

Flexible solid-solid phase change material with zero leakage via in-situ preparation for battery thermal management

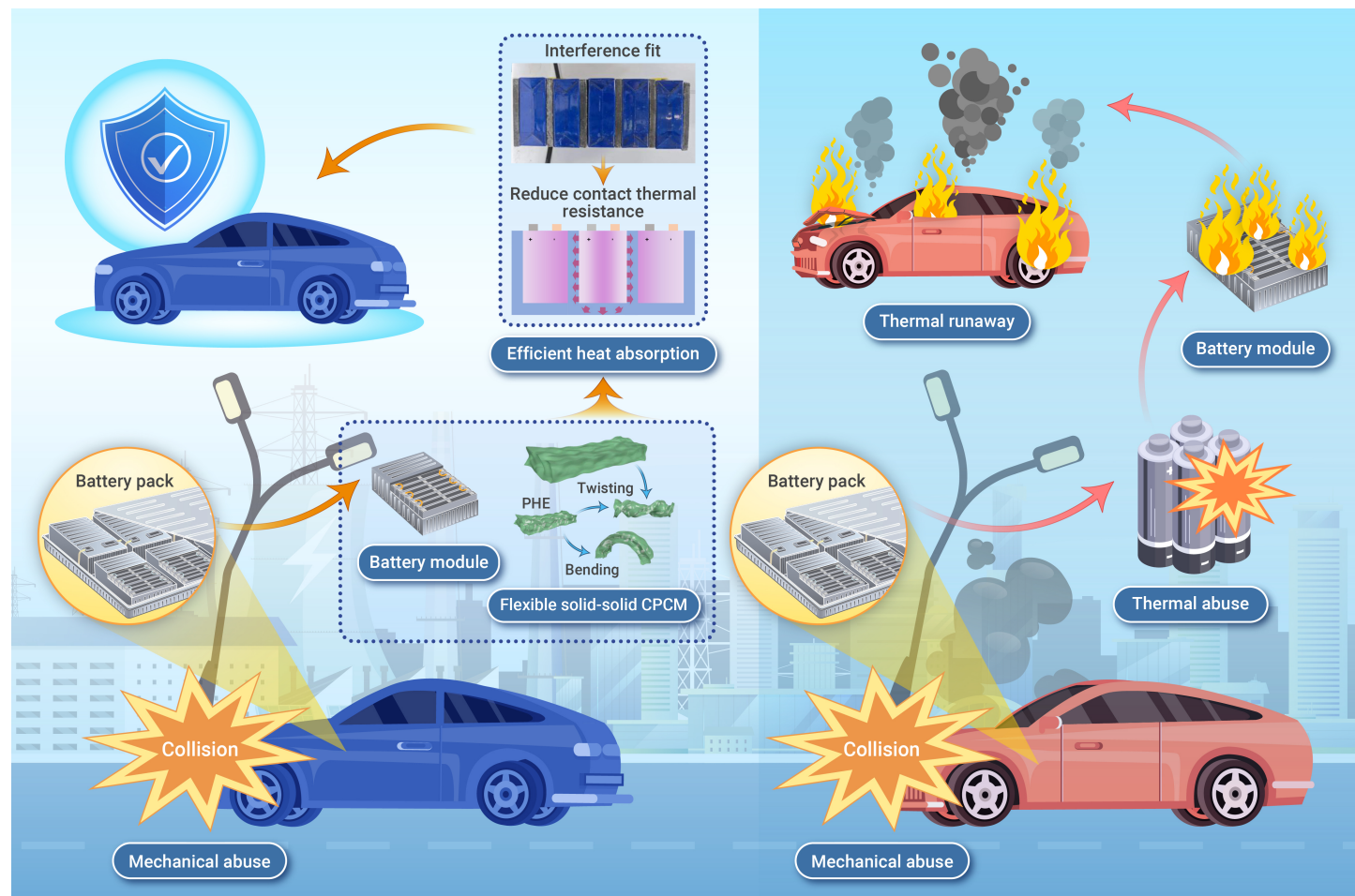
Xinxi Li,¹ Wensheng Yang,¹ Canbing Li,^{2,*} Jian Deng,¹ Qiqiu Huang,¹ Wei Jia,³ Ya Mao,³ Yuntao Zou,⁴ Yuhang Wu,² Juxiong Tian,⁵ Guoqing Zhang,¹ Xianwen Tang,⁶ Dan Shao,⁶ Yanrui Zhang,⁵ Siwei Zhu,⁵ and Xuxiong Li¹

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GRAPHICAL ABSTRACT



PUBLIC SUMMARY

- Polyurethane structured composite phase change material (CPCM) has been proposed and prepared via in-situ.
- Solid-solid CPCM (PUPCM) with polyurethane structure can improve flexible and anti-leakage properties.
- PUPCM sustain a constant mass with zero leakage even under 150°C heating condition.
- Flexibility and temperature control capability of PUPCM can effectively dissipate heat in battery module.
- The battery module with PUPCM can control the maximum temperature within 60°C at 3 C discharge rate.

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Composite phase change material (CPCM) has great potential in addressing the challenges associated with thermal energy storage and thermal management. However, the flexibility and latent heat capacity of CPCM exist contradiction, hindering its wide application, especially in thermal management field. Herein, a novel solid-solid polyurethane structured phase change material including as chain segments PEG4000 and hexamethylene diisocyanate coupling with expanded graphite (PHE5) has been proposed and prepared via in-situ approach. Expand graphite is uniformly distributed and the carbamate group is produced by in-situ preparation, the high latent heat and anti-leakage characteristics of PHE5 are beneficial to sustain a constant mass with zero leakage even under 150°C heating condition. At a 3 C discharge rate, the battery module with PHE5 can reduce the maximum temperature to 59°C, which is lower than the PE-based module. Additionally, the battery system can maintain the temperature difference below 4.5°C, ensuring uniform temperature within the battery module. The flexibility and controlling temperature capabilities of PHE5 can effectively dissipate heat during charge and discharge cycles, and the mechanistic analysis of PHE5 with anti-leakage property can enhance the battery thermal safety, achieving comprehensive protection throughout normal operating and extreme conditions. Thus, this research reveals that solid-solid CPCM with polyurethane structured can improve the flexible and anti-leakage properties via in-situ preparation, which will offer an effective thermal safety solution for battery module, substantially enhancing the safety of millions of drivers and passengers.

INTRODUCTION

The current shift in the energy sector towards renewable sources has coupled with significant progress in battery technologies, particularly lithium-ion batteries (LIBs), as a pivotal component in the future framework of energy systems. The LIBs with high energy density, long cycle life, and low self-discharge rate have been widely utilized in electric vehicles (EVs). However, the widespread application of LIBs in EVs has also brought the challenge to battery safety.^{1,2} At high charge and discharge rate during the driving condition, the heat of the LIBs is easily and quickly generated and accumulated, which increases the temperature of the battery modules.^{3,4} Moreover, an abnormal temperature rise can trigger uneven temperatures within the battery module, increasing the risk of thermal runaway.^{5,6} The battery accompanied by heat accumulation can bring about accelerating battery retirement and threaten the safety of passengers in EVs under high-temperature conditions.^{7,8} Generally, the battery has degraded approximately doubles with every 10°C increments. Thus, an efficient and reliable thermal management system (BTMS) is very vital for battery module,⁹ including air cooling,^{10,11} liquid cooling,^{12,13} phase change materials (PCM) cooling,^{14,15} and heat pipe cooling.¹⁶ Among them, PCM cooling has been established as an efficient thermal management approach for EVs. As a passive cooling method, PCM cooling requires no additional energy input and can absorb and release the latent heat undergoing a phase transition, rendering it particularly advantageous in BTMS.^{17,18} Extensive studies have demonstrated its viability for widespread

application in the EVs industry.^{19,20}

Polyethylene glycol (PEG) with high latent heat, reasonable phase change temperature, and low-cost has been suitably applied in battery module,^{21,22} but its poor anti-leakage capability,²³ high rigidity,²⁴ and low thermal conductivity²⁵ still severely affected the dissipating heat efficiency. To address these issues, different composite phase change materials (CPCM) have been developed by adding supporting material to encapsulate and absorb PEG like epoxy resin (ER)^{26,27} and metal foam (MF).^{28,29} The form-stable CPCM was synthesized through blending PEG with silicon dioxide (SiO₂) and expanded vermiculite (EVM),^{30,31} which can improve the enthalpy, anti-leakage capability, and maximum load force compared to pure PEG, indicating the enhancement of thermal and structural integrity performances. In addition, a micro-capsule structure was constructed to encapsulate CPCM, which prevented the phase change components from leakage and fully utilized the phase change latent heat.³² Particularly, to decrease the CPCM rigidity, different kinds of flexible CPCM (FCPCM) have been synthesized via adding flexible support skeletons including olefin block copolymer (OBC),³³ styrene-butadiene-styrene (SBS),³⁴ and thermoplastic ester elastomer (TPEE).³⁵ Moreover, the anti-leakage and flexibility properties of FCPCM can both be obtained via adding paraffin, ethylene-ethylene-butadiene-styrene block copolymers (SEBS), polyethylene octene co-elastomers (POE),³⁶ thermoplastic elastomer and polyolefin elastomer.³⁷ Besides, thermally conductive fillers such as graphite,³⁸ expanded graphite (EG),^{39,40} and metal nitride power^{41,42} are selected to improve thermal conductivity for CPCM in thermal management system for battery modules. Different structures CPCM with silicon carbide were prepared via vacuum impregnation and ethanol methods, which indicated that silicon carbide with nanofiber structure maximally adsorbed stearic acid phase change materials and endowed the composites with high thermal conductivity.⁴³ In our previous research, a highly thermally conductive FCPCM was prepared via the solvent volatilization method,⁴⁴ encapsulated by a backbone composed of SBS with AlN as adding material. Although these additions have enhanced the anti-leakage, flexibility, and thermal conductivity of CPCM based on the PEG, an inevitable leakage still appeared in FCPCM during long-term operation, owing to the incompatibility between the PEG and additions.⁴⁵

Considering the polyurethane structured phase change material (PUPCM) is formed with crystallizable linear chains onto the polyurethane, it has attracted attention due to its anti-leakage capability even in repeated phase transiting processes.⁴⁶ The mobility of soft chain material of PEG on the CPCM undergoing phase transition is restricted to remain solid. The PUPCM with polyethylene oxide as a side chain was prepared by reacting diethanolamine-modified monomethoxy polyethylene glycol with isophorone diisocyanate and 1,4 butanediol, which remained solid state within 100°C and possessed only 2% loss ratio of phase change enthalpy after 100 cycles.⁴⁷ PUPCM was synthesized with isophorone diisocyanate as the hard chain segment, PEG as the soft chain segment and butylene glycol as the chain extender. Although the long-term cycling stability, shape foldability and stretchability were all obtained, the latent heat of this PUPCM was only 61.48 J/g.⁴⁸ Through mixing with varying loadings of titanium dioxide nanoparticle

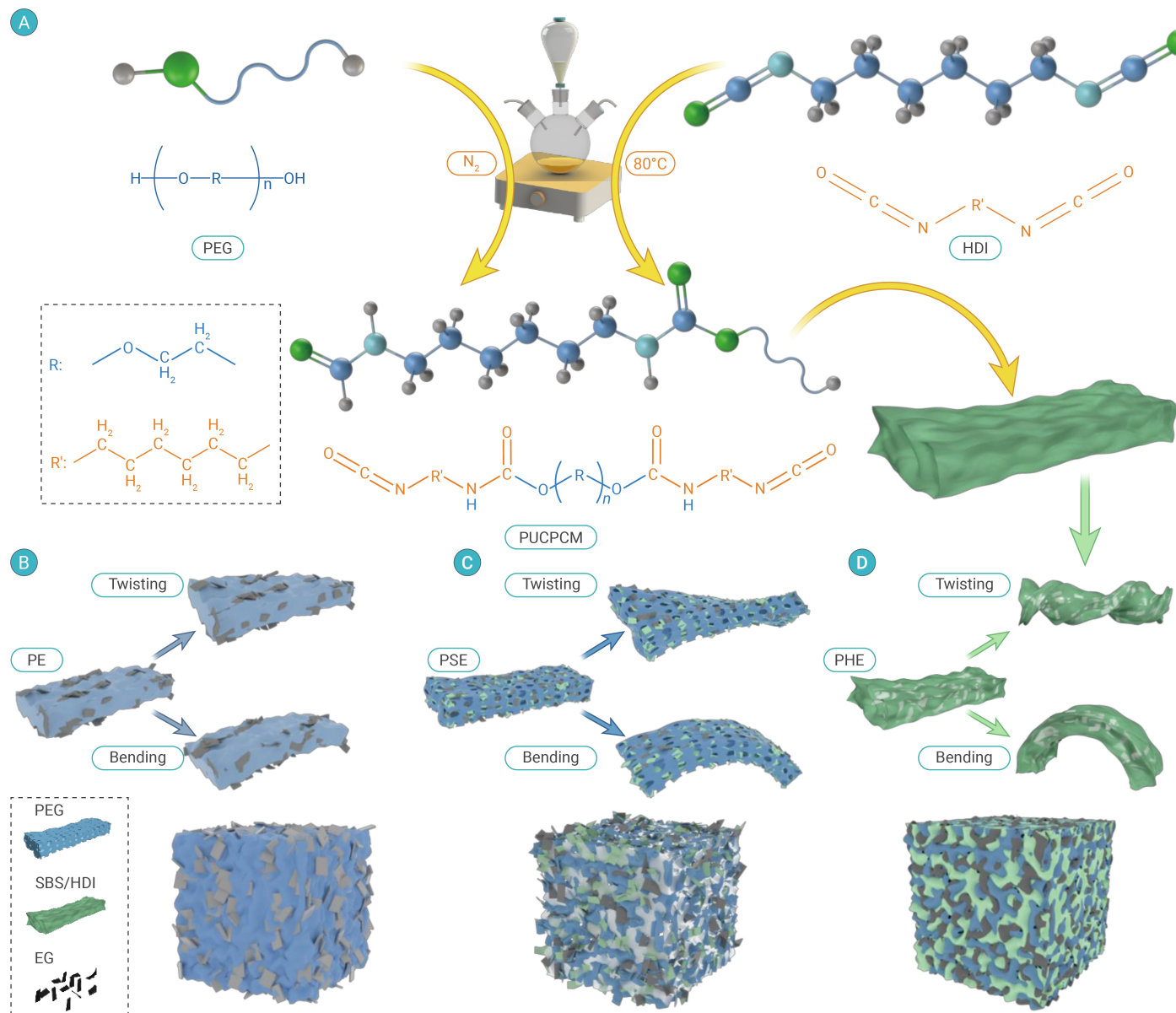


Figure 1. The designation and various structures of different CPCMs (A) the synthesizing mechanism of PUPCM. (B) PE with rigidity after twisting and bending. (C) PSE with enhancement on the flexibility. (D) PHE maintains excellent shape stability in the twisting and bending tests without cracks.

particles, the latent heat of PUPCM³ was improved from 65.59 J/g to 73.02 J/g.⁴⁹ A rubbery PUPCM with excellent thermal stability was obtained by adding dichloromethane, hexamethylene diisocyanate (HDI) and Dibutyltin dilaurate (DBTDL) to the dried PEG under an argon atmosphere. The PUPCM was synthesized using PEG with molecular weight from 300 to 1500, the latent heat was reached to 78 J/g.⁵⁰ Nevertheless, the existing bottleneck of PUPCM is still confronted with a contradiction between flexibility and a high latent heat capacity.^{51,52}

Among the inner structure of PUPCM, PEG molecules with long molecular chains exhibit high intermolecular interactions, thus leading to an augmentation of phase change enthalpy. In contrast, PEG-based polyurethane with low molecular weight exhibits an abundance of active groups that contribute to an increased degree of crosslinking, yielding enhanced flexibility.⁵³ Thus, this contradiction presents the PUPCM cannot simultaneously exhibit both excellent flexibility and exceptional thermal storage capability. In practical application of EVs, the battery modules have to endure highly frequent charging and discharging conversion during the cycling process at a high discharge rate, it is imperative for CPCM to exhibit a stable enthalpy value exceeding 100 J/g with sufficient flexibility, ensuring the thermal and shape stability of battery

module. Herein, the concurrent enhancement of flexibility and latent heat capacity of PUPCM (PHE) has been designed, which included PEG and Hexamethylene diisocyanate (HDI) coupling with expanded graphite that has successfully synthesized, the incorporation of different proportions of EG is employed to alleviate the reaction rate during the in-situ preparation, uniformly distributing in the PUPCM owing to its stratified structure, which can also strengthen the PUPCM flexibility properties. The in-situ synthesis can ensure the strong bonding effect between PEG and HDI, resulting in exceptional resistance to leakage and thermal stability. Furthermore, the battery module with different CPCMs has been employed to analyse thermal management effect. The PHE presents obviously mitigation volume change effect within the battery module. These outstanding flexible PUPCM endow the battery module exhibiting excellent cooling efficiency, adaptability, and durability, which is beneficial to improve the safety of millions of drivers and passengers in EVs.

MATERIALS AND METHODS

Materials

Polyethylene glycol (PEG, molecular weight 4000) was purchased from

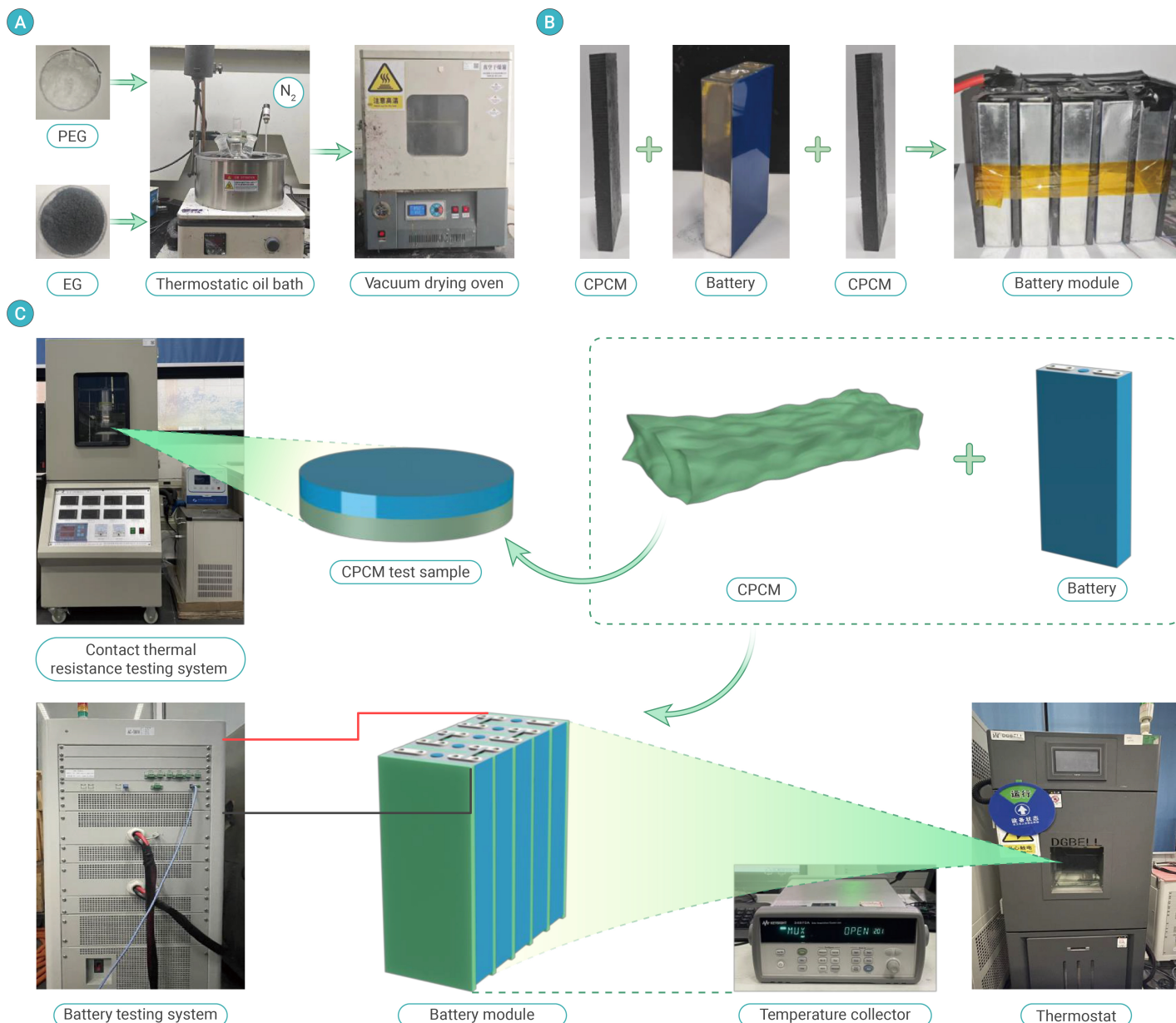


Figure 2. The assembling and measuring platform of prismatic battery module (A) Physical diagram of the CPCM preparing process. (B) Physical diagram of the battery module assembling process. (C) Battery thermal management system measuring platform.

Shanghai Macklin Biochemical Co., Ltd. Hexamethylene diisocyanate (HDI) purchased from Wanhua Chemical Co. Dibutyltin dilaurate (DBTDL), was from Shanghai Aladdin Biochemical Technology Co., Ltd., which acted as a catalyst during the reacting process. EG as a thermal conductivity additive was obtained by expanding at 850°C for 10 min.

PUPCM preparation and synthesis

As depicted in Figure 1A, the dehydrated PEG was placed in a three-neck flask at 80°C . EG was introduced and uniformly stirred using a mechanical stirrer. Following this, HDI and a small amount of DBTDL were added to the three-neck flask, and the mixture was stirred under a nitrogen atmosphere for 30 min. Finally, the thoroughly mixed solid was transferred into the mold. The ratio of HDI to PEG should also be 1:1 owing to the ratio of isocyanate group ($-\text{NCO}$) to hydroxyl group ($-\text{OH}$). However, to prepare PUPCM with better thermal stability, the amount of HDI should be excessive. Three sets of samples with different ratios were set up with R (HDI: PEG) of 1.5, 2, and 2.5, noted as PH1.5, PH2, and PH2.5 respectively. To investigate the effect of the content of the thermal conductivity additive EG on the PUPCM performance, 1, 3, 5, and 7 wt% of EG were added to the PH2 samples, denoted as PHE1, PHE3, PHE5,

and PHE7, respectively. In addition, there were two CPCMs prepared by physical blending. Among them, PE was a CPCM prepared by mixing PEG and EG. PS was an FCPCM prepared by using styrene-butadiene-styrene block copolymer (SBS) as a supporting backbone and PEG. All the component proportions details of CPCMs are shown in Table S1.

XRD and FT-IR

The chemical compatibility and crystalline structure of PUPCMs were characterized by XRD, Rigaku D/max-2550 using Cu K α radiation (0.154056 nm). The scanning angle 2θ range of XRD was $5\sim 50^{\circ}$, and the scanning speed was $10^{\circ}\cdot\text{min}^{-1}$. To research the functional groups of PUPCM, Fourier transform infrared spectroscopy (FT-IR, Bruker Tensor-27) was used to characterize PEG, PE, PSE, and PHE samples using KBr disks in the spectral range of $400\sim 4000\text{ cm}^{-1}$.

SEM and mechanical characterization

To reveal the morphological differences between PUPCM and pure PEG, as well as the distribution of EG in PUPCM, a Scanning Electron Microscope (SEM Hitachi S-3400 N, Japan) with an accelerating voltage of 20 kV was

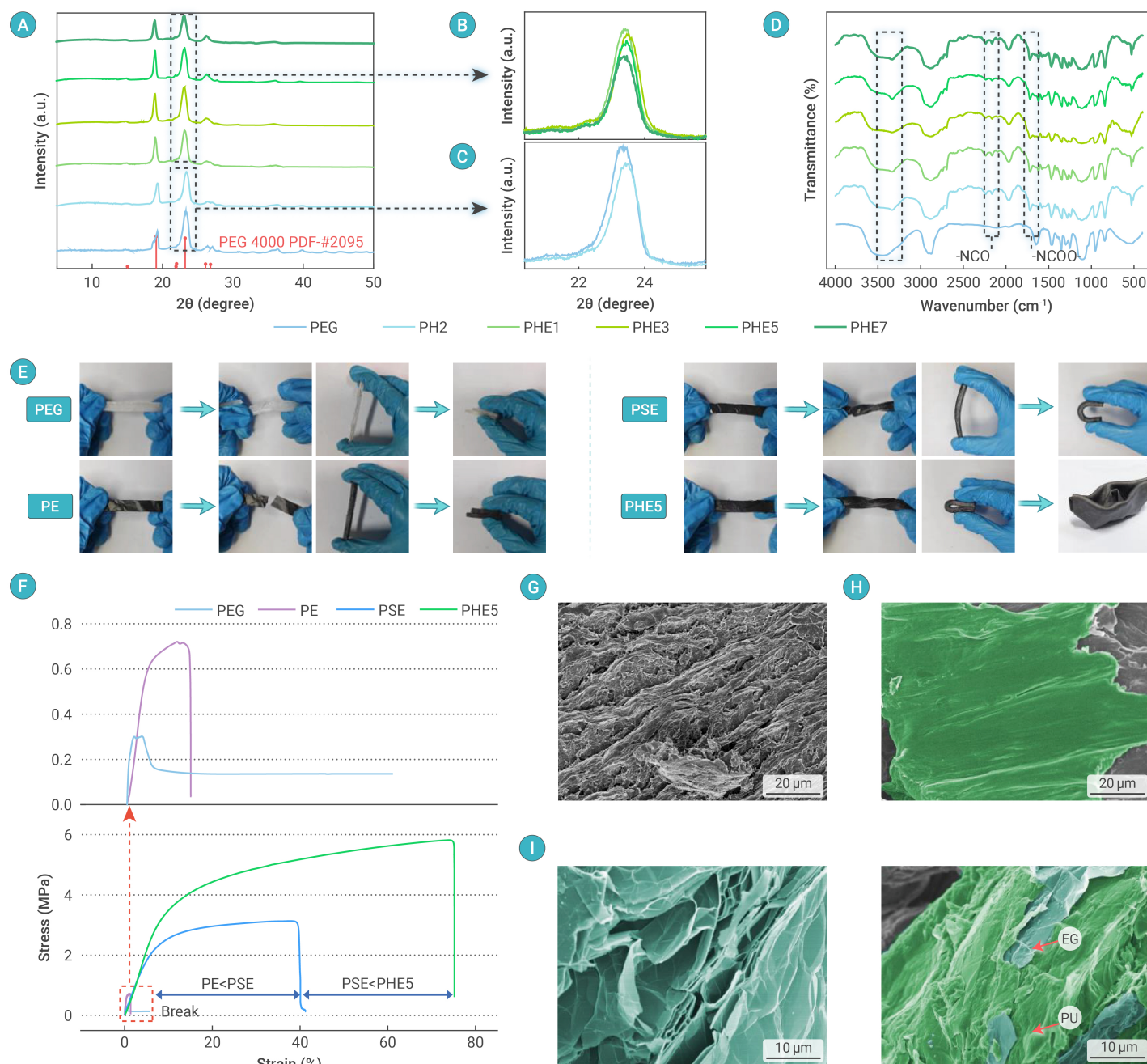


Figure 3. The structure characterization of different CPCMs (A) XRD curves of PEG, PH2, PHE1, PHE3, PHE5, PHE7 with scanning angle 2θ range, and the scanning speed is $10^\circ \cdot \text{min}^{-1}$. (B) XRD curves of PHE1, PHE3, PHE5 and PHE7 with EG. (C) XRD curves of PEG and PH2 without EG. (D) FT-IR spectra of PEG, PH2, PHE1, PHE3, PHE5 and PHE7. (E) Mechanical characterization of PEG, PE, PSE, PHE5. (F) Tensile strength test of PEG, PE, PSE, and PHE5. SEM image of (G) PEG, (H) PH2, (I) EG, (J) PHE5.

utilized to characterize the microscopic morphology of samples. The mechanical characterization of PUPCM included twist test and bend measurement. PUPCMs were fabricated into 10 mm x 6 mm x 4 mm size samples. The same magnitudes of force were applied to these samples and the deformation magnitude of the samples was observed in the twist test and the bend test.

Thermal stability and thermodynamic characterization

PUPCM shape stability was characterized by a thermostatically heating platform (Dongguan Jinfeng Electronics Co. LTD, China) and an electronic balance (Shenzhen Botu Electronic Technology Co., LTD, China, accuracy is 0.001 g). Samples of circular block shapes with a diameter of 35 mm and thickness of 20 mm were placed on a thermostatically heated platform and heated at 70°C for 72 h. The quality of the sample was measured by an electronic balance every 12 h. The quality maintenance rate (R) can be calculated

by $R = Q_n/Q_0$, where R represents the quality maintenance rate. Q_n represents the quality of the sample and Q_0 is the initial mass of the sample. In addition, to investigate the thermal stability of samples at different temperatures, these samples were placed on a thermostatically heated platform at 70°C to 150°C with a gradient of 20°C for 1 h. The variations in the morphology of the samples at 70°C , 90°C , 110°C , 130°C , 150°C were observed and photographs were taken. Differential scanning calorimetry (DSC, Q20, TA Instruments Inc.) was applied to the latent heat analysis of PUPCM. Each sample weighing 5 mg was heated from 20°C to 80°C at a rate of $5^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. The latent heat values and melting temperature peaks of the samples were obtained by analysing the heat flow versus time curves of each sample.

In addition, the thermal conductivity of each sample was tested using a thermal conductivity tester (DRL-2A, Xiangtan Instrument Co., Ltd., China) and the TCR was obtained by $\text{TCR} = \text{TR} - R_{\text{PUPCM}}$ and $R_{\text{PUPCM}} = D/\lambda$, where TR

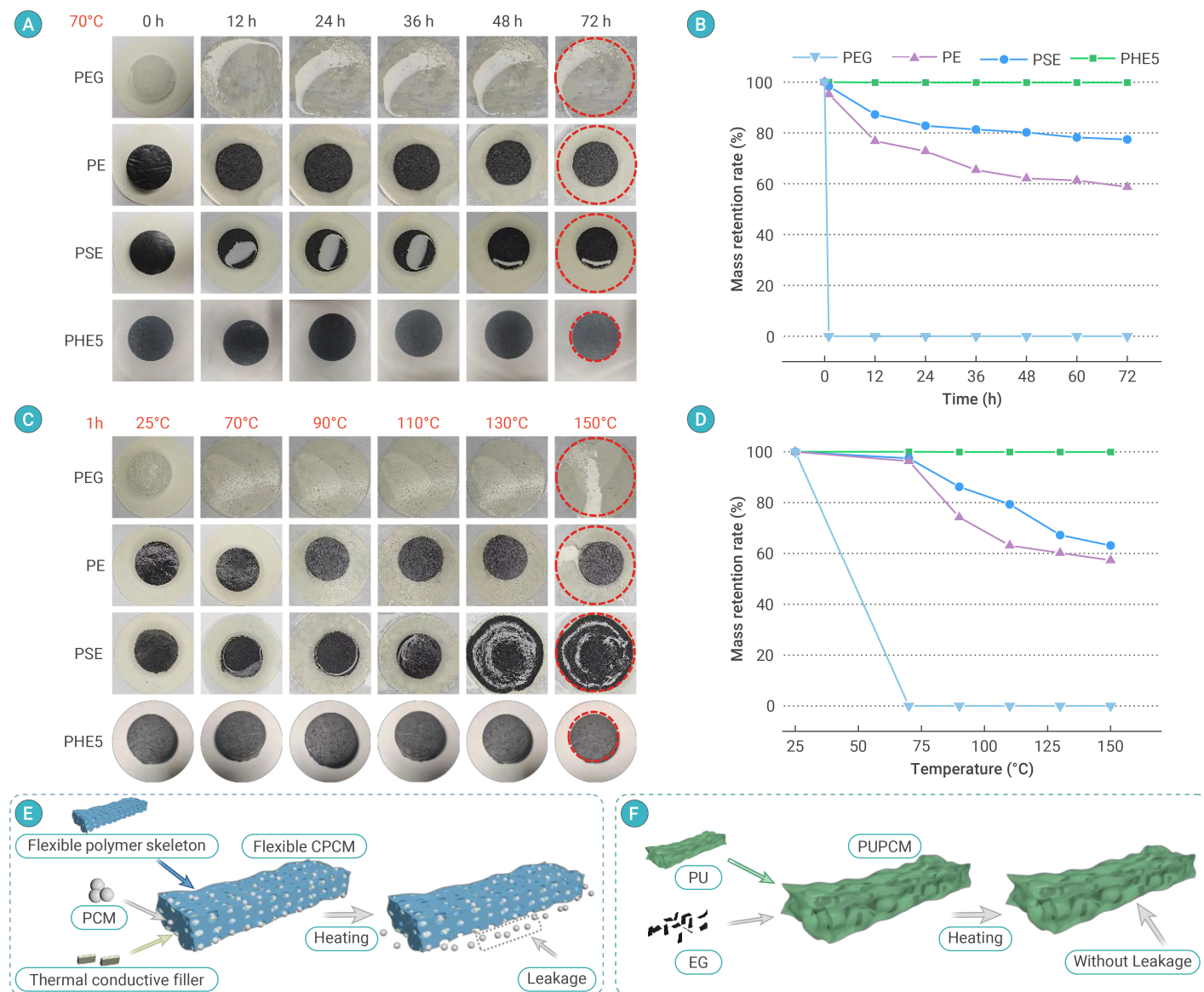


Figure 4. Characterization of PUPCM thermal stability under heating conditions (A) Picture and (B) mass retention rates of PEG, PE, PSE, and PHE5 under continuous heating at 70 °C. (C) Picture and (D) mass retention rates of PEG, PE, PSE, PHE5 heated at 25 °C, 70 °C, 90 °C, 110 °C, 130 °C, 150 °C in 1 h. (E) Schematic diagram of leakage resistance mechanism of FPCM and (F) PUPCM variations under heating conditions.

and R_{PUPCM} represent the experimentally measured and the theoretically calculated thermal resistance of PUPCM, respectively. D represents the thickness of PUPCM, measured by the thermal conductivity tester, and λ represents the thermal conductivity of PUPCM.

BTMS verification

The relevant parameters of the cell and the battery module are listed in Table S3. The three battery modules were placed in a 30°C thermostat and tested. Meanwhile, battery modules were connected to a temperature collector through thermocouples to record the temperature data. In the experiment, the thermocouple was adopted as T-type thermocouple. The testing range of the thermocouple was ranged from -50 to 300°C, and the testing accuracy was 0.01°C.

RESULTS AND DISCUSSION

Flexible characteristics of PUPCM and integrated design of battery modules

The PEG and HDI as materials are prepared PUPCMs with bulk polymerization reaction, as depicted in Figure 1A, PEG is reacted with HDI through esterification reaction to form PHE. Besides, PE, PSE and different propor-

tions of PUPCMs were synthesized to investigate the effect of HDI and EG contents on the PUPCM performance, respectively, as described in Table S1 and Table S2. It is worthy noted that these samples are denoted according to the ratio of PEG to HDI and the proportion of EG. It can be observed that PE synthesized from PEG and EG maintains a high degree of rigidity when subjected to twisting and bending in Figure 1B. Although the addition of the SBS skeleton enhances the flexibility of PSE, as indicated in Figure 1C, the physical mixing method restricts its twisting and bending performance due to insufficient material integration. However, PHE is synthesized via the in-situ preparation method, exhibiting superior flexibility compared to PE and PSE. In Figure 1D, it illustrates that PHE can be twisted up to 720° and bent up to 90° without cracks. This underscores the flexibility improvement achieved in the PHE.

As shown in Figure 2A, PUPCM was prepared with the bulk polymerization reaction of PEG and HDI. The dehydrated PEG was posited in a three-neck flask at 70°C. Then the EG was put in and stirred uniformly by a mechanical stirrer. Especially, the experiments including PEG and EG had preheated in an oven for 12 h to dissipate water. After that, the HDI and a small amount of DBTDL were added into the three-neck flask and stirred under a nitrogen atmosphere for 30 min. During mixing process, the mixture rapidly becomes

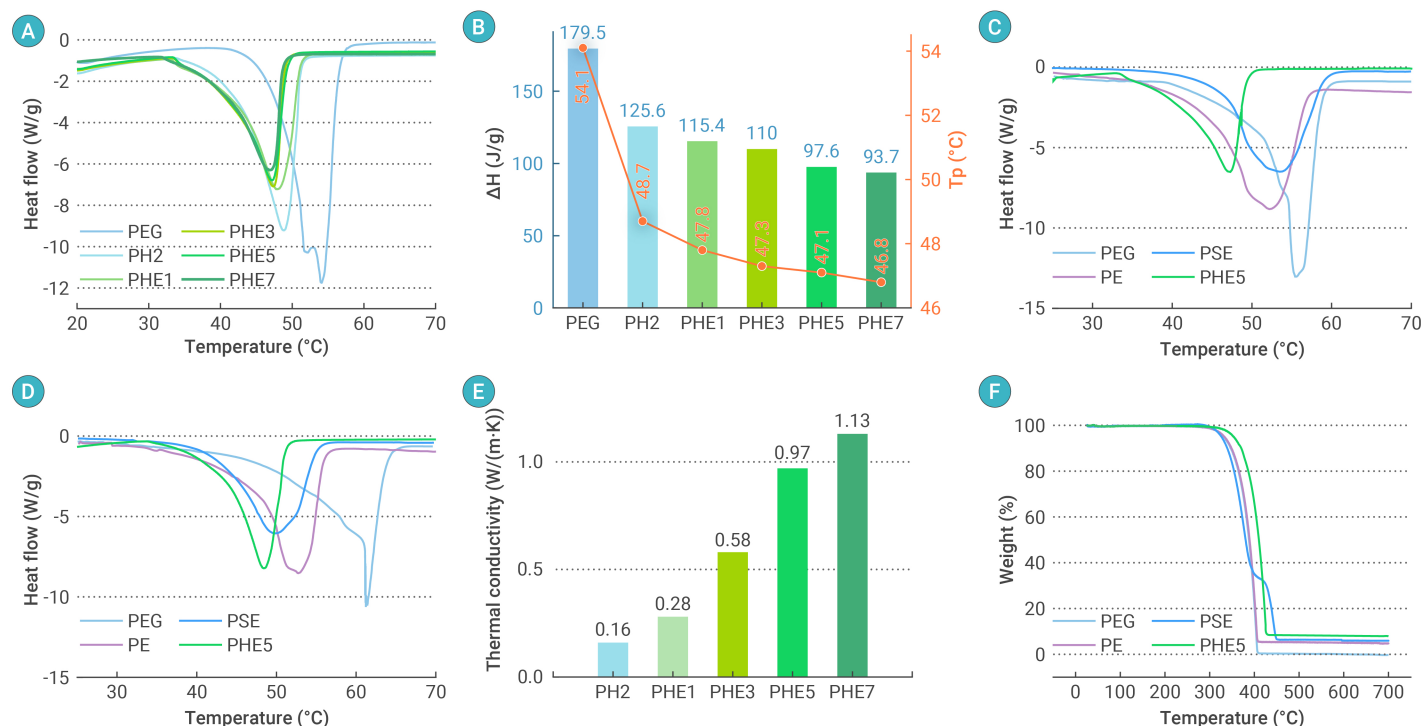


Figure 5. The thermodynamic characterization of PUPCM (A) DSC curves and (B) ΔH and T_g curves of PEG, PH2 and different PHE samples. DSC curves of PEG, PE, PSE, and PHE5 (C) before and (D) after thermal cycle. (E) Thermal conductivity of PH2 and different PHE samples. (F) The TGA curves of PEG, PE, PSE and PHE5.

viscous and a large number of air bubbles are generated. Therefore, it is necessary to utilize a powerful mechanical stirrer to ensure that the air bubbles in the mixture are removed. Finally, the well-stirred solid was poured into the module and the PUPCM was successfully prepared. Further, CPCMs prepared were used with 5 cells forming the same size battery module for temperature testing during charging and discharging (Figure 2B). To analyse the TCR reduction and battery thermal management effect of PUPCM, the CPCM was prepared as a circular block with a diameter of 30 mm and a thickness of 3 mm as shown in Figure 2C. The samples were closely laminated with aluminium blocks of the same size to characterize the TCR. The aluminium block was selected as the same material of the battery case for simulating the roughness of the battery case.

The PUPCM crystallization characteristic and chemical structure

The energy storage and release of PUPCMs are achieved by conversion between the crystalline and amorphous states. Therefore, the crystallization characteristics of PUPCMs can affect the thermal storage capacity. The crystallographic properties of the samples were characterized by X-ray diffractometer (XRD), as depicted in Figure 3A. It can be seen that the PUPCMs and PEG (PDF#49-2095) show distinct characteristic peaks at 19.2° and 23.3° , respectively, indicating that the PUPCMs exhibit a similar crystallization pattern to PEG. As displayed in Figure 3B, the diffraction peak intensity of PHE1, PHE3, PHE5, and PHE7 decreases with the EG increase. It is also observed that the diffraction peak intensity of PEG and PH2 decreases with the HDI increase, as depicted in Figure 3C. Owing to the positive correlations between the diffraction peak intensity and crystallization ability, it can be concluded that the crystallization performance of PUPCMs decreases with the increase of HDI and EG content addition. The main reason is that the hard chain of HDI and EG with worm-like structures restricts the movement of soft chain PEG between the amorphous and crystalline states of PUPCMs.

The chemical structures including PEG, PH, and different proportions of PHE samples were investigated by Fourier Transform Infrared Spectrometer (FTIR), as shown in Figure 3D. It can be observed that these PUPCMs exhibit additional characteristic peaks at 3318 cm^{-1} , 2238 cm^{-1} , 2159 cm^{-1} , 1724 cm^{-1} , and 1609 cm^{-1} compared to PEG. Among them, the absorption peaks of samples are observed at 2238 cm^{-1} , and 2159 cm^{-1} , respectively, which

present the result of isocyanate group ($-\text{NCO}$) vibration, produced by an excess of HDI. The characteristic peak appearing at 3318 cm^{-1} is attributed to the stretching vibration of $-\text{NH}-$, and the absorption peaks are presented with the vibration of the carbamate group ($-\text{NCOO}-$), as observed at 1724 cm^{-1} , and 1609 cm^{-1} , respectively. Thus, these results indicate the PUPCMs with designed chemical structures have been successfully synergized.

The stable flexibility and continuous structure enhancement of PUPCM

The twisting and bending tests of sample strips were compared, displayed in Figure 3E. The PEG is rigid and easy to break in the test. Even with the addition of EG, the PE is unable to withstand bending and twisting. The PSE prepared by physical mixing shows a certain degree of flexibility, but its twisting ability is still limited in a 180° range. However, the PHE5 can be easily twisted to 720° in the twisting test. The PHE5 possesses stable flexibility and can withstand substantial bending without cracks, even fabricated as a ship type. Furthermore, as shown in Figure 3F, both the PEG and PE samples break immediately during the tensile process. In contrast, the tensile strength of PSE and PHE5 reaches 3.2 and 4.9 MPa, respectively. This confirms that PSE prepared by physical mixing still retains the poor tensile strength of PEG and only SBS provides support during the stretching process, while PHE5 acts as a FCPCM as a whole and shows more excellent mechanical properties.

The microstructures of PEG, PH, and PHE5 were observed to illustrate the differences in mechanical properties. As displayed in Figure 3G, PEG exhibits a concave and uneven striped structure, thus, it does not own stable mechanical properties. However, after preparing PEG into PUPCM, its morphology becomes a smooth and compact sheet structure, achieving more stable mechanical properties, as shown in Figure 3H. The continuous sheet structure ensures that PUPCM maintains its shape without cracks during bending or twisting. It can be seen from Figure 3I that EG owns a scale-like structure, with a large specific surface area and exuberant pores, and it can be uniformly distributed in the PHE5 (Figure 3J). These results indicate that PUPCM has satisfactory compatibility with EG, which provides the possibility for the improvement of structural stability and thermal conductivity.

The characteristics of thermal stability and anti-leakage

The thermal cycle life of PUPCM depends on both the thermal stability and

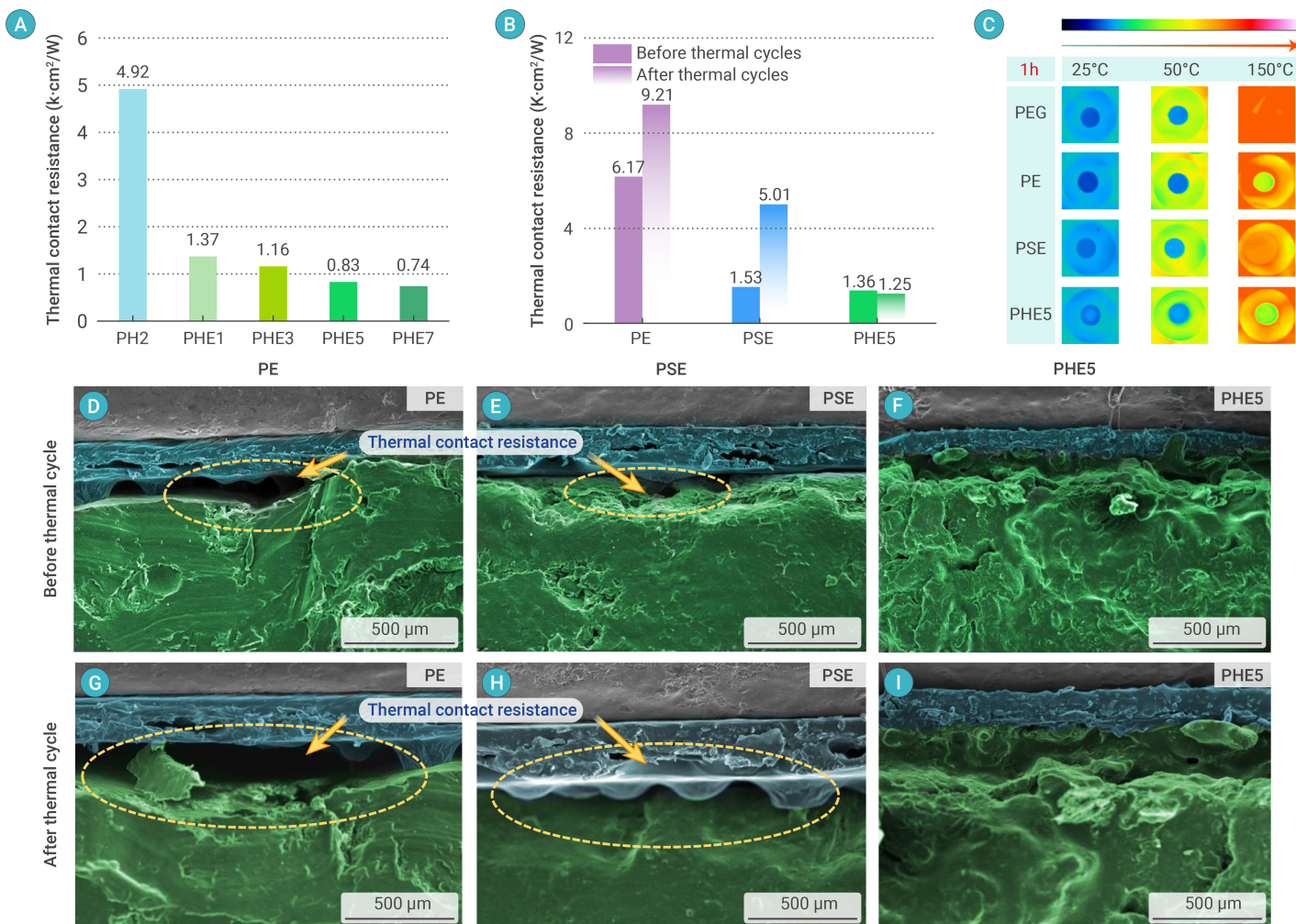


Figure 6. Characterization of contact thermal resistance of different CPCM samples (A) TCR of PHE samples. (B) TCR of PEG, PE, PSE, and PHE5 before and after thermal cycle. (C) Infrared thermal images of PEG, PE, PSE, and PHE5. SEM images of (D) PE, (E) PSE, (F) PHE5 before the thermal cycle, SEM images of (G) PE, (H) PSE, (I) PHE5 after thermal cycle.

anti-leakage capability during the repeated phase transition. As shown in Figure 4A, PEG is rapidly liquefied on the heating table at 70°C. The PE does not collapse under continuous heating owing to a three-dimensional supporting skeleton of EG, but it appears leakage. The PSE maintains structural stability during continuous heating conditions. However, the liquefied PEG is spilled from the SBS skeleton to the surface of PSE when the PEG surpasses to a certain degree. The PHE can maintain a stable structure throughout the whole heating test without leakage, indicating the PHE owns the thermal stability and anti-leakage capability under heating conditions.

In Figure 4B, it can be observed that PE is liquefied while EG delays the leakage compared with PEG. The mass retention rate is less than 60% after 72 h of continuous heating conditions. Following the heating test, the mass retention rate of PSE increases to 79%, while the mass of PHE5 remains unchanged. This indicates that PHE5 does not experience any leakage during continuous heating conditions. The morphological and structural stability of samples were tested as displayed in Figure 4C. The PEG is liquefied on a heating table above 70°C in 1 h. With the increase in heating temperature, the leakage and collapse of PE and PSE became more serious. There was a large amount of PEG leakage in PE, and only a loose EG skeleton remained. However, PSE not only leaked PEG at high temperature, but also collapsed due to the melting of SBS when the temperature exceeded 130°C. The PHE5 was heated from 25°C to 150°C without leakage. According to Figure 4D, the PEG, PE, and PSE were totally leaked when the temperature exceeded 75°C, at which PEG completely liquefied. Due to the encapsulation effect of SBS, the anti-leakage performance of PSE is better than that of PE lower than 125°C. However, when the temperature exceeded 125°C, the PSE and PE

exhibited a similar leakage phenomenon. The mass retention rate was only about 66% at 150°C. As for PHE5, it maintained the constant mass after heating at high temperatures. Thus, it can be demonstrated that PHE5 has possessed properties with anti-leakage and thermal stability during solid-solid phase transition under high-temperature conditions.

To investigate the anti-leakage mechanism of PUPCM, the material variation of FCPCM and PUPCM after heating are shown in Figures 4E-F. In Figure 4E, FCPCM is generally composed of a flexible polymer backbone, phase change matrix, and thermal conductive filler. Although flexible CPCM is encapsulated by a flexible polymer backbone to prevent leakage during the phase transition process, the flexible polymer can not completely adsorb the liquid-phase PCM under high temperatures. The liquid-phase PCM can penetrate through the pores of the flexible polymer surface to cause the leakage. In contrast, in Figure 4F, the anti-leakage mechanism of PUPCM is that PEG as a phase change component is formed a carbamate group by reacting with HDI. The soft chain segment PEG and the hard chain segment HDI are sufficiently linked in the presence of a carbamate group. Thus, PUPCM can achieve solid-solid phase transition during the heating process, presenting an optimum thermal stability and anti-leakage capability.

The EG reinforcement on thermodynamic characterization

The latent heat value (ΔH) of the CPCM determines the upper limitation of the material heat absorption ability. In Figure S1, it is demonstrated that the ΔH of PEG is 179.5 J/g, while the ΔH of PH1.5, PH2.5, and PH5.5 are 142.5 J/g, 125.6 J/g, and 114.7 J/g, respectively. This indicates that the ΔH of PUPCMs decreases accompanied by the increasing ratio of -NCO to -OH increment.

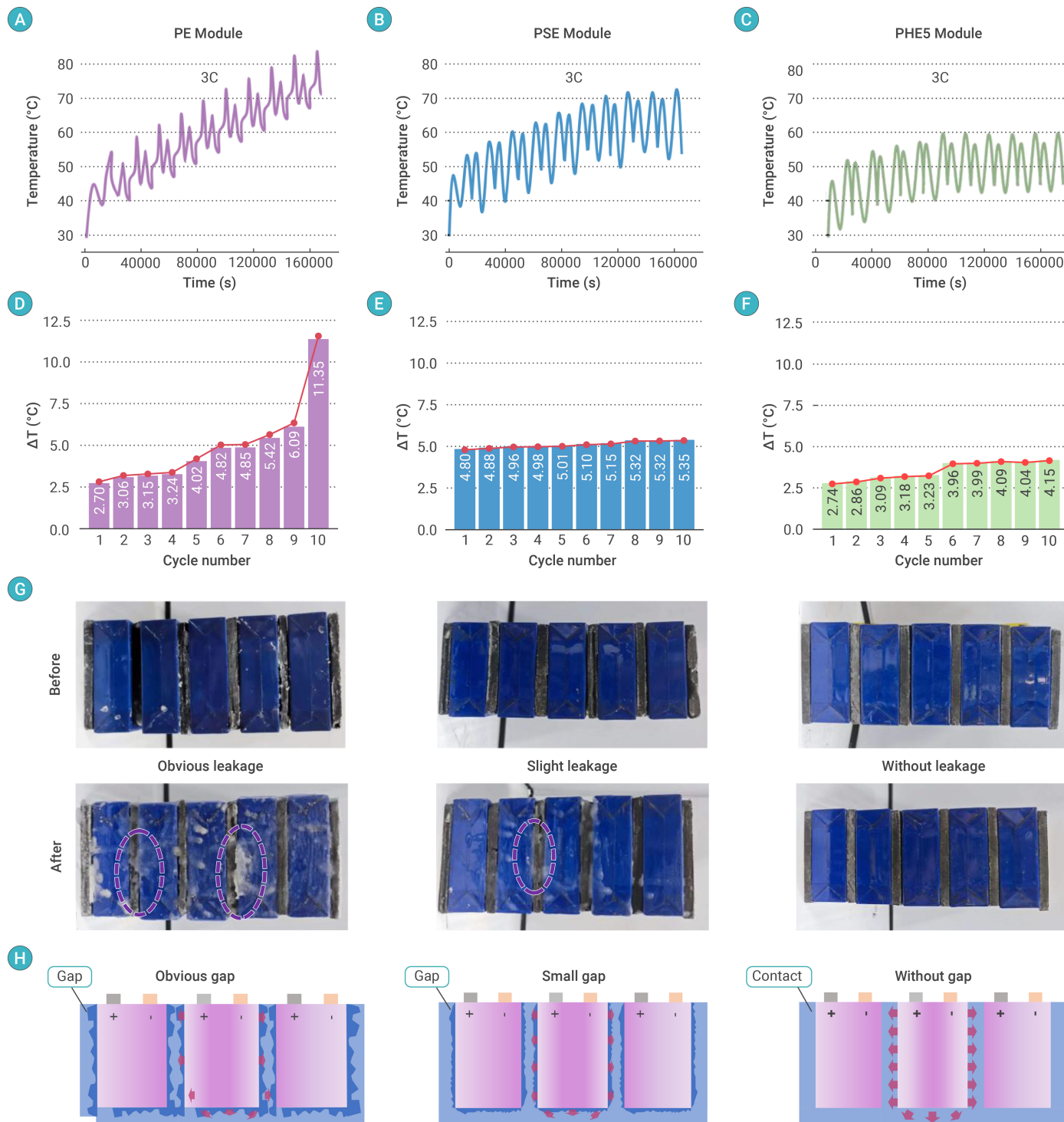


Figure 7. Characterization of PE, PSE and PHE5 Module Temperature curves of (A) PE Module, (B) PSE Module and (C) PHE5 Module at ten cycles charge-discharge test. Temperature different (ΔT) of (D) PE Module, (E) PSE Module and (F) PHE5 Module at ten cycles charge-discharge test. (G) Shape of the three battery modules with different CPCMs after the charge/discharge test. (H) Heat transfer and contact between PE, PSE, PHE5, and battery module.

The PH2 ratio was selected for subsequent experiments. In Figures 5A-B, it is demonstrated that the ΔH of PHE1, PHE3, PHE5, and PHE7 are 115.4 J/g, 110.0 J/g, 97.6 J/g, and 93.7 J/g, respectively. With the same ratio value, ΔH of PHE shows a decreasing trend with increasing EG content. The ΔH of PHE1 is 115.4 J/g, while ΔH decreases to 93.7 J/g in PHE7. The phase change temperature (T_p) shows a similar trend, which reveals that the T_p of PEG is about 59.6°C, and the PH2 is shifted forward to 55.5°C. The T_p of PHE1 and PHE7 is 54.9°C and 53.8°C, respectively. It indicates that EG accel-

erates the heat transfer.

The ΔH decreasing trend can be explained by the motion restrictions with the soft chain segments of PEG in PUPCM. The ΔH in the PUPCM is mainly derived from the heat required to transform the soft chain segment PEG from the low-entropy crystalline state to the high-entropy amorphous state. Compared with PEG, the soft chain segment of PEG in PUPCM is connected with the HDI hard segment during the phase transition, which limits the free motion of PEG. It eventually leads to less heat required and lower latent heat

value. As the HDI contents in PUPCM increase, the number of hard chain segments increases, further restricting the free movement of PEG soft chain segments. The T_g decreasing trend of PUPCM indicates that the hard chain segments in PUPCM can increase the lattice defects of PEG soft chain segments to promote the conversion of PEG into the amorphous state at lower temperatures.

The PUPCM exhibits anti-leakage and thermal stability properties during the heating process. Differential scanning calorimetry (DSC) curves of PEG, PE, PSE, and PHE5 before and after twenty thermal cycles were compared as shown in Figures 5C-D. It can be seen that there are no variations in the PHE5 DSC curves before and after the thermal cycle. However, after the thermal cycle, the DSC curves of physical mixing CPCMs show variations. As shown in Table S4, the ΔH of PEG, PE, and PSE before thermal cycles are 209.07 J/g, 171.95 J/g, and 138.04 J/g, respectively. After the thermal cycle, the ΔH of PEG, PE, and PSE decrease to 186.49 J/g, 143.99 J/g, and 112.88 J/g, respectively. It reflects that physical mixing CPCM cannot achieve the suppression of phase change component leakage. However, PHE5 showed better thermal cycle life with a latent heat value of 107.73 J/g. Thus, it indicates that PUPCM can achieve solid-solid phase transition and effectively prolong the thermal cycle life owing to the anti-leakage capability. In addition, Figure 5E shows the thermal conductivity of PHE samples. The thermal conductivity of PH2 without EG is only 0.16 W/(m·K), but when the EG content reaches 7 wt%, the thermal conductivity of PHE7 reaches 1.13 W/(m·K), six times higher than that of PH2. The main reason is that EG with high thermal conductivity can be uniformly distributed in PUPCM, which can form a stable and continuous heat transfer pathway to obtain rapid heat transferring rate. Thus, it can be concluded that EG can improve the thermal conductivity of PUPCM. In order to further analyze the thermal stability of different CPCMs, TGA analysis was performed under nitrogen atmosphere to quantitatively evaluate the thermal stability of PEG, PE, PSE and PHE5, and the results are shown in Figure 5F. It can be seen that PEG and PE exhibit similar weight loss curves, but the addition of 5 wt% to PE makes its final residual mass higher than that of PEG. In addition, the TGA curves of PHE5 exhibit a higher temperature at the onset of mass loss than that of PEG and PE, which indicates that the thermal stability of PHE5 sample has been enhanced.

In addition, the heat absorption process is determined by the thermal contact resistance (TCR) between the CPCM and the battery. The TCR of PUPCM was measured at 25 Pa pressure with a cold temperature of 30°C and a hot temperature of 70°C. In Figure 6A, it is observed that the TCR of PH2 without EG reaches 4.92 K·cm²/W. After adding EG, the TCR of the PUPCM decreases, and the TCR of PHE1 is only 1.37 K·cm²/W. With EG content increasing, the TCR of the samples further decreases. The main reason is that EG owns a high thermal conductivity and increases the contact site between CPCM and the battery, making the heat transfer more rapid, manifested as a decrease in TCR. It can be found in Figure 6B that the TCR of PE, PSE, and PHE5 before the thermal cycle test is 6.17 K·cm²/W, 1.53 K·cm²/W, and 1.36 K·cm²/W, respectively, which indicates that the FPCPM reduces the gap between contact surfaces and has lower TCR compared with rigid CPCM. After the thermal cycle, the TCR of PE and PSE increases to 9.21 K·cm²/W and 5.01 K·cm²/W, respectively. This is due to the loss of PEG after the thermal cycle test, which makes the surface roughness of the CPCM decrease and the cavity inside the CPCM increase, hindering the heat transfer process. On the other hand, the TCR of PHE5 after the thermal cycle test is 1.25 K·cm²/W. The reason is that the thermal cycle allows the softened PHE5 to form a tighter fit with the surface of the other contact material, reducing the space between the contact surfaces and allowing heat to be transferred quickly between them. To analyze the morphology differences of the heat transferring process among the PEG, PE, PSE, and PHE5, the heat transfer of them placed on the heating table was recorded by infrared thermal imaging intuitively, as depicted in Figure 6C. PHE5 maintains a stable structure and temperature distribution even under 150°C.

The contact between CPCMs and the material surface (conductive adhesive layer) before and after the thermal cycle was observed. Before the thermal cycle test, it can be seen that there are gaps between PE (Figure 6D) and PSE (Figure 6E) and the conductive adhesive layer, while PHE5 (Figure 6F) can form a tight fit with the conductive adhesive layer. This proves that PHE5, as a flexible PUPCM, has a better degree of coupling to the contact interface

than PE and PSE. As shown in Figures 6G-I, the contact gaps between PE and PSE and the conductive adhesive layer are enlarged after the thermal cycle, owing to leakage of PEG, leading to the formation of more voids. Conversely, the PHE5 can stay in close contact with the conductive adhesive layer after the thermal cycle test, confirming that it has a long service life, stable TCR and heat transfer performance. Therefore, as for the CPCM prepared by physical mixing, the contact gap between the CPCM and the battery increases owing to the leakage of the phase change components during the long-term use condition, affecting the thermal management ability. However, PUPCM can adapt to the long-term thermal cycle without leakage and can maintain close contact with the surface of the battery, ensuring heat transfer speed and thermal management ability.

The PUPCM manifestation in battery thermal management system

To analyze the practical performance of the PUPCM battery thermal management system, three battery modules that conducted ten cycles process at 30°C were analyzed, denoted as PE Module, PSE Module, and PHE5 Module. In Figures S2-S4, it displays the temperature curves and temperature difference results of battery modules at a 2 C charge rate. Further, in order to verify the temperature control and temperature equalization performance of the prepared CPCM for battery modules at high discharge rates, the cycle test results of three battery modules at 3 C discharge rates are shown in Figure 7 and compared with the battery module with forced air cooling in Figure S5. In Figures 7A-C, it displays the temperature curves of battery modules at a 3 C charge rate, indicating the maximum temperature of the PE Module rises to 57°C during the cycle process, and the maximum temperature of the PSE Module reaches 52°C. Correspondingly, the PHE5 Module presents the best temperature control property, reaching a maximum temperature of only 51°C. This indicates that PUPCM possesses better thermal conductivity, which can effectively optimize the heat transfer process in BTMS. Moreover, the temperatures of battery modules during the ten cycles were collected. As shown in Figure 7A, during the cycle test, the PE Module has a heat accumulation, and the temperature gradually increases with each cycle. After the tenth cycle test, the maximum temperature of the PE Module reaches 83°C, outside the battery's operation temperature range. Compared with the PE Module, the heat accumulation of the PSE Module is delayed, and its temperature rise rate also decreases. PSE Module reaches its maximum temperature on the eighth cycle and maintains 70°C (Figure 7B). It can be observed that there is little heat accumulation in the PHE5 module, and the maximum temperature during the cycle test is maintained at 59°C (Figure 7C). This demonstrates that PHE5 owns temperature control capability, and provides long and stable thermal management for the battery module due to its anti-leakage and low TCR properties.

In addition, the performance of the BTMS is also determined by the temperature difference (ΔT) of the battery module. Figures 7D-F displays the ΔT of the three battery modules during the cycle test. The trend of the ΔT of PE Module exhibits an upward trend, similar to its maximum temperature curve. In the first cycle, the ΔT of the PE Module is only 2.70°C, while the ΔT raises to 11.35°C after ten cycles. It should be noted that although the ΔT of the battery module with the PSE Module shows the same stable trend as that of the PHE5 Module, the ΔT of the PSE Module is higher than that of the PHE5 Module. During the initial charge and discharge procedure, the ΔT of the PSE Module reaches 4.80°C, which is 2.06°C higher than that of the PHE5 Module. This can be attributed to the higher TCR of PSE than that of PHE5, providing a worse temperature equalization effect. The leakage resistance of PE, PSE, and PHE5 can be characterized by comparing the morphology of the battery modules before and after the cycle test, shown in Figure 7G. There is a difference in the morphology of the PE Module before and after the cycle test, and it has collapsed in morphology, even exposing some batteries to air, which causes the PE thermal management capability failure, resulting in a continuous temperature rise in the battery. Since PSE can not achieve complete leakage resistance, a small amount of leaking PEG was found at the edge of the battery module after the cycle test, which is also the direct cause of the decrease of thermal management ability and the increase of TCR of PSE. However, there is no change in the morphology of the PHE5 Module before and after the cycle test. It can also be seen in Figure 7H that the gap between the CPCM and the battery module. The PE Module

possesses the obvious gap and PSE Module also has a minor gap, which severely restricts the capability of heat transfer from battery to CPCM. However, the gap of PHE5 Module is so tiny that the heat accumulation caused by the battery can be transferred efficiently, making the battery always operate at the optimal temperature range. Therefore, it can be concluded that PHE5 achieves solid phase transition successfully and provides efficient heat transfer and thermal storage capacity with the flexibility property to meet the long-term use of BTMS.

CONCLUSION

Composite phase change material (CPCM) as an efficient thermal storage medium has a great promising in various applications, but their low thermal stability is still restricted the achievable capacity. In this research, a novel solid-solid CPCM with polyurethane structured including as chain segments PEG4000 and hexamethylene diisocyanate coupling with expanded graphite (PHE5) has been prepared via in-situ method, simultaneously exhibiting excellent flexibility, high latent heat, and anti-leakage properties. The main results can be summarized as follows:

1) The PHE5 can demonstrate excellent long-cycle life and maintain TCR stability at $1.25 \text{ K}\cdot\text{cm}^2/\text{W}$ even after twenty thermal cycles, which can efficiently avoid the appearance of heat accumulation during the charge and discharge cycling process.

2) The PUPCM maintains a stable structure at 150°C for one hour with zero leakage, ensuring the safety of the battery module under extremely high temperature. It should be contributed that the soft chain segment of PEG and the hard chain segment HDI among PHE5 are linked together with carbamate group.

3) The maximum temperature of the battery module with PHE5 is controlled within 60°C , and the temperature difference is maintained within 4.5°C at 3 C discharge rate during ten cycles. It reveals that PHE5 can exhibit optimum thermal management effect owing to excellent flexible property, which will greatly decrease thermal contact resistance among battery module.

Therefore, the present research can offer a new insight into the development of multifunctional CPCM and solve the leakage of CPCM at high temperature, which will prolong the lifespan of battery packs, further improving the safety of millions of drivers and passengers in EVs.

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AUTHOR CONTRIBUTIONS

X.X.L., W.S.Y., and J.D. conceived and designed the experiments. W.S.Y., X.X.L., J.D., Q.Q.H., Y.T.Z. performed the experiments. X.X.L., W.S.Y., C.B.L., W.J., Y.T.Z., Y.R.Z., S.W.Z., X.X.L. analyzed the data. X.X.L., C.B.L., Y.M., Y.H.W., J.X.T., G.Q.Z., X.W.T. contributed reagents/materials/analysis tools. X.X.L., W.S.Y., C.B.L., J.D., D.S. wrote the paper. All authors contributed to the subsequent editing and improvement of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

ETHICAL STATEMENT AND PATIENT CONSENT

Not applicable.

DATA AND CODE AVAILABILITY

Data are available from the corresponding author upon reasonable request.

SUPPLEMENTAL INFORMATION

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