold storage

➢ Main hypotheses

(a) The thermo-physical properties are constant, independent of pressure and temperature for the liquid PCM;

(b) The liquid pressure within the shell is uniform;

(c) As a result of the micro-size capsule, convection heat transfer inside the shell is negligible;

(d) Viscous energy dissipation is also neglected;

(e) The solid phase of PCM possesses homogeneously constant values of thermo-physical properties;

(f) The solid phase of PCM is deformable along with the shell without effect on the shell deformation;

(g) The shell is considered to be a homogeneous, isotropic and exhibiting linear elastic behavior indicated by Young's modulus, with constant values of thermo-physical properties;

(h) The external surface of the shell is at known and uniform temperature and pressure;

(i) The conditions of temperature continuity and heat flux conservation are satisfied at the solidification front;

(j) There are equalities of temperature and pressure at the shell/PCM interface.

2.1 Thermo-mechanical models for cold storage

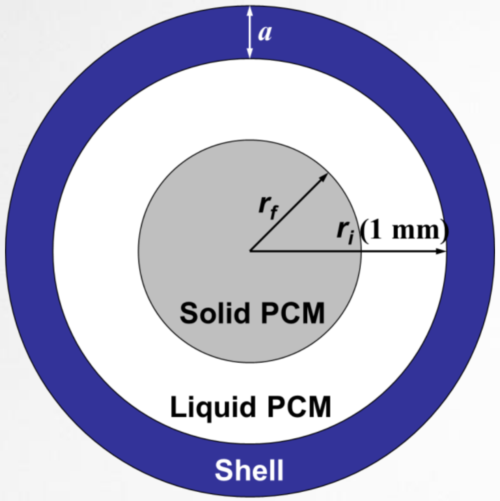
➢ Main hypotheses

Items	Key Equations	Boundary conditions
Energy conservation equations	$\frac{\partial\left[(\rho c_p)_{eq} T_i\right]}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(\lambda_{eq} r^2 \frac{\partial T_i}{\partial r}\right) - \frac{\partial(\rho_{eq}\Delta h_f)}{\partial t}$ for $0 \le r \le r_i$, $\frac{\partial(\rho_c c_{pc} T_c)}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(\lambda_c r^2 \frac{\partial T_c}{\partial r}\right)$ for $r_i < r \le r_e$, $\Delta h_f = f_l L_f$ $f_l(r,t) = \begin{cases} 1, & T_p \ge T_f \\ 0, & T_p < T_f \end{cases}$. $f^*(t) = 1 - \frac{3}{r_{i0}^3}\int_0^{r_i} r^2 f_l(r,t)\,dr$	$-\lambda_{eq}\frac{\partial T_i}{\partial r} = 0$ at $r = 0$ $T_i(r,0) = T_c(r,0) = T_0$ $\lambda_{eq}\frac{\partial T_i}{\partial r} = \lambda_c \frac{\partial T_c}{\partial r}$, and $T_i = T_c$ at $r = r_i$ $T_c = T_e(t)$ at $r = r_e$ $T_c(r_e, t) = T_0 - \beta t$
Lamé's equations	$\frac{d^2u}{dr^2} + \frac{2}{r}\frac{du}{dr} - \frac{2u}{r^2} = 0$ $\sigma_{rr} = \delta\left(\frac{du}{dr} + \frac{2u}{r}\right) + 2\mu\frac{du}{dr} - (3\delta + 2\mu)\alpha_c \Delta T$ $\Delta V = V_{l0}\left(\frac{\rho_l - \rho_s}{\rho_s}\right) f^*(t)$ $\Delta V = \frac{4}{3}\pi[(u(r_{i0}) + r_{i0})^3 - r_{i0}^3]$	$\sigma_{rr}(r = r_{i0}) = -P$ $\sigma_{rr}(r = r_{e0}) = -P_a$
Thermodynamic model	$g_j(T_f, P) = g_{j0} - s_{j0}(T_f - T_{f0}) + \frac{1}{\rho_{j0}}(P - P_0) - \frac{1}{2}\frac{c_{pj0}}{T_0}(T_f - T_{f0})^2 - \frac{1}{2}\frac{\beta_{j0}}{\rho_{j0}}(P - P_0)^2 + \frac{\alpha_{j0}}{\rho_{j0}}(T_f - T_{f0})(P - P_0)$, $g_l = g_s$ $L_f(T_f, P) = \Delta s_f(T_f, P) T_f$ $s_j \equiv -\left.\frac{\partial g_j}{\partial T}\right\vert_P$ $\frac{1}{\rho_j} \equiv \left.\frac{\partial g_j}{\partial P}\right\vert_T$	
Buckling theory	$\boxed{P_{cr} = \kappa\frac{2E_c a^2}{r_i^2\sqrt{3(1 - \nu_c^2)}}}$ $u_{b\theta} = \sum_{n=1}^{\infty} A_n \frac{dF_n(\cos\theta)}{d\theta}$ $u_{br} = \sum_{n=1}^{\infty} B_n F_n(\cos\theta)$ **Critical buckling pressure**	When the difference between external and internal pressures is equal to or larger than the critical buckling pressure, buckling occurs.

2.2 Thermo-mechanical models for heat storage

➢ Geometry and coupled approach

Melting



Solar salts/SiC

Cu/Ni

Energy conservation equation
(enthalpy method for phase change)
(1D, Non-dimensionalized, FVM)

$f_l(r,t)$ ⇒ $T(r,t)$

Lamé's equation
(couple volume displacement)
(couple pressure inside shell)

$T_f(P)$ ⇑ $H_f(P, T_f)$ $\rho(P, T_f)$

iterate

P

P (convergence)

Thermodynamic model
(liquid-solid equilibrium condition)

Von Mises' criterion
(equivalent pressure, cracking)

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2.2 Thermo-mechanical models for heat storage

➢ Main hypotheses

(a) The thermo-physical properties are constant for the solid phase of PCM with non-deformability;

(b) The thermo-physical properties except for the density are constant for the liquid phase of PCM;

(c) Convection heat transfer inside the small-sized capsule is negligible;

(d) Viscous energy dissipation of the liquid is also neglected;

(e) The liquid within the shell has uniform pressure;

(f) The shell is considered to be a homogeneous, isotropic and exhibiting linear elastic behavior indicated by Young's modulus, with constant values of thermo-physical properties;

(g) The pressure and temperature are known and uniform at the external wall of the shell;

(h) There are equalities of temperature and pressure at the shell/PCM interface.

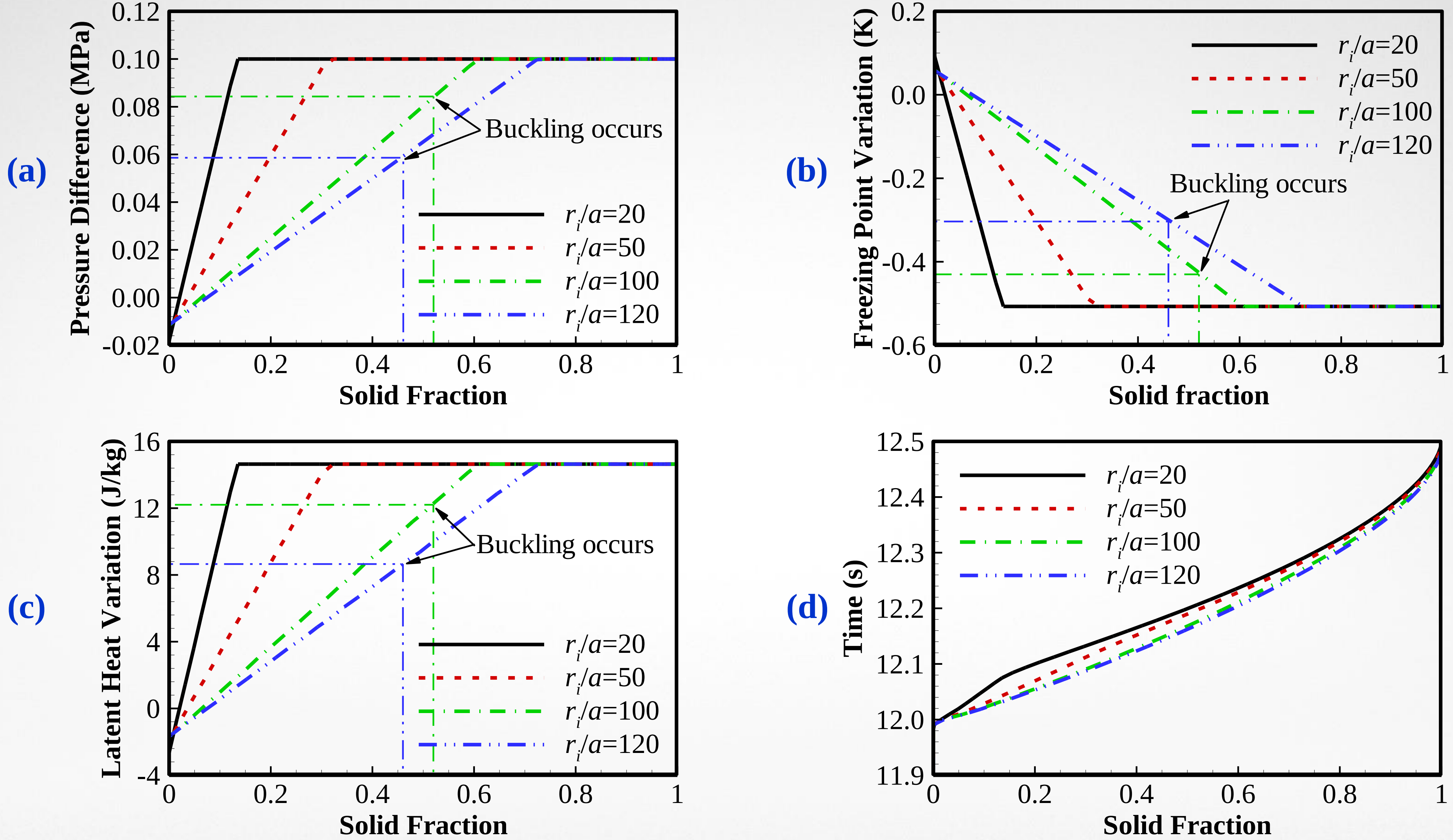
2.2 Thermo-mechanical models for heat storage

➢ Main hypotheses

Items	Key Equations	Boundary or initial conditions
Energy conservation equations	$\begin{cases} \frac{\partial\left[(\rho c_p)_{eq} T_i\right]}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(\lambda_{eq} r^2 \frac{\partial T_i}{\partial r}\right) - \frac{\partial(\rho_{eq}\Delta h_m)}{\partial t} & \text{for } 0 \le r \le r_i, \\ \frac{\partial(\rho_c c_{pc} T_c)}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(\lambda_c r^2 \frac{\partial T_c}{\partial r}\right) & \text{for } r_i < r \le r_e, \end{cases}$ $\Delta h_m = f_l L_m = (1-f_s)L_m$ $f_s(r,t) = \begin{cases} 0, & T_i \ge T_m \\ 1, & T_i < T_m \end{cases}$ $f^*(t) = 1 - \frac{3}{r_{i0}^3}\int_0^{r_i} r^2 f_s(r,t)dr$	$-\lambda_{eq}\frac{\partial T_i}{\partial r} = 0 \text{ at } r = 0$ $T_i(r,0) = T_c(r,0) = T_0$ $\lambda_{eq}\frac{\partial T_i}{\partial r} = \lambda_c\frac{\partial T_c}{\partial r}, \text{ and } T_i = T_c \text{ at } r = r_i$ $T_c = T_e(t) \text{ at } r = r_e$ $T_e(t) = T_0 + \gamma t$
Lamé's equations	$\frac{d^2u}{dr^2} + \frac{2}{r}\frac{du}{dr} - \frac{2u}{r^2} = 0$ $\sigma_{rr} = \delta\left(\frac{du}{dr} + \frac{2u}{r}\right) + 2\mu\frac{du}{dr} - (3\delta + 2\mu)\alpha_c\Delta T$ $\Delta V = V_{l0}\left(\frac{\rho_l - \rho_s}{\rho_s}\right)f^*(t)$ $\Delta V = \frac{4}{3}\pi[(u(r_{i0}) + r_{i0})^3 - r_{i0}^3]$	$\sigma_{rr}(r = r_{i0}) = -P$ $\sigma_{rr}(r = r_{e0}) = -P_a$
Thermodynamic model	$g_j(T_f,P) = g_{j0} - s_{j0}(T_f - T_{f0}) + \frac{1}{\rho_{j0}}(P - P_0) - \frac{1}{2}\frac{c_{pj0}}{T_0}(T_f - T_{f0})^2 - \frac{1}{2}\frac{\beta_{j0}}{\rho_{j0}}(P - P_0)^2 + \frac{\alpha_{j0}}{\rho_{j0}}(T_f - T_{f0})(P - P_0)$ $g_l = g_s$ $L_f(T_f,P) = \Delta s_f(T_f,P)T_f$ $s_j \equiv -\left.\frac{\partial g_j}{\partial T}\right\|_P$	
Von mises' criterion	$\sigma_v = \sigma_{\theta\theta} - \sigma_{rr}$ $\boxed{P_{eq} = \frac{2}{3}\left(1 - \frac{r_{i0}^3}{r_{e0}^3}\right)\sigma_t}$ **Critical equivalent cracking pressure**	When the internal pressure is equal to or larger than the critical equivalent cracking pressure, cracking occurs.

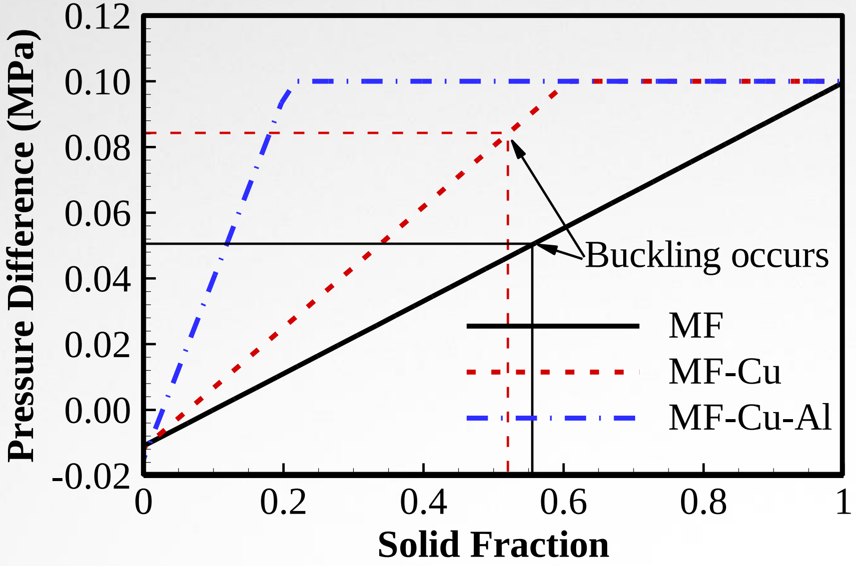
contents

3.1 Effects of shell thickness

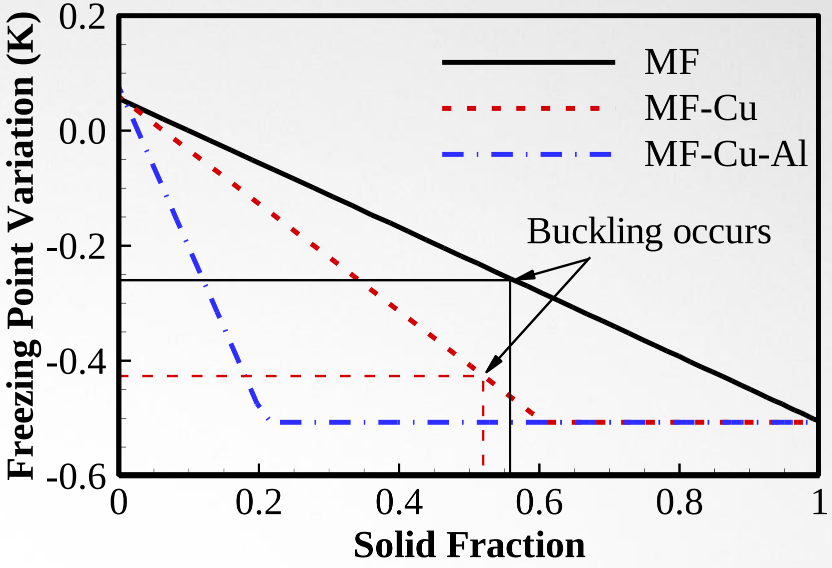


3.2 Effects of shell compositions

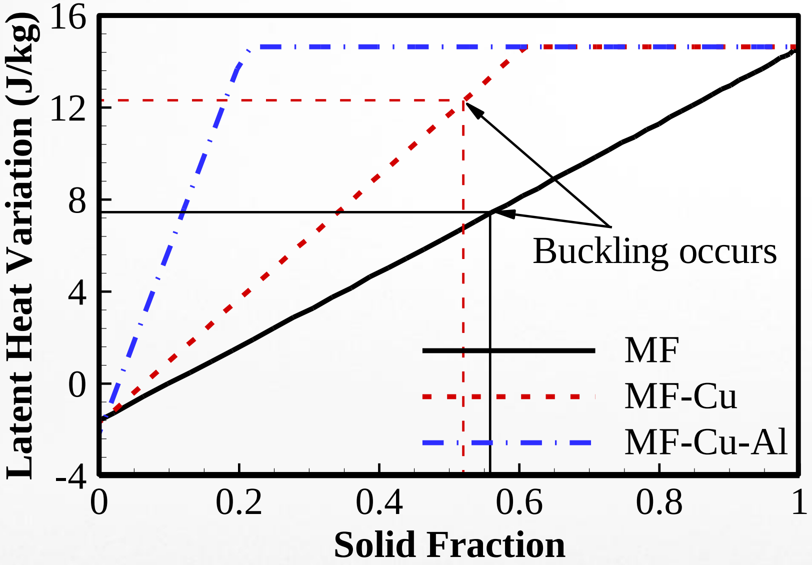
(a)



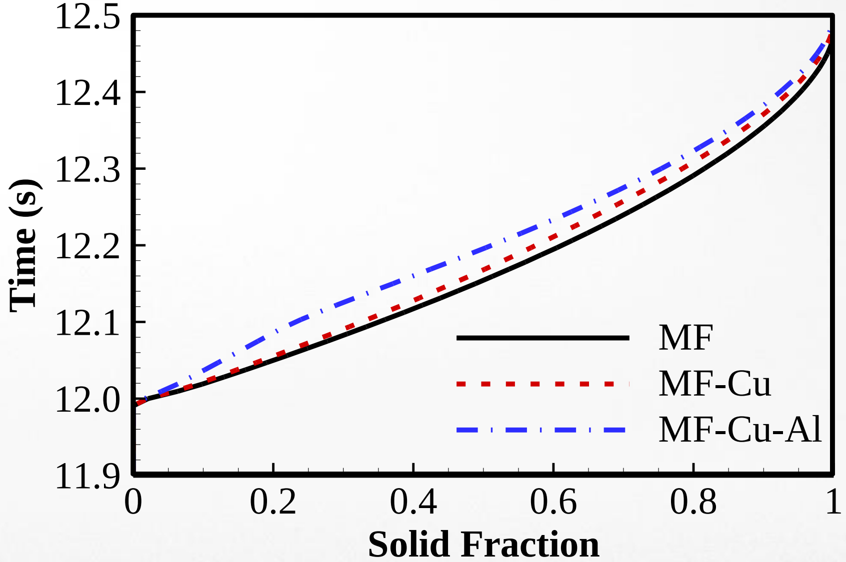
(b)



(c)

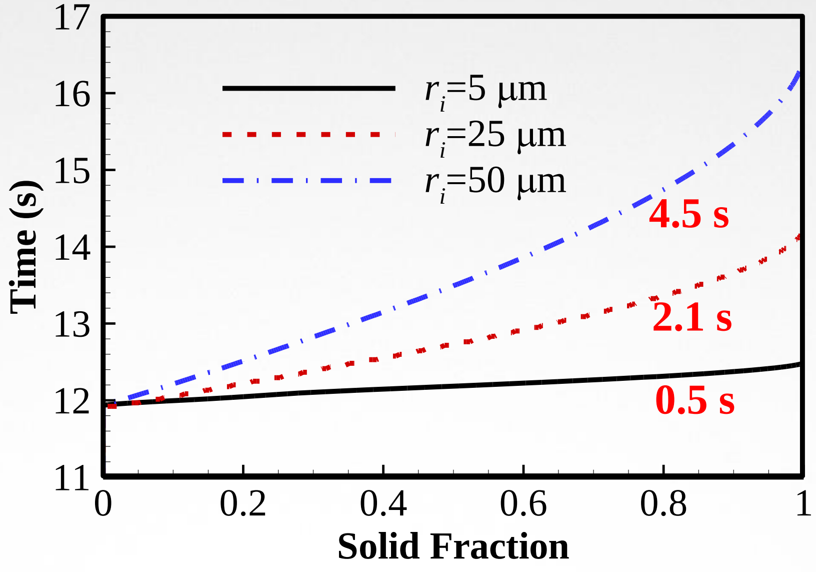


(d)

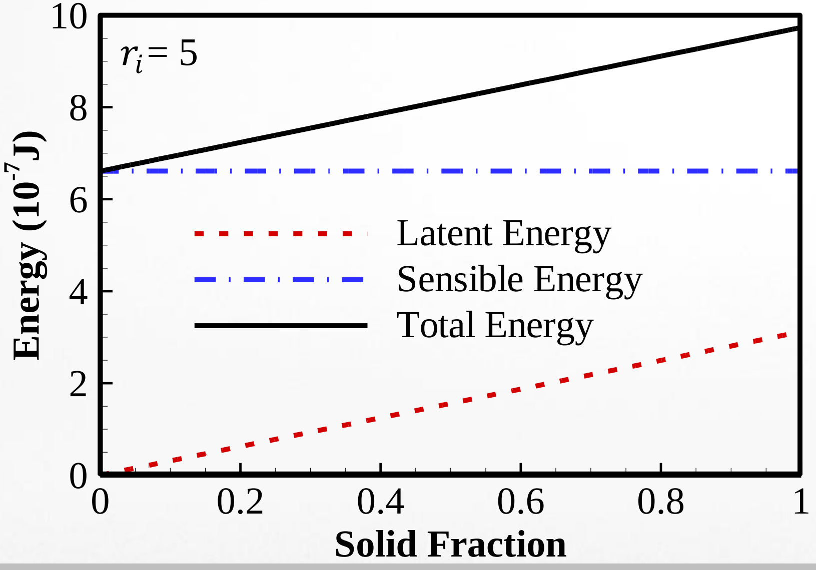


3.3 Effects of capsule sizes

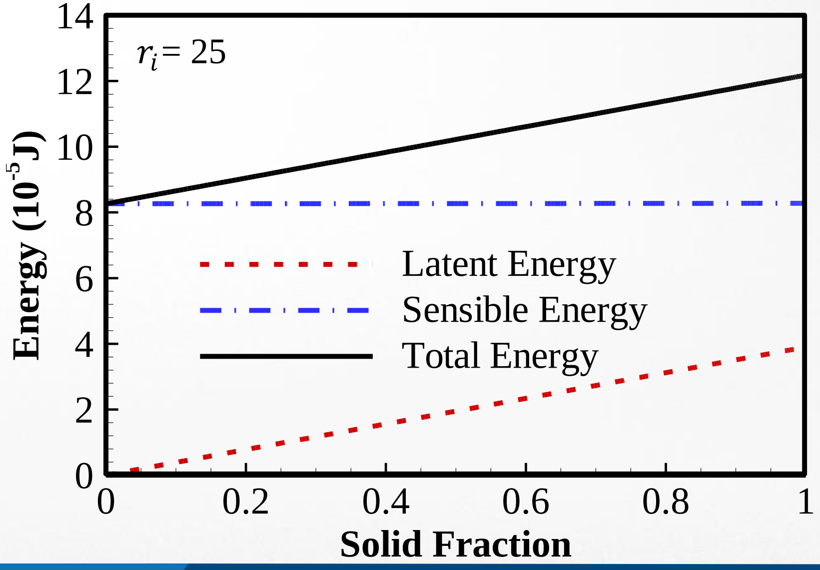
(a)



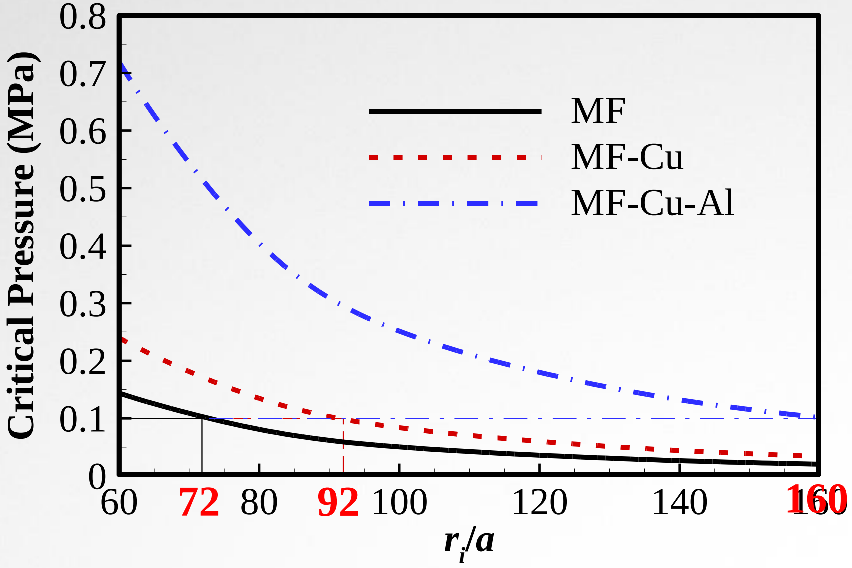
(b)

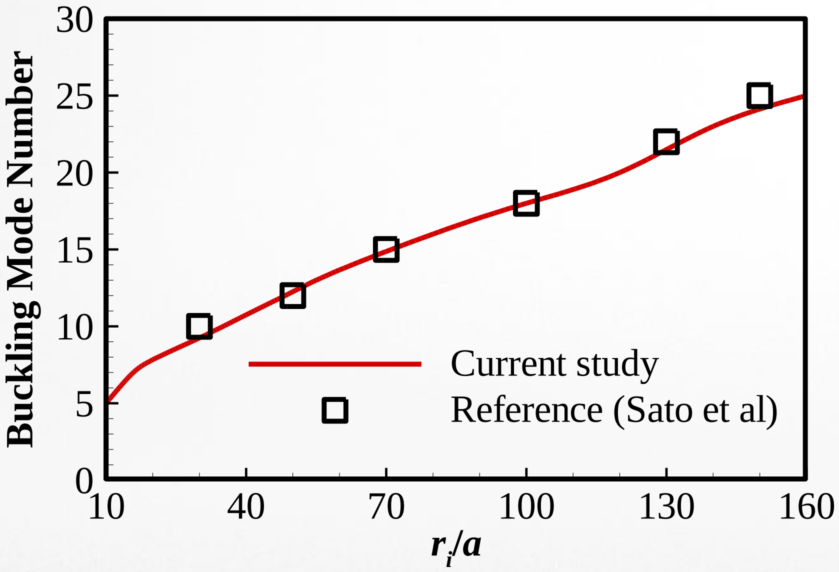


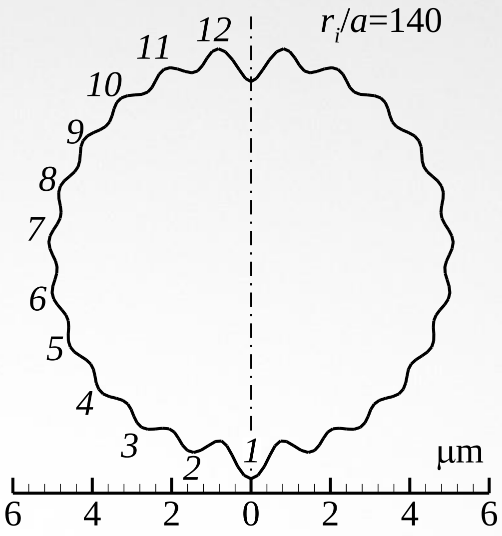
(c)

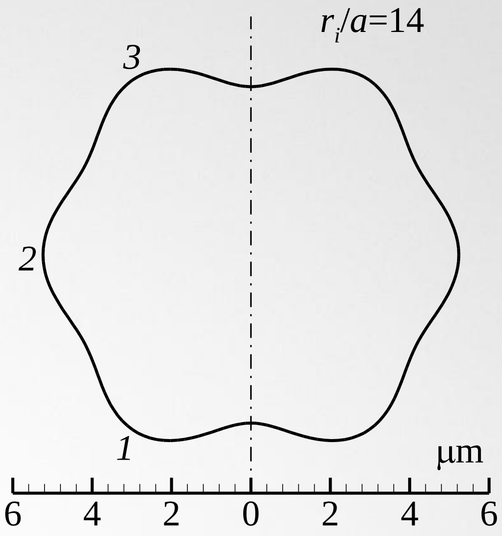


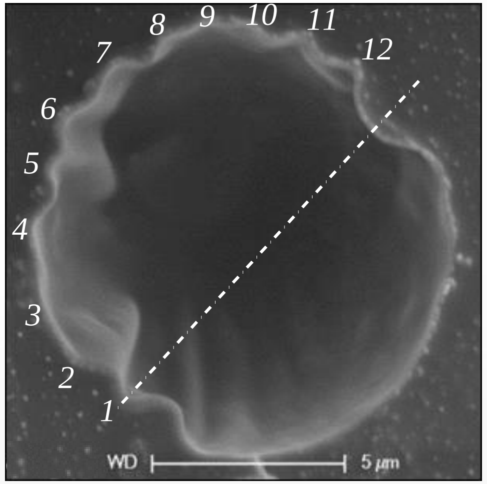
3.4 Critical bulking pressure and mode

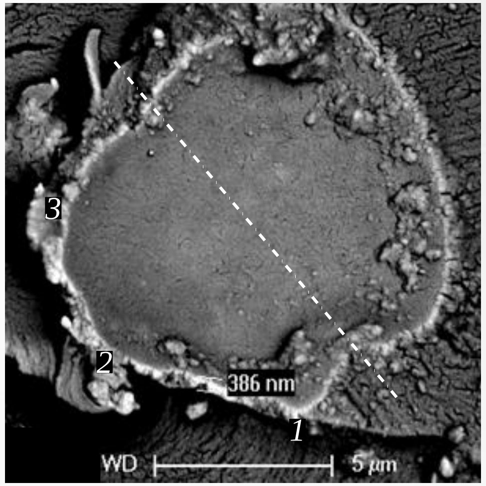










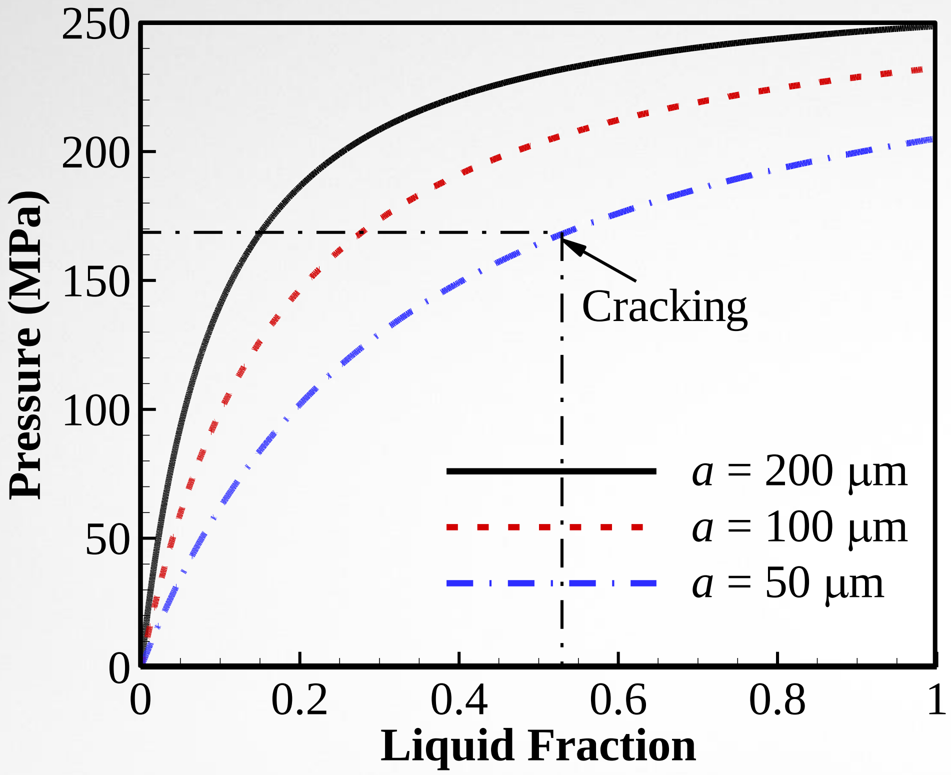


Predicted a = 36 nm $E \leq 23$ MPa

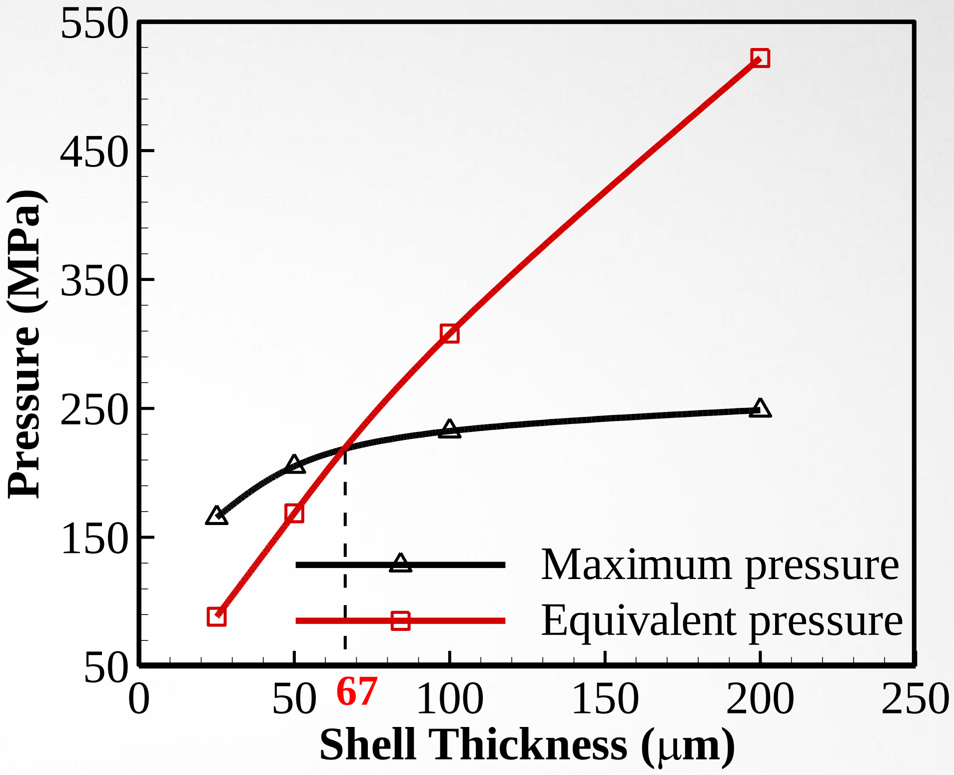
contents

4.1 Effects of shell thickness

➢ **salts/SiC capsule with r_i = 1 mm**



(a) Internal pressure VS. Liquid Fraction



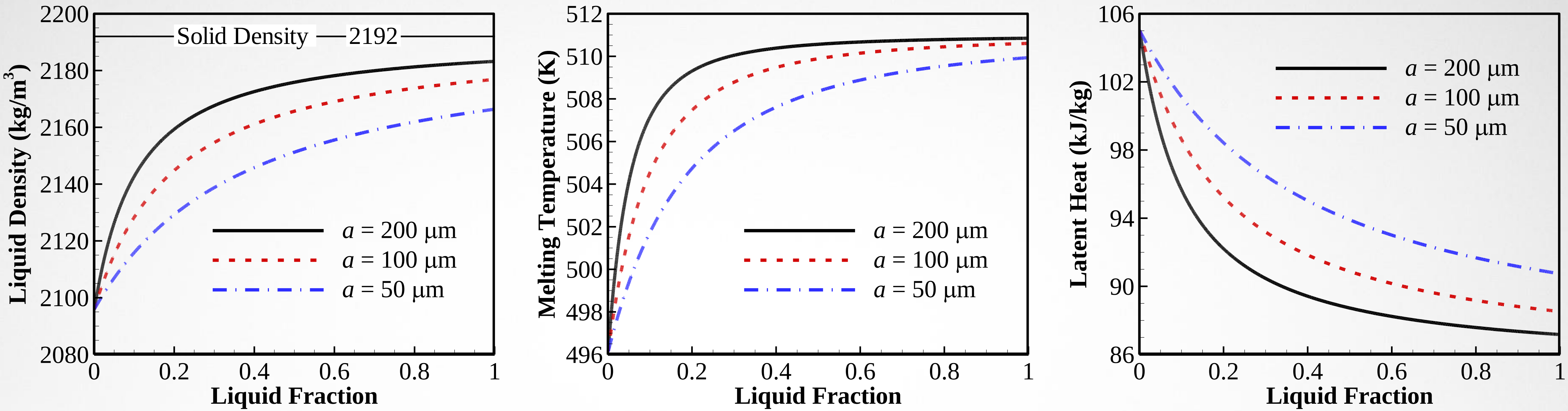
(b) Comparison between maximum and equivalent pressures

✓ **If the tensile strength of SiC could be augmented over 2.26 GPa the shell with *a*= 50μm can also avoid cracking**

✓ **The condition of avoiding cracking for different size salts/SiC capsules is $r_i/a \leq 14.9$.**

4.1 Effects of shell thickness

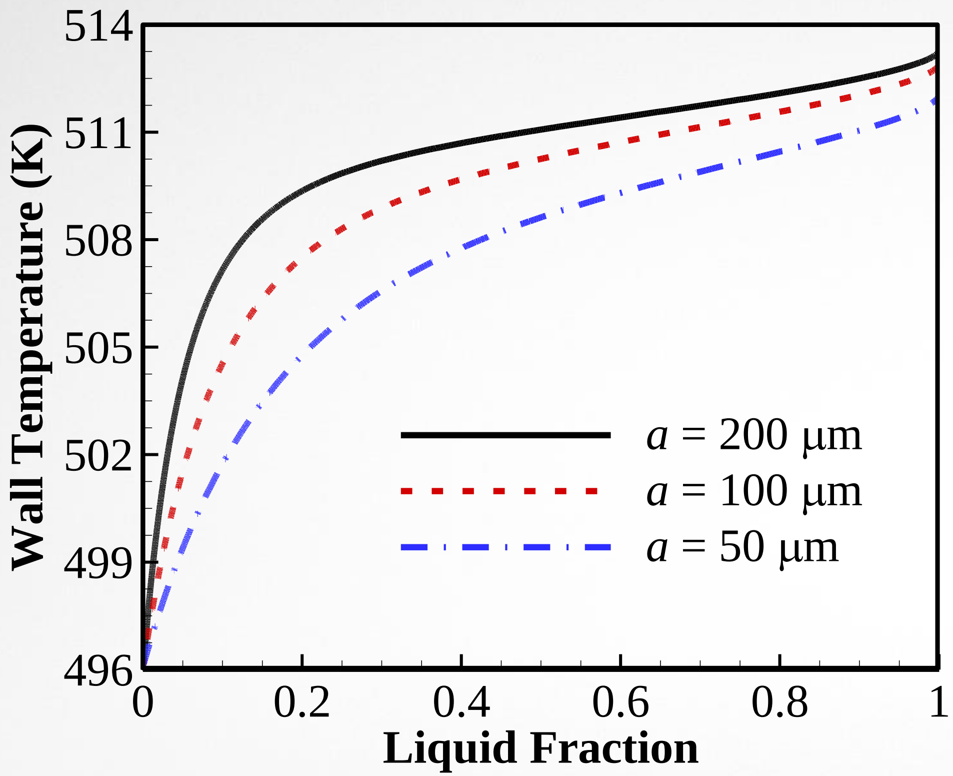
➢ **salts/SiC capsule with r_i = 1 mm**



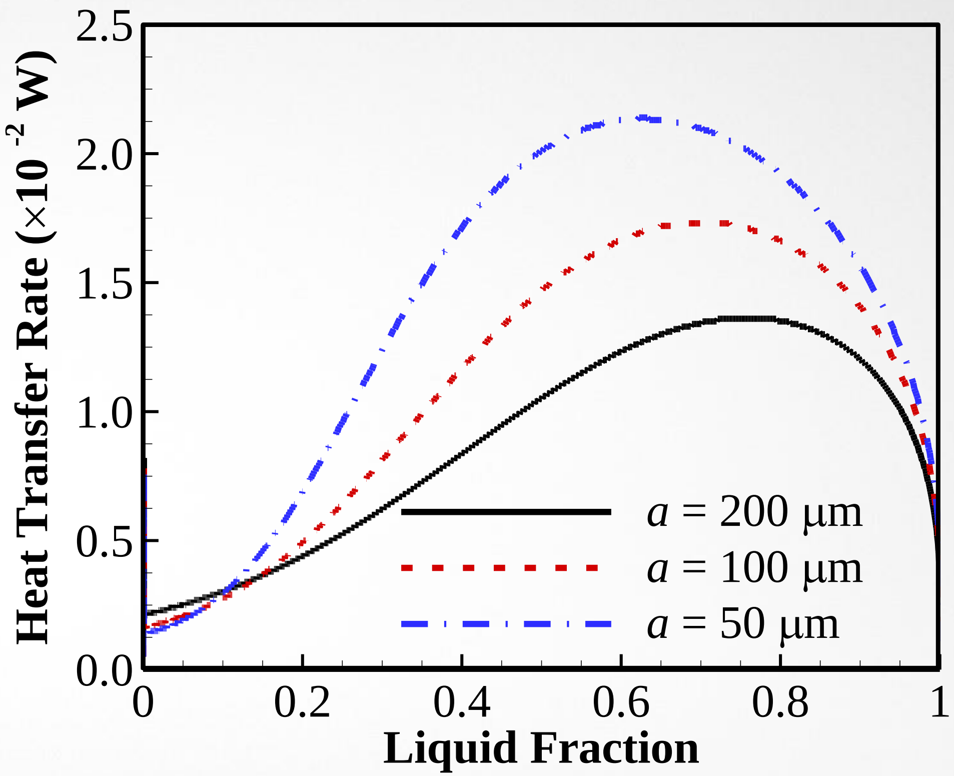
(a) Liquid density **(b) Melting temperature** **(c) Latent heat**

4.1 Effects of shell thickness

➢ **salts/SiC capsule with r_i = 1 mm**



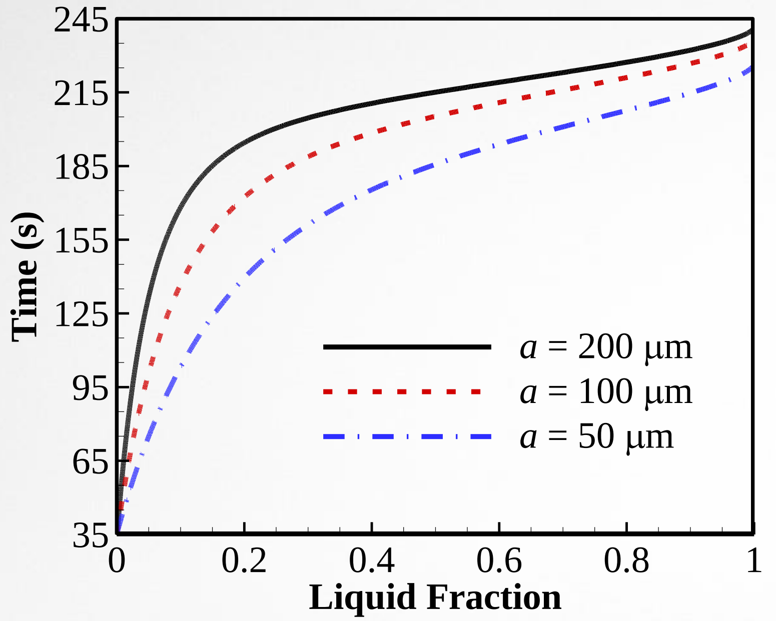
(a) Wall temperature



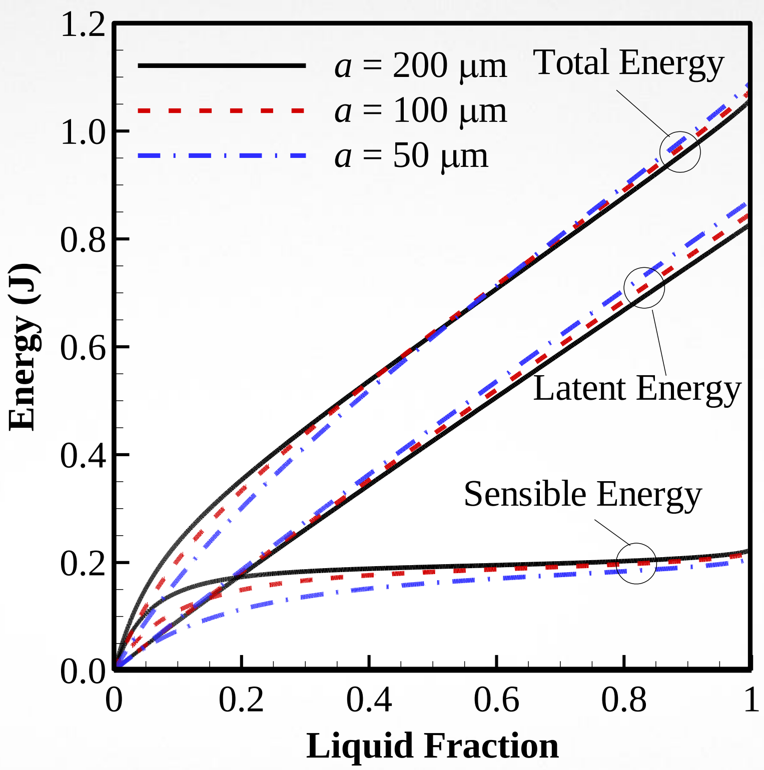
(b) Wall heat transfer rate

4.1 Effects of shell thickness

➢ salts/SiC capsule with r_i = 1 mm



(a) Melting time



(b) Stored energy

Shell thickness (μm)	Mass-based energy storage density (kJ/kg)	Volume-based energy storage density (MJ/m^3)
200	64.2	168.8
100	84.2	206.3
50	99.6	232.3

Heat storage density of a capsule

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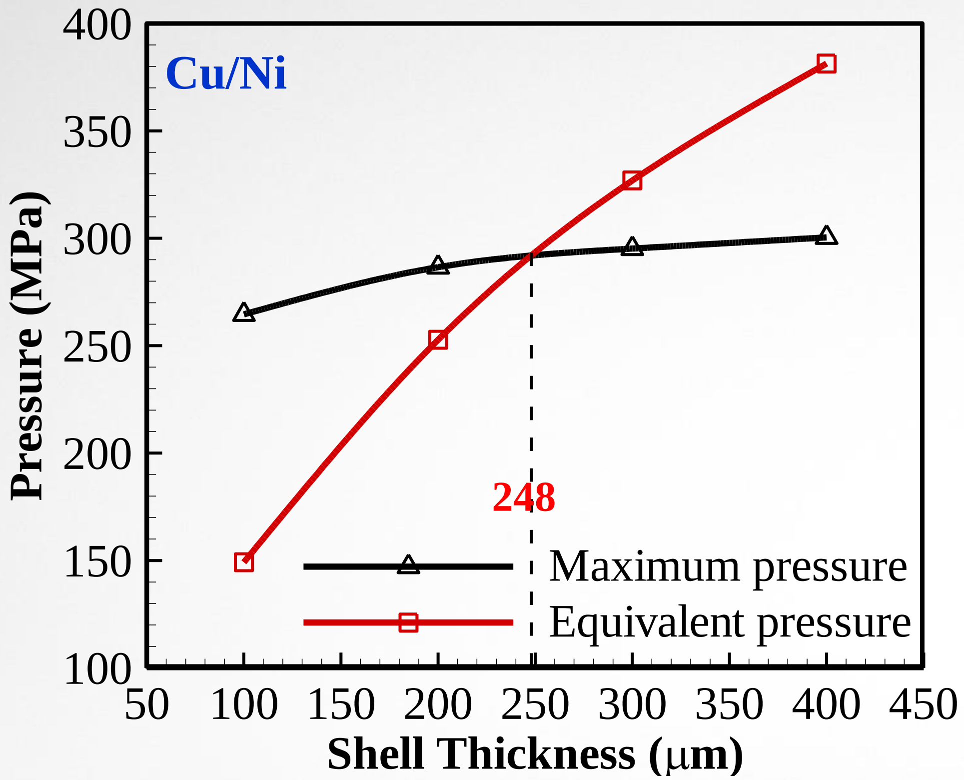
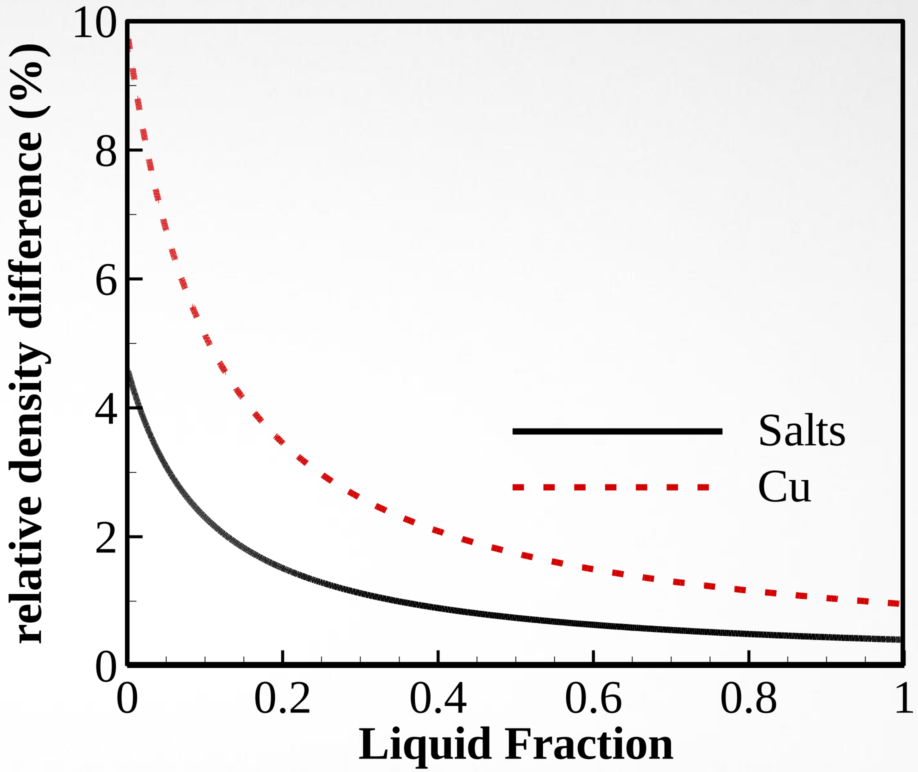
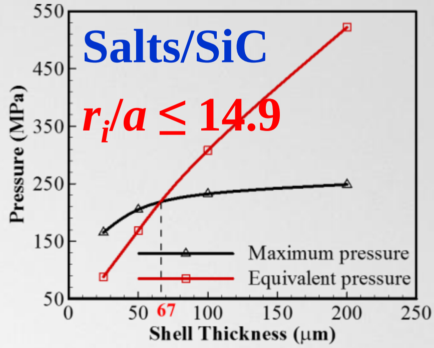
4.2 Comparison of different capsules with r_i = 1 mm





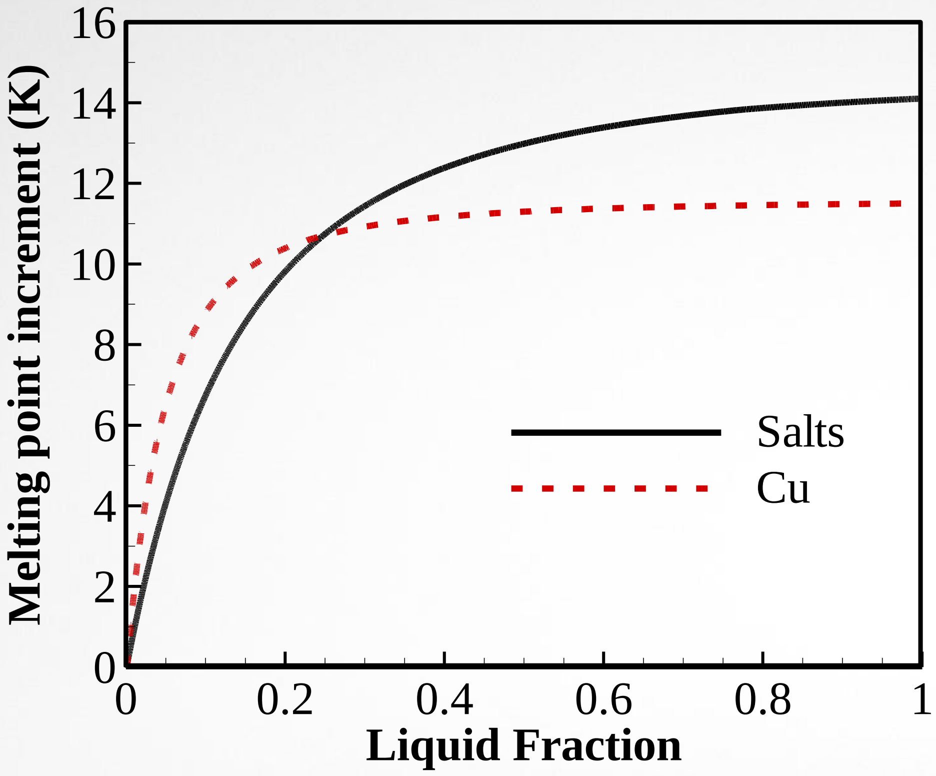


(a) Comparison between maximum and equivalent pressures

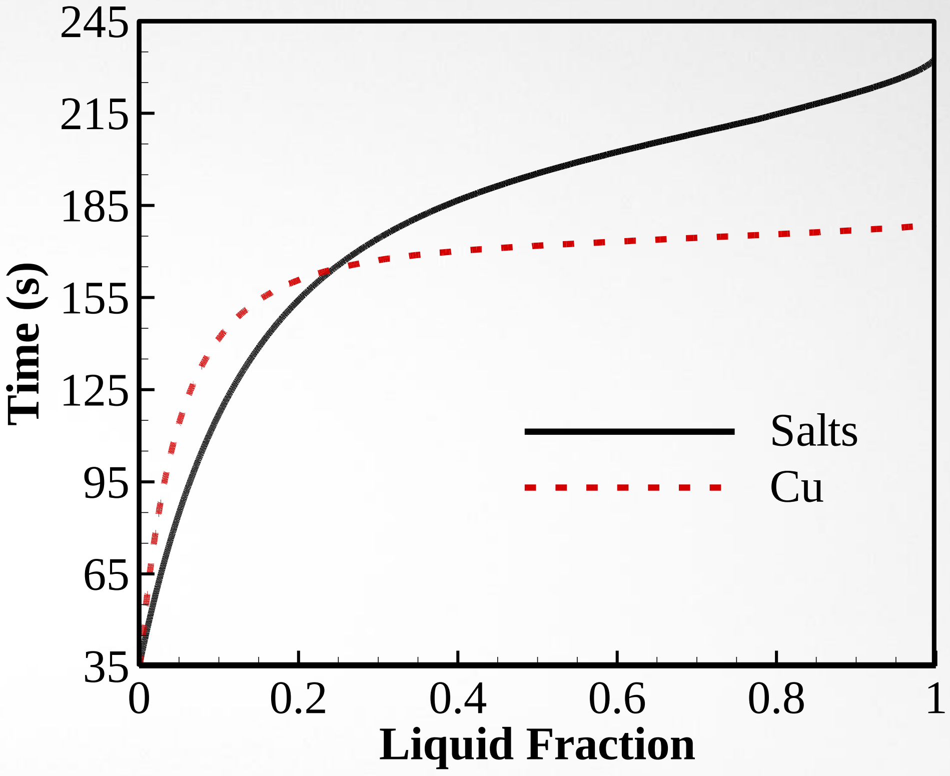
(b) Relative density difference

- ✓ **The result in Fig. (a) coincides with the experimental result of Zhang et al. (SEM&SC, 2014;128: 131-7.)**
- ✓ **The condition of avoiding cracking for different size Cu/Ni capsules is $r_i/a \leq 4.0$.**

4.2 Comparison of different capsules with r_i = 1 mm



(a) Melting point increment



(b) Melting time

contents

5 Conclusions and remarks

- ✓ We developed a coupled model which can effectively explore the thermo-behaviour of a single PCM microcapsule for cold or heat storage;
- ✓ For cold storage, the shell buckling can be avoided by adjusting shell thickness and shell compositions (i.e. Young’s module), and the critical values can be predicted by the developed model.
- ✓ For heat storage, the shell cracking can be avoided by adjusting shell thickness and shell tensile strength, and the critical values can be predicted by the developed model.
- ✓ Shell thickness and Young’s module have notable effects on the internal pressure and hence the phase change dynamics (phase change temperature, latent heat) and storage performance (charging time and storage density).
- ✓ Further work is required to figure out the link between the thermo-mechanical behaviours of a single microcapsule to the performance of thermal storage devices.

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Thank you for your attention!