



This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Preparation and application of composite phase change materials stabilized by cellulose nanofibril-based foams for thermal energy storage

Shen, Zhenghui; Kwon, Soojin; Lee, Hak Lae; Toivakka, Martti; Oh, Kyudeok

Published in: International Journal of Biological Macromolecules

DOI: 10.1016/j.ijbiomac.2022.10.075

Published: 01/12/2022

Document Version Accepted author manuscript

Document License CC BY-NC-ND

Link to publication

Please cite the original version:

Shen, Z., Kwon, S., Lee, H. L., Toivakka, M., & Oh, K. (2022). Preparation and application of composite phase change materials stabilized by cellulose nanofibril-based foams for thermal energy storage. *International Journal of Biological Macromolecules*, 222(B), 3001-3013. https://doi.org/10.1016/j.ijbiomac.2022.10.075

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Preparation and application of composite phase change materials stabilized by cellulose
nanofibril-based foams for thermal energy storage
Zhenghui Shen ^{a,b} , Soojin Kwon ^c , Hak Lae Lee ^b , Martti Toivakka ^d , Kyudeok Oh ^{e*}
^a Beijing Key Laboratory for Theory and Technology of Advanced Battery Materials, School of
Materials Science and Engineering, Peking University, Beijing 100871, P. R. China
^b Program in Environmental Materials Science, Department of Agriculture, Forestry and
Bioresources, College of Agriculture and Life Sciences, Seoul National University, Seoul
08826, Korea
° Department of Forest Biomaterials, North Carolina State University, Raleigh, North Carolina
27695, United States
^d Laboratory of Natural Materials Technology, Åbo Akademi University, Turku 20500, Finland
^e Department of Bio Based Materials, Chungnam National University, 99 Daehak-ro, Yuseong-
gu, Daejeon, 34134, South Korea
*Corresponding author: Kyudeok Oh (kyudeok.oh@cnu.ac.kr)
Tel: +82-42-821-5759, Fax: +82-42-821-6159

18 Funding: This work was supported by research fund of Chungnam National University.

19 Abstract: The leakage issue and inferior heat conduction of organic phase change materials 20 (PCMs) limit their actual applications. In present study, cellulose nanofibril (CNF)-based foams 21 were prepared as the porous scaffolds for polyethylene glycol (PEG) and paraffin wax (Pw) to 22 prevent their leakage, and multiwalled carbon nanotubes (CNTs) were incorporated to improve 23 the heat transfer performance. The prepared foams had low density (<67.3 kg/m³) and high 24 porosity (>94.5%). Selective chemical modifications of nanocellulose foams enhanced their 25 shape-stability and compatibility with PCMs. The highly porous foam structure and favorable 26 compatibility resulted in PCM loading levels (93.63% for PEG and 91.77% for Pw) and 27 negligible PCM leakage (<2%). CNTs improved the heat transfer performance of PCMs, as 28 evidenced by the improved thermal conductivities and boosted temperature rises during solar 29 heating. Meanwhile, the composite PCMs exhibited improved thermal stability over the control. 30 PEG-based composite PCM exhibited phase change enthalpy of 143 J/g with melting 31 temperature of 25.2 °C; Pw-based composite PCM exhibited phase change enthalpy of 184 J/g 32 with melting temperature of 53.4 °C. Novel PCM sandwich structures based on these composite 33 PCMs and a thermoelectric generator was designed and displayed promising potential for solar energy 34 harvesting and utilization.

- 35 Keywords: cellulose nanofibril, phase change materials, multiwalled carbon nanotubes, form-
- 36 stability, heat transfer enhancement, thermal energy storage

37 **1. Introduction**

38 Latent heat storage (LHS) owing to its advantages of high volumetric energy storage 39 density and small temperature swings represents a promising strategy for expanding the 40 utilization of renewable energies and coping with the energies tension. The fulfillment of a LHS 41 process relies on the reversible phase transitions of the energy storage medium (i.e. the phase 42 change materials, PCMs), where heat can be stored during heating and used later [1]. PCMs are 43 typically categorized into inorganic, organic and eutectic ones, and each type has their pros and 44 cons. Eutectics PCM systems compromises at least two different kinds of PCMs and show 45 complexity for composition design and property tuning. Inorganic PCMs, with salt hydrates as the most representative family, exhibited the advantages of high energy storage capacity, 46 47 relatively higher thermal conductivity, and inexpensiveness, widely extending their 48 applications in both domestic and industrial applications [2]. Nevertheless, salt hydrates exhibit devastating drawbacks such as phase segregation and supercooling during the charging and 49 50 discharging processes, which severely harm their energy storage performance in cyclic charging 51 and discharging and timely release of the stored energy [3,4]. On the contrary, organic PCMs 52 do not suffer from phase segregation, have no or little supercooling, and exhibit broad ranges 53 of working temperatures, non-corrosivity and chemical stability properties, making them 54 promising candidates for a variety of practical applications [5].

55 Polyethylene glycol (PEG) and paraffin wax (Pw) as typical organic PCMs provide 56 favorable characteristics for LHS such as high heat of fusion, negligible supercooling, 57 nontoxicity and non-corrosivity [6-8]. However, their solid-liquid phase transition features 58 make them suffer from the large volume change in their phase transitions, which causes the 59 leakage issue and limit its wide applications [9,10]. Therefore, fabricating form-stable 60 composite PCMs is of great importance for ensuring their efficient and reliable uses for LHS 61 systems. Porous materials, as the supporting matrix to stabilize PCMs, could absorb the liquid 62 PCMs into the pores and prevent their leakage in the melting process. Compared to other 63 approaches like core-shell microencapsulation, using porous scaffolds to prepare form-stable 64 composite PCMs is simple and effective. A variety of supporting skeletons, such as porous 65 carbon-based (e.g., expanded graphite, graphene aerogels, carbon nanotube sponges), mineral-based (e.g., expanded perlite and expanded vermiculite), metal-based (e.g., aluminum and copper foams),
polymer-based (e.g., polystyrene and polyurethane foams) and silica-based materials (e.g., silica
aerogels) [11], have been used to fabricate composite PCMs with stable form during their phase
transitions. However, most of these porous materials usually require harsh or energy-intensive
preparations and costly precursors. Moreover, the majority of these materials are not sustainable.
Therefore, the development of sustainable and high-performance porous scaffolds for organic
PCMs is of great importance to actual applications and provokes great interest to researchers.

73 Cellulose as the most abundant natural polymers on earth represents a promising material 74 for numerous fields because of its fascinating properties like biodegradability, renewability, 75 recyclability, safety and low price [12–14]. Cellulose surface has abundant hydroxyl groups, 76 and these functional groups endow the feasibility of various chemical modifications through 77 oxidation, esterification, polymer grafting, etc. [15]. Importantly, cellulose chains readily form 78 entangled networks even in low concentration aqueous suspensions [16], making it quite easy 79 to prepare porous structures from cellulose suspension after removing the solvent by drying. 80 One thing to consider is the compatibility between the foam scaffolds and PCMs, and this can 81 be easily fulfilled by tuning the surface chemistry of cellulose foams as explained above. 82 Compared to conventional PCM scaffolds like silica aerogels and carbon aerogels, cellulose-83 based porous supporting materials exhibit advantages of ease of preparation, superior environmentally friendliness, and cost-effectiveness. Moreover, cellulose materials are of low 84 85 density and low thermal expansion coefficient [17]. These superior properties of cellulose are 86 making them promising starting materials for next generation foams and aerogels.

87 Another intrinsic drawback of organic PCMs that hinders their LHS performance is the low thermal conductivity [18]. In practical uses, PCMs with high thermal conductivity are 88 89 preferred as their charging process can be shorter and cost-effective [19]. To enhance the 90 thermal conductivity of PCMs, various thermally conductive fillers including metal 91 nanoparticles, carbon spheres, graphite, graphene nanoplatelets, carbon fibers, carbon 92 nanotubes can be used [19,20]. In the present study, carbon nanotubes (CNTs) are selected due 93 to their ultrahigh thermal conductivity and high aspect ratio [21]. Carbon nanomaterials, 94 however, suffer from severe aggregation due to the high surface area and the strong van der Waals force between these nanoparticles [22]. Instead of environmentally unfriendly surfactants, nanocellulose can be applied as the dispersing agent for carbon nanomaterials thanks to their amphiphilic nature. Green nanocellulose facilitates the dispersion of carbon nanomaterials via hydrophobic-hydrophobic interactions and intercalation effect, and this, does not harm the intrinsic thermal properties of carbon materials [23]. Therefore, the preparation of nanocellulose/carbon foam as the supporting matrix for PCMs provides a solution for addressing the two intrinsic drawbacks of organic PCMs simultaneously.

102 In this work, form-stable composite PCMs with enhanced thermal conduction 103 performance were prepared by using nanocellulose based foam as a supporting matrix. To 104 improve the shape-stability of foams and their compatibility with PCMs, silane agent-induced 105 chemical modification was carried out, and the effect of surface chemistry tuning on PCM 106 stabilization was explored. Multiwalled CNTs as the heat transfer enhancers were applied in 107 the preparation of porous supporting foams. Herein, nanocellulose serves not only the skeleton 108 of the foam but also the dispersing agent of CNTs. The morphologies, structures, phase change 109 properties, thermal stability, and thermal reliability of the prepared composite PCMs were 110 investigated. In particular, leakage testing was performed to examine the form-stability of the 111 prepared composite PCMs. Moreover, special PCM sandwich structures were designed and tested for absorption and conversion of solar energy. By addressing the leakage issue and the 112 113 inferior thermal conduction of PEG and Pw, their efficient applications for LHS would be 114 expanded. Besides, the interest of using naturally occurring polymers such as polysaccharides 115 for stabilizing PCMs for sustainable energy applications is expected to increase.

116

117 **2. Experimental**

118 2.1 Materials

Bleached eucalyptus kraft pulp (BEKP) was the starting material to prepare CNF. (3-Aminopropyl)trimethoxysilane (APTMS) and Methyltrimethoxysilane (MTMS) silylation reagent, paraffin wax (Pw), and polyethylene glycol (PEG) PCMs were purchased from Sigma-Aldrich (St. Louis, MO, USA). Hydrochloric acid used to regulating pH was purchased from Duksan Pure Chemicals Co., Ltd. (Ansan-city, Korea). Multiwalled CNTs in powder form were

- 124 purchased from Research Nanomaterials, Inc. (Houston, TX, USA). Filter paper (quantitative
- 125 ashless, 11 cm in diameter; ADVANTEC, Tokyo, Japan) was used for leakage testing of the
- 126 prepared composite PCMs. Detailed information of the materials is available in Table 1.

Material	Specification	Role	Provider
BEKP	Commercial grade	CNF starting mateial	Moorim Paper Co., Ltd., Korea
APTMS	purity 97%	Silylation agent	Sigma-Aldrich, USA
MTMS	purity 98%	Silylation agent	Sigma-Aldrich, USA
Pw	Mw=436	Hydrophobic PCM	Sigma-Aldrich, USA
PEG	Mw=1000	Hydrophilic PCM	Sigma-Aldrich, USA
UC1	1 N,	DU regulator	Duksan Pure Chemicals Co., Ltd,
псі	laboratory grade	r n legulator	Korea
Multiwalled CNTs	purity >95%, outer	Thermal conductivity enhancer	Research Nanomaterials Inc. USA
With Wallow CIVIS	diameter 10–20 nm	Thermal conductivity enhancer	Research Nationaterials, Inc., USA
	Quantitative		
Filter paper	ashless, 11 cm in	Leakage testing substrate	ADVANTEC, Japan
	diameter		

127 **Table 1.** Detailed information of the materials used in the experiments.

128

129 **2.2 Methods**

130 **2.2.1 Preparation of CNF**

131 CNF was prepared by grinding a 2 wt% pulp suspension 30 times using a Super 132 Masscolloider grinder (Masuko Sangyo Co., Ltd., Kawaguchi-city, Japan) and the entire 133 grinding process consumed about 8 hours. The gap between the two grinding plates was -80134 µm, and the grinding speed was 1,500 rpm. The zeta potential of the resulting CNF, determined 135 using a Malvern Zetasizer (Nano-ZS, Malvern Instruments Ltd., Worcestershire, UK), was 136 -34.8 ± 0.5 mV. The charge density of the CNF, according to a titration method, was 0.16 meq/g 137 CNF.

138 **2.2.2 Preparation of CNF/CNT composites**

139 CNF/CNT composites were prepared by homogenizing CNTs in a 0.5% CNF suspension 140 using an Ultra-Turrax T50 homogenizer (Janke and Kunkel, IKA-Labortechnik, Staufen, 141 Germany) at 10,000 rpm for 60 min. The homogenized suspensions were then centrifuged with 142 a centrifugal (Combi R514, Hanil Scientific Inc., Gimpo, Korea) at 9,000 rpm for 30 min to 143 obtain the CNF/CNT composites. Different amounts of CNTs (10, 20, 30, and 50 wt%, based on CNF) were used for the preparation, and the resulting composites were coded as CNF/CNT_{10} , CNF/CNT₂₀, CNF/CNT_{30} , and CNF/CNT_{50} , where the subscript indicates the dose (wt%) of CNTs.

147 **2.2.3 Preparation of foams**

148 CNF-based foams were prepared by freeze-drying the corresponding suspensions. To tune 149 the surface chemistry of CNF, the pH of a 2% CNF suspension was adjusted to 4 by using HCl. 150 Then silane chemical APTMS or MTMS was added to the CNF suspension at the mass ratio of 151 2:1, and the silvlation reaction was continued while mixing at 1,500 rpm at room temperature 152for 2 h. The silvlated CNF suspension was then stored in a refrigerator (4° C) to minimize the 153possible cracking and shrinkage of foams during subsequent freeze-drying [24]. The precooled CNF suspension was frozen in liquid nitrogen, followed by a 72 h freeze-drying (FD8518 freeze 154 155dryer, Ilshin Lab. Co., Ltd., Yangju-city, Korea). Foams were cured at 120 °C for 3 h to ensure the completion of silvlation. The CNF/CNT foams were similarly prepared by freeze-drying 156 the corresponding silylated CNF/CNT suspensions. When APTMS was used as the silane agent, 157158 the prepared foams were labeled as CNF_{APTMS}, CNF_{APTMS}/CNT₁₀, CNF_{APTMS}/CNT₂₀, 159CNF_{APTMS}/CNT₃₀, and CNF_{APTMS}/CNT₅₀, where the subscript denotes the dose (wt%) of CNTs 160 based on the dry weight of CNF. When MTMS was used as the silane agent, the prepared foams were labeled as CNF_{MTMS}, CNF_{MTMS}/CNT₁₀, CNF_{MTMS}/CNT₂₀, CNF_{MTMS}/CNT₃₀, and 161 CNF_{MTMS}/CNT₅₀, where the subscript denotes the dose (wt%) of CNTs based on the dry weight 162 163 of CNF.

The apparent densities of the foams were calculated from their weights and dimensions, which were determined with a digital caliper (Absolute Origin, iGaging, San Clemente, CA, USA). The porosity (P, %) of the foams was calculated from their apparent densities and skeleton densities according to Equation (1) [25].

168
$$P = \left(1 - \frac{\rho_a}{\rho_s}\right) \times 100\% \tag{1}$$

169 where ρ_a is the apparent density of the foam (kg/m³) and ρ_s is the density of the foam 170 skeleton (kg/m³).

171 For silvlated CNF foams,
$$\rho_s = \frac{1}{\frac{W_{CNF} + W_{Silane}}{\rho_{CNF} + \rho_{Silane}}}$$
 (2)

and for silvlated CNF/CNT foams,
$$\rho_s = \frac{1}{\frac{W_{CNF} + \frac{W_{Silane}}{\rho_{SIIane}} + \frac{W_{CNT}}{\rho_{SIlane}}}$$
(3)

173 where w_{CNF} , w_{Silane} , and w_{CNT} are the weight fractions (%) of CNF, silane agent, and 174 CNTs in the foams, respectively. ρ_{CNF} was fixed at 1500 kg/m³, ρ_{APTMS} was fixed at 1027 175 kg/m³, ρ_{MTMS} was fixed at 1900 kg/m³, and ρ_{CNT} was fixed at 2100 kg/m³.

1.0

176 **2.2.4. Preparation of Composite PCMs**

177Composite PCMs were prepared by impregnating the prepared foams with molten PCM under 1-bar vacuum for 6 h. Excess PCM on the sample surface was carefully removed using 178 179 filter paper. The prepared Composite PCMs were named according to the type of the used PCM 180 and foam. For example, the obtained PEG-based Composite PCMs were coded as CNFAPTMS-CNF_{APTMS}/CNT₁₀-PEG, CNF_{APTMS}/CNT₂₀-PEG, 181 PEG. CNF_{APTMS}/CNT₃₀-PEG, and 182 CNF_{APTMS}/CNT₅₀-PEG when APTMS silvlated foams were used. Analogously, the obtained 183 Pw-based Composite PCMs were coded as CNF_{MTMS}-Pw, CNF_{MTMS}/CNT₁₀-Pw, CNF_{MTMS}/CNT₂₀-Pw, CNF_{MTMS}/CNT₃₀-Pw, and CNF_{MTMS}/CNT₅₀-Pw when MTMS silylated 184 185 foams were used. The PCM fraction of prepared Composite PCMs was calculated according to 186 Equation (4):

187
$$C = \left(\frac{w_b - w_a}{w_b}\right) \times 100\% \tag{4}$$

188 where w_a is the foam weight before impregnation with PCM (g) and w_b is the foam weight 189 after impregnation with PCM (g) (i.e., the weight of prepared Composite PCMs).

190 **2.2.5 Characterizations**

191 The morphologies of CNF, CNT, and CNF/CNT composites were studied by energy-192 filtering transmission electron microscopy (LIBRA 120, Carl Zeiss, Oberkochen, Germany). 193 The structures of foams and Composite PCMs were investigated by field-emission scanning 194 electronic microscopy (FE-SEM; Auriga; Carl Zeiss, Oberkochen, Germany). Water contact 195 angle (WCA) measurements were performed using a drop shape analyzer (DSA100, Krüss 196 GmbH, Hamburg, Germany).

Leakage testing of PCM samples was performed as follows. For PEG-based Composite
PCMs, they were placed on a filter paper, then heated in an oven at 50 °C for 30 min. For Pw-

based Composite PCMs, they were placed on a filter paper, then heated in an oven at 70 °C for
30 min. The area of leaked PCM on filter paper was recorded by a digital camera. The leakage
percentage (%) of PCM was calculated according to Equation (5):

202
$$L = \left(\frac{m_a - m_b}{m_a}\right) \times 100\%$$
 (5)

where m_a is the sample weight before the leakage test (g) and m_b is the sample weight after the leakage test (g).

205 Fourier transform-infrared spectroscopy (FT-IR, Thermo Scientific, Waltham, MA, USA) 206 was used to record the IR spectra of samples. A D8 Advance diffractometer (Bruker, Germany) 207 with Cu ka1 radiation (wavelength $\lambda = 1.5418$ Å) operating at 40 kV and 40 mA was used to 208 obtain the X-ray diffraction (XRD) patterns of samples. Differential scanning calorimetry (DSC, 209 Discovery DSC, TA Instruments Inc., New Castle, DE, USA) was employed to investigate the 210 phase change properties of samples. Samples were heated from 0 °C to the targeted temperature 211 (70 °C for PEG and 80 °C for Pw) at a temperature ramping rate of 5°C/min, followed by a 212 cooling process to 25 °C at the same rate. A thermogravimetric analyzer (Discovery TGA, TA 213 Instruments Inc.) was used to study the thermal stability of samples over the temperature range 214 of 40-600 °C at a heating rate of 10 °C/min under 20 mL/min of nitrogen gas purge. The heat 215 transfer performance of samples was investigated as follows. A thermocouple (Electronic 216 Temperature Instruments Ltd., Worthing, UK) was used to determine the real-time temperature 217 variations of samples under the heating of a solar simulator (CEL-HXF300-T3, Ceaulight, 218 Beijing, China) The temperatures of samples were collected by a ThermaData® logger 219 (Electronic Temperature Instruments Ltd.) and exported using ThermaData® Studio software 220 (version 5.1.4, Electronic Temperature Instruments Ltd.). The thermal reliabilities of PCM 221 samples were investigated by comparing their phase change properties before and after 100 222 melting/freezing cycles. The thermal conductivity of PCM samples was measured following a 223 laser flash method. Disk-shaped samples were prepared, and their dimensions and weights were 224 measured for determining their densities. Then the thermal conductivity of samples was 225 calculated using Eq. (6) [26]:

226
$$k = \alpha \cdot C_p \cdot \rho$$

(6)

227 where κ is the thermal conductivity [W/(m·K)], α represents the thermal diffusivity 228 (mm²/s), C_P denotes the specific heat capacity [J/(g·K)] and ρ is the density of pellets (g/cm³). 229 The application potential of the prepared composite PCM for thermal energy storage and 230 conversion was evaluated by using the designed PCM sandwich structures based on the 231 differences between the phase change performances of PEG and Pw. As illustrated in Fig.1., 232 Pw-based composite PCMs were positioned on the top (hot side), a thermoelectric generator 233 (TEG, SP1848-27145 SA, Shenzhen Chuangxin Microelectronics Co., Ltd., China) was 234 positioned in the middle and PEG-based composite PCMs were attached to the bottom of TEG, 235 respectively. The thermoelectric materials in the TEG is Bismuth Telluride. The dimension of 236 TEG was about 40 mm×40 mm×3.4 mm, operating temperature ranges from -40 °C to 150 °C. 237 The top side of the assembled sandwich-like structures was heated by the solar simulator, and 238 the light intensity of the solar simulator was 469 mW/cm² at a working current of 14 A. The 239 voltage generated by TEG was monitored by a 6½-Digit USB multimeter (2100 Series, Keithley 240 Instruments, Inc., Cleveland, OH, USA).





243

Fig. 1. Schematic illustrating the solar-heat-electricity system based on novel PCM

sandwich structures.

244 **3. Results and discussion**

245 **3.1 Effect of nanocellulose surface chemistry on PCM shape-stabilization**

246 Surface chemistry plays a critical role in the compatibility between two materials. In other 247 words, host and guest materials with good affinity are likely to contribute to more compatible 248 composites. One of the research aims of this work is to address the leakage issue of PCMs by 249 using CNF-based foams as the supporting material; thus, the surface chemistry of nanocellulose 250 skeleton should be carefully considered as well as the porous structure of nanocellulose foams. 251 In the present study, silane chemicals including APTMS and MTMS were used to tune the 252 surface chemistry of CNF. The reaction mechanism between silane chemicals and CNF is 253 schematically illustrated in Fig.2a. In the silvlation process, silane chemicals were hydrolyzed 254 to silanol and reacted with the hydroxyl groups of nanocellulose to form an interlaced network 255 [25], which would consequently enhance the foam-stability. The chemical structures of APTMS 256 and MTMS are shown in Fig.2b and Fig.2c, respectively. Regarding the fact that APTMS has 257 a hydrophilic amine group while MTMS has hydrophobic methyl groups on their structures, 258 each of them would impart different surface chemistry to CNF-based foams. The 3D network 259 structure of CNF foam is mainly dictated by hydrogen bonding and physical entanglement 260 between adjacent cellulose nanofibrils, which leads to poor mechanical properties of such 261 foams. Especially, cellulose nanofibers absorb water and swell under wet or humid conditions 262 owing to their hygroscopic nature, leading to the deterioration of network bonding between 263 adjacent fibers and then a loss of foam strength [27,28]. Therefore, although CNF has a good 264 affinity with PEG thanks to their abundant hydroxyl groups, surface modification of CNF by 265 APTMS-induced chemical crosslinking was conducted to enhance the shape-stability of foams 266 while retaining their intrinsic affinity with PEG. Considering Pw is hydrophobic, CNF was 267 hydrophobically modified by MTMS to improve the affinity between CNF-based foams and 268 Pw. Such surface chemistry modifications are expected to have a positive effect on the shape-269 stability of the resulting composite PCMs.



- 270
- 271 272

Fig. 2. (a) Chemistry tuning of CNF using trimethoxy silane and the involved reaction mechanism, (b) chemical structure of APTMS, and (c) chemical structure of MTMS.

273

274 Water contact angle (WCA) measurements were performed to quantitively investigate the 275 hydrophilicity of the prepared foams. As shown in Fig. S1a, it was difficult to measure the WCA 276 of pristine CNF foam as the foam surface quickly collapsed upon contact with water, which is 277 ascribed to the hygroscopic nature of cellulose materials. CNFAPTMS foam absorbed water 278 quickly due to its hydrophilicity and porous structure while the foam remained intact (Fig. S1b), 279 indicating successful hydrophilic treatment and the enhanced foam shape-stability. CNT_{MTMS} 280 foam, however, repels water and prevents its absorption and penetration (Fig. S1c). The measured WCA of CNT_{MTMS} foam was greater than 130° (Fig. S2), indicating strong 281 282 hydrophobicity. The shape-stability of pristine CNF foam, CNFAPTMS foam, and CNFMTMS foam 283 was tested, and the results are shown in Figs. S1d-f. As expected, pristine CNF foam collapsed 284 into pieces and lost its original shape during mixing with water, while the modified CNF foams 285 maintained their structures after mixing. Although these results indicate that by suitable 286 chemical modification both the surface chemistry and shape-stability of nanocellulose foams 287 can be assured, direct measurement of the wettability of molten PCMs on the surface of 288 supporting materials is interesting if their quick solidification could be resolved [29].

The effect of the chemical modifications of CNF foams on their PCM-stabilization was tested (Fig. 3). One thing to mention is that it is more reliable to evaluate the PCM leakage situation by weighing the mass of the leaked PCM, especially when the leakage areas of PCM samples do not differ much. For composite PCMs supported by pristine CNF foams, more leaked Pw rather than PEG was visible on the filter paper, and the leakage percentage of Pw is 294 higher than that of PEG (Tables 2 & 3), which suggests the importance of the affinity between 295 supporting materials and PCMs for a stable form. When CNF_{APTMS} foams were used to 296 encapsulate PCMs, it was found that PEG-based composite PCM exhibited less leakage while 297 Pw-based composite PCM exhibited more leakage, also evidenced by the results in Tables 2 & 298 3. Analogously, CNF_{MTMS} foams provided a greater stabilization effect to Pw, and less PCM 299 leakage was seen. In contrast, these hydrophobic foams imparted an inferior stabilization effect 300 on PEG, and PCM leakage increased accordingly. These results prove the importance of tuning 301 the surface chemistry of supporting materials on the shape-stability of PCMs, which 302 significantly affects their actual applications. Therefore, CNF_{APTMS} foams and CNF_{MTMS} foams 303 were used to fabricate PEG-based composite PCMs and Pw-based composite PCMs, 304 respectively.



305

- 306 **Fig. 3.** Effect of the chemical modifications of CNF foams on their PCM-stabilization effect:
- 307 leakage testing of (a) PEG-based composite PCMs and (b) Pw-based composite PCMs.
- 308

309 **Table 2.** PEG leakage percentage of different foam-stabilized composite PCMs.

Composite	Weight before test	Weight after test	Weight of the leaked PEC	G Leakage percentage
РСМ	(g)	(g)	(g)	(%)
CNF-PEG	0.675	0.662	0.013	1.93
CNF _{APTMS} -PEG	0.47	0.462	0.008	1.70
CNF _{MTMS} -PEG	0.489	0.472	0.017	3.48

Composite	Weight before test	Weight after test	Weight of the leaked Pw	Leakage percentage
РСМ	(g)	(g)	(g)	(%)
CNF-Pw	0.474	0.464	0.01	2.11
CNF _{APTMS} -Pw	0.431	0.419	0.012	2.78
CNF _{MTMS} -Pw	0.568	0.563	0.005	0.88

310 **Table 3.** Pw leakage percentage of different foam-stabilized composite PCMs.

312 **3.2 Morphologies and structures of composite PCMs**

313 The morphologies and structures of the prepared composite PCMs, supporting foams and 314 related starting materials CNF and CNT are presented in Fig. 4. Fig.4a shows the typical 315 morphology of CNF, i.e., dozens of nanometers in diameter and several micrometers in length, 316 and the high aspect ratio of CNF benefit the entanglement of the adjacent nanofibrils, which is 317 also visible in the TEM image. In the present work, CNTs were used as the heat transfer 318 enhancers for the prepared composite PCMs, and the morphology of an individual CNT is 319 shown in Fig. 4b. As noticed, CNT has a comparable diameter with CNF but is short in length. 320 Figs 4c and 4d present the porous structure of the prepared CNF-based foams, and these 321 nanocellulose-based foams exhibit lamellar architectures and open porosity, as reported 322 elsewhere [30]. The presented foams displayed irregular arrangements of thin plates in the form 323 of films or nanopapers that are connected by partially fibrillated fibers or dangling mass. In 324 particular, the porous structures of such foams can be easily controlled by the concentration of 325 CNF suspensions for foam preparation and processing parameters such as the freezing rate and 326 freezing direction of CNF suspensions [31,32]. In this work, the concentration of starting CNF 327 suspensions was fixed at 2% based on our previous results [31], and silvlation reaction and CNT 328 introduction were performed in these suspensions, followed by liquid nitrogen freezing and 329 freeze drying.

With the increased introduction of CNTs, the foams became denser, and their porosities decreased accordingly (Tables 4 and S1). The possible reason is that CNTs attached to the CNF surface, and the foam voids were partially filled with CNTs. Fig. S3 shows the distribution of CNTs in the CNF-based foam skeleton, and they are found to be uniformly located in the observed areas and partially filled the pores in the foams, which led to decreased PCM absorption capacity but greater PCM stabilization (Table S1). 336 Figs. 4e and 4f present the internal structure of composite PCMs that were prepared by 337 impregnating the porous foams with the molten PCMs. No holes or voids exist in the two 338 composites, which indicates favorable PCM absorption into the porous structures of the two 339 chemically modified CNF-based porous scaffolds. Given the low density and high porosity of 340 the two porous scaffolds (Table 4), the obtained PCM composites exhibit high loading factions of PCMs (i.e. 93.63% of PEG and 91.77% of Pw), which contributes to high phase change 341 342 enthalpy for practical uses. Moreover, no evident interfaces between the components are 343 noticed. Such features indicate good compatibility between the components [33], which was 344 mainly contributed by the chemistry tuning of CNF-based scaffolds.



345

Fig. 4. TEM images of (a) CNF and (b) CNT; SEM images of (c) CNF_{APTMS}/CNT₅₀ foam, (d)
 CNF_{MTMS}/CNT₅₀ foam, (e) CNF_{APTMS}/CNT₅₀-PEG composite and (f) CNF_{MTMS}/CNT₅₀-Pw
 composite.

349

The leakage testing of the prepared composite PCMs was conducted to confirm their formstability, and the results are shown in Fig. 5 and Table 4. For the CNF_{APTMS}/CNT_{50} -PEG composite, the PCM leakage percentage was 1.81%, which is slightly higher than that of the CNF_{APTMS} -PEG composite. The possible reason is that the introduction of CNTs may interfere 354 with the internal structure of foams and thus the absorption and stabilization of PCMs. Similarly, the CNF_{MTMS}/CNT₅₀-Pw composite also exhibits slightly higher PCM leakage than CNF_{MTMS}-355 356 Pw composite. Despite so, the as-prepared CNF_{APTMS}/CNT₅₀-PEG composite has PCM fraction 357 of 93.63%, and CNF_{MTMS}/CNT₅₀-Pw composite has a PCM fraction of 91.77%, a value higher 358 than previously reported results (40–50% [34], 40–70% [35], 77.5% [36], 85% [6], 70–90% 359 [37]). Composite PCMs with high loading levels of PCM are preferred for practical uses due to 360 their high energy storage density and cost-effectiveness. Meanwhile, the negligible PCM 361 leakage of the obtained composite PCMs favors their long-term energy storage applications 362



Fig. 5. Leakage testing of foam-stabilized composite PCMs on filter paper: (a) CNF_{APTMS} PEG, (b) CNF_{MTMS}-Pw, (c) CNF_{APTMS}/CNT₅₀-PEG and (d) CNF_{MTMS}/CNT₅₀-Pw.
 366

Table 4. The effect of CNF-based foams on the PCM absorption capacity and leakage
 percentage.

Foam	Foam density (kg/m ³)	Foam porosity (%)	PCM absorption capacity (%)	PCM Leakage percentage (%)
CNF _{APTMS}	59.88	94.78	94.40	1.70
CNF _{APTMS} /CNT ₅₀	67.26	94.52	93.63	1.81
CNF _{MTMS}	59.91	96.57	92.08	0.88
CNF _{MTMS} /CNT ₅₀	64.53	96.39	91.77	1.71

369

363

370 **3.3 Chemical and crystalline structure analyses**

The chemical structures of composite PCMs and their components were examined by FT-IR, and the collected spectra are presented in Figs. 6a and b. As shown in Fig. 6a, the spectrum of neat CNF exhibits absorption bands at 3328 cm⁻¹ and 897 cm⁻¹ that are ascribed to the hydroxyls groups and characteristic glucosidic linkages of cellulose structures, respectively

375	[38]; the spectrum of APTMS modified CNF (i.e. CNF _{APTMS}) displayed new banks at 1610,
376	1506, 1226, 1032, and 694 cm ⁻¹ that can be assigned to $-NH_2$ in-plane deformation, $-CH_2-$
377	scissoring, Si-C bending, Si-O stretching, and -NH2 out-of-plane bending vibrations,
378	respectively [39]; the spectrum of MTMS modified CNF (i.e. CNF_{MTMS}) displayed a
379	characteristic broad band at 897 cm ⁻¹ that is assigned to Si–OH stretching, and a sharp band at
380	777 cm ⁻¹ that is ascribed to Si-C and/or Si-O stretching [40]. These changes in FT-IR spectra
381	suggest the successful chemical modification of CNF. The FT-IR spectra of PEG and Pw are
382	displayed in Fig. 6b. In the FT-IR spectrum of pristine PEG, characteristics peak at
383	3342 cm ^{-1} ascribed to the stretching vibration of O–H group and 1107 cm ^{-1} due to the C–O–C
384	symmetric stretching vibration, peaks at 2887 cm^{-1} , 1469 cm^{-1} , 949 cm^{-1} and
385	841 cm ⁻¹ corresponding to the C–H vibration [41], are visible. In the spectrum of Pw, bands at
386	2916 cm ^{-1} and 2848 cm ^{-1} are ascribed to C–H stretching of –CH ₃ and –CH ₂ groups, respectively,
387	which are the characteristics of alkanes [42]. The spectra of the prepared CNF_{APTMS}/CNT_{50} -
388	PEG and CNF_{MTMS}/CNT_{50} -Pw composite PCMs are found to be simply the mixture of the
389	characteristic peaks of corresponding porous scaffolds (i.e., CNF/CNT foams) and PCMs, and
390	no extra peaks were generated (Fig. 6b), indicating the absence of chemical reactions between
391	the scaffolds and PCMs. Therefore, PCM was encapsulated in the porous foam via physical
392	absorption.





Fig. 6. FT-IR spectra of (a) pristine CNF and chemically modified CNF, and (b) composite PCMs
 and related components; XRD patterns of (c) pristine CNF and chemically modified CNF, and (d)
 composite PCMs and related components.

398 The crystalline structures of composite PCMs and their components were investigated, 399 and the obtained XRD patterns are shown in Figs. 6c and 6d. The XRD pattern of pristine CNF 400 shows the characteristic peaks at 16.2° and 22.2° that are assigned to the (110) and (200) crystal 401 planes of cellulose, respectively (Fig. 6c) [43]. The XRD pattern of silvlated CNF (i.e., CNF_{APTMS} and CNT_{MTMS}) differed from the XRD pattern of pristine CNF, i.e., the peak at 16.3° 402 403 shifted to left, which is assigned to the conversions of polymorphs from the original cellulose I to cellulose II and indicates the success of chemical modification of CNF [44]. Fig. 6d compares 404 the XRD patterns of neat PCM and the prepared composite PCMs. It was found that the patterns 405 of composite PCMs show two main diffraction peaks similar to those of neat PCMs, indicating 406 407 that using CNF-based hybrid foam to encapsulate PCMs did not affect their crystal structure [45]. Similar to the FT-IR results, the diffraction peaks of the composite PCMs contain all the 408 409 characteristic peaks from their corresponding components, and no new peaks appear. This again, 410 verified the absence of chemical reactions or interactions between the supporting scaffolds and411 PCMs.

412

413 **3.4 Phase change and thermal properties**

414 Thermal energy storage and release by PCMs are fulfilled through their phase transitions, 415 and the thermal properties of PCMs such as thermal conduction performance and thermal 416 stability are critical to the speed and efficiency of energy storage. Therefore, it is necessary to 417 examine the phase change and thermal properties of the prepared composite PCMs. The phase change enthalpies and transition temperature of PCM samples were determined by DSC method. 418 419 As illustrated by Fig. 7a, all DSC curves of PEG-based PCM samples displayed one main phase 420 change peak during both melting (endothermic) and freezing (exothermic) processes, which 421 corresponds to the solid-liquid phase transitions. However, the DSC curves of Pw-based PCM 422 samples exhibited two peaks during their phase transitions (Fig. 7b). The lower-temperature 423 peak was assigned to the solid-solid phase transition, and the higher-temperature peak was 424 attributed to the solid-liquid phase transition [46]. The phase change enthalpies and transition 425 temperature of PCM samples are extracted from the DSC curves and are listed in Tables 5 and 426 6. The phase change enthalpy of neat PEG is 151.1 kJ/kg, and the melting temperature, onset 427 temperature, is 26.1 °C during heating, and similar values were obtained during cooling. As 428 noticed, neat PEG exhibits quite close melting temperature and freezing temperature, indicating 429 the absence of supercooling problem, which is an advantage of organic PCMs. The phase 430 change temperatures of composite PCMs are slightly lower than that of neat PEG, which can 431 be attributed to the improved form-stability that enhances the heat transfer efficiency in phase 432 transitions [47]. The phase change enthalpies of the prepared composite PCMs are 4.6%–5.4% 433 lower than the enthalpy of neat PEG because non-phase change components (i.e., CNF and 434 CNTs) were incorporated. These enthalpy reductions roughly agree with the PEG fractions of 435 the prepared composite PCMs (Table S1). Similar findings can also be extracted for Pw-based 436 PCM samples, i.e., reason phase change temperatures and enthalpies were obtained. Besides, 437 composite PCMs prepared in this work exhibit relatively higher enthalpies than the composites 438 reported elsewhere [46,48–52]. The high loading levels of PCMs and the superior form-stability



439 of the composite PCMs would contribute to their favorable phase change performance for440 practical applications.

Fig. 7. DSC curves of (a) PEG and PEG-based composite PCMs and (c) their curves after 100
cycles of melting and freezing; (b) Pw and Pw-based composite PCMs and (d) their curves
after 100 cycles of melting and freezing.

Table 5. Melting points, freezing points and enthalpies of PEG-based PCM samples.

	Hea	ating process			Cooling process		
PCM sample	Melting point (°C)	Enthalpy (kJ/kg)	Enthalpy reduction (%)	Freezing point (°C)	Enthalpy (kJ/kg)	Enthalpy reduction (%)	
PEG	26.1	151.4	_	26.2	151.3	_	
CNF _{APTMS} -PEG	25.2	144.2	4.76	25.6	144.3	4.63	
CNF _{APTMS} /CNT ₅₀ -PEG	25.2	143.3	5.35	24.9	143.1	5.42	

	Hea	Heating process			Cooling process		
PCM sample	Melting point (°C)	Enthalpy (kJ/kg)	Enthalpy reduction (%)	Freezing point (°C)	Enthalpy (kJ/kg)	Enthalpy reduction (%)	
Pw	57.7	202.8	-	55.5	202.7	-	
CNF _{MTMS} -Pw	54.2	185.9	8.3	57.0	185.9	8.3	
CNF _{MTMS} /CNT ₅₀ -Pw	53.4	184.6	9.0	57.2	184.5	9.0	

449 **Table 6.** Melting points, freezing points and enthalpies of Pw-based PCM samples.

451 Thermal reliability of PCMs is desired for their reliable and durable applications. The 452 thermal reliabilities of the prepared composite PCMs were determined by measuring their phase 453 change properties after a number of thermal cycles. The phase change enthalpies and transition 454temperatures of the prepared composite PCMs after 100 melting/freezing cycles that are 455 extracted from DSC curves (Figs. 7c and 7d) are summarized in Tables S2 and S3. Results show 456 that the phase change enthalpies of PEG-based composite PCMs decreased approximately by 12%-14%, while the Pw-based composite PCMs decreased approximately by 2%-6%, 457 458 indicating their unfavorable thermal reliability for long-term applications. Unexpectedly, the 459 phase change enthalpies of neat PEG and Pw also decreased after 100 thermal cycles. This is 460 possibly related to their relatively low molecular weight, which may cause the potential 461 degradation of PCM in repeated heating and cooling. Despite so, the thermal reliability of the 462 prepared composite PCMs should be improved in future work.

463 Thermal stabilities of neat PCM and the prepared composite PCMs were evaluated by 464 thermogravimetric analysis (Fig. 8). As shown in Fig. 8a, the weight loss of neat PEG began at 465 220 °C, 50 wt% of this sample decomposed at 372.6 °C, and its decomposition completed at 420 °C, and the residual mass of neat PEG after heating approaches zero, and similar thermal 466 467 degradation process was reported elsewhere [50,53]. Compared to neat PEG, the prepared 468 composite PCMs exhibited slower rates of weight loss during heating, i.e., 50 wt% of 469 CNF_{APTMS}-PEG decomposed at 393.4 °C, and 50 wt% of CNF_{APTMS}/CNT₅₀-PEG decomposed 470 at 404 °C; and their weight losses completed at higher temperatures (approximately 425 °C for CNF_{APTMS}-PEG and 435 °C for CNF_{APTMS}/CNT₅₀-PEG), indicating their improved thermal 471

472 stabilities. The residual mass of composite PCMs is higher than that of neat PEG, which can be 473 correlated to the introduction of thermal stable ingredient CNTs that are even stable at 474 temperatures up to approximately 800 °C [54]. In particular, CNFs used in this work were 475 prepared from bleached kraft pulp where the amounts of hemicellulose and lignin can be 476 ignored. Considering that cellulose has a pyrolysis temperature of 315–400 °C [55], it may also positively contribute to the improved thermal stability of composite PCMs under heating. It is 477 478 reasonable that the final residual solid content of CNFAPTMS/CNT50-PEG was the highest among 479 all the tested PCM samples because of its higher addition levels of thermally stable CNTs. 480 Similar findings can also be seen for Pw-based composite PCMs (Fig. 8b), i.e., the decomposition temperature of composite PCMs (approximately 350 °C) are higher than that of 481 482 neat Pw (315 °C) and more residues retained for composite PCMs due to the incorporation of 483 relatively stable foam scaffolds. In conclusion, the prepared composite PCMs exhibit greater 484 thermal stabilities over neat PCMs, which is likely to benefit their high-temperature 485 applications.

486



Fig. 8. Thermogravimetric curves of (a) PEG and PEG-based composite PCMs and (b) Pw
 and Pw- based Composite PCMs.

490

487

491 **3.5 Application investigation of composite PCMs**

Solar energy harvesting and utilization is one of the most promising application scenarios for PCMs. To investigate the heat absorption behavior of PCM samples under sunlight, Xenon lamp with a full solar spectrum was used as the heat source, and the real-time temperature of 495 samples was recorded (Figs. 9a & 9b). The neat PCM samples were not tested because of their 496 rapid melting and serious leakage during heating. On the contrary, the tested composite samples 497 remained almost intact upon heating, which indicated their favorable form-stabilities. During 498 the whole heating process, the temperature of composite PCMs without CNTs is always lower 499 than that of composite PCMs containing CNTs. Moreover, a higher CNT content led to faster 500 temperature rise and higher final temperature before removing the heat source. These findings 501 are consistent with those in other reports [56–58]. After removing the lamp, the PCM samples 502 started to release the stored energy, after which the sample temperature gradually decreased to 503 ambient level. It was found that the heat release period of composite PCMs containing CNTs is 504 longer than that of neat PCMs and composite PCMs without CNTs, indicating that the former 505 samples absorbed and stored more latent heat during heating. Interestingly, the final 506 temperatures of all samples decreased to ambient temperature almost simultaneously, which 507 suggests that composite PCMs containing CNTs experienced more quick heat transfer from 508 samples to the surroundings. These observations verified the enhanced thermal conduction 509 performance of composite PCMs containing CNTs, which may contribute to more efficient heat 510 storage applications.

511 The measure thermal conductivities of PCM samples are presented in Fig. 9c. The results 512 indicate that CNT-containing PCM composites exhibited improved thermal conductivity over 513 pure PCM, which can be attributed to the excellent heat transfer performance of CNTs. The 514 thermal conductivity of CNF_{APTMS}/CNT₅₀-PEG and CNF_{MTMS}/CNT₅₀-Pw is 15.1% and 13.9% 515 higher than that of neat PEG and Pw, respectively. These results along with the results in Figs. 516 8a and b proved that the introduction of CNTs improved the heat transfer performance of PCM composites. Nevertheless, one thing to confess is that the improvement in thermal 517 conductivities of PCMs is not sufficiently high. Two reasons may account for the low absolute 518 519 values of the thermal conductivity of CNF_{APTMS}/CNT₅₀-PEG and CNF_{MTMS}/CNT₅₀-Pw. First of 520 all, the high PCM fractions (93.63% for PEG and 91.77% for Pw) in the PCM composites 521 suppressed the improvement in thermal conductivity [59]. Secondly, thermal conductive 522 properties along the CNT axis are very different from the transverse direction (estimated up to 523 3500 W/(m•K) in the axial direction vs. 10.23 W/(m•K) in the transverse direction [60]), thus

the anisotropic distribution of hollow CNTs in PCM composites directly affected the thermal conductivity values. Similar observations have been reported elsewhere [59]. Therefore, the type and dose of carbon nanomaterials should be care for when they are used to enhance the thermal conductivity of PCMs.

528 It is known that TEG is a type of solid-state semiconductor device that converts a temperature difference and heat flow into a useful DC power source, and PCMs-based heat 529 530 exchangers can be applied to transfer and dissipate heat for the optimization of the thermal 531 management system of TEGs [61]. Novel PCM sandwich structures (Fig. 1.) were designed for 532 actual application based on the differences between the phase change performances of PEG and Pw. Pw-based composite PCM with high CNT content (i.e. CNF_{MTMS}/CNT₅₀-Pw) was placed 533 534 on the top of TEG due to its high phase change enthalpy (184.6 kJ/kg) and relatively high phase 535 transition temperature (53.4 °C); PEG-based composite PCMs were attached to the bottom of 536 TEG because of its lower phase transition temperature (about 25 °C). A thermoelectric generator 537 is positioned in the middle of two pieces of composite PCMs for voltage generation. Due to 538 such a structure design, the original heat sink that is attached to the bottom of TEG for better 539 heat dissipation was replaced by the PEG-based composite PCM. As shown in Fig. 9d, the 540 control (i.e., TEG without any PCMs on it) generated a 0.05 V voltage during heating, a value 541 approximately half of that in Fig. S4. The reason might be that the original aluminum heat sink 542 structure was immersed in iced water, and this gave a faster heat dissipation to the TEG bottom 543 surface and then a greater temperature difference between TEG top and bottom surfaces, which 544 resulted in more efficient voltage generation [62]. When only CNF_{MTMS}/CNT₅₀-Pw was positioned on the top surface of TEG, the generated voltage gradually increased and then 545 546 leveled off at 0.10 V during sunlight irradiation. A similar tendency was observed when PCM 547 sandwich structure I was applied, and the higher voltage of 0.14 V can be ascribed to the 548 improved heat absorption and dissipation of the TEG bottom surface contributed by CNT_{APTMS}-549 PEG composite PCM. When PCM sandwich structure II was applied, the maximum voltage 550level was unaffected, but two voltage plateau regions appeared. The occurrence of steady 551 voltage generation can be attributed to the phase transitions of composite PCMs that create 552 stable temperature differences of TEG surfaces. When the sunlight irradiator was removed, all

the curves showed slower voltage decline than did the control, which can be attributed to the decrease of temperature difference of two TEG surfaces by the released heat from composite PCMs, as evidenced by the curves at the time length of 4000–5500 s. Therefore, the proposed PCM sandwich structures exhibit attractive heat absorption and dissipation, and more efficient voltage maintenance in the absence of heating power was observed. However, the voltage level should be improved when using these PCM sandwich structures for practical applications such as solar-thermal-electricity conversion systems, and this will be the focus of our future work.







Fig. 9. Temperature- heating time curves of (a) PEG based Composite PCMs and (b) Pw based
 PCM under solar simulator, (c) thermal conductivity of PCM samples and (d) time course of the
 open-circuit voltage of the thermoelectric generator with/without sandwich PCMs on it.

565 **4. Conclusion**

566 The present study suggests the importance of surface chemistry tuning and thermal conductivity enhancer introduction of supporting scaffolds for the performance improvement 567 568 of organic PCMs. Chemistry modification of CNF enhanced the foam shape-stability and its 569 affinity with PCMs. The prepared composite PCMs had compact structures with high loading 570 levels of PCMs (93.63% for PEG and 91.77% for Pw) due to the highly porous foam structure 571 and favorable foam-PCM compatibility. Meanwhile, the use of CNF-based foams remarkably 572 inhibited PCM leakage during their phase transitions. Consequently, the prepared composite 573 PCMs exhibited reasonable phase change enthalpies and phase transition temperatures. Due to 574 the introduction of CNTs, composite PCMs displayed enhanced thermal stability and heat 575 conduction performance, which benefit their applications in solar energy harvesting, storage 576 and utilization because of the enhanced sunlight absorption and heat transfer. Interestingly, the designed PCM sandwich structure in this research is also promising for voltage maintenance of 577 578 TEG-based power systems in the lack of sunlight irradiation. Nevertheless, the thermal 579 conductivity and thermal reliability of composite PCMs needs to be further improved for long-580 term LHS applications. Overall, the present work shows the potential of sustainable polymer-581 based supporting scaffolds for the preparation and energy application of form-stable composite 582 PCMs.

583

584 **Associated Content**

- 585 See supplementary data.
- 586

587 **CRediT authorship contribution statement**

Zhenghui Shen and Soojin Kwon contributed equally to this work. Zhenghui Shen:
Conceptualization, Methodology, Investigation, Writing-Original Draft. Soojin Kwon:
Conceptualization, Methodology, Investigation, Writing-Original Draft. Hak Lae Lee:
Writing-Review & Editing, Supervision. Martti Toivakka: Writing-Review & Editing.
Kyudeok Oh: Conceptualization, Methodology, Investigation, Writing-Review & Editing,
Funding acquisition.

594 **Declaration of Competing Interest**

- 595 The authors declare that they have no known competing financial interests or personal 596 relationships that could have appeared to influence the work reported in this paper.
- 597

598 Acknowledgments

- 599 This work was supported by research fund of Chungnam National University. Professor Hye 600 Jung Youn is thanked for her assistance in preparing CNF.
- 601

602 **References**

- W. Aftab, A. Usman, J. Shi, K. Yuan, M. Qin, R. Zou, Phase change material-integrated
 latent heat storage systems for sustainable energy solutions, Energy Environ. Sci. 14 (8)
 (2021) 4268–4291. https://doi.org/10.1039/D1EE00527H.
- S.A. Mohamed, F.A. Al-Sulaiman, N.I. Ibrahim, Md.H. Zahir, A. Al-Ahmed, R. Saidur,
 B.S. Yılbaş, A.Z. Sahin, A review on current status and challenges of inorganic phase
 change materials for thermal energy storage systems, Renew. Sust. Energ. Rev. 70 (2017)
 1072–1089. https://doi.org/10.1016/j.rser.2016.12.012.
- 610 [3] M.M. Farid, A.M. Khudhair, S.A.K. Razack, S. Al-Hallaj, A review on phase change
 611 energy storage: materials and applications, Energy Convers. Manag. 45(9–10) (2004)
 612 1597–1615. https://doi.org/10.1016/j.enconman.2003.09.015.
- [4] A. Safari, R. Saidur, F.A. Sulaiman, Y. Xu, J. Dong, A review on supercooling of phase
 change materials in thermal energy storage systems, Renew. Sust. Energ. Rev. 70 (2017)
 905–919. https://doi.org/10.1016/j.rser.2016.11.272.
- [5] D.G. Atinafu, Y.S. Ok, H.W. Kua, S. Kim, Thermal properties of composite organic phase
 change materials (PCMs): A critical review on their engineering chemistry, Appl. Therm.
 Eng. 181 (2020) 115960. https://doi.org/10.1016/j.applthermaleng.2020.115960.
- [6] M.R. Yazdani, R. Ajdary, A. Kankkunen, O.J. Rojas, A. Seppälä, Cellulose nanofibrils
 endow phase-change polyethylene glycol with form control and solid-to-gel transition for
 thermal energy storage, ACS Appl. Mater. Interfaces. 13 (5) (2021) 6188–6200.
 https://doi.org/10.1021/acsami.0c18623.

- [7] Y. Zhao, L. Jin, B. Zou, G. Qiao, T. Zhang, L. Cong, F. Jiang, C. Li, Y. Huang, Y. Ding,
 Expanded graphite-paraffin composite phase change materials: Effect of particle size on
 the composite structure and properties, Appl. Therm. Eng. 171 (2020) 115015.
 https://doi.org/10.1016/j.applthermaleng.2020.115015.
- 627 L. Liu, J. Chen, Y. Qu, T. Xu, H. Wu, G. Huang, X. Zhou, L. Yang, A foamed cement [8] blocks with paraffin/expanded graphite composite phase change solar thermal absorption 628 Sol. Cells. 200 (2019)629 material, Sol. Energy Mater 110038. 630 https://doi.org/10.1016/j.solmat.2019.110038.
- [9] S. Sundararajan, A.B. Samui, P.S. Kulkarni, Versatility of polyethylene glycol (PEG) in
 designing solid-solid phase change materials (PCMs) for thermal management and their
 application to innovative technologies, J. Mater. Chem. A. 5 (35) (2017) 18379–18396.
 https://doi.org/10.1039/C7TA04968D.
- [10] S. Ramakrishnan, J. Sanjayan, X. Wang, M. Alam, J. Wilson, A novel paraffin/expanded
 perlite composite phase change material for prevention of PCM leakage in cementitious
 composites, Appl. Energy. 157 (2015) 85–94.
 https://doi.org/10.1016/j.apenergy.2015.08.019.
- [11] K. Yu, Y. Liu, Y. Yang, Review on form-stable inorganic hydrated salt phase change
 materials: Preparation, characterization and effect on the thermophysical properties, Appl.
 Energy. 292 (2021) 116845. https://doi.org/10.1016/j.apenergy.2021.116845.
- [12] D. Klemm, B. Heublein, H.-P. Fink, A. Bohn, Cellulose: Fascinating biopolymer and
 sustainable raw material, Angew. Chem. Int. Ed. 44 (22) (2005) 3358–3393.
 https://doi.org/10.1002/anie.200460587.
- [13] D. Klemm, F. Kramer, S. Moritz, T. Lindström, M. Ankerfors, D. Gray, A. Dorris,
 Nanocelluloses: A new family of nature-based materials, Angew. Chem. Int. Ed. 50 (24)
 (2011) 5438–5466. https://doi.org/10.1002/anie.201001273.
- [14] S. Ummartyotin, H. Manuspiya, A critical review on cellulose: From fundamental to an
 approach on sensor technology, Renewable and Sustainable Energy Reviews. 41 (2015)
 402–412. https://doi.org/10.1016/j.rser.2014.08.050.
- [15] H. Lee, J. Sundaram, S. Mani, Production of cellulose nanofibrils and their application to

- food: A review, In: R. Prasad, V. Kumar, M. Kumar (Eds.), Nanotechnology, Springer
 Singapore, Singapore, 2017: pp. 1–33. https://doi.org/10.1007/978-981-10-4678-0 1.
- [16] M. Pääkkö, M. Ankerfors, H. Kosonen, A. Nykänen, S. Ahola, M. Österberg, J.
 Ruokolainen, J. Laine, P.T. Larsson, O. Ikkala, T. Lindström, Enzymatic hydrolysis
 combined with mechanical shearing and high-pressure homogenization for nanoscale
 cellulose fibrils and strong gels, Biomacromolecules. 8 (6) (2007) 1934–1941.
 https://doi.org/10.1021/bm061215p.
- [17] Q.-F. Guan, H.-B. Yang, Z.-M. Han, L.-C. Zhou, Y.-B. Zhu, Z.-C. Ling, H.-B. Jiang, P.-F.
 Wang, T. Ma, H.-A. Wu, S.-H. Yu, Lightweight, tough, and sustainable cellulose
 nanofiber-derived bulk structural materials with low thermal expansion coefficient, Sci.
 Adv. 6 (18) (2020) eaaz1114. https://doi.org/10.1126/sciadv.aaz1114.
- [18] X. Chen, P. Cheng, Z. Tang, X. Xu, H. Gao, G. Wang, Carbon-based composite phase
 change materials for thermal energy storage, transfer, and conversion, Adv. Sci. 8 (9)
 (2021) 2001274. https://doi.org/10.1002/advs.202001274.
- [19] K. Yuan, J. Shi, W. Aftab, M. Qin, A. Usman, F. Zhou, Y. Lv, S. Gao, R. Zou, Engineering 666 667 the thermal conductivity of functional phase-change materials for heat energy conversion, 668 30 storage, and utilization, Adv. Funct. Mater. (8) (2020)1904228. 669 https://doi.org/10.1002/adfm.201904228.
- [20] S. Wu, T. Yan, Z. Kuai, W. Pan, Thermal conductivity enhancement on phase change
 materials for thermal energy storage: A review, Energy Stor. Mater. 25 (2020) 251–295.
 https://doi.org/10.1016/j.ensm.2019.10.010.
- [21] J.N. Coleman, U. Khan, W.J. Blau, Y.K. Gun'ko, Small but strong: A review of the
 mechanical properties of carbon nanotube-polymer composites, Carbon. 44 (9) (2006)
 1624–1652. https://doi.org/10.1016/j.carbon.2006.02.038.
- [22] W. Yang, Z. Zhao, K. Wu, R. Huang, T. Liu, H. Jiang, F. Chen, Q. Fu, Ultrathin flexible
 reduced graphene oxide/cellulose nanofiber composite films with strongly anisotropic
 thermal conductivity and efficient electromagnetic interference shielding, J. Mater. Chem.
 C. 5 (15) (2017) 3748–3756. https://doi.org/10.1039/C7TC00400A.
- 680 [23] Y. Li, H. Zhu, F. Shen, J. Wan, S. Lacey, Z. Fang, H. Dai, L. Hu, Nanocellulose as green

- dispersant for two-dimensional energy materials, Nano Energy. 13 (2015) 346–354.
 https://doi.org/10.1016/j.nanoen.2015.02.015.
- [24] Q. Zheng, Z. Cai, S. Gong, Green synthesis of polyvinyl alcohol (PVA)-cellulose
 nanofibril (CNF) hybrid aerogels and their use as superabsorbents, J. Mater. Chem. A. 2
 (9) (2014) 3110–3118. https://doi.org/10.1039/C3TA14642A.
- [25] S. Jiang, M. Zhang, M. Li, L. Liu, L. Liu, J. Yu, Cellulose nanofibril (CNF) based aerogels
 prepared by a facile process and the investigation of thermal insulation performance,
 Cellulose. 27 (11) (2020) 6217–6233. https://doi.org/10.1007/s10570-020-03224-4.
- [26] Z.A. Qureshi, H.M. Ali, S. Khushnood, Recent advances on thermal conductivity
 enhancement of phase change materials for energy storage system: A review. Int. J. Heat
- 691 Mass Transf. 127 (2018) 838–856.
- 692 https://doi.org/10.1016/j.ijheatmasstransfer.2018.08.049.
- [27] K. Khwaldia, E. Arab-Tehrany, S. Desobry, Biopolymer coatings on paper packaging 693 694 9 materials, Compr. Rev. Food Sci. Food Saf. (1)(2010)82–91. https://doi.org/10.1111/j.1541-4337.2009.00095.x. 695
- [28] J.-W. Rhim, Effect of moisture content on tensile properties of paper-based food
 packaging materials, Food Sci. Biotechnol. 19 (1) (2010) 243–247.
 https://doi.org/10.1007/s10068-010-0034-x.
- [29] S. Wu, T. Li, Z. Tong, J. Chao, T. Zhai, J. Xu, T. Yan, M. Wu, Z. Xu, H. Bao, T. Deng, R.
 Wang, High-performance thermally conductive phase change composites by large-size
 oriented graphite sheets for scalable thermal energy harvesting. Adv. Mater. 31 () (2019)
 1905099. https://doi.org/10.1002/adma.201905099.
- [30] F. Martoïa, T. Cochereau, P.J.J. Dumont, L. Orgéas, M. Terrien, M.N. Belgacem,
 Cellulose nanofibril foams: Links between ice-templating conditions, microstructures and
 mechanical properties, Mater. Des. 104 (2016) 376–391.
 https://doi.org/10.1016/j.matdes.2016.04.088.
- [31] Z. Shen, S. Kwon, H.L. Lee, M. Toivakka, K. Oh, Cellulose nanofibril/carbon nanotube
 composite foam-stabilized paraffin phase change material for thermal energy storage and
 conversion, Carbohydr. Polym. 273 (2021) 118585.

710 https://doi.org/10.1016/j.carbpol.2021.118585.

- [32] K. Kriechbaum, P. Munier, V. Apostolopoulou-Kalkavoura, N. Lavoine, Analysis of the
 porous architecture and properties of anisotropic nanocellulose foams: A novel approach
 to assess the quality of cellulose nanofibrils (CNFs), ACS Sustain. Chem. Eng. 6 (9) (2018)
 11959–11967. https://doi.org/10.1021/acssuschemeng.8b02278.
- [33] X. Du, J. Qiu, S. Deng, Z. Du, X. Cheng, H. Wang, Alkylated nanofibrillated
 cellulose/carbon nanotubes aerogels supported form-stable phase change composites with
 improved *n*-alkanes loading capacity and thermal conductivity, ACS Appl. Mater.
 Interfaces. 12 (5) (2020) 5695–5703. https://doi.org/10.1021/acsami.9b17771.
- [34] S. Salimian, M. Montazer, A.S. Rashidi, N. Soleimani, A. Bashiri Rezaie, PCM nanofibrous composites based on PEG/PVA incorporated by TiO₂/Ag nanoparticles for thermal energy management, J. Appl. Polym. Sci. 138 (46) (2021) 51357. https://doi.org/10.1002/app.51357.
- 723 [35] B. Wu, Y. Jiang, Y. Wang, C. Zhou, X. Zhang, J. Lei, Study on a PEG/epoxy shape-724 stabilized phase change material: Preparation, thermal properties and thermal storage 725 performance. Int. J. Heat Mass Transf. 126 (2018)1134-1142. 726 https://doi.org/10.1016/j.ijheatmasstransfer.2018.05.153.
- [36] L. Zhen, G. Meng, B. Zhou, W. Ma, Y. Yang, X. Duan, Y. Fu, H. Wang, Efficient utilization of interparticle mesopores in aluminosilicate towards thermal energy storage, J. Energy Storage. 36 (2021) 102359. https://doi.org/10.1016/j.est.2021.102359.
- [37] C. Wang, L. Feng, W. Li, J. Zheng, W. Tian, X. Li, Shape-stabilized phase change
 materials based on polyethylene glycol/porous carbon composite: The influence of the
 pore structure of the carbon materials, Sol. Energy Mater Sol. Cells. 105 (2012) 21–26.
 https://doi.org/10.1016/j.solmat.2012.05.031.
- [38] D.A. Gopakumar, A.R. Pai, Y.B. Pottathara, D. Pasquini, L. Carlos de Morais, M. Luke,
 N. Kalarikkal, Y. Grohens, S. Thomas, Cellulose nanofiber-based polyaniline flexible
 papers as sustainable microwave absorbers in the X-band, ACS Appl. Mater. Interfaces.
 10 (23) (2018) 20032–20043. https://doi.org/10.1021/acsami.8b04549.
- 738 [39] H. Kono, T. Uno, H. Tsujisaki, T. Matsushima, K. Tajima, Nanofibrillated bacterial

- cellulose modified with (3-Aminopropyl)trimethoxysilane under aqueous conditions:
 Applications to poly(methyl methacrylate) fiber-reinforced nanocomposites, ACS Omega.
 5 (45) (2020) 29561–29569. https://doi.org/10.1021/acsomega.0c04533.
- 742 [40] S. Zhao, Z. Zhang, G. Sèbe, R. Wu, R.V. Rivera Virtudazo, P. Tingaut, M.M. Koebel, 743 Multiscale assembly of superinsulating silica aerogels within silylated nanocellulosic scaffolds: Improved mechanical properties promoted by nanoscale chemical 744745 compatibilization, Mater. 25 Adv. Funct. (15)(2015)2326-2334. 746 https://doi.org/10.1002/adfm.201404368.
- [41] Z. Liu, Y. Zhang, K. Hu, Y. Xiao, J. Wang, C. Zhou, J. Lei, Preparation and properties of
 polyethylene glycol based semi-interpenetrating polymer network as novel form-stable
 phase change materials for thermal energy storage, Energy Build. 127 (2016) 327–336.
 https://doi.org/10.1016/j.enbuild.2016.06.009.
- [42] T. Xu, Y. Li, J. Chen, H. Wu, X. Zhou, Z. Zhang, Improving thermal management of
 electronic apparatus with paraffin (PA)/expanded graphite (EG)/graphene (GN)
 composite material, Appl. Therm. Eng. 140 (2018) 13–22.
 https://doi.org/10.1016/j.applthermaleng.2018.05.060.
- [43] M. Wada, L. Heux, J. Sugiyama, Polymorphism of cellulose I family: Reinvestigation of
 cellulose IV, Biomacromolecules. 5 (4) (2004) 1385 1391.
 https://doi.org/10.1021/bm0345357.
- [44] J. Gong, J. Li, J. Xu, Z. Xiang, L. Mo, Research on cellulose nanocrystals produced from
 cellulose sources with various polymorphs, RSC Adv. 7 (53) (2017) 33486–33493.
 https://doi.org/10.1039/C7RA06222B.
- [45] X. Zhang, Z. Huang, B. Ma, R. Wen, M. Zhang, Y. Huang, M. Fang, Y. Liu, X. Wu,
 Polyethylene glycol/Cu/SiO₂ form stable composite phase change materials: Preparation,
 characterization, and thermal conductivity enhancement, RSC Adv. 6 (63) (2016) 58740–
 58748. https://doi.org/10.1039/C6RA12890D.
- [46] W.-m. Guan, J.-h. Li, T.-t. Qian, X. Wang, Y. Deng, Preparation of paraffin/expanded
 vermiculite with enhanced thermal conductivity by implanting network carbon in
 vermiculite layers, Chem. Eng. J. 277 (2015) 56–63.

- 768 https://doi.org/10.1016/j.cej.2015.04.077.
- [47] C.V. Podara, I.A. Kartsonakis, C.A. Charitidis, Towards phase change materials for
 thermal energy storage: Classification, improvements and applications in the building
 sector, Appl. Sci. 11 (4) (2021) 1490. https://doi.org/10.3390/app11041490.
- [48] Ö. Gök, C. Alkan, Y. Konuklu, Developing a poly(ethylene glycol)/cellulose phase
 change reactive composite for cooling application, Sol. Energy Mater Sol. Cells. 191
 (2019) 345–349. https://doi.org/10.1016/j.solmat.2018.11.038.
- [49] Y. Yan, W. Li, R. Zhu, C. Lin, R. Hufenus, Flexible phase change material fiber: A simple
 route to thermal energy control textiles, Materials. 14 (2) (2021) 401.
 https://doi.org/10.3390/ma14020401.
- [50] Y.-F. Shih, C.-H. Wang, M.-L. Tsai, J.-M. Jehng, Shape-stabilized phase change
 material/nylon composite based on recycled diatomite, Mater. Chem. Phys. 242 (2020)
 122498. https://doi.org/10.1016/j.matchemphys.2019.122498.
- [51] A. Karaıpeklı, A. Sarı, K. Kaygusuz, Thermal characteristics of paraffin/expanded perlite
 composite for latent heat thermal energy storage, Energy Source. Part A. 31 (10) (2009)
 814–823. https://doi.org/10.1080/15567030701752768.
- [52] C. Li, H. Yang, Expanded vermiculite/paraffin composite as a solar thermal energy
 storage material, J. Am. Ceram. Soc. 96 (9) (2013) 2793–2798.
 https://doi.org/10.1111/jace.12504.
- 787 [53] M. Senthilkumar, K.R. Balasubramanian, R.K. Kottala, S.P. Sivapirakasam, L. 788 Maheswari, Characterization of form-stable phase-change material for solar photovoltaic 789 cooling, J. Therm. Anal. Calorim. 141 (6)(2020)2487-2496. 790 https://doi.org/10.1007/s10973-020-09521-1.
- [54] Q. Liu, W. Ren, F. Li, H. Cong, H.-M. Cheng, Synthesis and high thermal stability of
 double-walled carbon nanotubes using nickel formate dihydrate as vatalyst precursor, J.
 Phys. Chem. C. 111 (13) (2007) 5006–5013. https://doi.org/10.1021/jp068672k.
- [55] H. Yang, R. Yan, H. Chen, D.H. Lee, C. Zheng, Characteristics of hemicellulose, cellulose
 and lignin pyrolysis, Fuel. 86 (12 13) (2007) 1781–1788.
 https://doi.org/10.1016/j.fuel.2006.12.013.

- [56] D. Zou, X. Ma, X. Liu, P. Zheng, Y. Hu, Thermal performance enhancement of composite
 phase change materials (PCM) using graphene and carbon nanotubes as additives for the
 potential application in lithium-ion power battery, Int. J. Heat Mass Transf. 120 (2018)
 33–41. https://doi.org/10.1016/j.ijheatmasstransfer.2017.12.024.
- [57] X. Li, X. Sheng, Y. Guo, X. Lu, H. Wu, Y. Chen, L. Zhang, J. Gu, Multifunctional
 HDPE/CNTs/PW composite phase change materials with excellent thermal and electrical
 conductivities, J. Mater. Sci. Technol. 86 (2021) 171–179.
 https://doi.org/10.1016/j.jmst.2021.02.009.
- [58] J. Lin, Y. Ouyang, L. Chen, K. Wen, Y. Li, H. Mu, Q. Ren, X. Xie, J. Long, Enhancing
 the solar absorption capacity of expanded graphite-paraffin wax composite phase change
 materials by introducing carbon nanotubes additives, Surf. Interfaces. 30 (2022) 101871.
 https://doi.org/10.1016/j.surfin.2022.101871.
- [59] M.M. Umair, Y. Zhang, A. Tehrim, S. Zhang, B. Tang, Form-stable phase-change
 composites supported by a biomass-derived carbon scaffold with multiple energy
 conversion abilities. Ind. Eng. Chem. Res. 59 (4) (2020), 1393 1401.
 https://doi.org/10.1021/acs.iecr.9b06288.
- [60] M.K. Hassanzadeh-Aghdam, M.J. Mahmoodi, M. Safi, Effect of adding carbon nanotubes
 on the thermal conductivity of steel fiber-reinforced concrete. Compos. B. Eng. 174
 (2019) 106972. https://doi.org/10.1016/j.compositesb.2019.106972.
- [61] S. Lv, Z. Qian, D. Hu, X. Li, W. He, A comprehensive review of strategies and approaches
 for enhancing the performance of thermoelectric module, Energies. 13 (12) (2020) 3142.
 https://doi.org/10.3390/en13123142.
- [62] S. Ozbektas, B. Sungur, B. Topaloğlu, Performance analysis of thermoelectric generator
 at different hot surface temperatures, J. Thermophys. Heat Trans. 35 (4) (2021) 814 823.
 https://doi.org/10.2514/1.T6212.
- 822

824 Tables

Material Specification Role Provider CNF starting mateial BEKP Moorim Paper Co., Ltd., Korea Commercial grade APTMS purity 97% Silylation agent Sigma-Aldrich, USA MTMS purity 98% Silylation agent Sigma-Aldrich, USA Pw Hydrophobic PCM Sigma-Aldrich, USA Mw=436 PEG Sigma-Aldrich, USA Mw=1000 Hydrophilic PCM 1 N, laboratory Duksan Pure Chemicals Co., Ltd, HCl PH regulator Korea grade purity >95%, outer Multiwalled CNTs Thermal conductivity enhancer Research Nanomaterials, Inc., USA diameter 10-20 nm Quantitative ashless, 11 cm in ADVANTEC, Japan Filter paper Leakage testing substrate diameter 827 828 829 830 831 832 833 834 835 836 837 838 839 840 841 842 843

826	Table 1.	. Detailed	information	of the 1	materials	used in	the experime	nts.
							1	

Composite	Weight before test	Weight after test	Weight of the leaked PEO	G Leakage percentage
PCM	(g)	(g)	(g)	(%)
CNF-PEG	0.675	0.662	0.013	1.93
CNF _{APTMS} -PEG	0.47	0.462	0.008	1.70
CNF _{MTMS} -PEG	0.489	0.472	0.017	3.48

Table 2. PEG leakage percentage of different foam-stabilized composite PCMs.

Composite	Weight before test	Weight after test	Weight of the leaked Pw	Leakage percentage
РСМ	(g)	(g)	(g)	(%)
CNF-Pw	0.474	0.464	0.01	2.11
CNF _{APTMS} -Pw	0.431	0.419	0.012	2.78
CNF _{MTMS} -Pw	0.568	0.563	0.005	0.88

Table 3. Pw leakage percentage of different foam-stabilized composite PCMs.

Foam	Foam density (kg/m ³)	Foam porosity (%)	PCM absorption capacity (%)	PCM Leakage percentage (%)
CNF _{APTMS} -PEG	59.88	94.78	94.40	1.70
CNF _{APTMS} /CNT ₅₀ -PEG	67.26	94.52	93.63	1.81
CNF _{MTMS} -Pw	59.91	96.57	92.08	0.88
CNF _{MTMS} /CNT ₅₀ -Pw	64.53	96.39	91.77	1.71

848 Table 4. The effect of CNF-based foams on the PCM absorption capacity and leakage

849

percentage.

PCM sample	Heating process			Cooling process			
	Melting point (°C)	Enthalpy (kJ/kg)	Enthalpy reduction (%)	Freezing point (°C)	Enthalpy (kJ/kg)	Enthalpy reduction (%)	
PEG	26.1	151.4	_	26.2	151.3	_	
CNF _{APTMS} -PEG	25.2	144.2	4.76	25.6	144.3	4.63	
CNF _{APTMS} /CNT ₅₀ -PEG	25.2	143.3	5.35	24.9	143.1	5.42	

Table 5. Melting points, freezing points and enthalpies of PEG-based PCM samples.

PCM sample	Heating process			Cooling process			
	Melting point (°C)	Enthalpy (kJ/kg)	Enthalpy reduction (%)	Freezing point (°C)	Enthalpy (kJ/kg)	Enthalpy reduction (%)	
Pw	57.7	202.8	-	55.5	202.7	-	
CNF _{MTMS} -Pw	54.2	185.9	8.3	57.0	185.9	8.3	
CNF _{MTMS} /CNT ₅₀ -Pw	53.4	184.6	9.0	57.2	184.5	9.0	

Table 6. Melting points, freezing points and enthalpies of Pw-based PCM samples.

858 Captions

- Fig. 1. Schematic illustrating the solar-heat-electricity system based on novel PCM sandwich
 structures.
- Fig. 2. (a) Chemistry tuning of CNF using trimethoxy silane and the involved reaction
- 863 mechanism, (b) chemical structure of APTMS, and (c) chemical structure of MTMS.
- Fig. 3. Effect of the chemical modifications of CNF foams on their PCM-stabilization effect:
- leakage testing of (a) PEG-based composite PCMs and (b) Pw-based composite PCMs.
- Fig. 4. TEM images of (a) CNF and (b) CNT; SEM images of (c) CNF_{APTMS}/CNT₅₀ foam, (d)
- 867 CNF_{MTMS}/CNT₅₀ foam, (e) CNF_{APTMS}/CNT₅₀-PEG composite and (f) CNF_{MTMS}/CNT₅₀-Pw
- 868 Fig. 5. Leakage testing of foam-stabilized composite PCMs on filter paper: (a) CNF_{APTMS}-
- PEG, (b) CNF_{MTMS}-Pw, (c) CNF_{APTMS}/CNT₅₀-PEG and (d) CNF_{MTMS}/CNT₅₀-Pw.
- Fig. 6. FT-IR spectra of (a) pristine CNF and chemically modified CNF, and (b) composite
- 871 PCMs and related components; XRD patterns of (c) pristine CNF and chemically modified
- 872 CNF, and (d) composite PCMs and related components.
- Fig. 7. DSC curves of (a) PEG and PEG-based composite PCMs and (c) their curves after 100
- cycles of melting and freezing; (b) Pw and Pw-based composite PCMs and (d) their curves
- after 100 cycles of melting and freezing.
- Fig. 8. Thermogravimetric curves of (a) PEG and PEG-based composite PCMs and (b) Pw
- and Pw- based Composite PCMs.
- Fig. 9. Temperature- heating time curves of (a) PEG based Composite PCMs and (b) Pw
- based PCM under solar simulator, (c) thermal conductivity of PCM samples and (d) time
- 880 course of the open-circuit voltage of the thermoelectric generator with/without sandwich
- 881 PCMs on it.
- 882







Fig. 1.























Fig. 7.









Fig. 9.