1 Nanoencapsulation and performance of water-insoluble sebacic acid

# as a phase change material for medium-temperature thermal energy storage

- Songping Mo<sup>1,2</sup>, Jiaxuan Li<sup>1</sup>, Yuxuan Lin<sup>1</sup>, Zhi Yang<sup>1,2</sup>, Zhibin Wang<sup>1,2</sup>, Lisi Jia<sup>1,2</sup>, Yanping Du<sup>3</sup>,
   Ying Chen<sup>1,2,\*</sup>
- 6 1 School of Materials and Energy, Guangdong University of Technology, Guangzhou 510006,
  7 China.

8 2 Guangdong Provincial Key Laboratory on Functional Soft Condensed Matter, Guangdong

9 University of Technology, Guangzhou 510006, China.

10 3 School of Engineering, Lancaster University, Lancaster LA1 4YW, UK.

11 Abstract Nanoencapsulation has emerged as an effective strategy to address challenges 12 such as leakage during phase change while enhancing thermophysical properties of 13 phase change materials. Dicarboxylic acids, characterized by high latent heat, low supercooling, and excellent thermal stability, are highly promising for medium-14 15 temperature thermal energy storage. However, research on the microencapsulation of 16 these materials remains limited, with only one prior study focusing on water-soluble 17 glutaric acid. This manuscript introduces a novel method for nanoencapsulating water-18 insoluble phase change materials with melting points exceeding 100 °C, demonstrated 19 through the nanoencapsulation of sebacic acid. The developed nanocapsules exhibited 20 spherical morphology with particle sizes uniformly distributed between 200 and 500 nm. 21 Key findings include a melting temperature of 130.5 °C, a melting enthalpy of 164.4 22  $kJ\cdot kg^{-1}$ , minimal supercooling of 2.0 °C, an encapsulation ratio of 73.9%, and a thermal 23 reliability of 94.5% after repeated thermal cycling. Encapsulation significantly enhanced 24 thermal degradation resistance, improved thermal conductivity by 15.0% with just 1.0 25 wt% nanocapsules in thermal fluid, and reduced pumping power requirements by up to 26 78.0% for 10.0 wt% nanocapsule suspensions at 25 °C compared to the base fluid. These 27 results highlight the great potential of sebacic acid nanocapsules for medium-

<sup>\*</sup> Corresponding author.

E-mail address: chenying@gdut.edu.cn (Y. Chen)

- 28 temperature thermal energy storage and transfer systems.
- Keywords: Thermal energy storage, Phase change material, Sebacic acid, Sodium
  silicate, SiO<sub>2</sub>

31

Nomenclature							
Cp	specific heat, kJ·kg <sup>-1</sup> ·K <sup>-1</sup>	Т	temperature, K				
DSC	differential scanning calorimeter	TES	thermal energy storage				
Ε	encapsulation efficiency	TSI	Turbiscan stability index				
FT-IR	Fourier transform infrared	и	flow velocity, $m \cdot s^{-1}$				
	spectroscopy						
G	volume flow rate, $m^3 \cdot s^{-1}$	W/O	water-in-oil				
H <sub>m</sub>	melting enthalpy, kJ·kg <sup>-1</sup>	$X_{\rm BS}$	average backscattered light				
			intensity				
$H_{\rm s}$	solidification enthalpy, kJ·kg <sup>-1</sup>	Xi	average transmitted light				
			intensity				
L	length, m	XRD	X-ray diffraction				
n	the number of scans	TGA	thermogravimetric analysis				
Ν	ratio of pumping power	Gree	ek letters				
NESA	nanoencapsulated SA	μ	dynamic viscosity, Pa·s				
O/W	oil-in-water	ρ	density, kg⋅m <sup>-3</sup>				
Р	pumping power, kW	З	the mass fraction				
PCM	phase change material	Δ	change in parameter				
PVP	polyvinylpyrrolidone	Subs	scripts				
Q	heat transfer rate, kW	1	latent				
R	encapsulation ratio	m	melting				
$R_{\rm rel}$	thermal reliability	0	heat transfer oil				
Re	Reynolds number	S	solidification				
SA	sebacic acid	sp	Span 80				
SEM-	scanning electron microscope and	se	sensible				
EDS	energy-dispersive						
Span 80	sorbitan oleate	t	total heat capacity				

## 32 1 Introduction

33 The adoption of clean and sustainable renewable energy sources has emerged as a 34 promising solution to numerous environmental challenges. However, these energy 35 sources are usually intermittent and inefficiently utilized, necessitating the development 36 of effective energy storage technologies. Among these, thermal energy storage systems 37 (TES) systems based on phase change materials (PCMs) have gained significant 38 attention due to their ability to provide high-density heat storage within a narrow 39 temperature range around the phase change temperature. Despite their advantages, 40 practical applications of solid-liquid PCMs are hindered by issues such as melt leakage, 41 corrosion, volume changes, low thermal conductivity, and high supercooling. Various 42 methods, including the provision of extended surfaces like fins or heat pipes [1], the 43 use of multiple PCMs [2], and enhancements targeting the PCM's performance [3], have 44 been proposed to address these limitations. For instance, the addition of thermally 45 conductive nanofillers, such as SiC [4], Cu/graphene oxide [5], boron carbide [6], and 46 carbon quantum dots [7], has been explored to improve thermal conductivity, stability, 47 and supercooling reduction. However, challenges such as particle aggregation, 48 sedimentation, and ensuring long-term cycling stability remain critical barriers [8]. 49 Shape-stable composite PCMs, prepared through porous material adsorption or 50 microencapsulation, offer alternative solutions. Porous material adsorption relies on 51 capillary forces and surface tension to confine PCMs, with expanded graphite being a 52 commonly used material [9]. Meanwhile, microencapsulation forms a core-shell 53 structure that minimizes chemical reactions between the PCM and its environment 54 while controlling volume changes during phase change process.

Despite these advancements, the development of PCMs for medium-temperature applications, such as concentrating solar power systems and industrial waste heat recovery [3, 10], remains insufficient. It was found that up to 5-6% of total energy consumption at 100-300 °C can be recovered and used [11]. Recent studies have highlighted the potential of organic medium-temperature PCMs, particularly sugar 60 alcohols, due to their minimal phase segregation and corrosion compared to inorganic 61 PCMs. However, sugar alcohols suffer from significant drawbacks, including high 62 supercooling and poor thermal stability. For example, erythritol [12], inositol [13], d-63 mannitol [14] and galactitol [15] exhibit supercooling up to 89.3 °C, 43.1 °C, 52.9 °C and 78.1 °C, respectively. High supercooling is undesirable for efficient energy storage 64 65 applications [16], while Solé et al. [15], Neumann et al. [17] and Garcia et al. [18] show 66 remarkable degradation of sugar alcohols under both aerobic and anaerobic conditions. 67 These limitations underscore the need for alternative PCMs with inherently lower 68 supercooling and enhanced thermal stability.

69 In contrast, dicarboxylic acids, another class of organic medium temperature 70 PCMs, exhibit desirable properties such as low supercooling, high latent heat and cost-71 effectiveness. Despite these advantages, their potential as PCMs has been largely 72 overlooked [19]. Sebacic acid (SA), for instance, is an attractive candidate due to its 73 phase change temperature around 130 °C, supercooling below 5 °C, and latent heat 74 exceeding 200 kJ·kg<sup>-1</sup>. Haillot et al. [20] demonstrated SA's excellent thermal stability 75 in nitrogen and air environments, considering it as a promising organic PCM for solar 76 industrial process heat supply and heat recovery. However, most study on SA has 77 focused on its use as a chemical raw material rather than its application in energy 78 storage. To address this gap, recent efforts have explored the encapsulation of DAs 79 using porous materials like expanded graphite [21-24] or carbon nanotube sponges [25, 80 26]. While these approaches mitigate leakage to some extent, the open-pore structure 81 of porous materials limits their sealing performance. Microencapsulation, on the other 82 hand, offers a denser protective shell and enhances heat transfer by reducing PCM size 83 to micrometers or nanometers [27, 28]. Furthermore, nanoencapsulated PCMs can be 84 dispersed in working fluids to form latent heat functional fluids, enabling efficient 85 thermal energy transport and storage [29]. Despite these advantages, research on the 86 encapsulation of water-insoluble dicarboxylic acids remains scarce, with only one study 87 reported on the microencapsulation of a water-soluble dicarboxylic acid for thermal 88 energy storage [8]. This highlights a critical knowledge gap that the current study aims89 to address.

90 To overcome the challenges associated with encapsulating water-insoluble PCMs 91 with melting points exceeding the boiling point of water, this study proposes a novel 92 encapsulation method. Traditional encapsulation methods typically rely on oil-in-water 93 (O/W) emulsion for water-insoluble PCMs or water-in-oil (W/O) emulsion for water-94 soluble PCMs [30-32]. To maintain emulsion stability, the PCM's melting temperature 95 must be significantly lower than the boiling point of the continuous phase. However, 96 for medium-temperature PCMs, where the melting temperature exceeds the boiling 97 point of water, conventional encapsulation methods based on O/W emulsion are 98 unsuitable. Similarly, for water-insoluble PCMs, W/O emulsion-based encapsulation 99 methods also prove ineffective. onsequently, this study focuses on developing a robust 100 encapsulation strategy specifically designed for water-insoluble PCMs. SA was used as 101 the core PCM. To the best of our knowledge, no one has reported nanoencapsulation of 102 SA. Among the available shell materials, inorganic shells like silica are preferred over 103 organic shells due to their superior thermal stability, flame retardancy, and higher 104 thermal conductivity [33, 34]. Silica, in particular, has demonstrated excellent coating 105 properties for carboxylic acid PCMs [8, 35-37], with precursors such as tetraethyl 106 orthosilicate (TEOS) commonly used. However, the high cost and potential toxicity of 107 TEOS limit its scalability for commercial applications. Sodium silicate, an alternative 108 silica precursor, offers a cost-effective and environmentally friendly solution due to its 109 abundance, low cost, and non-toxicity [37-39]. However, only a few experimental 110 studies have explored PCM encapsulation using sodium silicate as a precursor, often 111 resulting in a low encapsulation ratio. This presents another challenge that needs to be 112 addressed in this work. Building on previous research, this study utilizes sodium silicate 113 as the precursor and investigates the influence of pH on the nanoencapsulation process, a key factor in achieving high-quality nanocapsules. This study aims to advance the 114 115 nanoencapsulation of water-insoluble medium-temperature PCMs, providing a

116 foundation for their broader application in thermal energy storage and transfer systems.

# 117 2 Materials and methods

## 118 2.1 Materials

Sebacic acid (SA, C10H18O4, Purity: 99%, Density: 1210 kg·m<sup>-3</sup>, Specific heat of 119 solids: 2.38 kJ·kg<sup>-1</sup>·K<sup>-1</sup>. Specific heat of liquids: 2.41 kJ·kg<sup>-1</sup>·K<sup>-1</sup>, thermal conductivity: 120 0.42 W·m<sup>-1</sup>·K-1) [40] was used as core material and purchased from Shanghai Macklin 121 Reagent Co., Ltd. The precursor sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>•9H<sub>2</sub>O, with 19.3-22.8 wt% 122 of Na<sub>2</sub>O, Density: 2.61 kg·m<sup>-3</sup>) was purchased from Sinopharm Chemical Reagent Co., 123 124 Ltd. The surfactants polyvinylpyrrolidone (PVP, (C<sub>6</sub>H<sub>9</sub>NO)<sub>n</sub>, Purity: 99%, Molecular 125 mass: 284.2, Density: 1140 kg·m<sup>-3</sup>, Melting temperature: 130 °C) and sorbitan oleate 126 (Span 80, C<sub>24</sub>H<sub>44</sub>O<sub>6</sub>, Purity: Chemically Pure, Density: 986 kg·m<sup>-3</sup>) were supplied by 127 Shanghai Aladdin Reagent Co., Ltd. and Sigma-Aldrich Reagent Co., Ltd., respectively. Citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>, Purity: >99.5%, Density: 1670 kg·m<sup>-3</sup>, Melting temperature: 153-128 159 °C, Acidity coefficient: 3.14 pKa) was provided by Tianjin Zhiyuan Chemical 129 130 Reagent Co., Ltd. Heat transfer oil (Great Wall L-QB300, Purity: 99%) was purchased from Guangzhou Maorun Lubricating Oil Co., Ltd. All chemical reagents were of 131 132 reagent quality and were not further purified.

## 133 2.2 Synthesis of nanocapsules

134 The microencapsulation technique includes dispersing PCM particles in water, 135 making a stable aqueous suspension, and finishing the microencapsulation by 136 hydrolysis and condensation reactions of the precursor on the surface of the suspended 137 particles. In theory, this approach can be used to microencapsulate any water-insoluble 138 PCM. The detailed process for synthesizing nanoencapsulated SA (NESA) is as follows. 139 Initially, the SA particles were dispersed in 20 mL deionized water and ultrasonicated 140 for 3 h. The surfactant PVP was then added, maintaining an SA(g): surfactant(g) ratio 141 of 1:1, as referenced from Zhang et al [41]. This specific ratio was chosen to ensure optimal stabilization of the SA particles in the aqueous medium while minimizing 142 aggregation during the process. After continuous stirring at room temperature for 12 h 143

144 to securely attach the PVP to the surface of the SA, the modified SA was washed, 145 collected, and re-dispersed in a three-necked flask heated in an oil bath at 70 °C. 146 Separately, 10 mL of a 10 wt% Na<sub>2</sub>SiO<sub>3</sub>•9H<sub>2</sub>O solution was prepared, and the pH was 147 adjusted to a suitable range by adding citric acid solution. The mixture was constantly 148 agitated until it turned transparent, yielding a silica sol solution containing hydrolyzed 149 silica monomers and oligomers. The resulting silica sol was then introduced dropwise 150 to the flask, where it was attached to the SA particles' surfaces via hydrogen bonding 151 interactions with the surfactant. The polycondensation reaction was completed at 70 °C 152 for 6 h, followed by aging at 80 °C for 4 h. Finally, the product was washed, centrifuged, 153 and freeze-dried to obtain NESA in the form of a white powder.

154 Iler's study [42] demonstrated that neutralizing sodium silicate to an acidic 155 environment increases the Si-OH/Si-O ratio, enhancing the reactivity of functional 156 groups and promoting inter-particle bonding, which ultimately facilitates the formation 157 of 3D gel networks. Based on this finding, citric acid was selected in this study as a 158 safer alternative to hydrochloric acid to regulate and maintain an acidic reaction 159 environment. It is well-established that the pH of the solution significantly influences 160 the gelation process. According to Kristensen et al. [43], the impact of pH often 161 outweighs that of temperature. Numerous studies [42, 44, 45] have shown that silica 162 sols achieve maximum stability at their isoelectric point, where gelation occurs most 163 slowly. Conversely, in the strongly acidic region below the isoelectric point, gelation proceeds extremely rapidly. Both extremes are unfavorable for effective microcapsule 164 165 encapsulation, as overly slow or rapid gelation compromises the uniformity and 166 integrity of the encapsulation shell. To optimize the encapsulation process, we 167 conducted three sets of experiments with pH values ranging between 2.5 and 3.5, based 168 on prior studies [46-48] related to microencapsulation using sodium silicate. These pH 169 conditions were chosen to balance gelation kinetics and encapsulation efficiency, 170 ensuring the formation of robust and uniform nanocapsules.

171

The reaction flow and concept are illustrated in Fig. 1. The polycondensation

172 reaction is primarily driven by dehydrogenation, generating linear silica-oxygen chains 173 that ultimately form a three-dimensional network structure on the surface of the SA 174 particles. Static aging is employed to promote further dehydration and condensation of 175 the gel, thereby completing the consolidation of the silica three-dimensional network. 176 Studies have shown that residual silanol groups on the nanocapsule surface continue to 177 react after gelation, forming new siloxane bonds while releasing water. These newly 178 formed siloxane bonds link the particles closer together, causing the solid skeleton to 179 contract like a spring [49]. Additionally, research [50] has demonstrated that the rate of 180 dehydration and agglomeration accelerates with increasing temperature under acidic 181 conditions. However, achieving complete dehydration may require tens or even 182 hundreds of hours, potentially resulting in severe agglomeration, which negatively 183 impacts the performance of the samples. To address this challenge, we moderately 184 increased the aging temperature to 80 °C and limited the aging time to a few hours, 185 guided by the work of He et al. [46, 47]. This approach aimed to obtain a balance 186 between dehydration efficiency and minimizing nanocapsule agglomeration. The NESA samples produced at pH=2.5, 3.0, and 3.5 were designated as NESA-2.5, NESA-187 188 3.0, and NESA-3.5, respectively, to facilitate subsequent characterization and 189 comparison.





Fig. 1 Schematic of the synthesis process of NESA nanocapsules

## 192 **2.3 Characterization of nanocapsules**

193 The chemical composition and functional group changes of the nanocapsules were 194 analyzed using Fourier transform infrared spectroscopy (FT-IR) with the KBr pellet 195 method, within wavenumber a range of 400 to 4000 cm<sup>-1</sup>. The crystalline structure was 196 characterized by X-ray diffraction (XRD), performed at a scanning rate of 10°/min over 197 a  $2\theta$  range of 5° to 60°.

The phase change properties were measured by differential scanning calorimeter (DSC) at heating and cooling rates of 0.5 °C/min and 10 °C/min, within a temperature range of 90-160 °C. An empty crucible was used as the reference, and nitrogen gas with a flow rate of 50 ml/min served as the protective atmosphere. The thermal stability was assessed through thermogravimetric analysis (TGA), conducted at a heating rate of 200 °C/min over a temperatures range of 40–600 °C.

The morphology and elemental composition of the nanocapsules were examined using scanning electron microscope combined with energy-dispersive X-ray spectroscopy (SEM-EDS). Particle size distribution was measured using a particle size and Zeta potential analyzer (DelsaNano C). The homogeneity and dispersion stability of the nanocapsule suspensions were assessed using a Turbiscan LAB stability analyzer, based on the principle of multiple light scattering.

Thermal conductivity was measured at room temperature using the transient plane source method with a Hot Disk thermal constants analyzer. Specifically, the probe was fully submerged in the center of the liquid sample, and a constant heating power of 70 mW was applied for 5.0 s. The specific heat capacities of solids and liquids were measured using DSC over a temperatures range of -5 °C to 50 °C.

The viscosity of the heat transfer oil and NESA suspensions was measured using a Kinexus Ultra+ rotational rheometer, with the shear rate set between 10 and 1000 s<sup>-1</sup>. A parallel plate fixture with a diameter of 60 mm was used to load an appropriate amount of sample between the measuring plates, ensuring the sample spread evenly across the surface without overflowing. The torque required for rotation was provided

10

by a drag cup motor, which drove the fixture to generate relative motion. This rotational motion induced a shear flow in the sample within the annular gap, applying stress to the sample. The instrument measured the resulting strain or rotational speed and calculated the viscosity of the sample.

Density measurements were performed using a ZMD series electronic densitometer. Table 1 summarizes the instruments used for characterization and provides the accuracy of the respective measurements.

227

#### Table 1 Characterization instruments and their accuracy

Measurement	Instrument	Accuracy	
Morphology and microstructure, surface elemental distribution	SEM, EDS, Hitachi SU8010	NA	
Size distribution	DLS, DelsaNano C	$\pm 1\%$	
Chemical structure	FT-IR, Nicolet 6700	Resolution :2 cm <sup>-1</sup>	
Crystal structure	XRD, Ultima-IV	NA	
Phase change property Specific heat	DSC, Mettler Toledo DSC3	Enthalpy: $\pm 0.05$ % Supercooling degree: $\pm 0.02$ °C	
Dispersion stability of suspensions	Turbiscan LAB stability analyzer	Temperature control: $\pm$ 0.5 °C	
Thermal conductivity	TPS, Hot Disk TPS500S	± 5 %	
Thermal stability	TGA, TG 209 F1	NA	
Viscosity	Kinexus Ultra+ rotational rheometer	±1 %	
Density	ZMD series electronic density meter	$\pm 0.002 \text{ kg} \cdot \text{m}^{-3}$	

## 228 **3 Results and discussion**

## 229 **3.1** Chemical composition of nanocapsules

Fig. 2 presents the FT-IR spectra of SA, SiO<sub>2</sub> and NESA. It can be observed that the FT-IR spectra of these nanocapsules were comparable. The spectrum of SA exhibits two characteristic absorption peaks at 2932 cm<sup>-1</sup> and 2854 cm<sup>-1</sup>, corresponding to the alkyl C-H stretching vibrations of -CH<sub>3</sub> and -CH<sub>2</sub> groups, along with a strong C=O stretching band at 1695 cm<sup>-1</sup> [51, 52]. Additionally, a peak at 1427 cm<sup>-1</sup> is attributed to -CH<sub>2</sub> bending vibration, while the peak at 721 cm<sup>-1</sup> represents the in-plane -CH<sub>2</sub> rocking vibration [23, 25].

The SiO<sub>2</sub> spectrum shows an antisymmetric stretching vibration of Si-O-Si at 1075 cm<sup>-1</sup>, along with symmetrical stretching vibration of Si-O at 796 cm<sup>-1</sup> and 464 cm<sup>-1</sup> [39, 53]. Additionally, a broad absorption band at 3446 cm<sup>-1</sup> is assigned to the Si-OH stretching vibration [34].

All characteristic peaks of both SA and silica are clearly identifiable in the NESA spectra, confirming that the silica condensation was successfully achieved to form the nanocapsule shell under different pH conditions. Notably, no new peaks appeared or disappeared in the NESA spectra, indicating that the interaction between the core SA and shell SiO<sub>2</sub> is purely physical, with no chemical bonding occurring between them.





Fig. 2 FT-IR spectra of SA, SiO<sub>2</sub> and NESA nanocapsules

## 248 3.2 Crystal structure of nanocapsules

249 The crystal structures of SA, SiO<sub>2</sub> and NESA were further investigated by XRD,

and the results are shown in Fig. 3, where  $2\theta$  represents the angle between the incident

and the diffracted light.

252 This indicates that no chemical reaction occurred during the encapsulation process,

which is consistent with the findings from the FTIR analysis.

254 The prominent diffraction peaks observed at  $2\theta = 8.1^{\circ}$ ,  $21.5^{\circ}$ ,  $24.1^{\circ}$ ,  $26.4^{\circ}$ , and 30.1° confirm the regular crystallization of pure SA [23]. These characteristic peaks are 255 256 also present in the XRD patterns of all NESA samples; however, their intensities are 257 somewhat reduced, likely due to the crystallization process being constrained by the SiO<sub>2</sub> shell. Additionally, a broad and diffuse diffraction peak typically found between 258 20-30° for SiO<sub>2</sub>, is not visible in the patterns, suggesting that the SiO<sub>2</sub> synthesized in 259 260 this study is predominantly amorphous silica [54]. Overall, no new peaks emerged, nor 261 did any original peaks disappeared, and the positions of the peaks for all NESA samples 262 remained nearly identical to those of pure SA. This indicates that no chemical reaction 263 occurred during the encapsulation process, which is consistent with the findings from 264 the FTIR analysis.





Fig. 3 XRD patterns of SA, SiO<sub>2</sub> and NESA nanocapsules

## 267 **3.3 Phase change behavior of nanocapsules**

DSC analysis was used to study the thermal properties of the samples, including their melting and freezing temperatures as well as latent heat. Many researchers concur that lower heating and cooling rates, even below 1 °C/min, are beneficial for identifying phase change temperatures with greater accuracy. However, this often comes at the expense of increased enthalpy errors and longer measurement times [55, 56]. In fact, for PCMs with lower purity or polycrystalline morphology, a slower scan rate is typically preferred to prevent the disappearance or merging of peaks, as these materials
may undergo phase changes across multiple temperature ranges [57]. Consequently, the
choice of scan rate must be tailored to the specific cases.

277 We conducted DSC tests of SA samples at two different scan rates: 0.5 °C/min and 278 10 °C/min. The results are presented in Fig. 4 and Table 2. The phase change 279 temperature points ( $T_{\rm m}$  and  $T_{\rm s}$ ) were determined by intersecting the extrapolated 280 baseline with a tangent line drawn at the inflection point on the leading edge of the heat 281 flow curve's peak. It is evident that as the heating rate increases, the melting peaks shift 282 toward higher temperatures, and the peak profiles become broader, which aligns with 283 previous findings. Furthermore, the absence of multiple peaks indicates the high purity 284 of the SA sample. The deviations in melting and solidification temperatures were 285 calculated to be 0.68% and 1.48%, respectively, while the deviations in the enthalpy of 286 melting and enthalpy of solidification were found to be 3.64% and 3.21%, respectively, 287 for the two scanning rates. After comparing the uncertainty and test time costs at the 288 two scanning rates, we selected a scan rate of 10 °C/min, which is widely recognized 289 as the most common scan rate for conventional materials. Table 2 shows that the phase 290 change properties of the SA samples observed in this study are similar to those 291 published in the literature, indicating the validity of the experimental data in this work.





Fig. 4 DSC curves of SA at different heating and cooling rates

Table 2 Comparison of phase change properties of SA with literature

Ref.	Mass(mg)	Heating/cooling rate (°C/min)	$T_{\rm m}(^{\circ}{\rm C})$	$H_{\rm m}(\rm kJ\cdot \rm kg^{-1})$	T₅(°C)	$H_{\rm s}({\rm kJ}\cdot{\rm kg}^{-1})$
Present	9.72	0.5	133.2	230.5	128.0	224.8
Present	8.20	10	132.3	222.4	129.9	217.8
[23]	NA	10	133.3	222.4	128.9	217.6
[25]	NA	10	129.7	219.6	127.2	216.8
[26]	NA	5	131.7	222.3	129.8	222.1

295 Figure 5 and Table 3 demonstrate that both SA and NESA exhibit similar melting 296 and crystallization behaviors, characterized by a single fusion peak (downward) and 297 crystallization peak (upward). However, the phase change enthalpy of pure SA is 298 significantly higher than that of NESA. This difference can be attributed to the fact that 299 only SA absorbs and releases thermal energy during heating and cooling, while the SiO<sub>2</sub> 300 shell does not contribute to the phase change enthalpy and reduces the proportion of the 301 SA core within the nanocapsules. Two key parameters, the encapsulation ratio (R) and 302 the encapsulation efficiency (E), are used to characterize the phase change behavior of 303 NESA. These parameters can be calculated using the following equations.

304

305

$$R = (\Delta H_{\rm m,NESA} / \Delta H_{\rm m,SA}) \times 100\%$$
<sup>(1)</sup>

$$E = (\Delta H_{\rm m,NESA} + \Delta H_{\rm s,NESA} / \Delta H_{\rm m,SA} + \Delta H_{\rm s,SA}) \times 100\%$$
(2)

306 where  $\Delta H_{\text{m,NASA}}$  and  $\Delta H_{\text{s,NASA}}$  represent the melting enthalpy and freezing enthalpy of 307 NESA, respectively, while  $\Delta H_{m,SA}$  and  $\Delta H_{s,SA}$  represent the melting enthalpy and 308 freezing enthalpy of the pure SA, respectively. The NESA-3.0 nanocapsules exhibited 309 the highest encapsulation ratio and efficiency, reaching 73.9% and 74.0%, respectively. 310 Additionally, both the initial melting and solidification temperatures of the NESA 311 samples shifted slightly toward lower values, with the temperature change not 312 exceeding 2.0 °C. The decrease in melting temperature may be attributed to both weak 313 core-shell interactions and increased thermal conductivity [58]. Meanwhile, the 314 reduction in solidification temperature could be related to the small sample size used in 315 the DSC experiments, typically less than 10 mg [14].

316 Similar findings were reported by Fu et al. [59], who encapsulated stearic acid within a

SiO<sub>2</sub> shell, resulting in a melting point reduction ranging from 1.3 to 3.3 °C. Likewise, Cao et al. [60] encapsulated palmitic acid in a TiO<sub>2</sub> shell, observing decrease in melting and freezing temperatures of 0.9 and 3.8 °C, respectively. Furthermore, the broader peak shape observed for NESA compared to pure SA can be attributed to the constrained crystallization of SA caused by the silica shell, which restricts the mobility of SA molecules. Notably, the supercooling degree of all samples remained below 3.0 °C, which is advantageous for TES applications.



Table 3 DSC data of SA and the NESA nanocapsules

Samples	Mass(mg)	$T_{\rm m}(^{\circ}{\rm C})$	$H_{\rm m}({\rm kJ}{\cdot}{\rm kg}^{-1})$	$T_{\rm s}(^{\circ}{\rm C})$	$H_{\rm s}({\rm kJ}\cdot{\rm kg}^{-1})$	$\triangle T(^{\circ}C)$	<i>R</i> (%)	E(%)
SA	8.20	132.3	222.4	129.9	217.8	2.4	NA	NA
NESA-2.5	5.72	132.3	145.4	129.4	141.5	2.9	65.4	65.2
NESA-3.0	7.10	130.5	164.4	128.5	161.3	2.0	73.9	74.0
NESA-3.5	7.45	128.3	128.1	127.9	126.3	0.4	57.6	57.8



325 326

Fig. 5 DSC curves of SA and NESA nanocapsules

The NESA sample with the highest encapsulation ratio, designated as NESA-3.0, was selected and renamed NESA for subsequent testing. Table 4 compares the key parameters of the synthesized NESA with other micro/nanocapsules reported in the literature. The results reveal that the present nanocapsules are unique in containing water-insoluble PCM with a medium melting temperature, whereas other reported capsules typically encapsulate either water-soluble PCMs or water-insoluble PCMs 333 with melting temperatures below 100 °C. Notably, the current nanocapsules exhibit

334 significant competitive advantages, including a high phase change enthalpy, minimal

335 supercooling degree, and high encapsulation ratio and efficiency.

336	Table 4 Comparison of	present nanocansules	to those prepared w	with sodium silicate as a
550	Table 4 Comparison of	present nanocapsules	to mose prepared v	and source as a

337

precursor in the literature.

Ref.	Samples	$T_{\rm m}(^{\circ}{\rm C})$	$H_{\rm m}({\rm kJ}{\cdot}{\rm kg}^{-1})$	$H_{\rm s}({\rm kJ}\cdot{\rm kg}^{-1})$	$\triangle T(^{\circ}C)$	<i>R</i> (%)	E(%)
[47]	n-Octadecane@SiO <sub>2</sub>	28.0	87.5	84.9	6.1	41.8	41.5
[46]	n-Heptadecane@SiO <sub>2</sub>	21.9,10.5	60.3	61.4	NA	30.9	30.5
[46]	$n\text{-}Octadecane@SiO_2$	32.6	73.5	72.2	NA	35.6	35.2
[46]	n-Nonadecane@SiO <sub>2</sub>	36.9, 25.8	74.8	80.8	NA	41.1	40.6
[46]	n-Eicosane@SiO <sub>2</sub>	40.5	81.2	78.6	NA	33.0	32.5
[61]	Palmitic acid@SiO <sub>2</sub>	67.2	47.8	41.3	9.2	43.0	41.5
[62]	Na <sub>2</sub> SO <sub>4</sub> @SiO <sub>2</sub>	886.0	82.3	83.7	5.4	49.3	49.0
[63]	n-Dodecanol@SiO2	21.0	116.7	114.6	5.9	55.5	55.2
[52]	Paraffin@SiO <sub>2</sub>	26.1	111.7	110.8	2.8	61.9	61.8
[48]	Paraffin@SiO <sub>2</sub>	47.7	186.4	183.2	15.4	74.1	73.7
[64]	Paraffin@SiO <sub>2</sub>	55.2	94.4	93.2	8.30	74.5	75.6
[65]	Polyethylene glycol@SiO <sub>2</sub>	58.1	151.8	141.0	15.8	79.3	80.6
[66]	Palmitic acid@SiO <sub>2</sub>	61.3	163.1	166.5	4.2	82.0	82.5
Present	SA@SiO <sub>2</sub>	130.5	164.4	161.3	2.0	73.9	74.0

### 338 **3.4 Morphology and elemental composition of nanocapsules**

The morphology of SA and NESA was investigated using SEM, as shown in Fig. 6. Pure SA particles typically exhibit a smooth, irregularly surface with relatively large particle sizes ranging from tens to hundreds of micrometers. In contrast, the NESA samples display a more spherical shape with a uniform profile, and their particle sizes are reduced to the nanoscale scale. Undoubtedly, the smaller particle size and increased specific surface area of the nanocapsules contribute to enhanced heat transfer rates.

However, it is worth noting that the nanocapsules exhibit a considerable degree of agglomeration. This phenomenon can be explained by two factors: On the one hand, the free hydroxyl groups on the silica shells may attract nearby nanocapsules through hydrogen bonding [65], a common occurrence in the synthesis of microcapsules using sodium silicate as a precursor. On the other hand, agglomeration may result from
particle-particle interactions during sample preparation, such as drying for SEM
observation [67, 68].



352353

## Fig. 6 SEM of (a) SA and (b) NESA nanocapsules

Fig. 7 shows the particle size distribution of the NESA. The nanocapsules exhibit a particle size range of approximately 200–500 nm, with the most prominent peak occurring at 250 nm. The size distribution of the nanocapsules is reasonably uniform, consistent with the observations from the SEM image.



358 359

Fig. 7 Particle size distribution of NESA nanocapsules

Fig. 8 and Table 5 present the mapping image and energy-dispersive X-ray spectroscopy (EDS) analysis report of NESA, respectively, providing further confirmation of the successful preparation and element distribution of the nanocapsules. The mapping image of Si and O components closely align with the contour of the nanocapsules, confirming that the shell is composed silicon dioxide. Additionally, Table 365 4 provides the semi-quantitative EDS analysis results for the key elements C, O, and Si

366 [69]. It is worth noting that H could not be detected due to its low characteristic367 radiation energy.



369

370

### Fig. 8 EDS mapping of NESA

Table 5 EDS data of NESA							
Element	Atomic (%)	Conc. (wt.%)					
С	31.27	22.66					
0	53.65	51.79					
Si	15.08	25.55					

# **371 3.6 Thermal stability of nanocapsules**

372 Fig. 9 presents the TGA curves of SA and NESA. The NESA sample exhibits 373 minimal weight loss below 100°C, suggesting that water adsorbed on the sample's 374 surface and residual solvents were not fully evaporated prior to testing [70]. The initial 375 decomposition temperature of SA is approximately 200 °C, whereas for NESA, it is elevated to 250 °C. This increase in the initial decomposition temperature can be 376 377 attributed to the silica encapsulation, which prevents direct contact between SA and 378 oxygen, thereby reducing thermal degradation. This is further supported by the more 379 gradual thermal degradation curve observed for NESA [14].

Upon increasing the temperature to over 500 °C, nearly no residue remains for pure SA, indicating complete evaporation of the material. In contrast, NESA shows an 82.0% weight decrease. This slight deviation from the previously calculated encapsulation ratio of 73.9% is commonly observed in microcapsules synthesized using sodium silicate as a precursor [46, 63, 71]. The additional weight loss observed at high temperatures may be attributed to the subsequent condensation and dehydration of residual silanol groups within the silica shell, as discussed in Section 2.2.

387 In summary, the thermal degradation temperature of the synthesized NESA is

388 substantially higher than its phase change temperature, underscoring its suitability for







#### Fig. 9 TGA curve of SA and NESA nanocapsules

## 392 **3.7 Thermal reliability of nanocapsules**

The thermal reliability of NESA was assessed through 50 melt-solidification cycles. The NESA sample was heated from 25 °C to 160 °C at a rate of 10 °C/min in a chamber furnace and subsequently cooled to room temperature. Fig. 10 and Table 6 show the phase change characteristics of the samples over each ten representative cycles. The thermal reliability is defined as the ratio of post-cycling to pre-cycling encapsulation efficiency, as expressed in Eq. (3).

399

$$R_{\rm rel} = E_{\rm tc}/E_0 \tag{3}$$

where  $E_0$  and  $E_{tc}$  represent the encapsulation efficiency before and after thermal cycling, 400 respectively. Table 6 presents the thermal reliability results calculated using Eq. (3). The 401 402 thermal reliability of the nanocapsules stabilizes 94.5% after 50 thermal cycles, 403 suggesting that encapsulating SA within a silica shell effectively minimizes leakage. 404 Additionally, the DSC peak patterns before and after cycling were nearly identical, 405 indicating negligible changes in thermal storage performance and confirming that the 406 nanocapsules maintained their thermal stability through repeated heat absorption and 407 release cycles.



## 408



Fig. 10 Phase change curves of NESA before and after thermal cycling

410

Table 6 Phase change characteristics of NESA after different thermal cycles

Number of cycles	$T_{\rm m}(^{\circ}{\rm C})$	$H_{\rm m}(\rm kJ\cdot \rm kg^{-1})$	$T_{\rm s}$ (°C)	$H_{\rm s}({\rm kJ}\cdot{\rm kg}^{-1})$	$R_{\rm rel}$ (%)
1st	130.5	164.4	128.5	161.3	NA
10th	130.5	162.2	127.8	157.9	98.3
20th	130.5	159.9	127.3	156.1	97.0
30th	131.0	160.8	126.3	157.2	97.6
40th	130.7	154.3	125.8	149.9	93.4
50th	130.7	155.8	126.8	151.9	94.5

## 411 **3.8 Dispersion stability of naocapsule suspensions**

412 Suspensions of NESA and SA were evaluated for dispersion stability and thermal 413 conductivity. At room temperature, 1.0 wt% NESA or SA particles were dispersed in 414 heat transfer oil with an equal proportion of the surfactant Span 80. The mixtures were 415 sonicated for 30 min and magnetically stirred for an additional 20 min.

The dispersion stability of the suspensions over time was monitored using a Turbiscan® Stability Analyzer, with the results shown in Fig. 11. The transmission and backscattering light intensity profiles of the NESA suspension remain nearly horizontal at various heights and exhibit minimal changes over time, demonstrating good dispersion stability. In contrast, significant variations are observed in the transmission and backscattering light profiles of the SA suspension, likely due to aggregation and

## 422 sedimentation of the nanocapsules.



424 Fig. 11 Transmission and backscattering curves of (a) NESA suspension and (b) SA suspension 425 Furthermore, the Turbiscan stability index (TSI) of the suspensions was calculated 426 using the measured average transmitted light intensity  $(X_i)$ , average backscattered light 427 intensity  $(X_{BS})$ , and the number of scans (n), as shown in Eq. (4). The TSI results are 428 shown in Fig. 12. The NESA suspension exhibits lower TSI values, and since a lower 429 TSI corresponds to greater suspension stability [72], this confirms the superior stability of the NESA suspension. These findings align with the earlier analysis of the 430 431 transmission and backscattering data.

432 
$$TSI = \sqrt{\sum_{i=1}^{n} (X_i - X_{BS})^2 / (n-1)}$$
(4)





Fig. 12 TSI of the SA and NESA suspension

## 435 **3.9** Thermophysical properties, pumping power evaluation and economic analysis

436 Figure 13 shows that the base fluid exhibits a thermal conductivity of 0.124 W·m<sup>-</sup> 437 <sup>1</sup>·K<sup>-1</sup>, consistent with values reported in previous studies [73, 74]. Suspensions 438 containing particles demonstrated enhanced thermal conductivity, with NESA 439 suspensions showing the most significant improvement, approximately 15.0%. 440 Typically, nanoparticles with high intrinsic thermal conductivity are known to produce 441 nanofluids with high thermal conductivity [75]. Therefore, it is reasonable to attribute 442 the substantial enhancement in thermal conductivity of the NESA suspensions to their 443 nanoscale size and the incorporation of inorganic silica shells, which themselves 444 possess high thermal conductivity. Furthermore, maintaining uniform dispersion of the 445 nanoparticles further contributes to the improved thermal conductivity of the 446 suspensions [76].





Fig. 13 Thermal conductivity of suspensions and enhancement percentage

In heat storage systems, determining the power consumption for fluid pumping is critical since it directly impacts both energy efficiency and economic feasibility. Microencapsulation and dispersion of PCMs in base fluids allow them to be transported as latent heat functional fluids. This approach prevents PCM freezing on heat transfer surfaces during the phase change process, ensuring consistent fluidity regardless of the PCM's state. Such fluidity facilitates the efficient transportation and pumping of phase change slurries.

456 It is important to note that nanocapsule suspensions are more viscous than the base 457 fluid. However, the presence of latent heat significantly enhances the heat storage 458 capacity while reducing the required pumping flow rate to transfer the same heat load, 459 potentially lowering overall pumping power requirements. Based on the considerations, 460 we compared the pumping power consumption of the base fluid and the NESA 461 suspension when transferring the same amount of thermal energy. The goal was to 462 assess whether the NESA suspension offers an advantage in terms of reduced energy 463 consumption.

Considering the requirements of practical applications, a higher concentration gradient of 10.0 wt% was prepared. To further investigate the sensitivity of the thermophysical properties of NESA and its suspension to temperature variations, and to understand how these variations influence the power consumption for pipeline 468 pumping, experiments were conducted at 25 °C and 45 °C, respectively. Equation (5) is 469 used to calculate pumping power for heat transfer oil ( $P_o$ ) and NESA suspension 470 ( $P_{suspension}$ ), taking into account the viscosity ( $\mu$ ), velocity (u) and pipe length (L) of the 471 corresponding fluid.

472

$$P = 8L\mu\pi u^2 \tag{5}$$

473 Equation (6) defines N as the ratio of the NESA suspension's pumping power to474 that of the heat transfer oil.

475

$$N = P_{\rm suspension} / P_{\rm o} \tag{6}$$

The test data for viscosity are shown in Fig. 14, illustrating pipeline flows at 476 477 different temperatures for shear rates ranging from 10 to 1000 s<sup>-1</sup>. From Fig. 14(a), it is 478 evident that the viscosity (dynamic viscosity) of the NESA suspensions at 25 °C 479 increases with increasing NESA concentration. The 1.0 wt% NESA suspension exhibits 480 a low viscosity that is extremely close to that of the heat transfer oil base fluid. However, 481 as the concentration of NESA nanocapsules increases to 10.0 wt%, the viscosity rises 482 significantly. This increase is attributed to the reduction in interparticle distances, 483 leading to stronger nanocapsule interactions [77].

484 The viscosity of the NESA suspensions at 45 °C are shown in Fig. 14(b). The 485 viscosity of all samples decreases substantially with increasing temperature. This 486 phenomenon is caused by the intensified thermal motion of molecules at higher 487 temperatures, which weakens the intermolecular forces of attraction [78]. As shown in 488 Fig. 14(b), the viscosity of the 1.0 wt% NESA suspension remains relatively constant 489 across different shear rates, demonstrating Newtonian fluid behavior similar to the base 490 solution. This behavior is attributed to the high degree of dispersion and minimal 491 agglomeration of NESA in the suspension. In contrast, the 10.0 wt% NESA suspension 492 exhibits shear-thinning non-Newtonian fluid characteristics. At high mass 493 concentrations, the reduced nanocapsule spacing causes nanocapsule motion to be more 494 easily influenced and restricted by neighboring nanocapsules, varying with the shear 495 rate. At low shear rates, Brownian motion dominates, causing nanocapsules to 496 agglomerate into clusters, resulting in higher viscosity. As the shear rate increases, some 497 agglomerates break down into smaller aggregates or individual nanocapsules, leading 498 to shear thinning [79]. In fact, there exists a critical shear rate above which the 499 suspension will exhibit Newtonian fluid behavior, with higher concentrations requiring higher critical shear rates [80]. From an application standpoint, shear thinning is 500 501 advantageous because industrial processes and pumping operations are typically 502 conducted under medium- to high-velocity shear rates. For the calculations, the viscosity at a shear rate of 1000 s<sup>-1</sup> was selected, as this represents a typical shear rate 503 504 for pipeline flow [81].



506 Fig. 14 Viscosity of base fluid and NESA suspensions at (a) 25 °C and (b) 45 °C

505

507 Equations (7) and (8) were used to calculate the volumetric flow rate ( $G_{suspension}$ ) 508 of heat transfer oil ( $G_{o}$ ) and NESA suspension ( $G_{suspension}$ ), respectively.

$$G_o = Q/\rho_0 c_{\rm p,o} \Delta T \tag{7}$$

510 
$$G_{\text{suspension}} = Q/(\rho_{\text{suspension}}\Delta h_{t,\text{suspension}})$$
(8)

511 where Q is the heat transfer rate and  $\Delta T$  is the heat transfer temperature difference. The 512 density  $\rho_0$  and specific heat  $c_{p,0}$  of the heat transfer oil, the density  $\rho_{suspension}$  and total heat 513 capacity  $\Delta h_t$  of the NESA suspension were measured experimentally.

514 The total heat capacity of the NESA suspension consists of both latent and sensible515 heat components.

516 
$$\Delta h_{t,\text{suspension}} = \Delta h_l + \Delta h_{\text{se}}$$
(9)

517 
$$\Delta h_{t,\text{suspension}} = \varepsilon_{\text{NESA}} \Delta h_{\text{l,NESA}} + \varepsilon_{\text{o}} \Delta h_{\text{se,o}} + \varepsilon_{\text{sp}} \Delta h_{\text{se,sp}} + \varepsilon_{\text{NESA}} \Delta h_{\text{se,NESA}}$$
(10)

518 
$$\Delta h_{t,\text{suspension}} = \varepsilon_{\text{NESA}} \Delta h_{\text{l,NESA}} + \varepsilon_{\text{o}} c_{\text{p,o}} \Delta T + \varepsilon_{\text{sp}} c_{\text{p,sp}} \Delta T + \varepsilon_{\text{NESA}} c_{\text{p,NESA}} \Delta T \quad (11)$$

519 where  $\varepsilon_{\text{NESA}}$ ,  $\varepsilon_{0}$  and  $\varepsilon_{\text{sp}}$  represent the mass fraction of NESA, base fluid and surfactant 520 Span 80, respectively, and  $c_{p,NESA}$ ,  $c_{p,o}$  and  $c_{p,sp}$  represent the specific heat of NESA, base 521 fluid and surfactant Span 80, respectively. Chen et al. [82] demonstrated that, for a 522 specified heat transfer capacity, minimizing pumping power is more effectively achieved 523 by enhancing the heat storage density of the heat transfer fluid rather than transitioning 524 to turbulent flow conditions. This optimization is accomplished by adjusting the 525 concentration of nanocapsules dispersed in the fluid. Specifically, when the heat transfer 526 demand increases, the pumping power consumption associated with raising the 527 concentration of nanocapsules in the suspension is significantly lower than the pumping 528 power required to achieve turbulent flow. Consequently, table 7 presents flow conditions 529 and characteristics that align with the assumptions for operating within the laminar flow regime. It demonstrates that, although the NESA suspensions exhibit higher viscosity 530 531 compared to the base fluid, the presence of latent heat enables a lower flow rate to 532 transfer the same amount of heat.

533

Table 7 Flow conditions of heat transfer oil and NESA suspensions

Dawawaataw	Tananatana	II. at the offen all	NESA su	spensions	NECA	Span 80	
Parameter	Temperature	Heat transfer off	1.0 wt%	10.0 wt%	NESA		
D	25°C	769.8	654.1	188.0	NA	NA	
ĸe	45°C	2189.1	1936.5	507.1	NA	NA	
$C(m^3 r^{-1})$	25°C	0.94×10 <sup>-3</sup>	0.80×10 <sup>-3</sup>	0.35×10 <sup>-3</sup>	NA	NA	
$G(m^{1},s^{1})$	45°C	0.92×10 <sup>-3</sup>	0.79×10 <sup>-3</sup>	0.34×10 <sup>-3</sup>	NA	NA	
(m, a <sup>-1</sup> )	25°C	2.99	2.55	1.11	NA	NA	
u (m·s)	45°C	2.92	2.51	1.09	NA	NA	
(1-2, 2-3)	25°C	868.5	879.0	900.3	NA	NA	
$\rho(\text{kg·m}^{+})$	45°C	859.8	864.4	890.8	NA	NA	
$u(\mathbf{D}_{\mathbf{a}},\mathbf{a})$	25°C	0.06737	0.06842	0.1066	NT A	NTA	
$\mu$ (Pa·S)	45°C	0.02290	0.02237	0.03843	NA	NA	
a (let. lea-l. K-l)	25°C	1.74	NA	NA	1.51	2.20	
$C_{\rm p}({\rm KJ}^{\rm K}{\rm Kg}^{\rm K}{\rm K})$	45°C	1.80	NA	NA	1.97	2.53	
<i>d</i> (m)			0.02 [82]				
$\triangle T$ (°C)			6 [82]				

Q(kW)

534	The total heat capacity and pumping power for the NESA suspensions and heat
535	transfer oil are presented in Table 8. The results indicate that the total heat capacity of
536	the NESA suspensions increases with the mass fraction of nanocapsules. For instance,
537	the total heat capacity of the 10.0 wt% NESA suspension is more than twice that of the
538	base oil, allowing for enhanced heat exchange within the laminar flow range while
539	avoiding significant increases in pressure drop and pumping power. At 25 and 45 °C, the
540	10.0 wt% NESA suspension reduces pumping power by 78% and 76%, respectively,
541	achieving substantial energy savings.

	Heat transfer oil		1.0 wt% NESA suspension		10.0 wt% NESA suspension	
	25 °C	45 °C	25 °C	45 °C	25 °C	45 °C
$\Delta h_{\rm t} ({\rm kJ} \cdot {\rm kg}^{-1})$	10.44	10.80	12.10	12.50	21.02	27.78
P(kW)	15.08	4.89	11.14	3.53	3.32	1.16
N	1.00	1.00	0.74	0.72	0.22	0.24

## Table 8 Total heat capacities and pumping power

# 543 4 Conclusions

542

544 Silica-coated sebacic acid nanocapsules with industrial applications were prepared 545 using sodium silicate as precursor. A series of characterization means proved their 546 superior thermal properties. The specific conclusions are as follows.

547 (1) Sebacic acid was successfully encapsulated into nanocapsules, exhibiting a
548 spherical morphology and uniform particle size distribution in the range of 200–500
549 nm.

550 (2) The sebacic acid nanocapsules demonstrated a melting point of 130.5 °C, with 551 a latent heat of 164.4 kJ·kg<sup>-1</sup> and an encapsulation ratio of 73.9%. The supercooling 552 degree of the nanocapsules was less than 3.0 °C.

553 (3) The sebacic acid nanocapsules exhibited excellent thermal stability and 554 reliability. After 50 melting-solidification cycles, the melting enthalpy remained high 555 at 155.8 kJ·kg<sup>-1</sup>, achieving a steady thermal reliability of 94.5%. Under the effective protection of a silica shell, the nanocapsules also displayed a higher thermal degradationtemperature.

(4) Suspensions of sebacic acid nanocapsules exhibit significantly improved suspension stability and thermal conductivity. Due to their excellent thermal storage capacity, these nanocapsules can substantially reduce pumping power requirements in pipeline flow, thereby enhancing energy efficiency and decreasing reliance on fossil fuels.

However, this study has certain limitations that warrant further investigation in thefuture.

565 (1) In the preparation process, the influencing factors of the nanocapsule reaction 566 process can be explored more comprehensively. For instance, parameters such as the 567 reaction temperature, the amount of surfactant, and the concentration of precursor 568 solutions could be systematically optimized.

569 (2) Regarding performance characterization, a more thorough investigation of the 570 thermophysical properties of the nanocapsules and their suspensions is necessary. This 571 could include setting finer temperature gradients and concentration gradients to reveal 572 detailed trends governing their variation.

Although the nanoencapsulation of dicarboxylic acids remains at the laboratory synthesis and characterization stage, this study addresses a significant gap in the micro/nano-encapsulation of water-insoluble phase change materials with medium- and high-melting temperatures, advancing their application in the field of thermal energy storage.

## 578 Credit authorship contribution statement

Songping Mo: Conceptualization, Funding acquisition, Methodology, Project
administration, Supervision, Writing-original draft, Writing-review & editing. Jiaxuan
Li: Investigation, Methodology, Writing-original draft. Yuxuan Lin: Investigation. Zhi
Yang: Writing-review & editing. Zhibin Wang: Writing-review & editing. Lisi Jia:
Writing-review & editing. Yanping Du: Writing-review & editing. Ying Chen:

584 Resources.

#### **Declaration of competing interest** 585

- 586 The authors declare that they have no known competing financial interests or
- 587 personal relationships that could have appeared to influence this work.

#### **Data availability** 588

589 Data will be made available on request.

#### 590 Acknowledgements

591 This work was supported by the National Natural Science Foundation of China

592 [grant number 51976040].

#### Reference 593

594 [1] A. Tavakoli, J. Hashemi, M. Najafian, A. Ebrahimi, Physics-based modelling and 595 data-driven optimisation of a latent heat thermal energy storage system with corrugated 596 fins, Renew. Energ. 217 (2023) 119200.

- 597 [2] Z.P. Hu, A.G. Li, R. Gao, H.G. Yin, Enhanced heat transfer for PCM melting in the 598 frustum-shaped unit with multiple PCMs, J. Therm. Anal. Calorim. 120 (2015) 1407-599 1416.
- 600 [3] H. Nazir, M. Batool, F.J.B. Osorio, M. Isaza-Ruiz, X.H. Xu, K. Vignarooban, P. Phelan, Inamuddin, A.M. Kannan, Recent developments in phase change materials for 601 energy storage applications: A review, Int. J. Heat Mass Tran. 129 (2019) 491-523. 602
- [4] H. Fayaz, S. Ramesh, A. Afzal, Ü. Agbulut, S.A. Khan, M. Asif, V. Raja, E. Linul,
- 603 604 Investigation of numerical phase transition of nano-enhanced SiC/paraffin wax PCM in 605 solar-assisted water desalination system, Therm. Sci. Eng. Prog. 50 (2024) 102528.
- [5] M. Ghalambaz, S.A.M. Mehryan, A. Veismoradi, M. Mahdavi, I. Zahmatkesh, Z. 606
- Kazemi, O. Younis, M. Ghalambaz, A.J. Chamkha, Melting process of the nano-607 608 enhanced phase change material (NePCM) in an optimized design of shell and tube 609 thermal energy storage (TES): Taguchi optimization approach, Appl. Therm. Eng. 193 (2021) 116945. 610
- 611 [6] H.F. Öztop, E. Gürgenç, M. Gür, Thermophysical properties and enhancement
- behavior of novel B4C-nanoadditive RT35HC nanocomposite phase change materials: 612
- 613 Structural, morphological, thermal energy storage and thermal stability, Sol. Energ. Mat. 614 Sol. C. 272 (2024) 112909.
- 615 [7] J. Emeema, G. Murali, B.V. Reddi, V.L. Mangesh, Investigations on paraffin
- 616 wax/CQD composite phase change material - Improved latent heat and thermal stability,
- 617 J. Energy Storage. 85 (2024) 111056.

- [8] J.X. Li, S.P. Mo, B. Xiao, Q. Li, L.S. Jia, Y. Chen, A novel microencapsulated 618
- 619 medium-temperature phase change material employing dicarboxylic acid for thermal 620 energy storage, Appl. Therm. Eng. 255 (2024) 123970.
- 621 [9] A. Islam, A.K. Pandey, R. Saidur, V.V. Tyagi, Shape stable composite phase change 622 material with improved thermal conductivity for electrical-to-thermal energy 623 conversion and storage, Mater. Today Sustain. 25 (2024) 100678.
- 624 [10] Z. Li, Z.G. Wu, Development of medium-temperature composite phase change 625 material with high thermal stability and conductivity, Sol. Energ. Mat. Sol. C. 155 (2016)
- 626 341-347.
- 627 [11] R. Tamme, T. Bauer, J. Buschle, D. Laing, H. Müller-Steinhagen, W.D. Steinmann,
- 628 Latent heat storage above 120°C for applications in the industrial process heat sector 629 and solar power generation, Int. J. Energ. Res. 32 (2008) 264-271.
- 630 [12] Z.Y. Zhang, Q. Jiang, M. Chen, K.L. Diao, M.C. Yang, Y.Z. Zhu, Experimental
- study of erythritol SiO<sub>2</sub> phase change nanocapsules for medium temperature thermal 631 632 storage, Appl. Therm. Eng. 239 (2024) 122167.
- 633 [13] X.F. Shao, C. Wang, Y.J. Yang, B. Feng, Z.Q. Zhu, W.J. Wang, Y. Zeng, L.W. Fan, 634 Screening of sugar alcohols and their binary eutectic mixtures as phase change materials for low-to-medium temperature latent heat storage. (I): Non-isothermal 635 melting and crystallization behaviors, Energy. 160 (2018) 1078-1090. 636
- 637 [14] L.J. He, S.P. Mo, P.C. Lin, L.S. Jia, Y. Chen, Z.D. Cheng, Synthesis and properties 638 of nanoencapsulated D-mannitol for medium temperature thermal energy storage, Sol. 639 Energ. Mat. Sol. C. 209 (2020) 110473.
- [15] A. Solé, H. Neumann, S. Niedermaier, I. Martorell, P. Schossig, L.E. Cabeza, 640 641 Stability of sugar alcohols as PCM for thermal energy storage, Sol. Energ. Mat. Sol. C. 642 126 (2014) 125-134.
- 643 [16] L. Piquard, E. Gagnière, G. Largiller, D. Mangin, F. Bentivoglio, Xylitol used as phase change material: Nucleation mechanisms of the supercooling rupture by stirring, 644
- 645 J. Energy Storage. 48 (2022) 103922.
- 646 [17] H. Neumann, S. Niedermaier, S. Gschwander, P. Schossig, Cycling stability of D-
- 647 mannitol when used as phase change material for thermal storage applications, 648 Thermochim. Acta. 660 (2018) 134-143.
- 649 [18] M.M. Rodríguez-García, R. Bayón, E. Rojas, Stability of D-mannitol upon 650 melting/freezing cycles under controlled inert atmosphere, Proceedings of the 4th 651 international conference on solar heating and cooling for buildings and industry. 91 652 (2016) 218-225.
- 653 [19] K. Muraishi, Y. Suzuki, The thermal behaviour of dicarboxylic acids in various atmospheres, Thermochim. Acta. 232 (1994) 195-203. 654
- 655 [20] D. Haillot, T. Bauer, U. Kröner, R. Tamme, Thermal analysis of phase change
- materials in the temperature range 120-150°C, Thermochim. Acta. 513 (2011) 49-59. 656
- [21] G.T. Nguyen, H.S. Hwang, J. Lee, I. Park, Azelaic acid/expanded graphite 657
- 658 composites with high latent heat storage capacity and thermal conductivity at medium
- 659 temperature, Acs Omega. 6 (2021) 8469-8476.

- 660 [22] G.T. Nguyen, T.N. Ly, N.T. Tran, H.N.A. Tuan, N.H. Hieu, T.H. Bui, Glutaric 661 acid/expanded graphite composites as highly efficient shape-stabilized phase change 662 materials at medium-temperature, J. Energy Storage. 63 (2023) 107038.
- [23] S.P. Wang, P. Qin, X.M. Fang, Z.G. Zhang, S.F. Wang, X.C. Liu, A novel sebacic
   acid/expanded graphite composite phase change material for solar thermal medium-
- temperature applications, Sol. Energy. 99 (2014) 283-290.
- 666 [24] S. Liu, L.P. Han, S.L. Xie, Y.Z. Jia, J.H. Sun, Y. Jing, Q.Y. Zhang, A novel medium-667 temperature form-stable phase change material based on dicarboxylic acid eutectic
- temperature form-stable phase change material based on dicarboxylic acid e
   mixture/expanded graphite composites, Sol. Energy. 143 (2017) 22-30.
- 669 [25] O. Zhang, J. Liu, Sebacic acid/CNT sponge phase change material with excellent
- thermal conductivity and photo-thermal performance, Sol. Energ. Mat. Sol. C. 179
  (2018) 217-222.
- 672 [26] L.P. Han, G.X. Ma, S.L. Xie, J.H. Sun, Y.Z. Jia, Y. Jing, Preparation and 673 characterization of the shape-stabilized phase change material based on sebacic acid
- and mesoporous MCM-41, J. Therm. Anal. Calorim. 130 (2017) 935-941.
- 675 [27] A. Palacios, M.E. Navarro-Rivero, B. Zou, Z. Jiang, M.T. Harrison, Y. Ding, A
- 676 perspective on Phase Change Material encapsulation: Guidance for encapsulation 677 design methodology from low to high-temperature thermal energy storage applications,
- 678 J. Energy Storage. 72 (2023) 108597.
- [28] C.Y. Zhao, G.H. Zhang, Review on microencapsulated phase change materials
  (MEPCMs): Fabrication, characterization and applications, Renew. Sust. Energ. Rev.
  15 (2011) 3813-3832.
- [29] P.W. Griffiths, P.C. Eames, Performance of chilled ceiling panels using phase
  change material slurries as the heat transport medium, Appl. Therm. Eng. 27 (2007)
  1756-1760.
- [30] V. Pethurajan, S. Sivan, A.J. Konatt, A.S. Reddy, Facile approach to improve solar
  thermal energy storage efficiency using encapsulated sugar alcohol based phase change
  material, Sol. Energ. Mat. Sol. C. 185 (2018) 524-535.
- 688 [31] Z.H. Cao, L.Z. Dong, L. Li, Y. Shang, D.M. Qi, Q. Lv, G.R. Shan, U. Ziener, K.
- 689 Landfester, Preparation of mesoporous submicrometer silica capsules via an Interfacial
- 690 sol-gel process in inverse miniemulsion, Langmuir. 28 (2012) 7023-7032.
- 691 [32] C.B. Wu, G. Wu, X. Yang, Y.J. Liu, C.X. Gao, Q.H. Ji, M. Wang, H.Z. Chen,
- 692 Preparation of Mannitol@Silica core-shell capsules via an interfacial polymerization
  693 process from water-in-oil emulsion, Colloid. Surface. A. 457 (2014) 487-494.
- 694 [33] Y.C. Huang, A. Stonehouse, C. Abeykoon, Encapsulation methods for phase695 change materials-A critical review, Int. J. Heat Mass Tran. 200 (2023) 123458.
- 696 [34] H.Z. Zhang, X.D. Wang, D.Z. Wu, Silica encapsulation of n-octadecane via sol-
- 697 gel process: A novel microencapsulated phase-change material with enhanced thermal
- 698 conductivity and performance, J. Colloid. Interf. Sci. 343 (2010) 246-255.
- 699 [35] Z. Chen, L. Cao, F. Shan, G.Y. Fang, Preparation and characteristics of
- microencapsulated stearic acid as composite thermal energy storage material in
  buildings, Energ. Buildings. 62 (2013) 469-474.

- 702 [36] G.Y. Fang, H. Li, Z. Chen, X. Liu, Preparation and properties of palmitic acid/SiO<sub>2</sub>
- composites with flame retardant as thermal energy storage materials, Sol. Energ. Mat.Sol. C. 95 (2011) 1875-1881.
- 705 [37] S.K. Song, L.J. Dong, Z.Y. Qu, J. Ren, C.X. Xiong, Microencapsulated capric-
- stearic acid with silica shell as a novel phase change material for thermal energy storage,Appl. Therm. Eng. 70 (2014) 546-551.
- 708 [38] S. Paneliya, S. Khanna, Utsav, A.P. Singh, Y.K. Patel, A. Vanpariya, N.H. Makani,
- 709 R. Banerjee, I. Mukhopadhyay, Core shell paraffin/silica nanocomposite: A promising
- 710 phase change material for thermal energy storage, Renew. Energ. 167 (2021) 591-599.
- [39] G. Alva, X. Huang, L.K. Liu, G.Y. Fang, Synthesis and characterization of
  microencapsulated myristic acid-palmitic acid eutectic mixture as phase change
  material for thermal energy storage, Appl. Energ. 203 (2017) 677-685.
- 714 [40] W.S. Hua, J.S. Hu, Y.Z. Zhao, X.L. Zhang, S.W. Cai, J. Ji, Development and
- thermal property analysis of biobased binary composite heat storage materials, J.
  Energy Storage. 95 (2024) 112556.
- 717 [41] H.F. Zhang, D. Shin, S. Santhanagopalan, Microencapsulated binary carbonate salt
- 718 mixture in silica shell with enhanced effective heat capacity for high temperature latent
  710 heat store on Person 124 (2010) 1156 1162
- 719 heat storage, Renew. Energ. 134 (2019) 1156-1162.
- [42] Iler, K. Ralph, The chemistry of silica, solubility, polymerization, colloid andsurface properties, A Wiley-Interscience Publication(1979).
- [43] R. Kristensen, T. Lund, V.I. Titov, N.I. Akimov, Laboratory evaluation and field
   tests of a silicate gel system intended for use under North Sea conditions, Geological
- 724 Society, London, Special Publications. 84 (1995) 251-259.
- [44] B. Knoblich, T. Gerber, Aggregation in SiO<sub>2</sub> sols from sodium silicate solutions, J.
- 726 Non-Cryst. Solids. 283 (2001) 109-113.
- 727 [45] X.G. Cui, W.C. Zin, W.J. Cho, C.S. Ha, Nonionic triblock copolymer synthesis of
- SBA-15 above the isoelectric point of silica (pH=2-5), Mater Lett. 59 (2005) 22572261.
- 730 [46] F. He, X.D. Wang, D.Z. Wu, Phase-change characteristics and thermal performance
- 731 of form-stable n-alkanes/silica composite phase change materials fabricated by sodium
- rilicate precursor, Renew. Energ. 74 (2015) 689-698.
- [47] F. He, X.D. Wang, D.Z. Wu, New approach for sol-gel synthesis of
  microencapsulated n-octadecane phase change material with silica wall using sodium
  silicate precursor, Energy. 67 (2014) 223-233.
- 736 [48] D.F. Zhang, C. Liu, Y.M. Yang, X.H. Tang, Z.N. Jiang, L. Su, X.A. Li, Z.G. Chen,
- 737 W.B. Yang, Systematic investigation on preparation and characterization of silica shell
- 738 microencapsulated phase change materials based on sodium silicate precursor, Colloid.
- 739 Surface. A. 667 (2023) 131328.
- 740 [49] S. Wilhelm, M. Kind, On the relation between natural and enforced syneresis of
- acidic precipitated silica, Polymers. 6 (2014) 2896-2911.
- 742 [50] S. Wilhelm, M. Kind, Influence of pH, temperature and sample size on natural and
- reforced syneresis of precipitated silica, Polymers. 7 (2015) 2504-2521.

- 744 [51] A. Kumar, H. Jain, B.P. Tripathi, Synthesis and nanoencapsulation of poly(ethylene
- 745 glycol)-distearates phase change materials for latent heat storage and release, Acs Appl.
- 746 Energ. Mater. 3 (2020) 5965-5976.
- 747 [52] R.L. Luo, S.F. Wang, T.Y. Wang, C.Y. Zhu, T. Nomura, T. Akiyama, Fabrication of
- paraffin@SiO<sub>2</sub> shape-stabilized composite phase change material via chemical
  precipitation method for building energy conservation, Energ. Buildings. 108 (2015)
  373-380.
- 751 [53] Y.C. Zhou, S.S. Li, Y. Zhao, Z.Y. Ling, Z.G. Zhang, X.M. Fang, Compatible
- paraffin@SiO<sub>2</sub> microcapsules/polydimethylsiloxane composites with heat storage
  capacity and enhanced thermal conductivity for thermal management, Compos. Sci.
  Technol. 218 (2022) 109192.
- 755 [54] G.Y. Fang, Z. Chen, H. Li, Synthesis and properties of microencapsulated paraffin
- composites with  $SiO_2$  shell as thermal energy storage materials, Chem. Eng. J. 163 (2010) 154-159.
- 758 [55] C. Castellón, E. Günther, H. Mehling, S. Hiebler, L.F. Cabeza, Determination of 759 the enthalpy of PCM as a function of temperature using a heat-flux DSC-A study of
- 760 different measurement procedures and their accuracy, Int. J. Energ. Res. 32 (2008)
- 761 1258-1265.
- [56] E. Günther, S. Hiebler, H. Mehling, R. Redlich, Enthalpy of phase change materials
  as a function of temperature: required accuracy and suitable measurement methods, Int.
  J. Thermophys. 30 (2009) 1257-1269.
- [57] H. Fatahi, J. Claverie, S. Poncet, Thermal characterization of phase change
  materials by differential scanning calorimetry: A review, Appl. Sci-Basel. 12 (2022)
  12019.
- 768 [58] C.Y. Wang, L.L. Feng, W. Li, J. Zheng, W.H. Tian, X.G. Li, Shape-stabilized phase 769 change materials based on polyethylene glycol/porous carbon composite: The influence
- of the pore structure of the carbon materials, Sol. Energ. Mat. Sol. C. 105 (2012) 21-26.
- [59] Z.J. Fu, L. Dai, Y. Yi, J.S. Luo, B. Li, Structure and thermal properties of stearic
- acid/silica composites as form-stable phase change materials, J. Sol-Gel Sci. Techn. 87
- 773 (2018) 419-426.
- [60] L. Cao, F. Tang, G.Y. Fang, Preparation and characteristics of microencapsulated
- palmitic acid with TiO<sub>2</sub> shell as shape-stabilized thermal energy storage materials, Sol.
  Energ. Mat. Sol. C. 123 (2014) 183-188.
- 777 [61] H. Pourmohamadian, G.A. Sheikhzadeh, M. Rahimi-Nasrabadi, H.B. Tabrizi,
- Fabrication and characterization of microencapsulated PA with SiO<sub>2</sub> shell through sol gel synthesis via sodium silicate precursor, J. Mater. Sci-Mater. El. 28 (2017) 9990-
- 780 9997.
- 781 [62] Q. Guo, T. Wang, Preparation and characterization of sodium sulfate/silica
- 782 composite as a shape-stabilized phase change material by sol-gel method, Chinese J.
- 783 Chem. Eng. 22 (2014) 360-364.

- [63] L.X. Geng, S.F. Wang, T.Y. Wang, R.L. Luo, Facile synthesis and thermal
  properties of nanoencapsulated n-dodecanol with SiO<sub>2</sub> shell as shape-formed thermal
  energy storage material, Energ. Fuel. 30 (2016) 6153-6160.
- 787 [64] Z.T. Zhang, Y. Liu, J.C. Wang, L.Y. Sun, T.L. Xie, K.F. Yang, Z.J. Li, Preparation
- and characterization of high efficiency microencapsulated phase change material based
- on paraffin wax core and SiO<sub>2</sub> shell derived from sodium silicate precursor, Colloid.
  Surface. A. 625 (2021) 126905.
- 791 [65] T.T. Qian, J.H. Li, H.W. Ma, J. Yang, The preparation of a green shape-stabilized
- composite phase change material of polyethylene glycol/SiO<sub>2</sub> with enhanced thermal
- performance based on oil shale ash via temperature-assisted sol-gel method, Sol. Energ.
  Mat. Sol. C. 132 (2015) 29-39.
- 795 [66] J.H. Tan, K.J. Zhu, X. Ou, P.H. Xu, Y.X. Cheng, Process and performance of
- palmitic acid @silica phase-change microcapsules using chemical precipitation method,
  J. Appl. Polym. Sci. 139 (2022) 51962.
- 798 [67] F. De Jaeghere, E. Allémann, J.C. Leroux, W. Stevels, J. Feijen, E. Doelker, R.
- Gurny, Formulation and lyoprotection of poly(lactic acid-co-ethylene oxide)
  nanoparticles: influence on physical stability and in vitro cell uptake, Pharmaceut. Res.
  16 (1999) 859-866.
- 802 [68] S.P. Yeap, Permanent agglomerates in powdered nanoparticles: Formation and803 future prospects, Powder Technol. 323 (2018) 51-59.
- 804 [69] Y.T. Fang, L.H. Huang, X.H. Liang, S.F. Wang, H. Wei, X.N. Gao, Z.G. Zhang,
- Facilitated synthesis and thermal performances of novel SiO<sub>2</sub> coating Na<sub>2</sub>HPO<sub>4</sub>•7H<sub>2</sub>O
   microcapsule as phase change material for thermal energy storage, Sol. Energ. Mat. Sol.
- 807 C. 206 (2020) 110257.
- 808 [70] K.J. Yuan, H.C. Wang, J. Liu, X.M. Fang, Z.G. Zhang, Novel slurry containing
- 809 graphene oxide-grafted microencapsulated phase change material with enhanced
- thermo-physical properties and photo-thermal performance, Sol. Energ. Mat. Sol. C.143 (2015) 29-37.
- 812 [71] K. Tungkananurak, S. Kerdsiri, D. Jadsadapattarakul, D.T. Burns, Semi-micro
- 813 preparation and characterization of mesoporous silica microspheres from rice husk
- 814 sodium silicate using a non-ionic surfactant as a template: application in normal phase
- 815 HPLC columns, Microchim. Acta. 159 (2007) 217-222.
- 816 [72] Y.Y. Pan, Y.Y. Xu, L.J. Zhu, X.Y. Liu, G.X. Zhao, S.N. Wang, L.A. Yang, T. Ma,
- H. Liu, Stability and rheological properties of water-in-oil (W/O) emulsions prepared
  with a soyasaponin-PGPR system, Future Foods. 4 (2021) 100096.
- 819 [73] S.P. Mo, B. Xiao, J.X. Li, L.S. Jia, Y. Chen, LiNO<sub>3</sub>/NaCl nanocapsules with high
- 820 thermal properties for medium-temperature thermal energy storage, J. Energy Storage.
- 821 83 (2024) 110672.
- 822 [74] X. Yin, G.X. Kou, A.X. Xu, T. Fu, J. Zhu, Effects of TiO<sub>2</sub> nanoparticles on thermal
- 823 conductivity of heat transfer oil, J. Cent. South Univ. 26 (2019) 2129-2135.
- 824 [75] Y.J. Li, J.E. Zhou, S. Tung, E. Schneider, S.Q. Xi, A review on development of
- nanofluid preparation and characterization, Powder Technol. 196 (2009) 89-101.

- 826 [76] D.D. Kumar, A.V. Arasu, A comprehensive review of preparation, characterization,
- properties and stability of hybrid nanofluids, Renew. Sust. Energ. Rev. 81 (2018) 1669-1689.
- 829 [77] A.C.K. Sato, F.A. Perrechil, A.A.S. Costa, R.C. Santana, R.L. Cunha, Cross-830 linking proteins by laccase: Effects on the droplet size and rheology of emulsions
- stabilized by sodium caseinate, Food Res. Int. 75 (2015) 244-251.
- [78] Q.B. He, S.F. Wang, M.W. Tong, Y.D. Liu, Experimental study on thermophysical
  properties of nanofluids as phase-change material (PCM) in low temperature cool
  storage, Energ. Convers. Manage. 64 (2012) 199-205.
- 835 [79] M. Isaza-Ruiz, R. Mondragón, F.B. Osorio, J. Ventura-Espinosa, L. Hernández,
- 836 Viscosity and stability analysis of hitec salt-based alumina nanofluids, Sol. Energ. Mat.
  837 Sol. C. 222 (2021) 110923.
- 838 [80] Y.J. Zhuang, Z.B. Liu, W.B. Xu, Experimental investigation on the non-Newtonian
- to Newtonian rheology transition of nanoparticles enhanced phase change material
  during melting, Colloid. Surface. A. 629 (2021) 127432.
- 841 [81] C. Delgado-Sanchez, P. Partal, M.J. Martin-Alfonso, F.J. Navarro, Oil-in-Oil 842 emulsions of stearic acid dispersed in silicone oil with enhanced energy storage
- capability for heat transfer fluids, Sol. Energ. Mat. Sol. C. 245 (2022) 111893.
- 844 [82] J. Chen, P. Zhang, Preparation and characterization of nano-sized phase change
- emulsions as thermal energy storage and transport media, Appl. Energ. 190 (2017) 868-846 879.