

Recyclable, Flexible and Highly Thermally Conductive Phase Change Composites with Dynamic Networks for Thermal Management

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Abstract Flexible phase change materials (PCMs) have become increasingly critical to address the demand for thermal management in electronic technologies and energy conversion. However, their application remains challenging because of their rigidity, liquid leakage, and insufficient thermal conductivity. Herein, flexible glutamic acid@natural rubber/paraffin wax (PW)/carbon nanotubes-graphene nanoplatelets (GNR/PW/CGNP) phase change composites with high thermal conductivity, excellent shape stability, and recyclability were reported. Zn²⁺-based dynamic crosslinking was constructed through the reaction of zinc acetate and carboxyl groups on glutamic acid@natural rubber (GNR), which was used as a flexible matrix to physically blend with paraffin wax/carbon nanotubes/graphene nanoplatelets (PW/CGNP) to achieve uniform dispersion of PW/CGNP, continuous thermal conductivity networks, and good encapsulation of PW. The GNR/PW/CGNP composites showed excellent mechanical strength, flexibility, and recycling ability, and effective encapsulation prevented the outflow of melted PW during the phase transition. Also, the phase change enthalpy could attain 111.1 J/g with a higher thermal conductivity of 1.055 W/mK, 428% higher than that of pure PW owing to the formation of efficient thermal conductive pathways, which exhibited outstanding thermal management performance and superior temperature control behavior in electronic devices. The developed flexible composite PCMs may open new possibilities for next-generation flexible thermal management electronics.

Keywords Phase change composites; Mechanical flexibility; Shape stability; Recycling ability; Thermal management

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INTRODUCTION

The global energy crisis has drawn significant attention, and maximizing the efficient use of renewable energy has emerged as a key focus for advancing sustainable development.^[1,2] Phase change materials (PCMs) provide a novel pathway for enhancing clean energy utilization as potential solar-thermal media owing to their high energy storage capacity, suitable phase transition temperatures, and chemical stability.^[3–5] PCMs can store and release latent heat during the phase change process, which has attracted significant attention in thermal energy storage fields. Moreover, with the rapid development of electronic technology and artificial intelligence, microelectronic devices are increasingly being designed to be thin, light, compact, and high-powered.^[6–9] The long-term operation of electronic devices inevitably leads to the generation and accumulation of heat inside the equipment, which causes irreversible damage to its service life and safety. Efficient heat dissipation and maintaining an appropriate operating temperature are crucial for

electronic devices to ensure safety and improve their reliability of electronic devices.^[10,11] Therefore, an effective solution to the problem of heat accumulation has become a key factor in promoting the development of electronic devices.

Phase change materials (PCMs), which are promising candidates for thermal energy storage, are capable of absorbing and releasing latent heat and are considered as effective thermal responsive materials in electronic equipment systems.^[12,13] The implementation of PCMs as thermal management materials at the device's thermal interface can achieve a solder-like effect, maximize the filling of interface gaps, and effectively reduce contact thermal resistance.^[14–16] Therefore, flexible PCMs can be used for thermal management to regulate the optimal operating temperature of electronic components. Therefore, there is an urgent need to develop high-performance phase-change materials with high thermal conductivity and good mechanical flexibility. Nonetheless, PCMs are prone to leakage during phase transformation, which seriously reduces their service life and is unfavorable to the surroundings. In addition, the significantly lower thermal conductivity of PCMs considerably restricts their use in energy conversion and thermal management applications.^[17] Therefore, great efforts have been made to de-

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velop shape-stabilized PCMs and improve their thermal conductivity by filling them with various thermally conductive nanofillers.

Various methods have been explored to address the leakage problem of PCMs, including polymer blending and integration into 3D network matrices to enhance encapsulation. Hu *et al.*^[18] developed flexible composite PCMs using paraffin wax (PW) as a phase-change component *via* melt blending with EPDM rubber, which exhibited outstanding shape stability, flexibility, and high thermal storage capacity. Golnoosh *et al.*^[19] successfully constructed shape-stabilized nano-encapsulated PCMs by encapsulating PW within a polyurethane shell structure *via* mini-emulsion polymerization. Hu *et al.*^[20] reported flexible PW/SBS/CNT composites with excellent enthalpy and encapsulation efficiency, and PW was embedded in a 3D skeleton formed through the chemical crosslinking of styrene-butadiene block copolymer (SBS) and carbon nanotubes (CNTs). Encapsulating PCMs with flexible polymers is a practical approach for large-scale production of flexible PCMs.^[21] Although the above reports obtained good shape stability, achieving a high energy storage capacity remains a significant challenge. There is currently an urgent need for an efficient method for producing form-stable flexible composite PCMs to satisfy application requirements.

Considering the low thermal conductivity of PCMs, incorporating thermally conductive fillers is still an important strategy owing to both effective and simple processes.^[22] Li *et al.*^[23] introduced graphene oxide (GO) into composite phase change materials *via* aqueous chemical plating followed by high-temperature calcination processes, resulting in flexible composites with improved heat transfer. Kang *et al.*^[24] developed a flexible PW composite by combining aligned carbon fiber bundles (CF) with a polyolefin elastomer (POE), which demonstrated high thermal enthalpy and excellent thermal conductivity. Zhang *et al.*^[25] produced a highly thermally conductive flexible composite film by combining polyvinylidene fluoride-boron nitride (PVDF-BN) with PW, and the enthalpy of melting was 105.63 J/g. Although a high filler loading could enhance the thermal conductivity, it inevitably led to a reduction in the thermal energy capacity owing to the decrease in the mass ratio of the PCMs. Achieving both high thermal conductivity and phase-change enthalpy while maintaining good flexibility remains a significant challenge.

Natural rubber (NR), which exhibits excellent elasticity and insulation over a wide temperature range, is a promising candidate as a thermal interface material for thermal management.^[26] Paraffin wax (PW) exhibits various advantages, including a proper phase-change temperature, high thermal enthalpy, and non-corrosiveness,^[27] and has been extensively used in phase-change thermal management. However, the ease of leakage and low thermal conductivity restrict its practical application. To address these issues, flexible composite PCMs with high thermal conductivities and excellent shape stabilities were successfully prepared. Specifically, CNTs-GNP (CGNP) was uniformly dispersed in molten PW under heating conditions, and CGNP was the first to encapsulate PW (PW/CGNP). NR latex was coated with glutamic acid (Glu) *via* physical blending to produce flexible Glu@NR (GNR). The GNR

and PW/CGNP were mixed through two-roll milling using zinc acetate as a crosslinking agent, and the obtained compound was hot compression molded to obtain flexible GNR/PW/CGNP phase-change composites, achieving the second encapsulation for PW. Continuous thermal pathways were formed in the GNR/PW/CGNP matrix, which were anticipated to remarkably improve the thermal conductivity of the phase change composites. This strategy provides an effective approach for fabricating flexible composite PCMs with excellent shape stability and thermal conductivity that are suitable for efficient electronic thermal management.

EXPERIMENTAL

Materials

Analytical-grade PW (melting point ~46 °C) was supplied by Suzhou Kangzhilv Tech Co., Ltd. Graphene nanoplatelets (GNPs) with a particle size of ~10 µm were purchased from Nanjing XF-NANO Materials Tech Co., Ltd. CNTs with a length of 10–20 µm and a diameter of 4–8 nm were provided by Nanjing FAME Bearing Co., Ltd. Natural rubber latex (solid content of 60 wt%) was supplied by Nanjing Orientleader Technology Co., Ltd. Glutamic acid (Glu) with biochemical reagent was obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

Preparation of Glu@NR (GNR)

Fifty grams of distilled water were added to 50 g of NR latex to form a 30 wt% latex solution. Glu was added under ultrasonic treatment for 30 min and stirred for another 30 min at 50 °C to form a stable emulsion. The obtained emulsion was then flocculated and dried at 50 °C for 48 h to obtain functionalized NR (Glu@NR, GNR).

Preparation of GNR/PW/CGNP

Paraffin wax (PW) was heated to completely melt at 50 °C, and a certain amount of CNTs and GNPs powder was added to the molten PW under mechanical stirring for 30 min and sonicated for 1 h to obtain a PW/CGNP mixture. After cooling, the mixture was crushed to particles. The mass ratio of the CNTs to GNPs was maintained at 1:3. The contents of the CNT-GNPs (CGNP) were set as 3 wt%, 5 wt%, 7 wt%, and 10 wt% in terms of the weight of PW.

The prepared GNR and PW/CGNPs were mixed uniformly by two-roll milling at room temperature, and a small amount of zinc acetate was added as a crosslinking agent. The mass ratio of PW to NR was 6:4. GNR/PW/CGNP composites were obtained by hot pressing for 5 min, and the composites were denoted as GNR/PW/CGNP-*x*, where *x* is the CGNP content. GNR/PW and GNR/PW/CGNP0% represent the same sample. For comparison, NR/PW/CGNPs were prepared using the same procedure.

Characterization

The chemical structures were investigated using Fourier-transform infrared (FTIR) spectroscopy on a Nicolet Nicolet-iS10 spectrophotometer (USA). The crystalline structures of the samples were determined using a Philips X'pert Pro X-ray diffractometer (XRD) ($\lambda=0.154$ nm). The thermal properties were tested using a NETZSCH STA 449F3 thermal analyzer (Germany). The phase-change enthalpy was measured using a NETZSCH 214 DSC instrument (Germany). The morphologies of the samples were

recorded using a JEOL JSM-5900LV SEM (Japan). The mechanical properties of the samples were tested using a CMT-4304 Universal Testing Machine (USA). Thermal diffusivity was tested using a Netzsch LFA 467 laser scintillator (Germany). The surface temperature change in the heating-cooling state was recorded using an infrared camera (FLUKE 60S⁺).

RESULTS AND DISCUSSION

Construction and Microstructure of GNR/PW/CGNP

NR latex was modified with glutamic acid (Glu) via a simple physical blending method to produce Glu@NR (GNR). CNTs-GNP (CGNP) was introduced into the molten PW under sonication to obtain PW/CGNP to improve the thermal conductivity. The GNR and PW/CGNP were mixed through two-roll milling using zinc acetate as a crosslinking agent, and the obtained compound was hot compression molded to produce flexible GNR/PW/CGNP phase-change composites. The preparation process is illustrated in Fig. 1. PW was mixed with a flexible GNR matrix, and the CGNP was dispersed into the system to build a continuous thermal conductivity network. Zn²⁺-based exchangeable crosslinking was achieved through the reaction of zinc acetate with carboxyl groups on the GNR. PW is expected to be encapsulated in crosslinking networks to achieve shape stability.

Figs. 2(a) and 2(b) show the FTIR spectra of all samples. The characteristic functional groups of olefins for NR were clearly identified, and the absorptions at 2963 and 2851 cm⁻¹ and 1457 and 1373 cm⁻¹ were attributed to the asymmetric and symmetric telescopic and deformation vibrations of methyl (—CH₃) or methylene (—CH₂—).^[26] The characteristic peaks at 1638 and 842 cm⁻¹ are attributed to the stretching vibrations of the C=C bond in the NR chain and the vibrations of the trisubstituted olefins in polyisoprene, respectively.^[27] For Glu, the absorption peaks at 3433 and 1618 cm⁻¹ were attributed to the stretching vibrations of the N—H and C=O groups, respectively. GNR showed characteristic amino (—NH₂) peaks at 3380 cm⁻¹, a C=O peak at 1645 cm⁻¹ and amide bond peaks at 1607 cm⁻¹, suggesting the successful coating of Glu on the NR surface.^[28] For GNPs and CNTs, the peak at 1610 cm⁻¹ was assigned to O—H—H and C=C skeletal ring vibrations.^[29] The absorption peaks at 2966 and 2843

cm⁻¹ were attributed to the C—H stretching vibrations of methylene (—CH₂—) on the surface of the CNTs. The peaks of GNR/PW/CGNP at different CGNP contents were almost identical (Fig. 2b). The peaks at 2920, 2850, and 1730 cm⁻¹ were attributed to the C—H and C=O stretching vibrations, and the characteristic peak at 718 cm⁻¹ was assigned to the out-of-plane bending vibration of the O—H group. The characteristic peaks of GNR/PW/CGNP indicate the successful complexation of GNR, CGNP, and PW.

Figs. 2(c) and 2(d) show the XRD patterns of GNP, CNTs, PW, NR, GNR, and GNR/PW/CGNP. The diffraction peak of GNP at 11.06° corresponds to the (001) crystal plane.^[30] The peak at 2θ=25.52° for the CNTs corresponds to the (002) crystal plane. For GNR, the peak of NR moved to lower angles as a result of grafting the Glu molecule, and was observed at 2θ=18.6°. The diffraction peaks of PW at 21.6° and 23.84° are ascribed to the (110) and (200) crystal planes, respectively. Additionally, the XRD spectra of the GNR/PW/CGNP composites showed characteristic peaks of PW, demonstrating no obvious effect on the crystal structure of PW. The thermal stability indicates the reliability of the composite PCMs in heat storage applications. Figs. 2(e) and 2(f) show the TG curves of the NR, GNR, and GNR/PW/CGNP composites. GNP exhibited approximately 15% weight loss below 130 °C owing to the evaporation of water retained within the interlayers,^[31] and a second significant weight loss of approximately 20% occurred between 180 and 230 °C owing to the elimination of oxygen-containing groups from the GNP surface. The CNTs showed excellent thermal stability even at 800 °C without significant weight loss. The mass loss of NR decreased rapidly because of the decomposition of the molecular chains of NR at higher temperatures. For GNR, the decomposition of the NR chain is limited by the grafting of Glu. Therefore, the onset decomposition temperature of GNR increased to 350 °C, and the final weight residue was ~22%, which was higher than that of NR. In comparison with PW, the thermal decomposition temperature of GNR/PW/CGNP were higher, revealing the outstanding thermal stability.

Fig. 3 shows photographs of the equilibrium dissolution experiments for the same weight of GNR and GNR/Zn. GNR was completely dissolved in xylene at room temperature. The

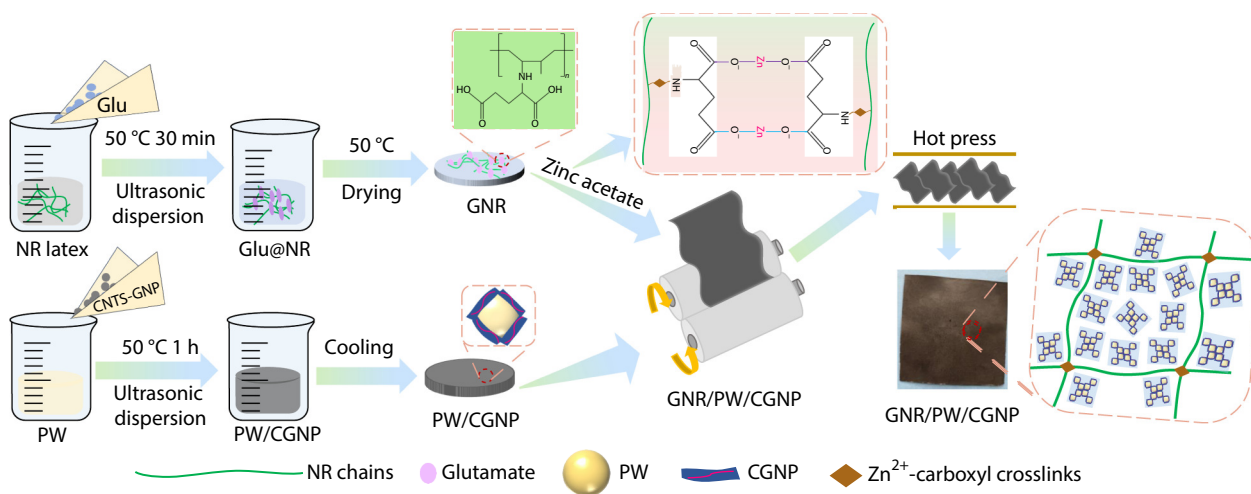


Fig. 1 Scheme for preparation of GNR/PW/CGNP composites.

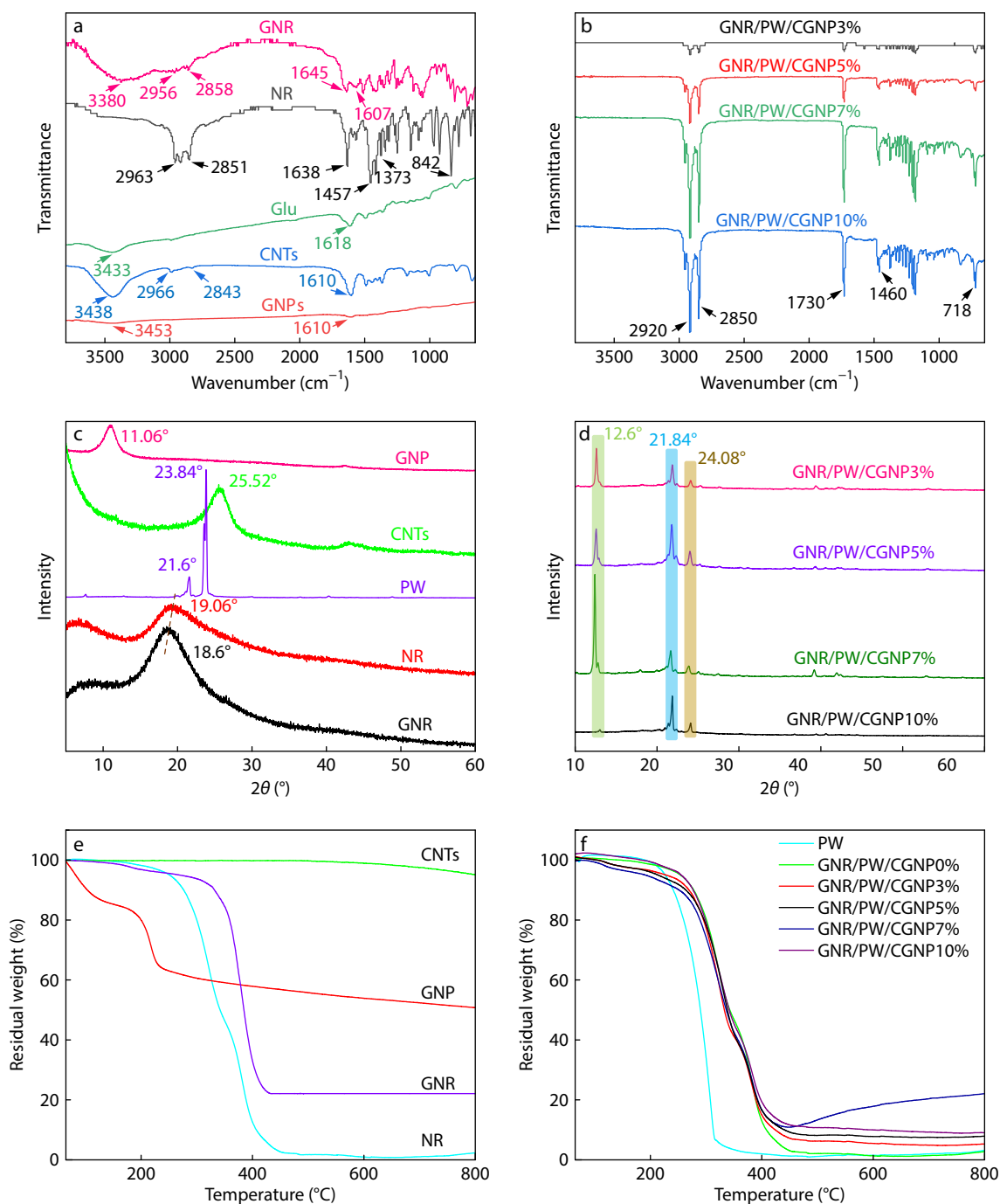


Fig. 2 FTIR spectra (a,b), XRD patterns (c,d) and TG curves (e,f) of NR, GNR, CNTs, GNP, PW and GNR/PW/CGNP.

GNR/Zn sample was swollen and did not dissolve even after setting for 96 h, which strongly indicated the formation of a crosslinked network structure. The strategy of constructing a crosslinked structure improved the tolerance of NR to organic solvents. However, GNR/Zn could be completely dissolved in a mixed xylene/chloroacetic acid solvent under stirring for 24 h, suggesting that a Zn^{2+} -based crosslinking network was formed in GNR/Zn. Ionic bonds can be dissociated using dichloroacetic acid, and the constructed Zn^{2+} -based crosslinks are sensitive to organic acids and break easily, which is consistent with our previous reports.^[32,33] NR/PW/

CGNP without Zn^{2+} -based crosslinks could be completely dissolved in xylene at room temperature, leaving only the CGNP fillers.

The cryogenically fractured surface morphologies of the GNR/PW/CGNP are shown in Fig. 4. The 3D network in the GNR was clearly observed, and the construction of the crosslinked network resulted in excellent interfacial contact between the GNR and PW, which improved the interfacial interaction and facilitated the uniform dispersion of CGNP, enabling CGNP to fully contribute to toughening and thermal conductivity.^[34] The PW was uniformly loaded into the GNR,

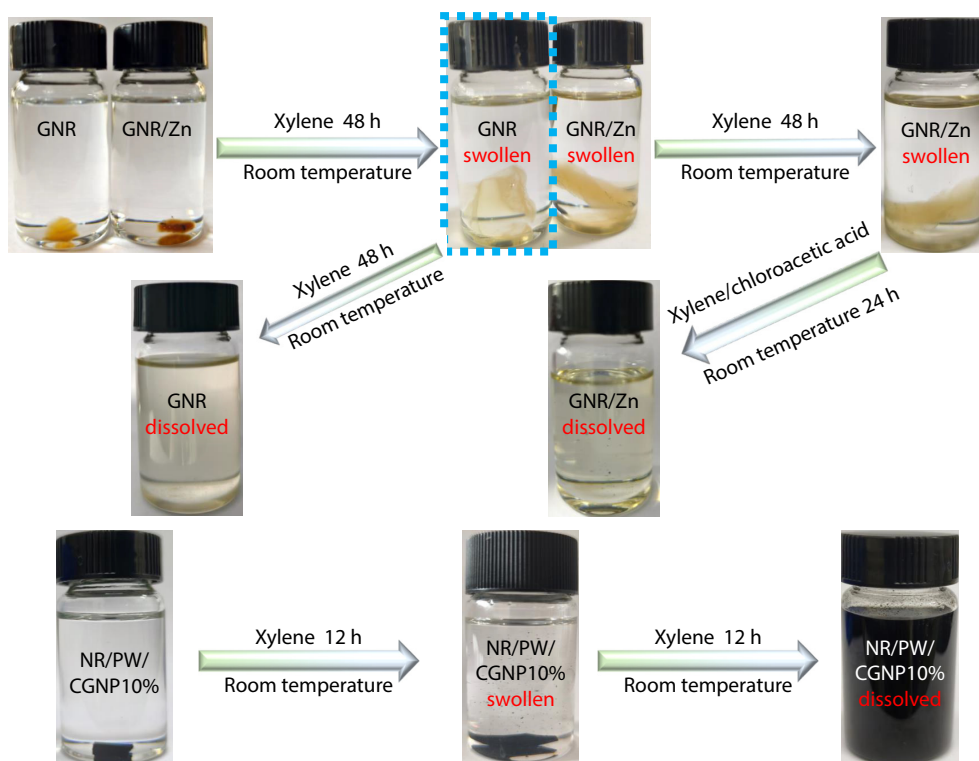


Fig. 3 Photographs of GNR, GNR/Zn and NR/PW/CGNP samples in the dissolution experiment.

which was encapsulated by the networks formed by GNR and CGNP, thus maintaining the good shape-stability of PW-based composite PCMs.^[35] A 3D network for the GNR/PW/CGNP composites can be clearly observed, as shown in Fig. 4 (a,a₁,a₂–d,d₁,d₂), which was the basis for the high PW encapsulation rate. In addition, with an increase in the CGNP content, PW and CGNP exhibited a more obvious stacking arrangement in the GNR matrix, indicating that a continuous three-dimensional thermal conductivity channel was formed.

Mechanical Property of GNR/PW/CGNP Phase Change Composites

Adequate mechanical strength is crucial for the effectiveness of GNR/PW/CGNP phase-change composites, particularly in situations that require folding, stretching, or bending. As illustrated in Figs. 5(a)–5(f), the GNR/PW/CGNP composites showed good mechanical strength and considerable flexibility, which could be stretched, bent, twisted, and folded by bearing an external force. In addition, the GNR/PW/CGNP composites could be shaped into various patterns, like “JOU.” GNR/PW/CGNP composites (thickness 0.5 mm) can easily lift a weight of 100 g, revealing the good mechanical strength and toughness of the composites. To meet the requirements of electronic devices, composites have been fabricated into different shapes depending on the application scenario while maintaining excellent thermal storage properties and ensuring optimal compatibility.^[36] The tensile strength of GNR/PW/CGNP0% was 2.48 MPa, indicating that the mechanical strength increased through exchangeable Zn²⁺-based crosslinking bonds and enhanced interfacial interactions.^[37] By addition of CGNP, the tensile strength for GNR/PW/CGNP overall showed an upward trend, attaining up to 2.72 MPa at 10 wt% content of CGNP,

which was mainly ascribed to the reinforcing effect of CGNP and interfacial interaction in the composite system, resulting in the effective stress transfer upon stretching. Compared to GNR/PW/CGNP0%, the tensile strength of GNR/PW/CGNP10% increased by 181%, as shown in Figs. 5(g) and 5(h). However, the elongation at break decreased as the CGNP content increased, and the loading of CGNP restricted the movement of the GNR molecular chain and deformation of the composites. In addition, the CGNP fillers hindered the dynamic features of the interfacial crosslinking network, especially at higher CGNP loadings, resulting in a reduction in stretchability. While for NR/PW/CGNP10%, the tensile strength was much lower than that of GNR/PW/CGNP10%, confirming the reinforcing effect of the Zn²⁺-based crosslinking networks.

Traditional flexible PCMs lack a reprocessing ability. However, by incorporating dynamic ionic crosslinking bonds into a flexible matrix, PCMs can be recycled under specific conditions.^[32] GNR/PW/CGNP utilized exchangeable ionic crosslinking between Zn²⁺ and carboxyl groups, enabling network topology and stress relaxation.^[38] The recyclability of GNR/PW/CGNP was verified by cutting it into smaller fragments, followed by reshaping through hot pressing or two-roll milling, as illustrated in Fig. 6(a). After hot pressing at 50 °C for 5 min, the GNR/PW/CGNP samples were reshaped even after recycling three times. The mechanical properties of the reprocessed GNR/PW/CGNP samples are shown in Figs. 6(c) and 6(d). Owing to the presence and change in the distribution of rigid PW, the tensile strength and elongation at break decreased after recycling, but the recycled samples recovered most of the initial mechanical strength owing to the existence of Zn²⁺-based crosslinking networks. The dynamic Zn²⁺-carboxyl crosslinks maintained excellent flexibility and

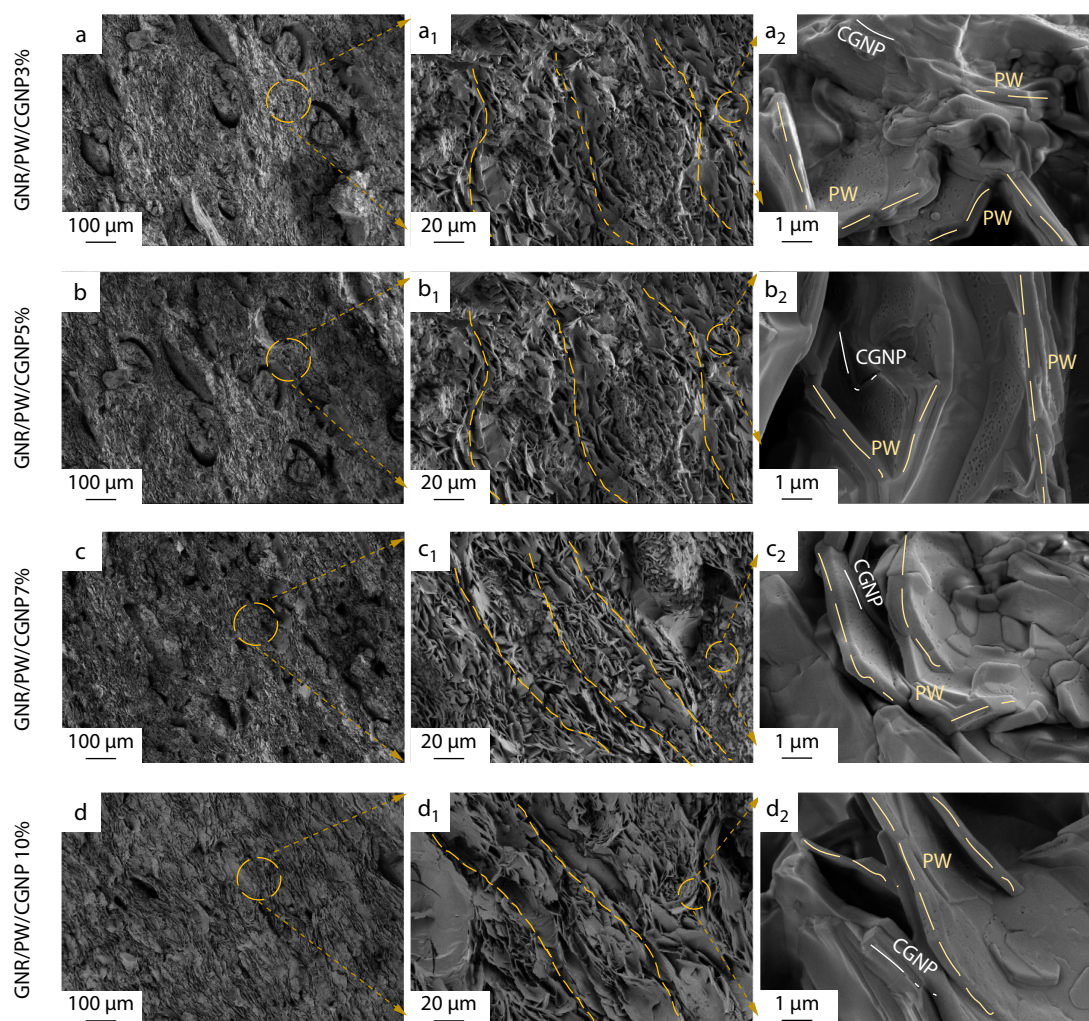


Fig. 4 Cross-sectional SEM images of GNR/PW/CGNP composites (a, a₁, a₂–d, d₁, d₂).

mechanical strength after multiple cycles. The reversible network of Zn^{2+} -carboxyl groups during the reprocessing is illustrated in Fig. 6(b). The phase transition behavior of the recycled GNR/PW/CGNP is shown in Figs. 6(e) and 6(f). The phase enthalpy (ΔH_m), crystallization enthalpy (ΔH_c), and phase change temperatures of the recycled sample after recycling three times showed almost no obvious changes compared to those of the original sample. The slight loss of mass-specific latent heat for PW indicated the successful encapsulation of GNR/CGNPs, which prevented PW from leaking during reprocessing.

Phase Change Characteristics and Shape Stability of GNR/PW/CGNP

Thermal energy storage capacity is critical for composite PCMs in practical applications.^[39] Fig. 7(a) illustrates the thermal energy storage and phase change performance of the composites. The corresponding phase change parameters are listed in Table 1. Pure PW melted at 44 °C with a latent heat of melting of 236.4 J/g. The temperature of crystallization was 36.4 °C and the latent heat of crystallization was 235.5 J/g. For the GNR/PW/CGNP composites, the melting latent heat and crystallization latent heat were reasonably reduced owing to the encapsulation

of GNR/CGNP and reduction in the mass fraction of PW. In addition, the encapsulation of PW within GNR/CGNP hindered the movement of the molecular chains, thus preventing the phase transition of PW.^[40,41] The melting temperature of GNR/PW/CGNP5% was 47.3 °C, and the latent heat was 111.1 J/g, while the crystallization temperature was 34.6 °C with a crystallization latent heat of 105.8 J/g, as shown in Fig. 7(b).

As shown in Figs. 7 (c) and 7(d), the heating and cooling curves of 50 cycles for PW and GNR/PW/CGNP were measured. The values of T_m , T_c , ΔH_m and ΔH_c for the 1st, 10th, 30th, and 50th cycle were presented in Table 2. Both the T_m and T_c values showed minimal changes after 50 cycles. The phase-change enthalpy of PW was 98.5%, while GNR/PW/CGNP maintained 99.7% of the initial enthalpy, indicating that GNR/PW/CGNP had excellent cycling reliability. This property extends the service life of composite PCMs in the thermal-management field.

Figs. 8(a)–8(f) show the leakage behavior of the PW and GNR/PW/CGNP composites in an oven at 70 °C for 1 h. PW, NR/PW/CGNP, and GNR/PW/CGNP composites maintained a stable shape. After 5 min, the pure PW began to melt into the liquid and flowed readily even when soaked in the filter paper at the bottom after heating for 20 min. The GNR/PW/

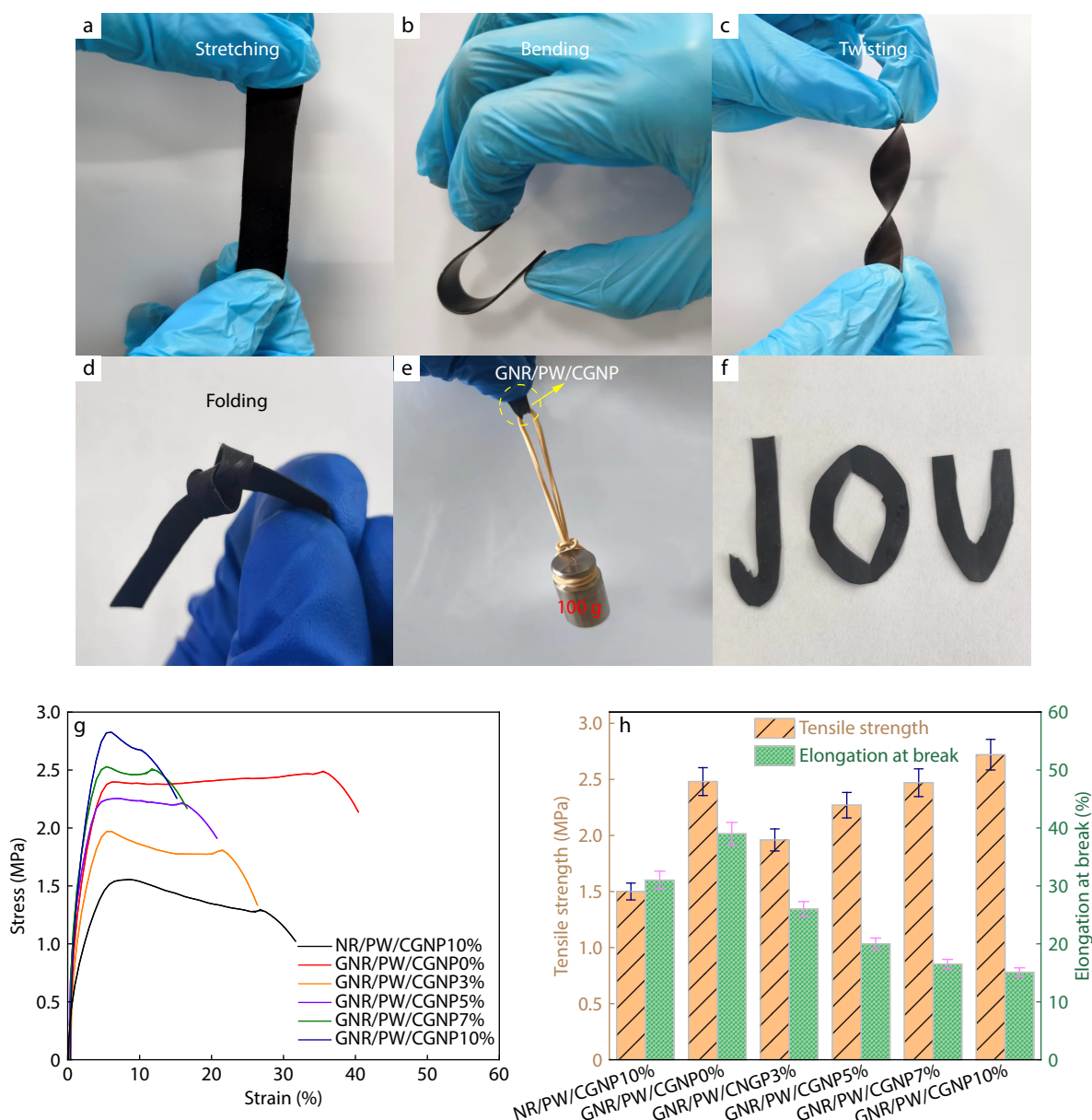


Fig. 5 Digital photos of GNR/PW/CGNP composites at different deformations of stretching, bending, twisting and folding (a–d). Digital photos of the composite lifting 100 g weight (e) and various shapes (f). Tensile stress-strain curves (g) and mechanical properties (h) of NR/PW/CGNP and GNR/PW/CGNP composites.

CGNP0% and GNR/PW/CGNP3% samples started to leak after heating for 10 and 20 min, respectively, and NR/PW/CGNP and GNR/PW/CGNP0% became deformed and collapsed at 30 min. However, when the CGNP content gradually increased to 5%–10%, the GNR/PW/CGNP composites maintained excellent shape stability without obvious leakage during the entire heating process, with only a slight PW trace at the bottom of the heating plate. The mass losses of PW and GNR/PW/CGNP are shown in Fig. 8(g). PW melted entirely, resulting in a complete mass loss of 100%, and the mass loss of all GNR/PW/CGNP composites was below 3%. The mass loss of NR/PW/CGNP was 1.59%, which was higher than that of GNR/PW/CGNP owing to the lack of a cross-linking network. The mass loss progressively decreased with increasing CGNP

content. The double-layer encapsulation of PW by GNR and CGNP limited the mobility of PW without leakage at elevated temperatures, suggesting that the GNR/PW/CGNP composites had excellent shape stability. As shown in Fig. 8(h), the PW started to melt when the temperature exceeded the phase transition temperature. However, PW was encapsulated by CGNP and GNR, which restricted the movement of the molten PW. Fig. 8(i) shows the cross-sectional morphologies of the GNR/PW/CGNP before and after heating at 70 °C for 1 h. The results showed that GNR/PW/CGNP had an interfacial gap owing to the physical encapsulation interaction between GNR, PW, and CGNP before heating. After heating, PW melted between the GNR and CGNP, and strong interactions between GNR/CGNP and PW resulted in smaller or even no in-

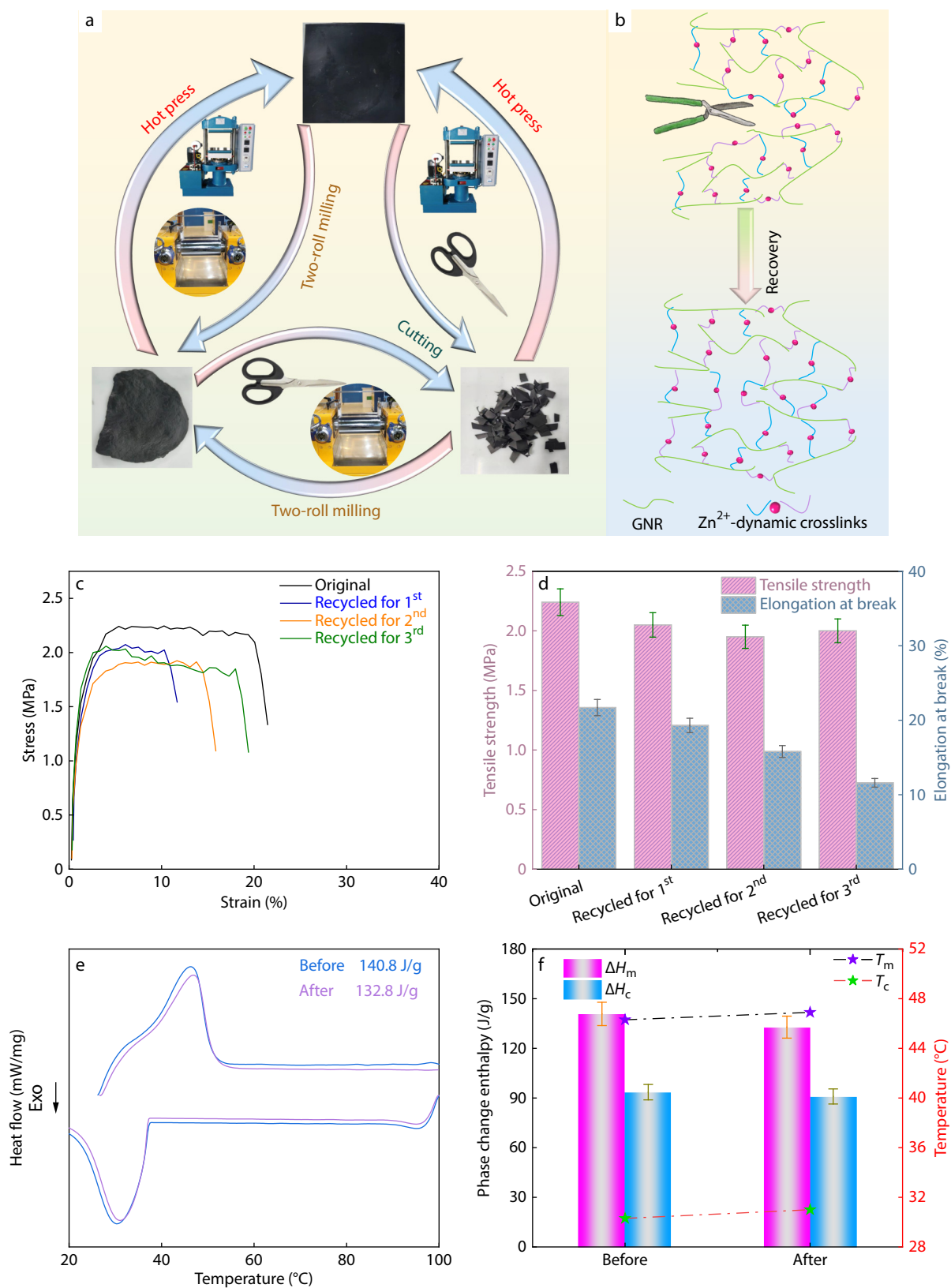


Fig. 6 Recycling process of GNR/PW/CGNP by hot pressing (a). Schematic illustrating multiple crosslinking networks (b), stress-strain curves (c) and mechanical properties after recycling (d) of GNR/PW/CGNP composites. DSC curves (e) and the enthalpy change, T_m and T_c (f) of GNR/PW/CGNP before and after recycling.

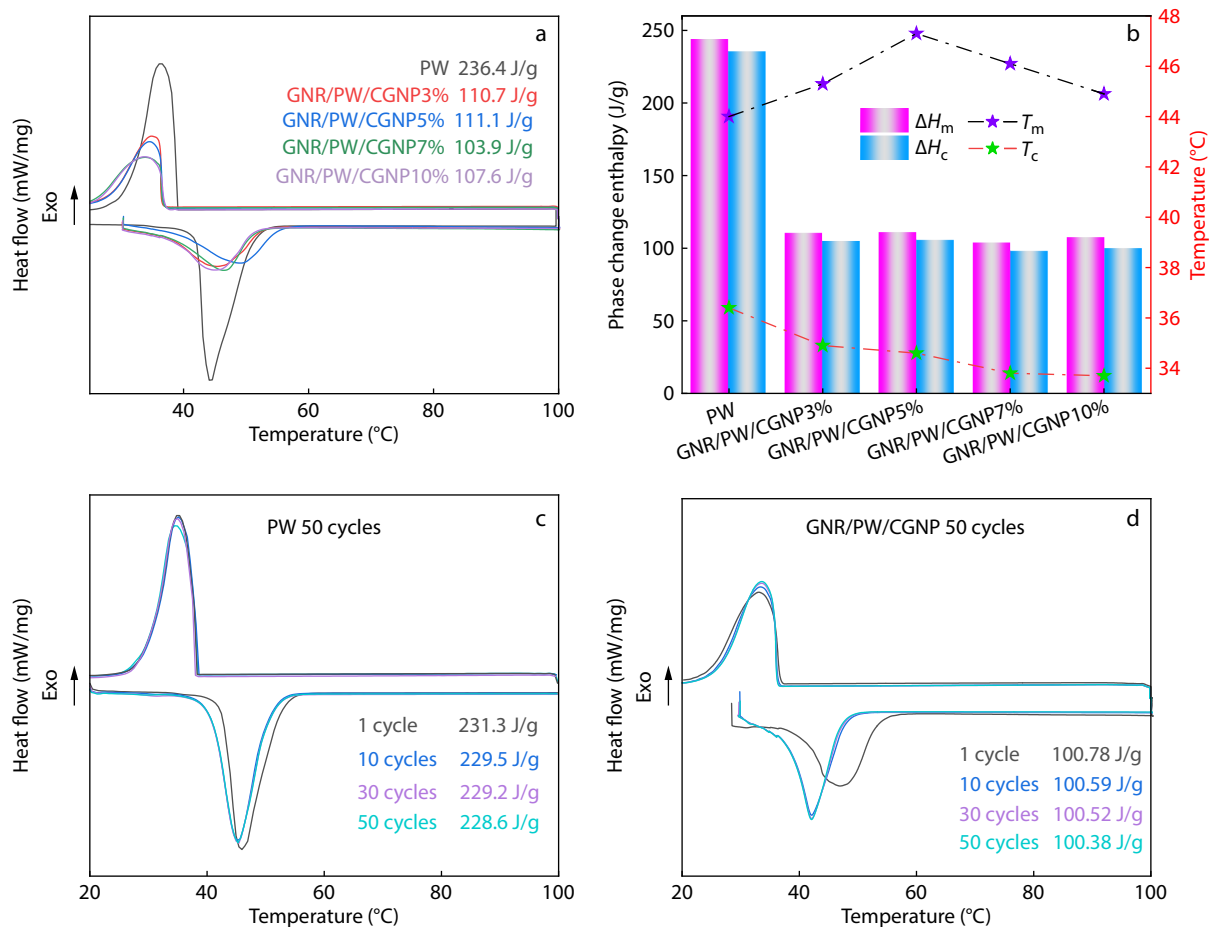


Fig. 7 DSC melting-solidifying curves (a), phase change enthalpy (b) and DSC cycling curves (c,d) for PW and GNR/PW/CGNP composites.

Table 1 DSC characteristic parameters of PW, GNR/PW/CGNP.

Sample	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
PW	44	236.4	36.4	235.5
GNR/PW/CGNP3%	45.3	110.7	34.9	105.1
GNR/PW/CGNP5%	47.3	111.1	34.6	105.8
GNR/PW/CGNP7%	46.1	103.9	33.8	98.1
GNR/PW/CGNP10%	44.9	107.6	33.7	100.1

Table 2 DSC cycling parameters of PW and GNR/PW/CGNP.

Sample	Cycle	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
PW	1 st	45.7	231.3	34.6	228.9
	10 th	45.2	229.5	35.1	226.5
	30 th	45.3	229.2	35.2	224.6
	50 th	45.3	228.6	35.1	218.4
GNR/PW/CGNP	1 st	46.8	100.78	32.9	83.25
	10 th	42.1	101.6	33.4	87.63
	30 th	42.1	100.59	33.6	86.39
	50 th	42.1	100.52	33.6	86.03

terfacial gaps, and no obvious larger gaps were observed, indicating that the GNR/PW/CGNP composites had superior shape stability. Furthermore, the addition of CGNP to the composites contributed to the improvement of heat transfer, which effectively avoided leakage of the PW during the melting process and facilitated the GNR/PW/CGNP to maintain

shape stability.

Thermal Behavior of GNR/PW/CGNP

The thermal conduction property plays a key role in phase-change composites, which directly affects the efficiency of energy storage and release during the phase-change process.^[42] The

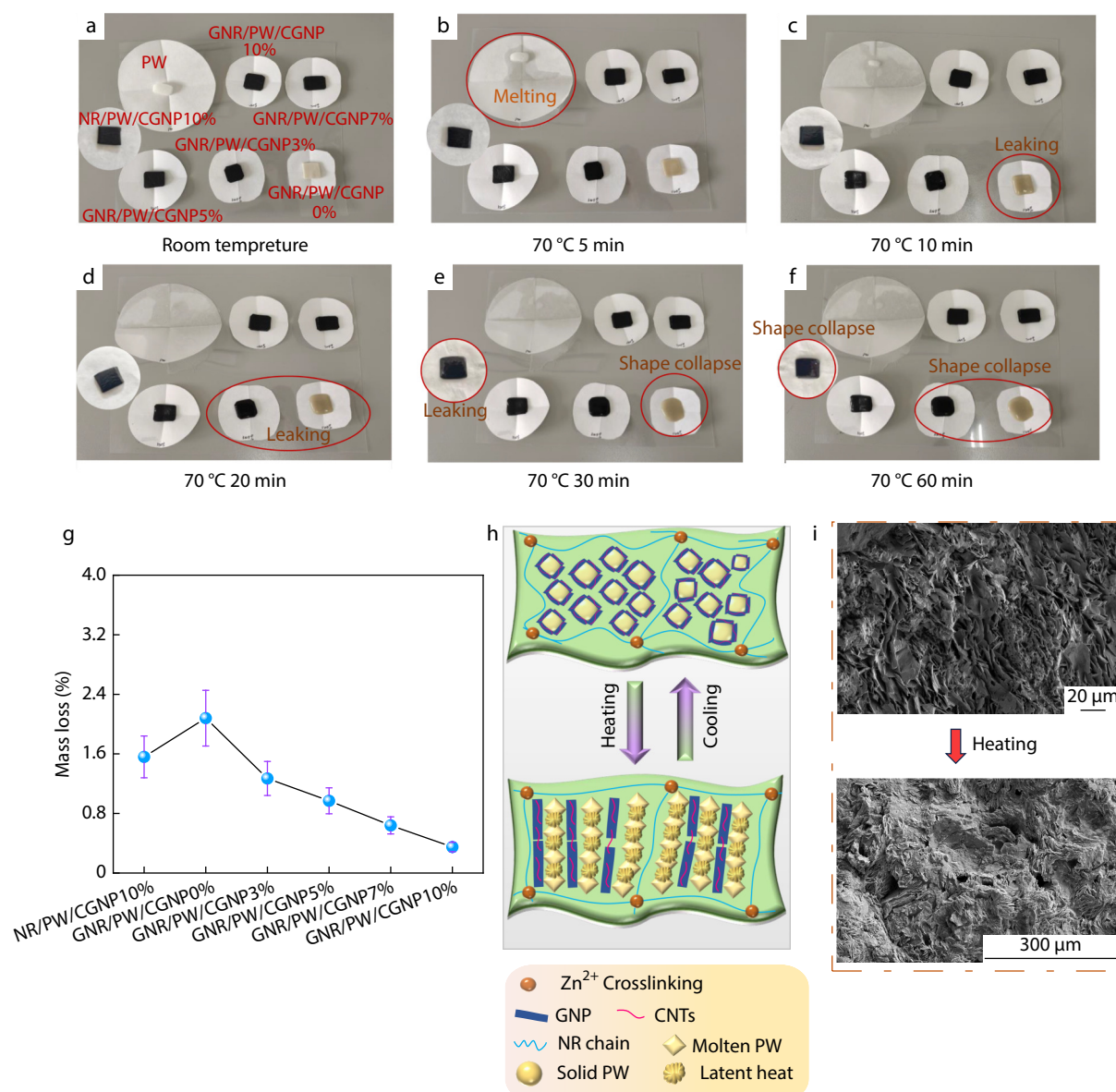


Fig. 8 Photos of shape change (a–f) and the mass loss (g) of PW, NR/PW/CGNP and GNR/PW/CGNP composites during heating process at 70 °C. Scheme for the heating-cooling mechanism of GNR/PW/CGNP (h). Cross-sectional SEM images of GNR/PW/CGNP composites captured before and after heating (i).

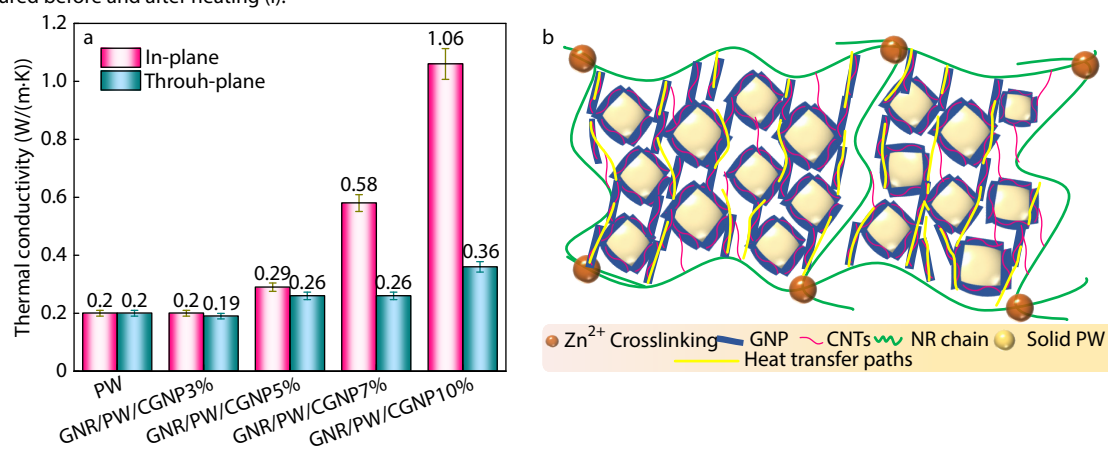


Fig. 9 In-plane and through-plane thermal conductivities of PW, GNR/PW/CGNP (a). Heat transfer mechanism of GNR/PW/CGNP composites (b).

thermal conductivity of pure PW showed an inherently low value of 0.2 W/mK, as shown in Fig. 9(a), the thermal conductivity of previous report.^[43] The thermal conductivity of pure NR is also very low, mainly originating from the disordered molecular chain structure.^[44] Upon the addition of CGNP, the in-plane

thermal conductivity showed an obvious upward trend, while the through-plane thermal conductivity showed a less noticeable change. The in-plane thermal conductivity was much higher than the through-plane thermal conductivity, exhibiting obvious anisotropic characteristics. Therefore, the stacked arrange-

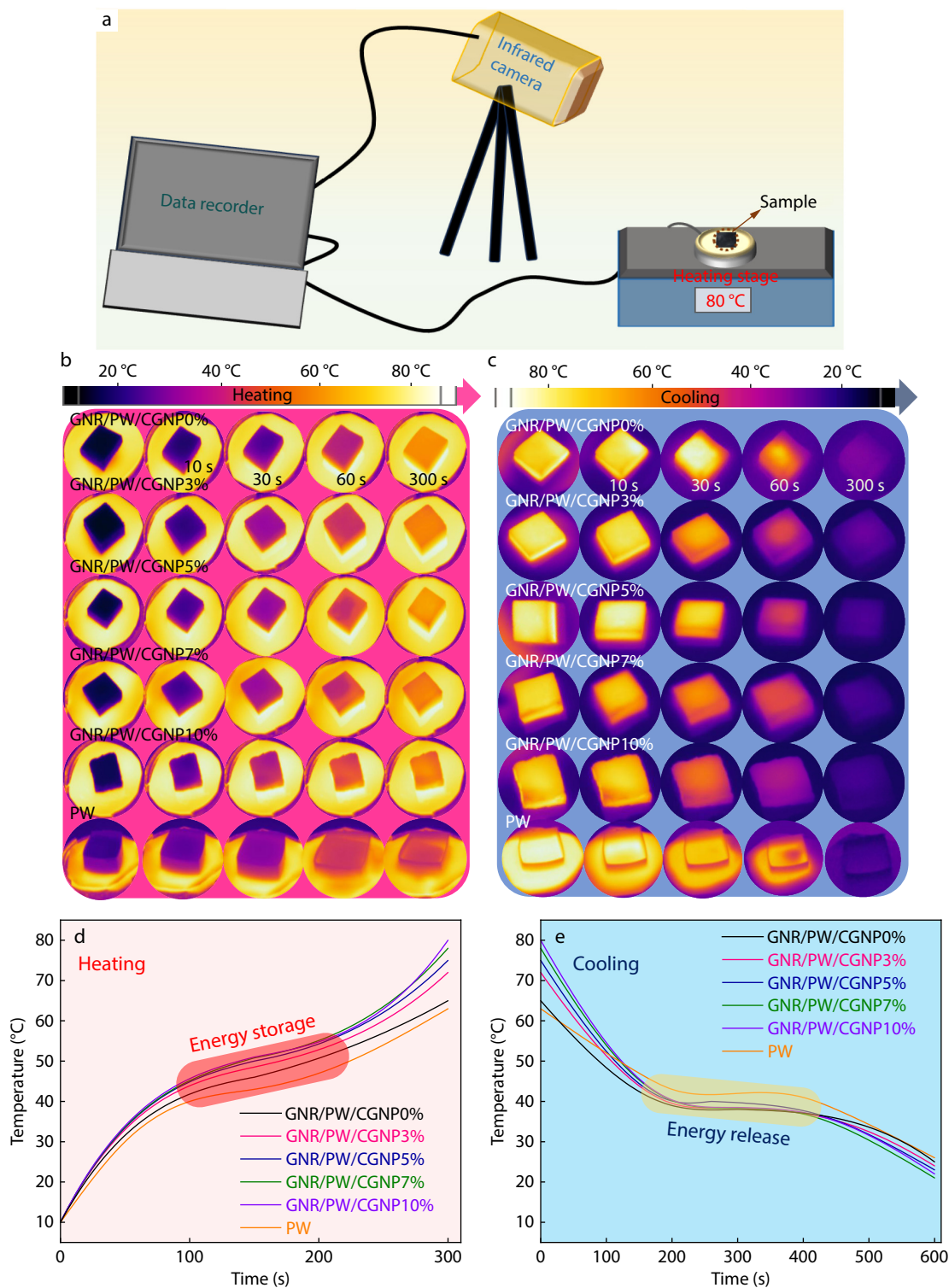


Fig. 10 Schematic illustrating the IR thermal imaging procedure (a). IR thermal images of PW and GNR/PW/CGNP composites (b,c). Corresponding temperature evolution of PW and GNR/PW/CGNP composites as a function of heating and cooling time (d,e).

ment structure of CGNP along the in-plane direction in the matrix (Fig. 4) was beneficial for improving the thermal conductivity. It is worth noting that GNR/PW/CGNP10% displayed a superior thermal conductivity of 1.055 W/mK, which is 428% higher than that of pure PW. The PW/CGNP was well distributed within the GNR network with an excellent layered structure, improving the interfacial compatibility between the PW/CGNP and GNR matrix, which contributed to the construction of efficient heat conduction pathways. Fig. 9(b) illustrates the mechanism of thermal conductivity enhancement of the GNR/PW/CGNP composites. Effective phonon transport serves as the primary mode of heat transfer in thermally conductive rubber nanocomposites.^[45] The incorporation of CGNP provided a continuous thermal conductivity path through the GNR/PW/CGNP composites, forming a 3D thermal conductivity network, which promoted phonon transport in the composites.^[46]

Fig. 10(a) shows the thermal images of the PW and GNR/PW/CGNP composites obtained using an infrared camera. The composites were heated using a heating plate and allowed to cool naturally, and the temperature was continuously monitored using an infrared camera to evaluate the thermal regulation properties. As shown in Fig. 10(b), the addi-

tion of CGNP improved the thermal response of the GNR/PW/CGNP composites, resulting in a much faster temperature change with increasing CGNP content. During heating, GNR/PW/CGNP10% underwent a swift transition from dark blue to red, indicating a rapid increase in surface temperature. In contrast, GNR/PW/CGNP0% and PW exhibited a delayed alteration in color, indicating that the incorporation of CGNP significantly improved the heat transfer efficiency of GNR/PW/CGNP. Thermal energy was stored in the GNR/PW/CGNP composites through the latent heat effect during the PW phase transformation. No leakage of the GNR/PW/CGNP composites was observed during the process. After removing the heating source, the stored thermal energy began to be released, leading to an evident temperature decrease. As shown in Fig. 10(c), the temperature change was faster with increasing CGNP content, further revealing the effectiveness of the CGNP-enhanced thermally conductive network. The temperature-time relationship of the GNR/PW/CGNP composites under the heating-cooling process is shown in Figs. 10(d) and 10(e). The “solid-liquid” and “liquid-solid” phase transition stages corresponded to PW were founded,^[47] respectively. Similarly, GNR/PW/CGNP10% exhibited a faster heat-trans-

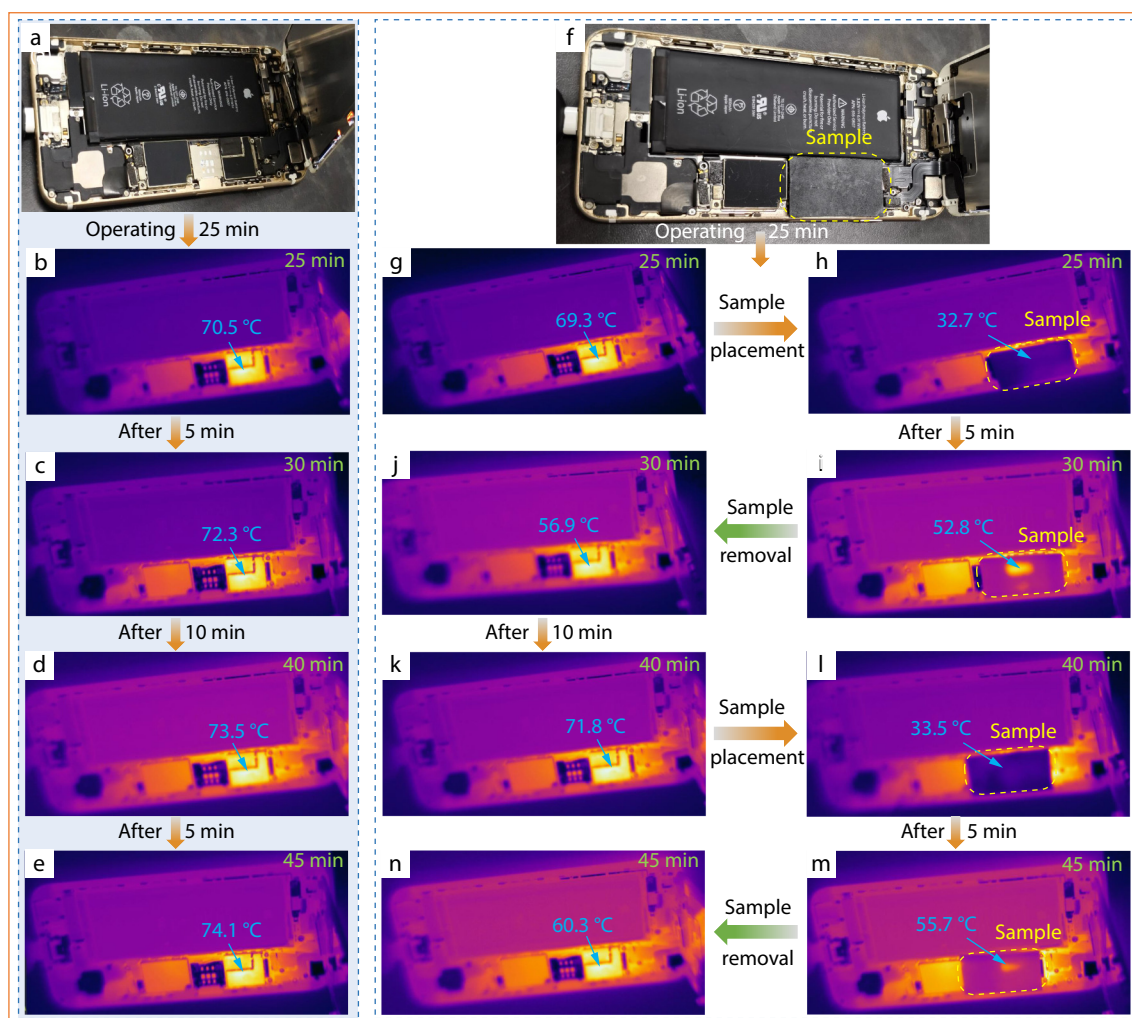


Fig. 11 Thermal management monitoring of operating electronic device without (a–e) and with GNR/PW/CGNP sample (f–n).

fer rate owing to its higher thermal conductivity.

To illustrate the potential application of the composite PCMs, as shown in Fig. 11, the thermal management of the operating smartphone with and without the GNR/PW/CGNP composite was evaluated. The GNR/PW/CGNP sample was installed in the core area of the iPhone Central Processing Unit (CPU) (Fig. 11f), and the thermal change in the phone after running for the same time was monitored by infrared thermography. With an increase in the running time of the iPhone, the CPU temperature gradually increased to 74 °C (Figs. 11a–11e). After the iPhone run for 25 min, the CPU surface temperature increased to 69.3 °C (Fig. 11g). When the GNP/PW/CGNP sample was placed on the CPU, the GNP/PW/CGNP surface temperature was 32.7 °C after running for 25 min, and gradually rose to 52.8 °C after running for another 5 min (Figs. 11h and 11i). However, the CPU surface temperature was only 56.9 °C when the GNP/PW/CGNP sample was immediately removed (Fig. 11j), 15.4 °C lower than that of the CPU without GNP/PW/CGNP (Fig. 11c). After continuously running for another 10 min, the CPU surface temperature increased again to 71.8 °C (Fig. 11k). When the GNP/PW/CGNP sample was placed once again on the CPU surface, the GNP/PW/CGNP surface temperature was 55.7 °C after running for 45 min (Figs. 11l and 11m). After the GNP/PW/CGNP sample was immediately removed, the CPU surface temperature was 60.3 °C (Fig. 11n), 13.8 °C lower than that of the CPU without GNP/PW/CGNP (Fig. 11e). The heat produced by the operating iPhone was transferred through the GNP/PW/CGNP phase change composite, indicating the significant temperature regulation effect of GNR/PW/CGNP. The thermal response of the position close to the heat source of the CPU core was almost entirely determined by the phase transition process, confirming the practical significance of GNR/PW/CGNP phase change composites in thermal control management systems for electronic devices.^[48]

CONCLUSIONS

In this study, an effective strategy was proposed to fabricate flexible GNR/PW/CGNP composite PCMs with high thermal conductivity, outstanding shape stability, and recycling ability via physical blending of GNR and PW/CGNP through a Zn²⁺-based crosslinking reaction. The dynamic Zn²⁺-carboxyl network was capable of reversible shredding and reforming, endowing GNR/PW/CGNP with excellent mechanical strength, flexibility, and recyclability. The phase change enthalpy of recycled GNR/PW/CGNP showed almost no obvious change compared to the original values, indicating that the encapsulation of the GNR/CGNP hindered the leakage of PW during reprocessing. CGNP and GNR were encapsulated twice in PW, effectively preventing PW leakage. PW/CGNP was uniformly dispersed in the GNR matrix, and continuous thermal pathways were formed, which enabled GNR/PW/CGNP to retain both effective energy storage and better thermal conductivity. GNR/PW/CGNP showed a sufficient latent heat of 111.1 J/g and outstanding cycling stability. The addition of CGNP remarkably strengthened the thermal conductivity to 1.055 W/mK, representing a 428% improvement over pure PW owing to the efficient thermal conductive pathways, which could be a good candidate for electronic thermal management. This demonstrates the significant

thermal management benefits of GNR/PW/CGNPs for electronic applications. This study is expected to broaden the applications of composite PCMs in thermal management and energy storage.

Conflict of Interests

The authors declare no interest conflict.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request. The author's contact information: licj_poly@jou.edu.cn.

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