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Thermo-mechanical analysis of microcapsules containing phase change materials for cold storage

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HIGHLIGHTS

- Thermo-mechanical model is established for microencapsulated PCMs for cold storage.
- Embedding Al_2O_3 nanoparticles into MF shell increases its resistance to buckling.
- Young's modulus or thickness of shell can be predicted according to buckling mode.
- The condition for avoiding buckling is proposed to improve the mechanical stability.
- Microencapsulated PCM slurries have higher energy storage capacity than packed beds.

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ABSTRACT

Microencapsulated phase change material slurries (MEPCMSs) offer a potentially efficient and flexible solution for cryogenic-temperature cold storage. In this paper, the phase change material (PCM) microcapsules prepared to form MEPCMSs for cryogenic-temperature cold storage consist of Dowtherm J (DJ) as core material and melamine formaldehyde (MF) as primary shell material. DJ is an aromatic mixture with diethylbenzene as the main component. Composite shell materials are adopted to avoid cracking by adding aluminium oxide (Al_2O_3) nanoparticles or copper (Cu) coating into/on MF shell. In order to explore the heat transfer behaviour and mechanical stability of the microcapsules during the solidification process of PCM, a thermo-mechanical model is established by taking into account of energy conservation, pressure-dependent solid-liquid equilibria, Lamé's equations and buckling theory. Based on the proposed model, the effects of shell thickness, shell compositions and microcapsule size are therefore studied on the variations of pressure difference, freezing point, and latent heat. The cause of shell deformation is clearly explained and the shell buckling modes are predicted using the model, which agree well with the experimental observations. The critical core/shell size ratios of avoiding buckling are proposed for the microcapsules with different compositions. Simultaneously incorporation of Al_2O_3 nanoparticles and Cu coating into/on MF shell can markedly enhance the resistant to buckling. In addition, special attention is paid to cold energy storage capacity of MEPCMSs, which has considerable superiority compared to packed pebble beds.

1. Introduction

Liquid air energy storage (LAES) and pumped thermal electricity storage (PTES) are two emerging grid scale thermal storage technologies, which are good solutions for the intermittency and instability of electricity from renewable energy sources [1–3]. Cryogenic-temperature cold storage is key to improving the overall performance of LAES and PTES systems [4–6]. At present, the two systems generally utilize packed beds for cryogenic-temperature cold storage. However, packed beds have much room for improvement in energy storage capacity, efficiency and flexibility [7–10]. Microencapsulated phase change material slurries (MEPCMSs) have great potential for dynamic and static cryogenic-temperature cold storage applications as they combine the advantages of phase change materials (PCMs) and liquid sensible energy storage materials, and are both transport media (heat transfer fluids) and thermal storage media. MEPCMSs consist of a carrier liquid and PCM microcapsules with a diameter of $< 100\,\mu m$, in general, small enough to be suspended in a carrier liquid. Such partially melting and

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Nomenclature

Roman letters

a	shell thickness (m)
c_p	specific heat (J·kg^{-1}·K^{-1})
E	Young's modulus (Pa)
ES	stored energy (J)
f	volumetric fraction
F	Legendre function
g	chemical potential (kJ·kg^{-1})
h	enthalpy (kJ·kg^{-1})
k_f	foundation modulus (N/m^3)
L	latent heat (kJ·kg^{-1})
n	buckling mode number
P	pressure (Pa)
r	radius (m)
s	entropy (J·kg^{-1}·K^{-1})
t	time (s)
T	temperature (K)
u	displacement (m)
V	volume (m^3)

Greek letters

α	thermal expansion coefficient (K^{-1})
β	isothermal compressibility (Pa^{-1})
γ	surface tension (N·m^{-1})
δ, μ	Lamé's constant
ε	strain
$\varkappa$	correction factor
λ	thermal conductivity (W·m^{-1}·K^{-1})
ν	Poisson's ratio
ρ	density (kg·m^{-3})
σ	stress (Pa)

Subscripts

0	reference or initial
a	atmospheric
b	buckling
c	shell
cr	critical
e	external surface of shell
eq	equivalent
f	freezing or freezing front
i	shell/PCM interface or PCM
l	liquid
m	microcapsule
r, θ, φ	spherical coordinates system
s	solid

Superscripts

$*$	holistic

solidifying slurries can offer very high energy storage densities and heat transfer rates in charging/discharging processes [11]. The good flowability of the MEPCMSs allows them to be transported through pumping, and thus their flow rate can be easily adjusted to realize the desired stored amount of cold energy and objective temperature. Furthermore, their apparent specific heats at set temperatures can be designed by addition of microcapsules with different melting point core PCM, in order to meet the significant specific heat changes of transcritical/supercritical fluids [12]. Therefore, the MEPCMSs can offer a much more flexible strategy for cold storage, which is extremely difficult to achieve using the conventional packed bed.

The utilisation of MEPCMSs will also have a significant impact on the cryogenic industry such as natural gas liquefaction and cold recovery in re-gasification, and air separation/liquefaction [13,14]. However, most of the research has been conducted only on moderate or high temperature MEPCMSs with melting points above $-20\,^{\circ}$C [15–18], whereas little research can be found on cryogenic MEPCMSs. Technically, the cryogenic MEPCMSs are more challenging compared to MEPCMSs applied at moderate temperatures due to deformation or fragility of the shell of microcapsules and poor heat transfer under cryogenic conditions. The success of MPCMSs in cryogenic temperature cold storage is dependent on the stability of microcapsules under repeated pumping, cyclic heating and cooling as well as long-term storage. As a result, it is important to understand the thermo-mechanical behaviour of MEPCMs in particular during the PCM solidification process.

Several studies have been devoted to the thermo-mechanical behaviour of encapsulated PCM. A composite of mixed graphite and nitrate salts is considered as a solid sphere of PCM encapsulated in a thick shell of graphite by Lopez et al. [19] and the shell was modelled as a closed elastic spherical shell with a mobile internal wall and a non-moving external wall. Based on this model, the effects of the shell Young's modulus on the internal pressure, melting point and latent heat, were examined. Pitié et al. [20] extended the model to a shell of silicon carbide (SiC) with a free mobile external wall by incorporating the Lamé equations. The variation of internal pressure due to the volume change during the melting process was analytically calculated based on the extended model with a given volume fraction of melted salts, leading to variations of melting point, enthalpy and stored energy. This indicates that the coated PCM should have a low volumetric expansion causing a lower pressure increase so that the coating SiC shell can avoid cracking. Based on the model, the temperature and pressure evolutions during the melting and solidification processes of copper-encapsulated nitrate spheres were simulated at a constant surrounding temperature by Parrado et al. [21]. In the simulations the heat transfer equation was decoupled with the mechanical stress equation. Zhao et al. [22] compared the time of the melting/solidification process between metal and non-metal encapsulated PCM particles using numerical simulations of heat transfer regardless of pressure variation. The above investigations are only based on high-temperature thermal energy storage and thermo-mechanical analysis of millimeter-scale encapsulated PCM particles. Mechanical response and properties of microcapsules near room temperature were also evaluated via experiments by Giro-Paloma et al. [23] and Su et al. [24], without considering the heat transfer behaviour. However, the thermo-mechanical behaviours of PCM microcapsules have rarely been studied for the purpose of cold storage. In particular, the effects of shell thickness and compositions on the thermo-mechanical behaviours have not been clearly addressed by previous studies.

It should be noted that the PCM solidification processes in cold storage are different from those in heat storage in terms of internal pressure and deformation mechanism of shells [20,25,26]. Because of the volume shrinkage of PCM during solidification in cold storage application, the internal pressure of microcapsule decreases while the external pressure is constant [27,28]. When the external pressure is higher than the internal pressure, the spherical microcapsule shell is only subjected to uniform external pressure. The morphology or deformation of such a pressurised spherical shell is then crucial to its properties, such as optical, electromagnetic and heat transfer. The analytical studies of structural behaviour or buckling of complete