

Research papers

A form-stable photothermal conversion phase change material based on CuS for efficient solar energy collection

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ABSTRACT

Copper sulfide (CuS) has been considered as an excellent photothermal conversion material in solar energy applications. The integration of CuS into phase change material (PCM) enables the unification of photothermal conversion and thermal energy storage. In this study, to avoid sedimentation of CuS particles in (PW), two kinds of thermoplastic elastomer (TPE) are simultaneously used as supporting materials to fabricate form-stable PCM. The form-stable, thermal properties, and photothermal effect of PW/TPE/CuS composite PCMs are analyzed. The results show that the shape stability of composite PCM improves with the increase of the content of TPE. The TPE with 20 wt% concentration can prevent the leakage of PCM and sedimentation of CuS particles, and the composite PCM also exhibits excellent flexibility. The melting latent heat of the composite PCM decreases with the increase of TPE and CuS, and the minimum latent heat is as high as 129.5 J/g. The solar absorption of composite PCM increases with the increase of CuS, and the photothermal conversion efficiency of composite PCM with 15 wt% CuS is calculated as 88.7 %. Furthermore, the composite PCM is employed in a solar water heater. The water temperature can be heated to 67.9 °C, and the composite PCM also has the capacity to decelerate the cooling of water. The water temperature can still maintain above 40 °C after 24:00 p.m. In conclusion, the prepared PW/TPE/CuS composite PCM demonstrates potential for utilization in solar energy storage applications.

1. Introduction

The efficient utilization of solar energy offers a promising opportunity to address the global energy crisis in an environmentally friendly, efficient, and sustainable manner [1]. Solar energy can be converted to thermal and electrical energy. Photothermal conversion technology is more easily and simplified, and has been used for a long time [2,3]. However, the application of solar energy suffers from its intermittency and instability [4]. How to obtain more stable thermal energy from the solar has been a hot topic in recent years [5]. Fortunately, latent heat thermal energy storage (LHTES) technology can be introduced into the solar energy system due to its high energy storage capacity at an approximately constant temperature. The LHTES system can store a large amount of thermal energy when solar energy is abundant, and release this heat when needed [6,7].

In the field of LHTES technology, paraffin wax (PW) is a commonly

utilized solid-liquid phase change material (PCM) due to its advantageous characteristics, including a suitable phase change temperature, non-toxicity, a plentiful resource, and a low cost [8,9]. However, PW and other traditional PCMs are unable to directly absorb solar energy and convert it into thermal energy for LHTES. To overcome this limitation, photothermal conversion fillers have been widely introduced into PCMs [10–14]. Recently, semiconductors represented by metal oxides and chalcogenides have been identified as a new type of photothermal nanomaterial [15–17]. Among them, copper sulfide (CuS) has been conformed as a promising candidate due to its excellent photothermal conversion efficiency and low cost. Comparison to other carbon materials, noble metal nanoparticles and organic dyes, CuS exhibits both localized surface plasmon resonance and high absorption for near-infrared which promote efficient photothermal conversion [16]. Fang et al. [18] first synthesized CuS nanorods and added them to water to prepare CuS emulsions. The CuS emulsions have strong optical

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absorption in both visible and near infrared light bands, and possess good photothermal conversion performance. And the maximum temperature of the CuS emulsion is measured to be 74.44 °C under 1000 W/m². Dong et al. [19] added CuS nanoparticles to polyethylene glycol (PEG) with the polyethylene pyrrolidone (PVP) as stabilizer to prepare photothermal conversion composite PCM. The photothermal conversion efficiency of PEG/PVP/CuS is tested as 87.36 %.

In fact, due to the high surface energy and van der Waals forces, CuS nanoparticles are prone to agglomeration and sedimentation in liquid PCMs [20]. In order to improve this issue, Li et al. [21] combined CuS with sugarcane-derived carbon to prepare C600-CuS-OC photothermal composite PCMs. The maximum loading of PCM in porous support material is 78 wt%. The photothermal conversion efficiency of C600-CuS-OC is calculated to be 83.2 %. Yan et al. [22] designed cuboidal and 3D flower-shaped CuS to prepare photothermal composite PCMs. They found that 3D flower-shaped CuS is more suitable for the supporting material and the photothermal conversion efficiency of PA/F-CuS can reach 70.3 %. Another way of immobilizing photothermal conversion medium is to prepare form-shaped PCMs by polymers. Thermoplastic elastomer (TPE) is a kind of polymer with excellent flexibility and strong shape plasticity. The compatibility of TPE and organic PCM is noteworthy. The 3D network structure of molecular chains of TPE can prevent the liquid leakage of PCM. Moreover, TPEs show good flexibility, which features the composite PCMs also flexible [23]. And the flexibility of composite PCMs can be improved in a broad temperature range by synergistically strengthen of multiple TPEs. A lot of works have been used TPE as supporting material to prepare form-stable PCMs [24–27]. Lately, several works have been reported related to the favorable miscibility, about the combination of PW and styrene-*b* (ethylene-co-butylene)-*b*-styrene (SEBS). PW/SEBS exhibits favorable shape stability and flexibility [28–30]. Another TPE, olefin block copolymer (OBC), compatible with PW, also provides shape stabilization, albeit with restricted flexibility enhancement [31]. Zhang et al. [32] discovered that blends of SEBS and OBC demonstrate a synergistic enhancement in shape stability within a wide temperature range. Deng et al. [33] developed polymer-based composite PCMs by adding expanded graphite (EG), the shape of PW/OBC/EG remains stable at 100 °C. Jing et al. [23] prepared ultra-flexible composite PCMs based on SEBS and OBC by chemical cross-linking for wearable thermal management with no leakage, possessing excellent shape stability over a wide temperature range. The studies demonstrate that the cross-linked 3D network structure of the two kinds of TPE when added simultaneously, can provide superior encapsulation performance for PCMs. The 3D network structure of TPE restricts the flow of liquid PCMs, thereby inhibiting the phase separation.

Traditional PCMs face challenges in solar thermal conversion applications, such as low efficiency and difficulties in heat storage, falling short of practical user needs. Therefore, developing PCMs for photothermal conversion is crucial to drive solar technology towards greater effectiveness and sustainability. In this work, to develop a novel functional PCMs integrating photothermal conversion and LHTES, SEBS and OBC are used together as shaping framework and CuS is used as the efficient photothermal conversion filler. The 3D network formed by the intertwining of resin and rubber segments of SEBS and OBC can keep the shape stability of PCM and ensure the uniform distribution of CuS particles in the PCM. Firstly, the preparation process of PW/TPE/CuS composite PCMs with excellent comprehensive performance is explored. Then, the morphology and structures, form stability, light absorption, and photothermal conversion efficiency of the composite PCMs are tested. Finally, the application of the composite PCMs used in the solar water heater is detected.

2. Experimental

2.1. Materials

Paraffin wax (PW, technical grade) with a melting point of 42 °C was supplied by Hangzhou Ruhr Energy Technology Co., Ltd. (China). Styrene-*b*(ethylene-co-butylene)-*b*-styrene (SEBS) triblock copolymer triblock copolymer (FG1901) powder was obtained from Kraton Corporation (USA). Olefin block copolymer (OBC, 0.887 g/cm³, melting point at 119 °C), Dow Chemical (UAS) Co., Ltd. CuS (99 %) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

2.2. Preparation of PW/TPE/CuS

Firstly, the mixture of PW/TPE was prepared by heat treatment and melt blending method (Fig. 1): PW and SEBS were treated in a drying oven at 70 °C for 180 min to obtain the form-stable PW/SEBS gels and without any flowability. The PW/SEBS gels were stirred with a speed of 120 rpm for 30 min in an oil bath at 180 °C. OBC was slowly added into the PW/SEBS and stirred for 60 min. And the PW/TPE mixture, which is colorless and transparent, was obtained. At 180 °C, the material exhibits optimal fluidity, thereby ensuring effective mixing. This fluidity also facilitates self-leveling and self-healing properties. Above 180 °C, the material oxidizes and turns yellow. Then, CuS was added into the PW/TPE mixture and stirred for another 30 min. Finally, composite material gradually loses the fluidity when the temperature drops to 120 °C, and the PW/TPE/CuS composite PCM was obtained after cooling to room temperature. The schematic diagram of the PW/TPE/CuS is presented in Fig. 1 and the identifier and fraction are shown in Table 1.

2.3. Characterization and measurements

The micromorphology of the sample was observed by scanning electron microscopy (SEM, Thermo Fisher FEI Inspect F, USA). FT-IR spectra of the samples were recorded with a Nicolet iS50 spectrophotometer (Thermo Scientific Co., Ltd., USA) in the wavenumber range of 4000–400 cm^{−1} range. The crystal structures and crystallization behaviors of the samples were investigated using an X-ray diffractometer (XRD, Malvern Panalytical, UK).

In the leakage test, samples were cut into uniform square shapes and subsequently positioned onto a heating stage. Record the mass change of samples after each heat treatment at 70 °C. The phase change properties of PCMs in the range of 10–70 °C were collected at a heating and cooling rate of 5 °C/min on a differential scanning calorimetry (DSC, TA Instruments Co., Ltd., USA). In addition, the thermal stability of the composites was determined on a TGA/DSC3+ (METTLER TOLEDO Co., Ltd., Switzerland) in the temperature range of 0–600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. The laser thermal conductivity meter (LFA457, NETZSCH Instruments GmbH) is used to test the thermal conductivity and specific heat capacity of materials.

A spectrophotometer (Shimadzu UV-3600, Japan) was employed to determine the absorbance of the samples. A xenon lamp with an intensity of 1000 W/m² (CEL-s500, CEAULIGHT, China) was used to simulate sunlight to test the photothermal performance of the samples. Samples were cut into equal-sized squares and placed under the xenon lamp, the temperature at the surface was recorded using an infrared thermal imager every other minute.

3. Results and discussion

3.1. Shape stability

In order to obtain a highly stable PW/TPE/CuS composite PCM, composite PCMs with varying contents of TPE were subjected to 40 cycles of heat treatment at 75 °C on the filter paper. The photograph and the mass loss of the composite PCMs before and after heat treatment are

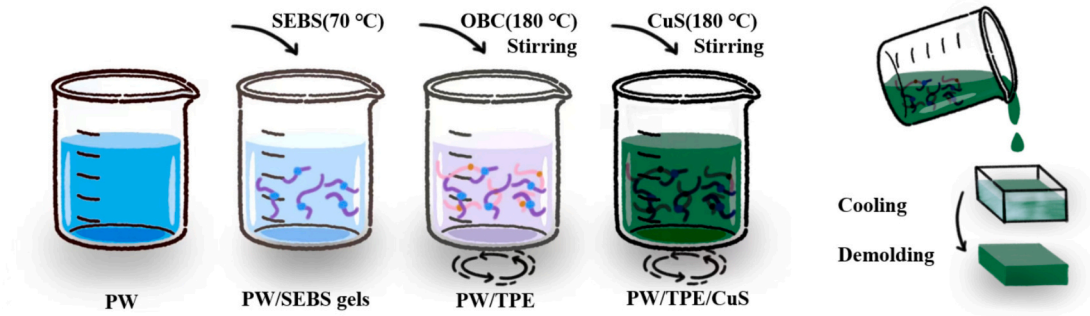


Fig. 1. Schematic diagram of PW/TPE/CuS preparation.

Table 1

Identifier and fraction of the PW/TPE/CuS composite PCMs.

Sample	PW (wt %)	TPE (wt%)	TPE in PW/TPE (wt %)	CuS (wt %)
		SEBS:OBC = 1:2		
PW/TPE ₁₀	90	10	10	0
PW/TPE ₁₅	85	15	15	0
PW/TPE ₂₀	80	20	20	0
PW/TPE/CuS ₅	76	19	20	5
PW/TPE/CuS ₁₀	72	18	20	10
PW/TPE/CuS ₁₅	68	17	20	15

shown in Fig. 2 (a). It can be found that PW phase changes into liquid at temperatures above 45 °C. TPE can prevent the liquid leakage of PW. The PW/TPE and PW/TPE/CuS keep their shape stable under a temperature of 75 °C. However, there are some liquid PW precipitates on the surface, and the amount of precipitation decreases with the increase of the content of TPE. When the content of TPE in the composite is 20 wt%, there is almost no liquid PW on the surface. The liquid leakage rate of the composite PCM after multiple heat treatments can be calculated by formula (1). And the results are shown in Fig. 2 (b).

$$L = \frac{M_0 - M_n}{M_0} \times 100\% \quad (1)$$

where, M_0 is the initial mass of the sample, and M_n is the mass after n cycles of heating and cooling.

The leakage rate of all PW/TPE composites increases as heat treatment times increase. In addition, the leakage rate of all PW/TPE composites decreases as the content of TPE increases. When the content of TPE is 20 wt%, the leakage rate of PW/TPE₂₀ is only 4.0 % after 40

cycles of heat treatment. This indicates that the 3D network structure formed by 20 wt% TPE can effectively encapsulate PCM, thereby obtaining a form-stable PCM. Therefore, in subsequent work, the TPE in the composites is 20 wt%. In addition, the result of heat treatment of PW/TPE/CuS₅ is also shown in Fig. 2. The PW/TPE/CuS₅ exhibits remarkable shape stability at 75 °C, with a minimal leakage rate of 0.8 % after 40 thermal cycles. Similarly, PW/TPE/CuS₁₀ and PW/TPE/CuS₁₅ also demonstrate good form stability. This is attributed to the reduction of PCM in the composite and the enhancement of the compatibility between TPE and PW by CuS nanoparticles [20].

The TPE not only improves the shape stability of composite PCMs, but also improves the flexibility of the form-stable PCMs. As illustrated in Fig. 3, both PW/TPE₂₀ and PW/TPE/CuS₁₅ can be bent at a 180° angle at 45 °C without exhibiting any signs of breakage or tearing. The composite PCMs exhibit a gradual return to their original form in the absence of an external driving force (Fig. 3 c, d). This permits close contact of form-stable PCMs with the heat exchange surface, which mitigates the adverse effect of air thermal resistance.

The tensile length of the sample at 45 °C is recorded by applying a tensile force of 5 N. The length of the sample is 80 mm and the length of PW/TPE₂₀ after stretching is 350 mm. This length is 4.38 times that of the original sample. As the content of CuS increases, the tensile length of PW/TPE/CuS decreases. Even though the addition of CuS resulted in a decrease in the mechanical properties of the composites, PW/TPE/CuS₁₅ was still able to be stretched to 2.88 times its original length.

3.2. Morphologies and chemical properties

The microstructure of the composite PCM and the dispersion state of CuS within it were further explored by SEM. As shown in Fig. 4 (a, c), PW crystals are dispersed in the amorphous phase of TPE, and it is challenging to discern the presence of nanosized CuS on the brittle fracture surface of the sample. Therefore, the distribution of CuS within the composite PCM was investigated through the scanning of the Cu

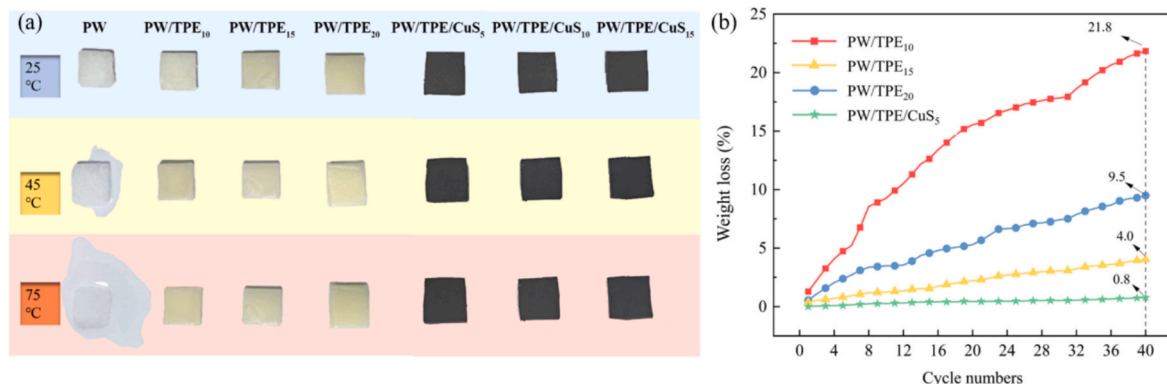


Fig. 2. (a) Photographs of the shape change at 25 °C, 45 °C and 75 °C. (b) Plot of the rate of sample mass loss as a function of cycle number.

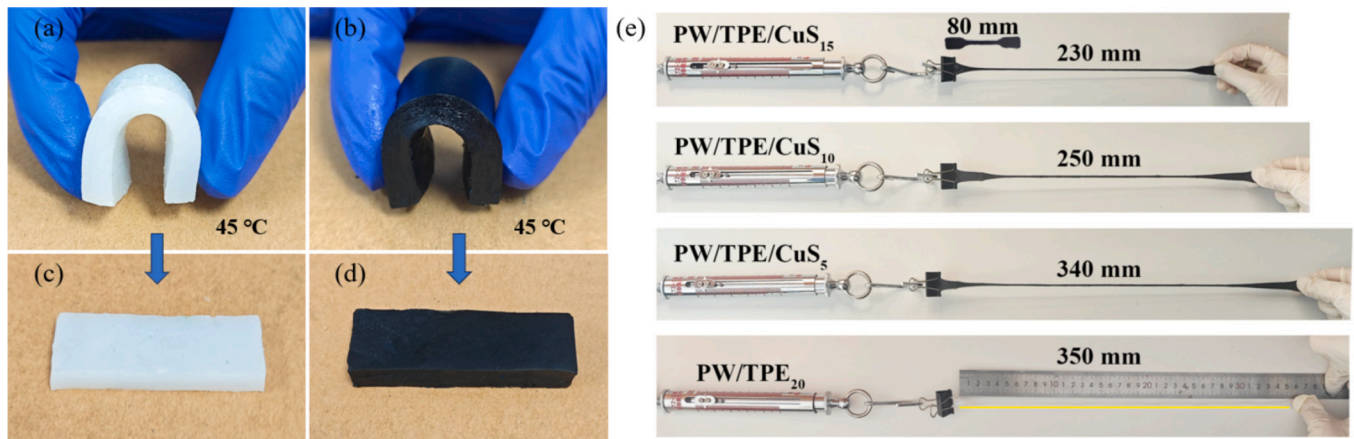


Fig. 3. Flexibility (a–d) and flexibility index (e) performance tests of PW/TPE and PW/TPE/CuS at a temperature of 45 °C.

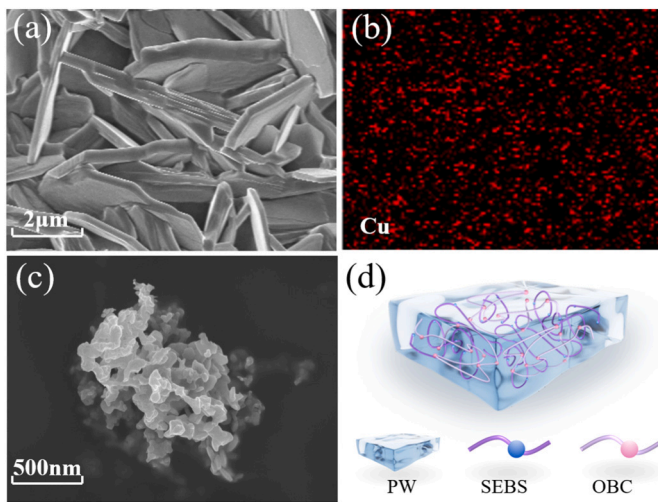


Fig. 4. (a) The brittle fracture surface microstructure of PW/TPE. (b) EDS mapping images of PW/TPE/CuS. (c) The microscopic morphology of CuS nanoparticles. (d) The 3D network structure of the TPE formed by cross-linking of SEBS and OBC in composite PCM.

elemental distribution by energy-dispersive spectroscopy (EDS). As shown in Fig. 4 (b), the dispersion of CuS within the composite PCM is homogeneous and devoid of agglomeration. The TPE network constrains the flow and phase separation of PW and CuS. The mechanism by which TPE enhances shape stability of PCM is revealed in Fig. 4 (d). SEBS and

OBC are cross-linked to form long polymer chains, and the 3D network structure is formed by the intertwining of long chains. This network is compatible with paraffin and exhibits excellent encapsulation capabilities.

As illustrated in Fig. 5 (a), the FT-IR spectrum reveals an absorption band in the 3000–2700 cm^{-1} , which can be attributed to the stretching vibration of the $-\text{CH}$ ($-\text{CH}_2$ and $-\text{CH}_3$) group. For PW, the absorption peaks are observed at 2912 cm^{-1} , 2847 cm^{-1} , and 1470 cm^{-1} . These peaks are attributed to the counter symmetric telescopic vibration, symmetrical telescopic vibration, and in-plane bending vibration of the $-\text{CH}_2$ group in PW, respectively. The absorption peak situated in the vicinity of 717 cm^{-1} is associated with the in-plane rocking vibration of the $-(\text{CH})_{2n}$ group. For SEBS, the absorption peaks located near 2920 cm^{-1} , 2847 cm^{-1} , 1470 cm^{-1} , and 698 cm^{-1} are associated with the counter symmetric telescopic vibration, symmetrical telescopic vibration, in-plane bending vibration, and in-plane rocking vibration of the $-\text{CH}_3$ group, respectively. The absorption peaks of OBC at 2962 cm^{-1} and 2850 cm^{-1} are indicative of counter-symmetric and symmetrical telescopic vibrations of the $-\text{CH}_2$ group, respectively. No significant characteristic peaks are discerned in the spectra of CuS. In summary, the spectra of PW/TPE and PW/TPE/CuS exhibit notable superposition peaks associated with PW, SEBS, and OBC. And no distinctive characteristic peaks are observed, indicating that there is no chemical reaction between PW, SEBS, and OBC. The PW is constrained within the 3D network of TPE exclusively by physical cross-linking reactions.

As shown in Fig. 5 (b), the XRD profile of PW exhibits narrow, sharp, and symmetrical diffraction peaks at diffraction angles of 7.6°, 21.9°, and 23.9°, which proves that PW shows good crystallization characteristics. The XRD profile of OBC shows a strong diffraction peak at the

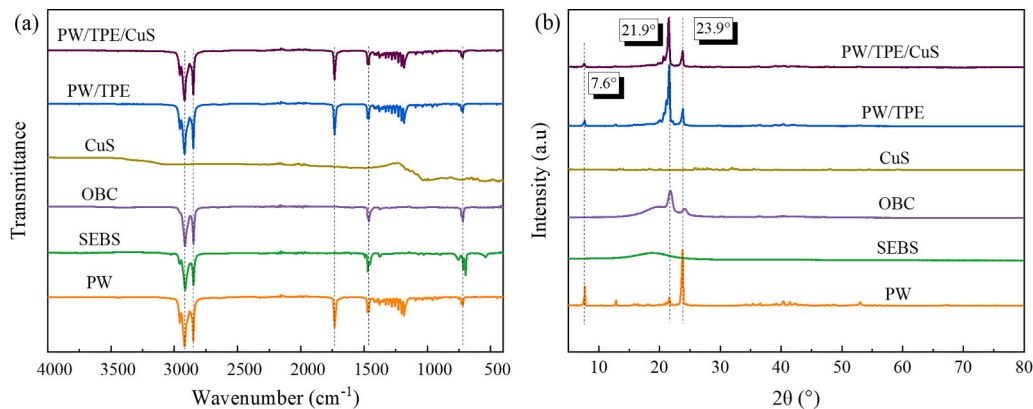


Fig. 5. The FT-IR spectral (a) and XRD patterns (b) of samples.

diffraction angle of 21.9° , indicating that OBC has crystallizable segments. SEBS has only a broad peak around 20° , indicating that SEBS exists in an amorphous form. No significant diffraction peaks are found in the XRD profiles of CuS. The XRD profiles of PW/TPE and PW/TPE/CuS contain the strong diffraction peaks of PW, SEBS, and OBC, indicating that the crystal form of PW does not change after physical cross-linking. The diffraction peak intensity of PW/TPE and PW/TPE/CuS at 23.9° decreases because PW is confined to the gaps between SEBS and OBC, and the crystallization process is inhibited. This may reduce the thermal energy storage capacity of composite PCMs.

3.3. Thermal properties

The DSC curves of PW and composite PCMs are shown in Fig. 6, and the detailed thermal properties are summarized in Table 2. The Fig. 6 shows that the endothermic peak and the exothermic peak of composite PCMs are similar to those of pure PW. The phase change trend of PW is not changed by the addition of functional fillers. TPE and CuS only play the role of shaping and enhancing the photothermal conversion ability in the composite PCMs.

It can be observed from Table 2 that as the mass fraction of PW decreases, the phase change temperature decrease. This is because of the addition of TPE and CuS can disrupt the crystal lattice structure of the PW, making the arrangement of the molecules less ordered. This disruption leads to a loss of close packing of molecules, which affects the phase change temperature [34,35]. Meanwhile, as the mass fraction of PW decreases, the latent heat of the composite material decreases. The test latent heat of the composite PCM is slightly lower than the theoretical latent heat. Given the known latent heat and mass ratio of the PW, the theoretical value of the latent heat of the composite PCM can be determined by the following equation [36]:

$$\Delta H_c = (1 - \eta) \times \Delta H_{pw} \quad (2)$$

where, ΔH_c is the latent heat of composite PCM; η is the mass proportion of CuS and TPE in the composite PCM; ΔH_{pw} is the latent heat of PW.

This difference can be attributed to the 3D network. The crystal arrangement and orientation of PW are restricted by the 3D network of TPE, and the high symmetry of the PW lattice is destroyed, causing the lattice energy to decrease. These factors lead to a decrease in the energy required for the phase change, phase change temperature and the latent heat. Although the addition of TPE and CuS decreases the occupation ratio of PW, PW/TPE/CuS₁₅ still possessed a latent heat of 129.5 J/g.

3.4. Thermal reliability

The thermal reliability of the prepared composite PCMs was explored by comparing the thermophysical parameters before and after the accelerated thermal cycling test. Fig. 7 (a) and (b) shows the DSC curves after 100 and 200 thermal cycles, and the detailed results are summarized in Table 3. After the accelerated thermal cycling test, the variation

Table 2

The DSC test results of PW, PW/TPE₂₀, PW/TPE/CuS₅, PW/TPE/CuS₁₀ and PW/TPE/CuS₁₅.

Sample	T _m (°C)	ΔH_m (J/g)		T _s (°C)	ΔH_s (J/g)	
		Test	Theoretical		Test	Theoretical
PW	41.1	202.1	—	40.0	202.8	—
PW/TPE ₂₀	37.4	151.2	161.6	37.7	144.4	162.2
PW/TPE/ CuS ₅	36.9	136.6	149.5	37.4	127.7	150.0
PW/TPE/ CuS ₁₀	36.1	132.6	144.9	36.9	125.1	146.6
PW/TPE/ CuS ₁₅	35.4	129.5	142.8	36.7	122.4	141.1

Notes: T_m - Melting temperature; T_s - Solidification temperature; ΔH_m - Melting latent heat, ΔH_s - Solidification latent heat.

range of T_m and T_s is less than 0.9°C , and the loss ratio of ΔH_m and ΔH_s is less than 3.9 %. The reference for comparison here is the non-cyclic parameters in Table 2.

The ΔH of the composite PCMs shows a decreasing trend. Due to the extremely low loss ratio, the trend is related to many factors, such as phase separation, aging, and water vapor content in the sample. The phase change temperature and latent heat vary within a narrow range and can be ignored. These findings suggest that CuS has no significant effect on the thermal performance of PW/TPE/CuS after multiple cycles, and the composite PCMs exhibit superior thermal reliability.

3.5. Thermal stability

The thermal stability and operating temperature range of composite PCMs below 500°C were tested by TG. Based on the results of multi-stage weight loss measurements, the decomposition order of different components can be explained. Fig. 8 shows the TG curves from 25°C to 500°C . As a single component, PW volatilizes and thermally decomposes in the range of $180\text{--}330^\circ\text{C}$, while the decomposition of SEBS and OBC usually occurs above 360°C . PW/TPE₂₀ and PW/TPE/CuS₅ will undergo a series of decomposition steps, starting with the degradation of PW and subsequently the TPE blends. However, the PW in the composites underwent thermal decomposition at a higher temperature than the pure PW. The excellent encapsulation efficiency of SEBS and OBC delays the thermal decomposition of PW.

3.6. Light absorption and photothermal conversion performance

The spectral range of solar illumination is concentrated in the UV-Vis-NIR band of $300\text{--}2500\text{ nm}$. The absorbance in this spectral range is a determining factor in the photothermal conversion efficiency of the materials. The absorbance of PW, PW/TPE₂₀, PW/TPE/CuS₅ was measured and the results are shown in Fig. 9.

The absorption peaks of PW and PW/TPE₂₀ are found to be

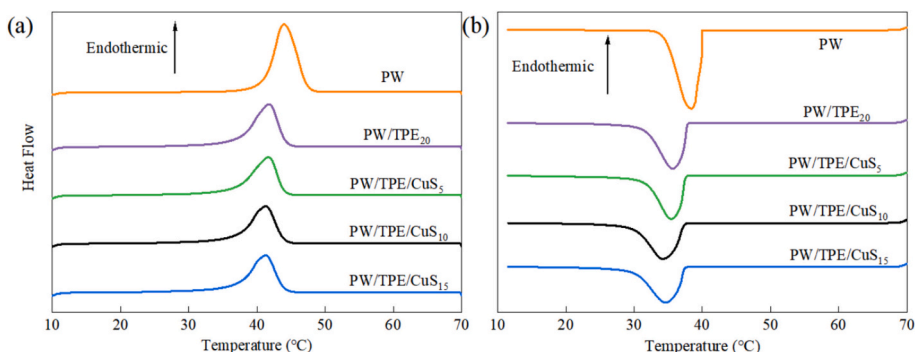


Fig. 6. The DSC diagram of the melting (a) and solidification (b) process.

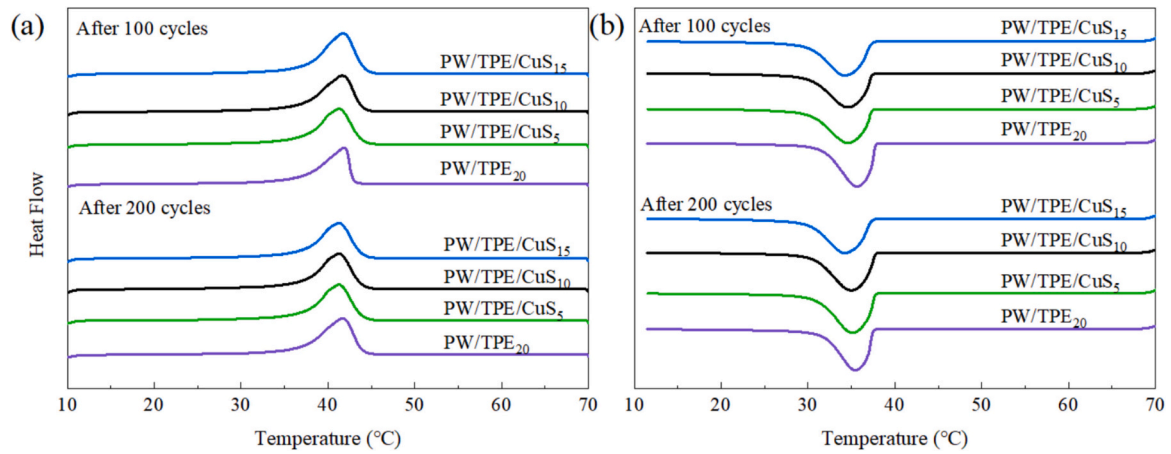


Fig. 7. DSC curve after accelerated thermal cycling tests.

Table 3

DSC results after accelerated thermal cycling test.

Sample	Cycle-index	T_m (°C)	ΔH_m (J/g)	T_s (°C)	ΔH_s (J/g)
PW/TPE ₂₀	100	37.6	148.5	37.7	140.7
	200	37.9	145.3	37.6	135.6
PW/TPE/CuS ₅	100	37.0	134.0	37.3	126.2
	200	37.2	131.4	37.7	125.0
PW/TPE/CuS ₁₀	100	36.2	132.2	37.8	124.2
	200	36.8	128.6	37.4	122.8
PW/TPE/CuS ₁₅	100	36.0	129.4	37.1	120.5
	200	35.8	126.6	37.6	118.2

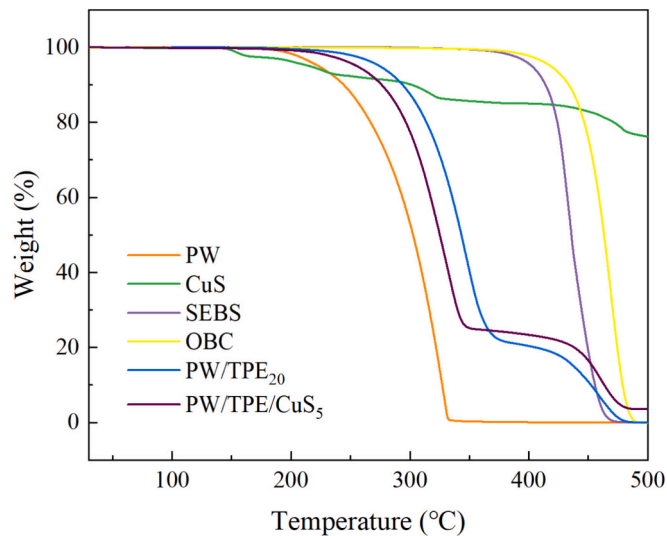


Fig. 8. The TG curves of samples.

consistent, with the exception of a slight increase in intensity observed for PW/TPE₂₀ in the majority of bands. This phenomenon can be attributed to the microphase interface between the paraffin and TPE, which can cause light scattering and thereby reduce the transparency of PW/TPE₂₀. Concurrently, the destruction of the crystalline structure of paraffin can also result in light scattering [1]. A further comparison reveals that the absorbance of PW/TPE/CuSs is markedly higher than that of PW and PW/TPE₂₀, with an incremental increase observed with the addition of CuS. The results demonstrate that CuS is an effective enhancer of light absorption in composite PCMs.

CuS is classified as an indirect bandgap semiconductor material [15]. Since the band gap of CuS matches the wavelengths of visible and near-

infrared light, CuS can absorb light of a specific wavelength, resulting in excited-state electron and hole pairs. Once electron-hole pairs are formed, they interact and are converted into heat. This process is known as thermal relaxation [37]. In the case of electron-phonon interaction, the electron-hole pairs in CuS are excited to vibrate in the lattice, and the energy of these vibrations is transferred to the surrounding crystals, which are ultimately converted into heat energy. The photoexcited states of CuS therefore undergo non-radiative recombination through two different relaxation processes. During this process, CuS remains excited until the energy is finally converted to heat and dissipated into the surrounding environment. The modes of heat exchange are radiation and heat convection.

The xenon lamp photothermal conversion test and the photothermal conversion performance of composite PCM are documented in practical applications (Fig. 10 a). Fig. 10 (b) illustrates the schematic diagram of the test apparatus and the results of IR imaging. As the duration of light irradiation increases, the surface temperature rises gradually. Concurrently, the surface temperature of PW/TPE/CuS₁₅ is the highest and that of PW is the lowest.

The results of the temperature change process for samples with varying quantities of CuS addition are shown in Fig. 10 (c). When the test point is within the phase change temperature range, a temperature platform emerges in the temperature-time curve, and the temperature rises gradually. During the phase change process, a large amount of latent heat energy is stored until the phase change is complete at the bottom. Composite PCMs with higher CuS quality scores exhibit a more rapid increase in temperature. The time required for the bottom of PW/TPE₂₀ to reach 55 °C is 3806 s, while the time required for PW/TPE/CuS₁₅ to reach 55 °C is 1040 s. These findings are in accordance with the outcomes of the absorbance test, which demonstrated that composite PCM with elevated CuS mass fractions exhibited enhanced light absorption. Following the deactivation of the xenon lamp, the sample undergoes a natural cooling process. As the temperature approaches the solidification point, the stored latent heat is released, resulting in a temperature plateau until the latent heat is fully released.

The efficiency of the photothermal conversion can be calculated according to the following formula [38]:

$$\varphi = \frac{mC_p(T_1 - T_0) + m\Delta H}{IS(t_1 - t_0)} \quad (3)$$

where, the m is the mass of the sample; the C_p is the specific heat capacity of the sample; the T_0 and T_1 are the temperature at the beginning and end of the phase change, respectively; the I is the intensity of irradiation, and the S is the surface area receiving the light intensity; t_0 and t_1 are the start and end time of the phase change, respectively.

The photothermal conversion efficiency of PW/TPE₂₀ is 65.9 %. An

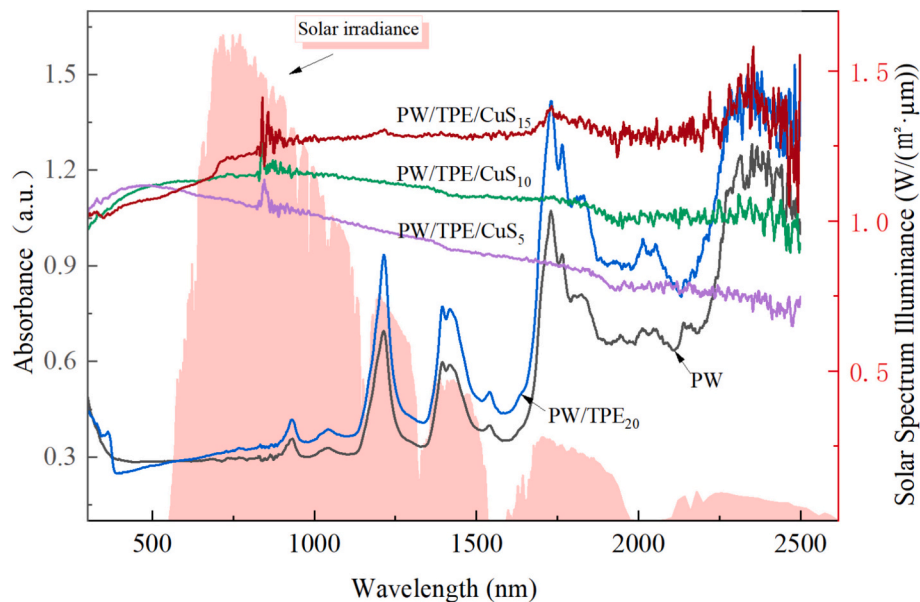


Fig. 9. UV-Vis-NIR absorption spectra of PW, PW/TPE₂₀, PW/TPE/CuS₅, PW/TPE/CuS₁₀, and PW/TPE/CuS₁₅.

increase in the concentration of CuS filler results in a proportional enhancement in the photothermal conversion efficiency of PW/TPE/CuS₅, PW/TPE/CuS₁₀, and PW/TPE/CuS₁₅, reaching 74.3 %, 82.6 %, and 88.7 %, respectively. Compared to PW/TPE₂₀, PW/TPE/CuS₅, PW/TPE/CuS₁₀, and PW/TPE/CuS₁₅, these materials illustrate the integrated capabilities of photothermal conversion and energy storage, and present a diverse range of prospective applications in solar thermal technology.

Fig. 10 (d) shows a comparison of the photothermal conversion curves of the samples before and after 200 accelerated thermal cycles. PW/TPE/CuS₁₅ exhibits similar photothermal conversion characteristics to the PW/TPE/CuS₁₅ after 200 accelerated thermal cycling tests.

In subsequent studies, it is anticipated that the light absorption properties of CuS nanoparticles will be further optimized through the precise tuning of their size and morphology. In addition, the introduction of other types of photothermal conversion fillers (e.g., carbon materials and organic dyes) is expected to make up for the shortcomings of existing materials in terms of a single photothermal conversion mechanism. A comparison of the experimental results of other researchers in Table 4 reveals that the composite PCM prepared in this paper exhibits superior shape stability and photothermal conversion efficiency.

3.7. Application of photothermal conversion PCM on solar water heating system

The implementation of solar water heating systems has historically been constrained by two factors: the intermittent nature of solar energy and the capacity limitations of water tanks. The daily fluctuations and meteorological conditions can result in intermittent alterations in light intensity, which can have a significant impact on the photothermal conversion efficiency of solar water heating systems. The dimensions of the water tank are constrained by the spatial configuration and load-bearing capacity of the building. It will be unable to meet the fundamental requirements of the users if the water tank with insufficient heat capacity.

The excellent photothermal conversion performance and shape stability of CuS composite PCMs have prompted their application to solar water tanks for the purpose of investigating their impact on the performance of solar water heating systems under natural sunlight [44].

As shown in Fig. 11, a quarter cylindrical water tank was designed, and photothermal PCMs were placed on its circular surface (schemes B) and right-angled surface (schemes C), respectively. The capacity of the

water tank is 1 l, and the thickness of the composite PCM is 15 mm. The control group is defined as the tank without photothermal conversion materials (schemes A). It is exhibited that the different structures of the PCM coupled to a solar thermal water tank and record the temperature fluctuations at disparate locations inside the tank. The tank is composed of transparent acrylic, with an arc on the side that receives the light, as illustrated in Fig. 11 (g). In practice, a transparent enclosure is employed on the exterior to insulate the surface of the system from convective heat flow to the outside world. The experiment was conducted in Chengdu, China, where the local temperature ranged from 20 to 30 °C, the atmosphere was clear, and the solar radiation intensity was 600–800 W/m². The results are presented in Fig. 11 (d, e, f).

The temperature of schemes B and C is higher than that of scheme A when exposed to solar radiation, due to the photothermal conversion effect. Scheme C exhibits the highest water temperature with a maximum value of 67.9 °C. The application of direct irradiation (schemes A and C) results in a more uniform distribution of water temperature. The maximum discrepancy in water temperature is 22 °C (scheme B). The photothermal PCM with high temperature at the bottom transfers heat to the water above. As a consequence of the temperature gradient, the heated water rises and creates a convective heat circulation within the water tank. P3 and P6 also experienced localized high temperatures as a result, which is also related to the inclined solar radiation and the small amount of water here. The results of the infrared imaging analysis corroborate the findings of the heat transfer analysis. The images reveal that thin layers of water in proximity to the photothermal PCM exhibit elevated temperatures, while the internal temperature of the water tank remains relatively constant (Fig. 11 h). The findings indicate that the photothermal PCM results in a delay in the decline of water temperature. The water temperatures at 24:00 p.m. for the three schemes are 27.2 °C, 29.6 °C, and 43.2 °C, respectively. The combination of photothermal conversion and energy storage allows for the realization of passive phase change energy storage in solar water tanks.

The functionality of scheme C was evaluated over a three-day period, encompassing both cloudy and sunny conditions (Fig. 11 i). The photothermal PCM ceases to generate heat when sunlight is obstructed. However, the system exhibits high efficiency on sunny days, and the water temperature can be maintained above 40 °C before 24:00 p.m. The prepared photothermal PCMs demonstrated high photothermal conversion and energy storage performance, which extends the operational time of solar water heating systems can be extended.

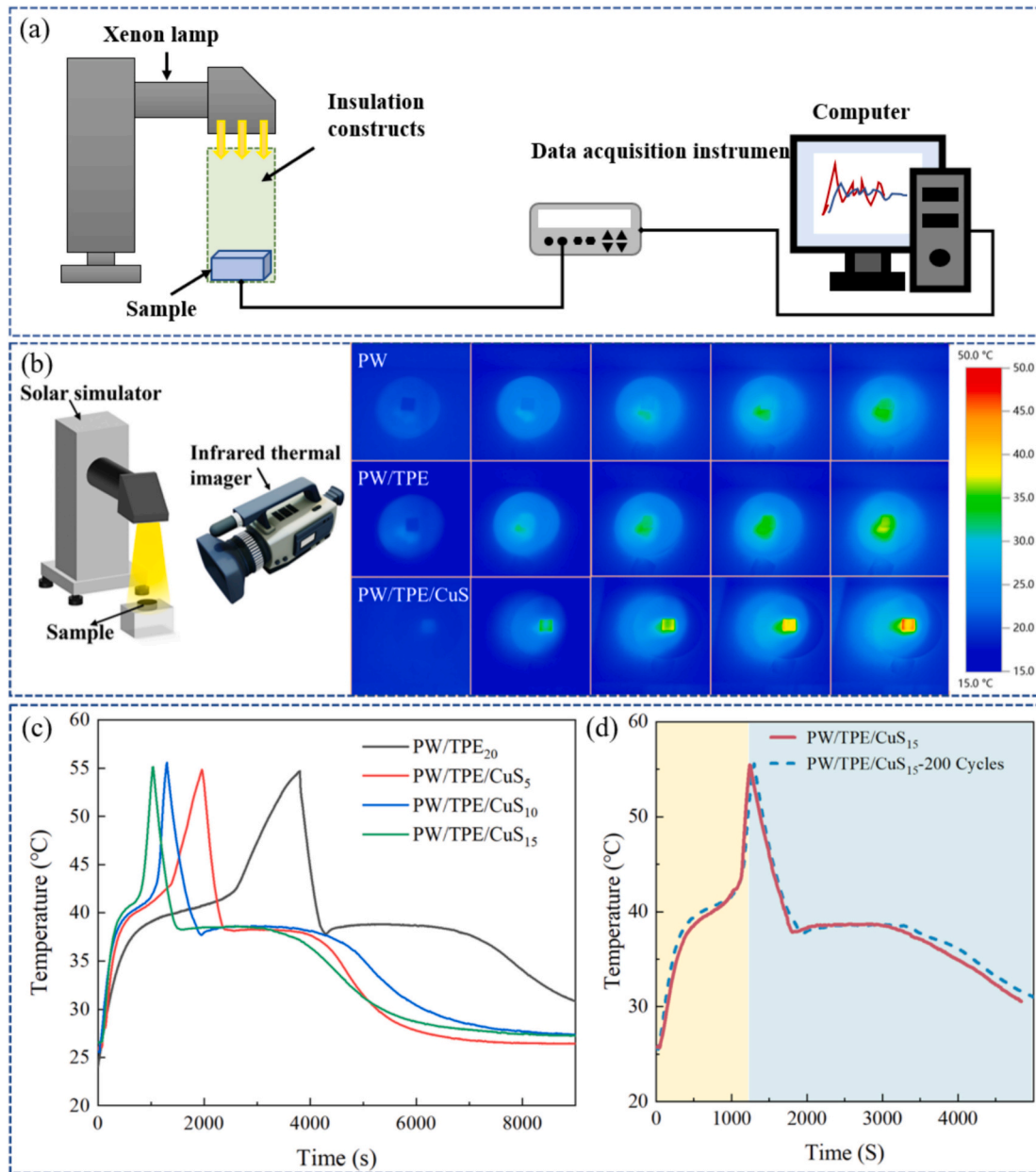


Fig. 10. The test of photothermal energy conversion. (a) Photothermal conversion test apparatus. (b) Schematic of testing apparatus and results of IR imaging. (c) Temperature-time profiles of the photothermal conversion test. (d) Temperature variation law of PW/TPE/CuS₁₅ and PW/TPE/CuS₁₅ after 200 accelerated thermal cycling tests.

Table 4
Comparison of leakage rate, latent heat and photothermal conversion efficiency.

PCM	Formed elements	Leakage (%)	ΔH (J/g)	ϕ (%)	Ref.
PW	WCC/PP	0.45	131.5	/	[25]
PW	EPDM/Graphene	0.62	96.1	/	[39]
PW	CTF/EG	0.18	111.3	/	[40]
LA	94LA/EG	1.10	193.2	93.8	[41]
PEG	VRBP	0.82–1.81	114.5	92.1	[42]
PW	CF/RGO/PW	/	111.5	86.7	[43]
LA	Ag-EG/LA	/	129.5	81.2	[10]
PW	SEBS/OBC/CuS	0.80	129.5	88.7	This work

However, in this study, the heating rate of the photothermal conversion PCM is faster due to the smaller volume of the water tank. Conversely, if the water tank is of a larger size, it may not be capable of meeting the heating demands at higher temperatures. It is imperative to

ensure sufficient sunlight exposure and maintain optimal contact between the PCM and the water tank to optimize the performance of system. The development of a reasonable light path and PCM-tank structure has the potential to enhance the operating efficiency of the system. Environmental temperature and solar radiation intensity are important factors affecting water temperature. In such circumstances, the most effective solution may be the combined operation of the equipment with other heating systems. Combined heat storage with electrically assisted heating devices and photothermal conversion PCM under low solar radiation is also a future research topic. In addition, the prepared PCMs can be used in energy-saving installations such as solar air collectors, grain drying or roof envelopes.

4. Conclusion

In this work, the integration of photothermal conversion and energy

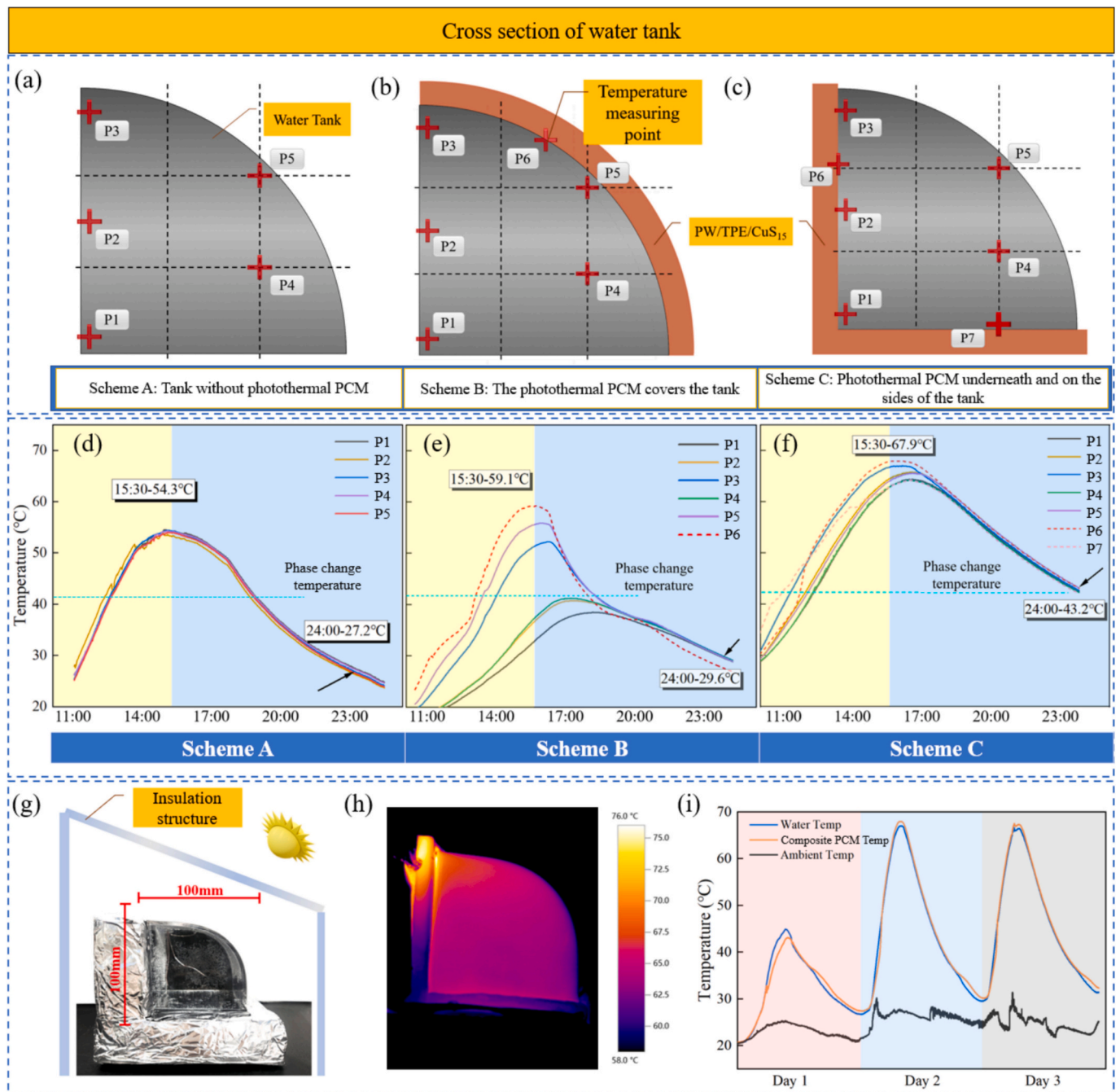


Fig. 11. Tank test of a solar water heating system combined with photothermal conversion PCM. (a, b, c) Three installation schemes (A, B, C) of photothermal PCM and thermocouple arrangement. (d, e, f) Test temperature profiles for schemes A, B, and C. (g) Physical picture of photothermal conversion phase change water tank. (h) The infrared imaging figure of tank cross-section of scheme C. (i) Water temperature trends of scheme C under different weather conditions.

storage in form-stable composite PCMs is achieved through the introduction of polymer TPE and CuS. Compared with traditional form-stable PCM, the PW/TPE/CuS₁₅ exhibits a low leakage rate of 0.8 % while maintaining a high latent heat of 129.5 J/g. The PW/TPE/CuS₁₅ can be stretched up to 2.88 times longer at phase change temperatures. The 3D network structure of TPE enhances the shape stability and inhibits the phase separation of CuS. The introduction of CuS improves the light absorption of composite PCMs in the solar radiation band. The photothermal conversion efficiency of PW/TPE/CuS₁₅ is 88.7 %. Three schemes combining composite PCMs are designed for the charging and endurance of solar water heating systems. In scheme C, a maximum water temperature of 67.9 °C can be achieved due to the self-photothermal conversion. Natural convection occurs inside the water

tank due to its unique structural design, resulting in a more uniform temperature distribution. The water temperature can be maintained above 40 °C before 24:00 p.m. on a sunny day. This work achieves the application of passive PCM in photothermal conversion and renewable energy storage systems.

CRediT authorship contribution statement

Xiaohan Li: Writing – review & editing, Writing – original draft, Visualization, Data curation. **Nan Zhang:** Methodology, Funding acquisition, Conceptualization. **Zhaoli Zhang:** Software, Data curation. **Xinrong Zhu:** Writing – review & editing, Supervision, Resources. **Hasan Köten:** Validation, Project administration, Formal analysis.

Yanping Yuan: Writing – review & editing, Validation, Supervision.

Declaration of competing interest

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

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Data availability

Data will be made available on request.

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